1

of

4

4

75-T-1651

**Synthesis and Characterization of Novel Ternary and Quaternary Reduced
Molybdenum Oxides**

by George Schemik

thesis submitted to Iowa State University

Ames Laboratory, U. S. DOE

Iowa State University

Ames, Iowa 50011

Date Transmitted: July 1993

Prepared for the U. S. Department of Energy

Under contract no. W-7405-eng-82.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

MASTER

dk
DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

**Synthesis and characterization of novel
ternary and quaternary reduced molybdenum oxides**

George Louis Schimek

**Under the supervision of Robert E. McCarley
From the Department of Chemistry
Iowa State University**

Novel ternary reduced molybdenum oxides containing infinite chains of trans edge-shared molybdenum octahedra have been well explored. In the past decade, synthetic efforts have examined "cutting" these infinite chains of Mo octahedra into smaller segments, termed oligomers. The oligomers can be formulated from the general formula, $M_{n-x}Mo_{4n+2}O_{6n+4}$, where n equals the number of trans edge-shared Mo octahedra. The major emphasis of this research was to synthesize and characterize tetrameric oligomers, where $n=4$. New oligomeric materials with $n=2,3,4$, & 5 were discovered. These members are: $K_{0.06}M_{1.94}Mo_{10}O_{16}$ ($M=Ca, Sr$), $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$, $SrBaMo_{10}O_{16}$, $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$, $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$, $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$, $Ba_3Mo_{18}O_{28}$, and $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$.

The structural features and properties of the oligomers were compared and contrasted in terms of electron counting methods. The dimeric oligomers have a consistent, strong apical Mo-Mo bond and a very strong intercluster metal-metal bond that varies in length based on electron count. For the trimeric oligomers, the apical-apical bonds are arranged in a short-long fashion for the members with less than $44e^-$ and the apical-apical bonds become nearly equivalent for materials with greater than $44e^-$. The intercluster metal-metal bonds for the $n=3$ members are long if less than $43e^-$ are available, short if between 43 and $44e^-$, and long if greater than $44e^-$. The $n=4$ oligomer, $Ba_3Mo_{18}O_{28}$, has four short and two long

apical-apical bonds and a long intercluster bond. $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$, the $n=5$ member, has four short and four long apical-apical bonds and a long intercluster metal-metal distance.

Two ternary reduced molybdenum oxide phases containing infinite chains of trans edge-shared Mo octahedra, connected in different manners, were prepared and characterized. The two materials are $Ti_{0.31}Fe_{1.69}Mo_4O_7$ and $RE_4Mo_4O_{11}$, where RE = Y, Nd, and Sm-Lu.

Many of the known ternary and quaternary reduced molybdenum oxides have superstructural ordering, due in part, to mixed metal and/or partial occupation of cation sites. Transmission electron microscopy was used to explore the superstructures present in $Fe_{1.89}Mo_{4.11}O_7$, $Sn_{0.9}Mo_4O_6$, $InMo_4O_6$, and $Mn_{1.5}Mo_8O_{11}$. Proposed structural models consistent with the observed electron diffraction were presented.

Synthesis and characterization of novel
ternary and quaternary reduced molybdenum oxides

by

George Louis Schimek

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Inorganic Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1993

DEDICATION

In Memory of Louie Schimek

**He taught me, through his actions, to live every day
to its fullest: by doing the activities that bring you joy,
with the people who are your friends.**

TABLE OF CONTENTS

GENERAL INTRODUCTION	1
Explanation of Dissertation Format	6
 SECTION 1. SYNTHESIS AND CHARACTERIZATION OF $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$: AN OLIGOMER WITH FOUR TRANS EDGE-SHARING Mo OCTAHEDRA	7
 INTRODUCTION	8
EXPERIMENTAL	9
Materials and Methods	9
Physical Measurements	10
Molybdenum analysis	10
X-ray powder diffraction	10
Magnetic susceptibility	10
Electrical resistivity	11
Scanning electron microscopy	11
Transmission electron microscopy	11
Microprobe analysis	12
Synthesis	12
X-ray Powder Diffraction	16
X-ray Single Crystal Data Collection	16
Structure Solution and Refinement	20
 RESULTS AND DISCUSSION	28
Description of Structure	28
Discussion of Properties	36
Bond length-bond strength relationships	36
Magnetic and resistivity properties	40
 CONCLUSIONS	44

SECTION 2. SYNTHESIS AND CHARACTERIZATION OF $K_xM_yMo_{14}O_{22}$ (M=Sn,Pb,Sr): OLIGOMERS WITH THREE TRANS EDGE-SHARING Mo OCTAHEDRA	45
INTRODUCTION	46
EXPERIMENTAL	47
Materials and Methods	47
Physical Measurements	48
X-ray powder diffraction	48
Magnetic susceptibility	48
Scanning electron microscopy	49
Microprobe analysis	49
Electron spin resonance	49
Synthesis	50
X-ray Powder Diffraction	52
X-ray Single Crystal Data Collection	52
Structure Solution and Refinement	57
RESULTS AND DISCUSSION	74
Description of Structure	74
Discussion of Properties	92
Bond length-bond strength relationships	92
Magnetic properties	98
Electron spin resonance	101
CONCLUSIONS	103

SECTION 3. SYNTHESIS AND CHARACTERIZATION OF	
$K_{0.19}Ba_{3.81}Mo_{22}O_{34}$: AN OLIGOMER WITH FIVE	
TRANS EDGE-SHARING Mo OCTAHEDRA	104
INTRODUCTION	105
EXPERIMENTAL	106
Materials and Methods	106
Physical Measurements	107
X-ray powder diffraction	107
Magnetic susceptibility	107
Scanning electron microscopy	108
Microprobe analysis	108
Electron spin resonance	108
Synthesis	109
X-ray Powder Diffraction	110
X-ray Single Crystal Data Collection	112
Structure Solution and Refinement	113
RESULTS AND DISCUSSION	122
Description of Structure	122
Discussion of Properties	130
Bond length-bond strength relationships	130
Magnetic susceptibility	135
Electron spin resonance	135
CONCLUSIONS	138

SECTION 4. SYNTHESIS AND CHARACTERIZATION OF $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$: A MATERIAL CONTAINING CLOSEST-PACKING OF INFINITE CHAINS OF OCTAHEDRAL MOLYBDENUM CLUSTERS	139
INTRODUCTION	140
EXPERIMENTAL	141
Materials and Methods	141
Physical Measurements	142
X-ray powder diffraction	142
Magnetic susceptibility	142
Scanning electron microscopy	142
Transmission electron microscopy	142
Microprobe analysis	143
X-ray photoelectron spectroscopy	143
Synthesis	143
X-ray Powder Diffraction	145
X-ray Single Crystal Data Collection	146
Structure Solution and Refinement	146
RESULTS AND DISCUSSION	153
Description of Structure	153
Discussion of Properties	157
Bond length-bond strength relationships	157
X-ray photoelectron spectroscopy	160
Magnetic susceptibility	162
Cation size effect	166
Oxidation state summary	166
Other important synthetic relationships to $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$. .	168
CONCLUSIONS	170

SECTION 5. SYNTHESIS AND CHARACTERIZATION OF	
K _x M _{2-x} Mo ₁₀ O ₁₆ (M=Ca,Sr,Gd): OLIGOMERS	
WITH TWO TRANS EDGE-SHARING	
Mo OCTAHEDRA 172	
INTRODUCTION	173
EXPERIMENTAL	174
Materials and Methods	174
Physical Measurements	175
X-ray powder diffraction	175
Scanning electron microscopy	175
Microprobe analysis	175
Synthesis	176
X-ray Single Crystal Data Collection and Structure Refinement	178
RESULTS AND DISCUSSION	195
Description of the Structure	195
CONCLUSIONS	206
SECTION 6. SYNTHESIS AND CHARACTERIZATION OF	
THE RE ₄ Mo ₄ O ₁₁ SERIES: RE =	
Y,Nd,Sm,Eu,Gd,Tb,Dy,Ho,Er,Tm,Yb, & Lu 207	
INTRODUCTION	208
EXPERIMENTAL	209
Materials and Methods	209
Physical Measurements	209
X-ray powder diffraction	209
Magnetic susceptibility	210
Electrical resistivity	210
Scanning electron microscopy	211
Transmission electron microscopy	211

Synthesis	211
RESULTS AND DISCUSSION	214
Discussion of Properties	214
X-ray powder diffraction	214
Magnetic susceptibility	219
Electrical resistivity	220
CONCLUSIONS	224
SECTION 7. SYNTHESIS AND CHARACTERIZATION OF Pb_{0.31}WO₃: A TETRAGONAL TUNGSTEN BRONZE CONTAINING LEAD	225
INTRODUCTION	226
EXPERIMENTAL	227
Materials and Methods	227
Physical Measurements	227
X-ray powder diffraction	227
Magnetic susceptibility	228
Scanning electron microscopy	228
Transmission electron microscopy	229
Microprobe analysis	229
Synthesis	229
X-ray Powder Diffraction	230
X-ray Single Crystal Data Collection	233
Structure Solution and Refinement	233
RESULTS AND DISCUSSION	238
Description of Structure	238
Discussion of Properties	244
Bond length-bond strength relationships	244
Magnetic properties	244
CONCLUSIONS	247

SECTION 8. EXAMINATION OF THE SUPERSTRUCTURE IN $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$, $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, InMo_4O_6 AND $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ BY ELECTRON MICROSCOPY	248
INTRODUCTION	249
EXPERIMENTAL	250
Materials and Methods	250
Physical Measurements	250
X-ray powder diffraction	250
Transmission electron microscopy	250
Scanning electron microscopy	251
Synthesis	251
RESULTS AND DISCUSSION	253
$\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	254
$\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	267
$\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	278
InMo_4O_6	285
CONCLUSIONS	286
GENERAL SUMMARY	287
REFERENCES	291
ACKNOWLEDGEMENTS	295
APPENDIX A: MEASURED AND CALCULATED D-SPACINGS FOR THE $\text{RE}_4\text{Mo}_4\text{O}_{11}$ SERIES: RE = Y, Nd, Sm, Gd, Tb, Dy, Ho, Er, Tm, Yb, & Lu	297
APPENDIX B: MAGNETIC SUSCEPTIBILITY FIGURES FOR SELECTED $\text{RE}_4\text{Mo}_4\text{O}_{11}$ MEMBERS	311

LIST OF FIGURES

Figure 1.1.	SEM micrograph at 130X of transported $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ crystals on quartz tubing	15
Figure 1.2.	X-ray powder diffraction pattern of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ using $\text{Cu K}\alpha_1$ radiation	19
Figure 1.3.	An ORTEP drawing of the tetrameric cluster unit, $\text{Mo}_{18}\text{O}_{42}$, of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	29
Figure 1.4.	An ORTEP representation (70% thermal ellipsoids) of the tetrameric cluster unit emphasizing Mo-O intercluster connections in a stair-step manner	32
Figure 1.5.	An ORTEP drawing of the coordination environment surrounding bariums in $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	33
Figure 1.6.	A view down the c axis of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$, parallel to the Mo octahedral chains	35
Figure 1.7.	Molar and inverse molar susceptibility versus temperature of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	42
Figure 1.8.	Resistivity ratio of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ plotted versus temperature. The inset shows the nearly linear relationship between the natural logarithm vs $1/T$	43
Figure 2.1.	An ORTEP representation of the $\text{Mo}_{14}\text{O}_{34}$ cluster observed in $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	75
Figure 2.2.	An ORTEP representation of the $\text{Mo}_{14}\text{O}_{34}$ cluster observed in $\text{K}_{1.66}\text{Pb}_{1.34}\text{Mo}_{14}\text{O}_{22}$	76
Figure 2.3.	An ORTEP view perpendicular to the c axis of $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$ with fragments of neighboring clusters included to indicate the stair-step manner in which the oligomeric units interconnect	79

Figure 2.4.	An ORTEP view perpendicular to the c axis of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ with fragments of neighboring clusters included to indicate the stair-step manner in which the oligomeric units interconnect and the intercluster metal-metal bond.	80
Figure 2.5.	An ORTEP view (70% thermal ellipsoids) of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ nearly parallel to the c axis, indicating the manner in which the chains interconnect, thus creating pockets for the cations	82
Figure 2.6.	An ORTEP view (70% thermal ellipsoids) of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ nearly parallel to the c axis. One adjacent set of trimeric cluster units is included in the c direction to indicate the cation pocket	84
Figure 2.7.	Oxygen coordination around the potassium at the origin and the tin satellites located on either side of the origin in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$	86
Figure 2.8.	Cation coordination environment of the second major cation site, Sn2, and its satellite, K2A, in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$	87
Figure 2.9.	Oxygen coordination around the potassium/lead at the origin in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	90
Figure 2.10.	Oxygen coordination environment of the second cation site, Pb2/K2, in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	91
Figure 2.11.	Molar and inverse molar susceptibilities versus temperature for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$	99
Figure 2.12.	Molar and inverse molar susceptibilities versus temperature for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	100
Figure 2.13.	ESR spectrum for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ taken at 112 K	102
Figure 3.1.	An ORTEP drawing (70% thermal ellipsoids) of the n=5 metal oxide cluster unit in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ as they are found parallel to the c axis	123

Figure 3.2.	An ORTEP drawing (70% thermal ellipsoids) emphasizing the interconnection of the metal oxide cluster units in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	125
Figure 3.3.	An ORTEP drawing (70% thermal ellipsoids) of the coordination environment surrounding barium/potassiums in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	128
Figure 3.4.	An ORTEP drawing, viewed down the c axis, emphasizing the interconnected metal oxide cluster units found in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	129
Figure 3.5.	Molar susceptibility versus temperature of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	136
Figure 3.6.	ESR spectrum at 105 K for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	137
Figure 4.1.	An ORTEP drawing (70% thermal ellipsoids) of $Ti_{0.31}Fe_{1.69}Mo_4O_7$ as viewed parallel to the molybdenum-oxide infinite chains, b direction	154
Figure 4.2.	Fe 2p core x-ray photoelectron spectrum	161
Figure 4.3.	Molar and inverse molar susceptibility versus temperature of $Ti_{0.31}Fe_{1.69}Mo_4O_7$	163
Figure 4.4.	Nonlinear least squares fit of high temperature data of $Ti_{0.31}Fe_{1.69}Mo_4O_7$	164
Figure 4.5.	The oxidation state flexibility of titanium & iron in $Ti_{0.31}Fe_{1.69}Mo_4O_7$ at a fixed effective moment	165
Figure 5.1.	An ORTEP representation (70% thermal ellipsoids) of the basic building block found in $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$, as viewed perpendicular to the a axis	196
Figure 5.2.	An ORTEP representation (70% thermal ellipsoids) indicating the stair-step manner in which the bioctahedral units interconnect in $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	197

Figure 5.3.	An ORTEP representation indicating the manner in which the biotetrahedral units interconnect to form a cation pocket in $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	199
Figure 5.4.	An ORTEP representation indicating the cation coordination sphere in $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	200
Figure 6.1.	X-ray powder diffraction pattern of $Y_4Mo_4O_{11}$ from 8-80° two theta.	213
Figure 6.2.	Variation of the a axis lattice parameter as a function of rare earth for $RE_4Mo_4O_{11}$	215
Figure 6.3.	Variation of the b axis lattice parameter as a function of rare earth for $RE_4Mo_4O_{11}$	216
Figure 6.4.	Variation of the c axis lattice parameter as a function of rare earth for $RE_4Mo_4O_{11}$	217
Figure 6.5.	Variation of the unit cell volume as a function of rare earth for the $RE_4Mo_4O_{11}$ series	218
Figure 6.6.	Resistivity ratio of $Gd_4Mo_4O_{11}$ versus temperature. The inset shows the nearly linear relationship between the $\log(\rho/\rho_{295})$ versus $1/T$	221
Figure 6.7.	Resistivity ratio of $Y_4Mo_4O_{11}$ versus temperature. The inset shows the nearly linear relationship between the $\log(\rho/\rho_{295})$ versus $1/T$	222
Figure 7.1.	The ORTEP representation of the $Pb_{0.31}WO_3$ unit cell, as viewed parallel to the c axis	239
Figure 7.2.	An ORTEP drawing (70% thermal ellipsoids) of the Pb1 coordination environment by oxygen	240
Figure 7.3.	The ORTEP drawing (70% thermal ellipsoids) of the Pb2 coordination environment by oxygen	242
Figure 7.4.	The octahedral coordination of oxygen around (a) W1 and (b) W2, drawn with 70% thermal ellipsoids	243

Figure 7.5.	Molar susceptibility versus temperature for $\text{Pb}_{0.31}\text{WO}_3$	246
Figure 8.1.	a) Selected area diffraction pattern for the [100] and b) the [110] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. All observed reflections, for both patterns, were indexed for the subcell.	255
Figure 8.2.	a) Simulated SAD for the [100] and b) the [110] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	256
Figure 8.3.	a) Convergent beam electron diffraction pattern and b) selected area diffraction pattern for the [001] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	257
Figure 8.4.	Simulated SAD of the [001] for $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	258
Figure 8.5.	a) Selected area diffraction pattern for the [101] and b) the [011] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	259
Figure 8.6.	a) Simulation of the SAD for the [101] and b) the [011] in $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	260
Figure 8.7.	a) SAD for the [010] and b) its simulation for $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	261
Figure 8.8.	The unit cell of $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ is isostructural to $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	263
Figure 8.9.	Two layers of MO_6 indicating the Mo/Fe ordering in a superstructure of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	264
Figure 8.10.	Two layers of MO_6 indicating the Mo/Fe ordering in a superstructure of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	265
Figure 8.11.	Two layers of FeO_6 units in a superstructure of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$	266
Figure 8.12.	a) CBED of the [001] and b) SAD of the [001] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	268
Figure 8.13.	SAD simulation of the [001] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	269
Figure 8.14.	a) SAD of the [101] and b) the [110] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	270

Figure 8.15.	a) Simulation of the [101] and b) the [110] in $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	271
Figure 8.16.	a) SAD of another [110] and b) the [111] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	272
Figure 8.17.	SAD simulation of the [111] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$	274
Figure 8.18.	View parallel to the c axis of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, indicating the tunnels in which the tin cations reside	275
Figure 8.19.	a) Subcells, 2x2x2, of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ emphasizing the alternating {111} planes. b) The new supercell of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ showing the orthorhombic symmetry of the tin atoms in the supercell	277
Figure 8.20.	a) SAD of the [100] and b) [110] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	279
Figure 8.21.	a) Simulation of the [100] and b) the [110] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	280
Figure 8.22.	a) SAD of the [101] and b) [010] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	281
Figure 8.23.	a) Simulation of the [101] and b) the [010] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	282
Figure 8.24.	a) SAD of the [011] and b) the [111] of $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	283
Figure 8.25.	SAD simulation of a) the [011] and b) the [111] in $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$	284

LIST OF TABLES

Table 1.1.	X-ray powder diffraction data for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	17
Table 1.2.	X-ray crystallographic data for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	22
Table 1.3.	Atomic coordinates for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	23
Table 1.4.	Anisotropic temperature factors for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	24
Table 1.5.	Selected metal-metal interatomic distances (Å) for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	25
Table 1.6.	Selected metal-oxygen bond distances (Å) for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	26
Table 1.7.	Selected bond angles (degrees) for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	27
Table 1.8.	Bond length-bond strength relationships for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	38
Table 2.1.	X-ray powder diffraction data for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	53
Table 2.2.	X-ray powder diffraction data for $\text{K}_{2.6}\text{Sr}_{0.4}\text{Mo}_{14}\text{O}_{22}$	55
Table 2.3.	X-ray crystallographic data for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	60
Table 2.4.	Atomic coordinates for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	61
Table 2.5.	Anisotropic temperature factors for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	62
Table 2.6.	Selected interatomic distances (Å) for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	63
Table 2.7.	Selected bond angles (degrees) for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	65

Table 2.8.	X-ray crystallographic data for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	68
Table 2.9.	Atomic coordinates for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	69
Table 2.10.	Anisotropic temperature factors for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	70
Table 2.11.	Selected bond distances (Å) for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	71
Table 2.12.	Selected bond angles (degrees) for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	73
Table 2.13.	Bond distance-electron counting relationships in $M_xMo_{14}O_{22}$	77
Table 2.14.	Bond length-bond strength relationships for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$	94
Table 2.15.	Bond length-bond strength relationships for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$	96
Table 3.1.	X-ray powder diffraction data for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	111
Table 3.2.	X-ray crystallographic data for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	116
Table 3.3.	Atomic coordinates for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	117
Table 3.4.	Anisotropic temperature factors for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	118
Table 3.5.	Selected metal-metal interatomic distances (Å) for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	119
Table 3.6.	Selected metal-oxygen bond distances (Å) for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	120
Table 3.7.	Selected bond angles (degrees) for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	121
Table 3.8.	Intercluster bond distances and electron counts for selected oligomeric members of the series, $M_xMo_{4n+2}O_{6n+4}$	126

Table 3.9.	Bond length-bond strength relationships for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$	131
Table 4.1.	X-ray powder diffraction data for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	145
Table 4.2.	X-ray crystallographic data for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	149
Table 4.3.	Atomic coordinates for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	150
Table 4.4.	Anisotropic temperature factors for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	151
Table 4.5.	Selected bond distances (Å) for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	151
Table 4.6.	Selected bond angles (degrees) for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	152
Table 4.7.	Metal-metal bond distances for seven $M_2Mo_4O_7$ compounds	156
Table 4.8.	Bond length-bond strength relationships for $Ti_{0.31}Fe_{1.69}Mo_4O_7$	158
Table 4.9.	Unit cell parameters for all known $M_2Mo_4O_7$	167
Table 4.10.	Other reactions to prepare $Ti_{0.31}Fe_{1.69}Mo_4O_7$	168
Table 5.1.	X-ray powder diffraction data for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	177
Table 5.2.	X-ray crystallographic data for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	180
Table 5.3.	Atomic coordinates for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	181
Table 5.4.	Anisotropic temperature factors for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	182
Table 5.5.	Selected bond distances (Å) for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	183
Table 5.6.	Selected bond angles (degrees) for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	184

Table 5.7.	X-ray crystallographic data for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$	185
Table 5.8.	Atomic coordinates for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$	186
Table 5.9.	Anisotropic temperature factors for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$	187
Table 5.10.	Selected bond distances (Å) for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$	188
Table 5.11.	X-ray crystallographic data for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$	189
Table 5.12.	Atomic coordinates for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$	190
Table 5.13.	Anisotropic temperature factors for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$	191
Table 5.14.	Selected bond distances (Å) for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$	192
Table 5.15.	Selected bond angles (degrees) for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$	193
Table 5.16.	Supplementary crystallographic information for $K_xM_{2-x}Mo_{10}O_{16}$	194
Table 5.17.	Important metal-metal distances in the $M_2Mo_{10}O_{16}$ series	195
Table 5.18.	Bond length-bond strength relationships for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$	202
Table 5.19.	Bond length-bond strength relationships for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$	203
Table 5.20.	Bond length-bond strength relationships for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$	204
Table 5.21.	Bond length-bond strength summations for $M_2Mo_{10}O_{16}$	205
Table 6.1.	Lattice parameters for $RE_4Mo_4O_{11}$	214
Table 6.2.	Magnetic properties of the $RE_4Mo_4O_{11}$	220

Table 7.1.	X-ray powder diffraction data for $\text{Pb}_{0.31}\text{WO}_3$	231
Table 7.2.	X-ray crystallographic data for $\text{Pb}_{0.31}\text{WO}_3$	235
Table 7.3.	Atomic coordinates for $\text{Pb}_{0.31}\text{WO}_3$	236
Table 7.4.	Anisotropic temperature factors ($\text{\AA}^2 \times 10^3$) for $\text{Pb}_{0.31}\text{WO}_3$	236
Table 7.5.	Select interatomic distances ($\text{\AA}$) and angles (degrees) for $\text{Pb}_{0.31}\text{WO}_3$	237
Table 7.6.	Bond length-bond strength relationships for $\text{Pb}_{0.31}\text{WO}_3$	245

GENERAL INTRODUCTION

Since the discovery of the first ternary reduced molybdenum oxide containing trans edge-shared molybdenum octahedra, $\text{NaMo}_4\text{O}_6^1$, a variety of structure types with this basic building mode have been synthesized. This diversity is achieved by the manner in which the molybdenum octahedra are interconnected or the number of edge-shared octahedra that occur in a chain segment. There are essentially 8 classes of materials, to date, that exemplify the above variations.

One theme that generalizes all of these various classes of materials is the method in which the connectivity of the systems can be described. Schäfer and von Schnering² use "i" for inner and "a" for ausser to represent the manner in which ligands or atoms are bound to clusters. This method can also be applied to the reduced molybdenum-oxide systems. The following definitions will be used: O^i are oxygens that are edge-bridging only within a cluster, O^{i-i} are oxygens that are edge-sharing between neighboring clusters, O^{i-a} and O^{a-i} are edge-bridging oxygens of one cluster that are terminal to the neighboring cluster (or vice versa), and O^a designate oxygens that are only terminal to a given cluster.

Perhaps, the most explored class of ternary reduced molybdenum oxide phases, containing Mo octahedra, is the series of the parent member, $\text{M}_x\text{Mo}_4\text{O}_6$. This structure type consists of infinite chains of trans edge-shared molybdenum octahedra ($[\text{Mo}_4\text{O}_6]^{nX-}$) running parallel to the c axis. These chains are interconnected via bridging oxygens with $\text{M}_x^{nX+}[(\text{Mo}_2\text{Mo}_{4/2}\text{O}_{8/2}^{i-i}\text{O}_{2/2}^{i-a})\text{O}_{2/2}^{a-i}]^{nX-}$, where n=cation valence, describing the connectivity. This arrangement of molybdenum oxide chains creates infinite tunnels in which a variety of cations can reside. The following compounds are known: $\text{NaMo}_4\text{O}_6^1$, $\text{InMo}_4\text{O}_6^3$, $\text{Pb}_{0.77}\text{Mo}_4\text{O}_6^4$, $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6^5$, $\text{Ba}_{0.62}\text{Mo}_4\text{O}_6^6$, $\text{Sr}_{0.62}\text{Mo}_4\text{O}_6^7$, $\text{KMo}_4\text{O}_6^{7,8,9}$,

$\text{Li}_x\text{Mo}_4\text{O}_6$ and $\text{Rb}_x\text{Mo}_4\text{O}_6$ ¹⁰, $\text{Eu}_x\text{Mo}_4\text{O}_6$ ¹¹, and $\text{Cs}_x\text{Mo}_4\text{O}_6$ ¹²

The second class contains only one member, $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$.¹³ This phase also has infinite chains of trans edge-shared Mo octahedra, $[\text{Mo}_4\text{O}_{5.5}]$ ^{1,5-}. However, they are interconnected via three different types of Mo-O bonds. $\text{Mn}_{1.5}[(\text{Mo}_2\text{Mo}_{4/2}\text{O}_{6/2}^{\text{i-i}}\text{O}_{2/3}^{\text{i-a}}\text{O}_{2/2}^{\text{i-a}})\text{O}_{1/3}^{\text{a-i}}\text{O}_{1/2}^{\text{i-i}}]$ describes the connectivity of this compound. The interconnectivity of these molybdenum chains creates an infinite tunnel quite different from the first class. Here, the manganese are found in low symmetry sites, resulting in coordination numbers of four or five, although neither of the sites are fully occupied. X-ray diffraction data from single crystals and TEM indicate that a poorly understood superstructure does exist.

A third class of ternary or quaternary reduced molybdenum oxides can be given the general formula ${}^t\text{A}^o\text{A}_{1-x-y}{}^o\text{B}_x{}^o\text{Mo}_y\text{Mo}_4\text{O}_7$ where t and o superscripts denote tetrahedral and octahedral coordination sites. The infinite chains of molybdenum octahedra, $([\text{Mo}_4\text{O}_7]^\text{P})$, in this phase form layers which are bound together by O-A-O and O-B-O bonds. The connectivity of these phases can be written as $[\text{AB}]_4[(\text{Mo}_6\text{Mo}_{4/2}\text{O}_{12/2}^{\text{i-i}}\text{O}_4^{\text{i}})\text{O}_4^{\text{a}}]$. This formulation takes into account the pairwise bonding of the apical molybdenum atoms that causes a tilting of the octahedra and, thereby, doubles the repeat unit. This phase has been structurally characterized for $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$ and $\text{Ti}_{0.5}\text{Zn}_{1.5}\text{Mo}_4\text{O}_7$ ¹⁴ and $\text{Sc}_{0.5}\text{Fe}_{1.5}\text{Mo}_4\text{O}_7$, $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$, $\text{Al}_{0.5}\text{Zn}_{1.4}\text{Mo}_{4.1}\text{O}_7$, and $\text{Al}_{0.41}\text{Fe}_{1.51}\text{Mo}_{4.08}\text{O}_7$.¹⁵ $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ was discovered and characterized in the present work, and will be discussed in Section 4, with reference to the previously reported members of this series. Also, the superstructural ordering of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$, as observed by electron microscopy, will be discussed in Section 8.

Compounds with the formula $\text{MMo}_8\text{O}_{10}$ constitute a fourth class which contain infinite chains of edge-shared molybdenum octahedra. In this phase, orthogonal, nonintersecting chains of molybdenum octahedra run parallel to the a

and b axes. Crosslinking of these chains through Mo-O-Mo bonds results in a still different connectivity, written as $M[(Mo_6Mo_{4/2}O_2^iO_{8/2}^{i-i}O_{4/3}^{i-a}O_{2/2}^{i-a})O_{2/3}^{a-i}O_{2/2}^{a-i}]$. In this system, there are no large open tunnels, but, rather, tetrahedral cavities between the orthogonal chains where the cations contribute to interlinking of the molybdenum octahedra. Only two compounds with this structural composition have been isolated, $LiMo_8O_{10}$ and $ZnMo_8O_{10}$.¹⁷

If one dilutes a compound so that isolated infinite chains of trans edge-shared molybdenum octahedra are formed, one arrives at the fifth class, the $RE_4Mo_4O_{11}$ phase. In these compounds, there are no direct Mo-O-Mo linkages between chains; thus the following connectivity results: $[RE_8O_6]^{12+}[(Mo_6Mo_{4/2}O_8^iO_{8/2}^{i-i})O_4^a]^{12-}$. As written, these materials can be considered a ceramic coating of RE-oxide around wires of molybdenum octahedra. This system is stabilized by $M=Y$, Nd, and Sm-Lu.^{18,19} The synthesis and properties of these compounds will be discussed in Section 6.

The $M_xMo_{18}O_{32}$ system is unique because it is constructed from three kinds of infinite chains, and constitutes the sixth class. Single molybdenum atom chains, chains of infinite trans edge-shared rhomboidal clusters, and infinite chains of trans edge-shared molybdenum octahedra make up the three building blocks. $M_x(MoO_3)_2(Mo_2O_{3.5})_4(Mo_4O_6)_2$ describes these separate entities. All chains run parallel to the b axis and the cations reside in a distorted bicapped trigonal prismatic geometry of oxygens created by the connectivity of the three types of chains. The $M_xMo_{18}O_{32}$ phase can be formed by Y, Nd, Sm, Gd, Tb, Dy, and Er-Lu²⁰ where $x=4$ and by Ca where $x=5.45$.³

The seventh class contains Mo_8 units, that is, bicapped molybdenum octahedra, with the general formula MMo_8O_{14} . Each Mo_8 unit is connected to neighboring Mo_8 units via bridging oxygens, and this connectivity can be formulated as $M[(Mo_8O_6^iO_{6/2}^{i-a})O_{6/2}^{a-i}O_{6/3}^{a-a}]$. The cations are located within the cluster layers and are twelve coordinate in oxygen as tetracapped cubes. This

$\text{MMo}_8\text{O}_{14}$ phase has been isolated for Nd, Pr, Sm, Gd²¹, and La.²²

The eighth class is perhaps the largest and fastest growing area of ternary and quaternary reduced molybdenum oxides, compounds of the general formula $\text{M}_{n-x}\text{Mo}_{4n+2}\text{O}_{6n+4}$, where n equals the number of trans edge-sharing molybdenum octahedra. This formula represents a system where the infinite chains may be viewed as having been "cut" into discrete oligomeric cluster units. The first compound in this series, $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ ²³, was discovered in 1986; this phase actually contains a 1:1 ratio of $n=4$ and 5 molybdenum octahedra. To date, it is the only reported member with mixed oligomers. Since 1986, a large effort has been put into synthetic work that involves "cutting" the infinite chains of molybdenum octahedra into varying lengths (different values of n) and studying their properties.

The first oligomer reported with $n=1$ was $\text{BaMo}_6\text{O}_{10}$.²⁴ This orthorhombic compound has molybdenum octahedra arranged in a zig-zag fashion, thereby, allowing strong Mo-Mo bonding between basal molybdenums of one octahedron and apical molybdenums of adjacent octahedra. This material can be formulated as $\text{Ba}^{2+}[(\text{Mo}_6\text{O}_2^{\text{i}}\text{O}_{4/2}^{\text{i-i}}\text{O}_{6/2}^{\text{i-a}})\text{O}_{6/2}^{\text{a-i}}]^{2-}$. The cation resides in a pocket created by the zig-zag molybdenum oxide framework. The crystalline powder phase of $\text{PbMo}_6\text{O}_{10}$ is the only other known oligomer with $n=1$.⁷

The first reported material containing bioctahedra of molybdenum, $\text{La}_2\text{Mo}_{10}\text{O}_{16}$, was discussed in 1988²⁵, although the calcium end member was alluded to in 1981.⁴ The lanthanum member was structurally analyzed by Rietveld techniques. Subsequently, single crystal work was obtained for the ternary metals: Pb²⁶, Sn²⁷, Gd^{28a}, Ba⁷, and Ca, Sr, La, Ce, Pr, Nd, Sm, and Eu.²⁹ The bioctahedra interconnect in a stair-step fashion, resulting in monoclinic symmetry, and are characterized by a strong intercluster Mo-Mo bond and two apical-apical molybdenum bonds. This interconnectivity can be formulated as $[\text{M}_2]^{x+}[(\text{Mo}_{10}\text{O}_6^{\text{i}}\text{O}_{4/2}^{\text{i-i}}\text{O}_{8/2}^{\text{i-a}})\text{O}_{8/2}^{\text{a-i}}]^{x-}$. Again, the cations reside in the pockets formed

by the molybdenum oxide framework. The synthesis and characterization of the first four quaternary $(\text{Mo}_{10}\text{O}_{16})^{x-}$ clusters, $\text{K}_{0.33}\text{Gd}_{1.67}\text{Mo}_{10}\text{O}_{16}$, $\text{K}_{0.06}\text{Ca}_{1.94}\text{Mo}_{10}\text{O}_{16}$, $\text{K}_{0.06}\text{Sr}_{1.94}\text{Mo}_{10}\text{O}_{16}$, and $\text{BaSrMo}_{10}\text{O}_{16}$, will be briefly compared and contrasted in light of the known ternary members in Section 5.

A derivative structure of the $\text{M}_2\text{Mo}_{10}\text{O}_{16}$ series has recently been reported by Gougeon.^{28b} $\text{Ce}_{16}\text{Mo}_{21}\text{O}_{56}$ consists of two crystallographically unique Mo_{10} bioctahedra with the typical complement of oxygens bridging edges and capping apical molybdenum atoms of the octahedra. Both pair of octahedra still have the typical short apical-apical molybdenum bond. However, all of these metal-metal bonded units are isolated. The voids between the bioctahedral units are filled with isolated Mo atoms octahedrally surrounded by oxygen and cerium cations in a variety of coordination sites. This is the first oligomeric member found as isolated units.

The first oligomer with $n=3$, $\text{Ti}_{1.6}\text{Sn}_{1.2}\text{Mo}_{14}\text{O}_{22}$, was reported in 1989^{26a} and then a more detailed study was given in 1991.³⁰ The trimers (three edge-shared Mo octahedra) in this compound are isolated, i.e. there is no intercluster Mo-Mo bonding, and the apical-apical molybdenum distances appear to be dependent upon the number of electrons available for metal-metal bonding. These systems have been found to be monoclinic, owing to their stair-step interconnections. The connectivity in this system can be written $[\text{M}_{3-x}]^{y+} [(\text{Mo}_{14}\text{O}_{10}^i\text{O}_{4/2}^{i-i}\text{O}_{10/2}^{i-a})\text{O}_{10/2}^{a-i}]^{y-}$. This Ti-Sn member is the first example of a nonstoichiometric oligomer, with respect to the cation, and indicates the ability of the molybdenum cluster to accept a variety of electron counts. Four other trimers have been synthesized and characterized in this group, $\text{K}_3\text{Mo}_{14}\text{O}_{22}$ by Chen⁷ and $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$, $\text{K}_{0.76}\text{Pb}_{1.53}\text{Mo}_{14}\text{O}_{22}$, and $\text{K}_{2.6}\text{Sr}_{0.4}\text{Mo}_{14}\text{O}_{22}$ which will be discussed in Section 2.

The tetrameric oligomer, $n=4$, had not been reported as a single phase constituent until the discovery of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ ¹⁶, discussed here in Section 1. The Mo_{18} unit is similar to the related cluster found in $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ ²³, with four

of the possible six apical-apical molybdenum interactions found as strong metal-metal bonds and no intercluster bonding. The tetramers are arranged in a stair-step fashion and have monoclinic symmetry. The general formulation for this oligomer is $\text{Ba}_3^{6+}[(\text{Mo}_{18}\text{O}_{14}^{\text{i}}\text{O}_{4/2}^{\text{i-i}}\text{O}_{12/2}^{\text{i-a}})\text{O}_{12/2}^{\text{a-i}}]^{6-}$.

$\text{In}_6\text{Mo}_{22}\text{O}_{34}$ has been characterized by X-ray crystallography and received a brief mention in 1986.³¹ It is the pentameric oligomer with a zig-zag arrangement of $(\text{Mo}_6)_5$ units that crystallizes with orthorhombic symmetry. The general formula, $\text{M}_{5-x}\text{Mo}_{22}\text{O}_{34}$ can be written to indicate its connectivity in the following manner: $[\text{M}_{5-x}]^{y+}[(\text{Mo}_{22}\text{O}_{18}^{\text{i}}\text{O}_{4/2}^{\text{i-i}}\text{O}_{14/2}^{\text{i-a}})\text{O}_{14/2}^{\text{a-i}}]^{y-}$. The barium end member, $\text{Ba}_{5-x}\text{Mo}_{22}\text{O}_{34}$ briefly discussed in Section 3, is isostructural to the $\text{In}_6\text{Mo}_{22}\text{O}_{34}$. However, another arrangement, with a stair-step organization of the $(\text{Mo}_6)_5$ units has been identified for $\text{Ba}_{4.2}\text{Mo}_{22}\text{O}_{34}$ and $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$.³² These members will also be discussed in Section 3.

At this time, no larger oligomers of molybdenum octahedra have been definitively isolated, although HREM has verified their presence in the In-Mo-O system.³¹

Explanation of Dissertation Format

This dissertation consists of eight sections. A General Introduction and a General Summary prelude and follow the main text, respectively. All references are given after the General Summary.

SECTION 1**SYNTHESIS AND CHARACTERIZATION OF $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$:
AN OLIGOMER WITH FOUR TRANS EDGE-SHARING Mo OCTAHEDRA**

INTRODUCTION

The discovery of NaMo_4O_6 ¹ opened up a new field in ternary reduced molybdenum oxide chemistry, materials with infinite chains of trans edge-shared molybdenum octahedra. One of the goals of the research in this laboratory since then has been to "cut" the infinite chains into segments, in order to form new compounds, and thereby determine how the properties of these new materials differ from the $\text{M}_x\text{Mo}_4\text{O}_6$ phases. These oligomeric compounds can be derived from the general formulation, $\text{M}_{n-x}\text{Mo}_{4n+2}\text{O}_{6n+4}$, where n is equal to the number of edge-sharing molybdenum octahedra. The first such reported compound, $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ ²³, contained a one to one ratio of Mo_{18} (four edge-sharing octahedra) and Mo_{22} (five edge-sharing octahedra). High resolution electron microscopy on the products from the indium-containing oligomers indicated that fragments with four, five, and six membered chains were possible, and that they did not necessarily grow in an ordered manner. This observation indicates, to some extent, the small differences in thermodynamic stability that must occur among these oligomers. With this insight, the difficulty in synthesizing pure oligomers with only one type of cluster fragment can be appreciated. In this section the synthesis, structure, and physical properties of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$, the first pure n=4 oligomeric compound, will be discussed. The structural aspects of this new oligomer will be compared to the Mo_{18} cluster found in $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated ($\sim 1 \times 10^{-4}$ torr) vessels made of fused silica. All reactants were thoroughly ground to produce an intimate mixture before being used as loose powders or pressed pellets. Mixed starting materials were subsequently stored in a desiccator.

The starting reagents included BaMoO_4 , MoO_2 , and Mo. Barium molybdate was prepared by mixing an aqueous solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Baker Analyzed Reagent, 99.6%) with an aqueous solution containing a stoichiometric quantity of sodium molybdate dihydrate (Fisher Certified). The white precipitate was filtered, washed with copious amounts of distilled water, and then dried overnight at 130°C under dynamic vacuum. During the initial grinding, streaks of white material were found within the black chunks of molybdenum dioxide (Alfa, 99%). Based upon the Guinier powder diffraction pattern, this white material was identified as molybdenum trioxide. Molybdenum analyses indicated that the real composition was $\text{MoO}_{2.18(1)}$. Approximately ten grams of the starting " MoO_2 " was ground into a fine powder and cleaned by successive washings with 3M NH_4OH , distilled H_2O , and 3M HCl . This cycle was repeated three times and finally the solid was rinsed with distilled water and then acetone. The clean molybdenum dioxide was air dried and then dried *in vacuo* at 150°C overnight. Molybdenum analyses indicated the final material could be formulated as $\text{MoO}_{1.99(1)}$. Molybdenum powder (Aldrich, 99.99%) was dried under dynamic vacuum at 120°C overnight. All reagents were stored in a desiccator.

Physical Measurements

Molybdenum analysis

Molybdenum analyses were performed on the starting MoO_2 reagent. Approximately 250 mg samples of " MoO_2 " were loaded into tared crucibles. The samples were fired in a muffle furnace at 520°C for eight hours to convert all the material to molybdenum trioxide. Then the samples were cooled in a desiccator and brought to constant weight by subsequent firing and cooling cycles.

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540562\text{\AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard. Some samples were also analyzed with a Scintag 2000 powder θ - θ diffractometer using $\text{Cu K}\alpha_1$ radiation. For the Scintag, the sample was pressed into a recessed region of a single crystal quartz plate.³²

Magnetic susceptibility

The magnetic properties were examined on samples of selected crystals with a Quantum Design SQUID magnetosusceptometer. The samples were loaded into a 3mm inner diameter quartz tube that had been sealed on the bottom half with 3mm outer diameter quartz rod. A quartz rod also was placed in the top half of the loaded sample tube which then was mounted in an apparatus that allowed evacuation of the sample tube and purging with helium gas. To eliminate water, the system was heated to 120°C for an hour under dynamic vacuum. After cooling, the system was pumped and purged with helium three more times. The upper quartz rod was pushed into place under a partial pressure of helium (to facilitate temperature equilibration during measurements), sandwiching the

sample between "solid" quartz, and sealed off. This procedure was used to eliminate oxygen contamination, which has an antiferromagnetic transition at ~50 K. The experimental data were corrected for the diamagnetic contribution from the quartz. Measurements on empty quartz tube/rod assemblies, with varying gap sizes, indicated that the diamagnetic contribution from the quartz was related to the size of the gap. Since the signal versus gap size could be fit by a line, the correction was simply employed by measuring the length of the gap containing the sample.

Electrical resistivity

Electrical resistivity measurements were carried out on a pressed pellet (8800 psi) that had been sintered in an evacuated fused silica ampoule at 1230°C for twelve hours. This measurement was based on the van der Pauw³⁴ four probe method for electrical conductivity. The basic method employs passage of a constant current through two leads of the sample while concurrently measuring the potential drop across the other two leads at a given temperature. Platinum wire leads were used and attached to the sample pellet via Epo-Tech silver epoxy resin.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Powdered samples and/or crystals were loaded on a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Transmission electron microscopy

A Philips CM30 transmission electron microscope was used to determine the presence or absence of any superstructure ordering. An approximate one to one

mixture of microcrystalline sample and G-1 Epoxy from Gatan was placed between lens paper, pressed between aluminum plates, and cured at 120°C for ten minutes. A three millimeter disk was punched out, thinned to ~20 µm by dimpling, put on a 200 mesh copper grid for support, and subsequently ion milled until a hole was observed. The sample and supporting grid assembly were subsequently loaded into the TEM sample holder for investigation.

Microprobe analysis

Elemental analyses were completed by Dr. Alfred Kracher (Department of Geological and Atmospheric Sciences) on an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers (WDS) and operated at 15 kV and 25 nA. Samples were mounted in Epo-Tek 301-2 epoxy resin, dried, and polished to produce a flat surface. Prior to examination, the samples were sputtered with carbon to insure conductivity. Peak profiles and backgrounds were measured for the standards, which included BaSO₄ and Mo metal. Data were analyzed using Probe³⁵ software.

Synthesis

The tetrameric oligomer was first discovered as black, chunk-like crystals in a multiphase product obtained from a reaction prepared and fired by Dr. Dick Nagaki. This initial reaction was prepared to form the quaternary dimeric oligomer, LaBaMo₁₂O₂₀, from stoichiometric quantities of La₂O₃, BaMoO₄, MoO₂, and Mo. The reagents were thoroughly ground and loaded into a fused silica tube with approximately forty weight percent BaCl₂ added as a potential flux (melting point = 963°C). The crystals of the tetrameric phase came from the reaction fired at 1230°C for one week.

An x-ray single crystal diffraction data set was collected at 24°C on a crystal with a Rigaku AFC6R diffractometer. The unit cell indexed as monoclinic with $a=9.939(2)\text{\AA}$, $b=9.354(3)\text{\AA}$, $c=13.058(1)\text{\AA}$, $\beta=100.945(9)^\circ$ and met the conditions for the space group $P2_1/a$ (#14). All atomic positions for molybdenum, oxygen, and cations were determined, thermal parameters varied, and occupancies checked, but the structure would not refine below $R=8.5\%$. Perhaps this crystal was twinned. Most bond distances had large standard deviations, thermal parameters were irregular, and the difference between La and Ba, and their population, could not be discerned. Many other crystals from the same reaction were indexed, but most were badly twinned. Further synthetic work, to grow better quality crystals, was undertaken.

SEM EDS on some of the crystals from Nagaki's reaction indicated that lanthanum, chlorine, or silicon were not present. Subsequent reactions to prepare $\text{Ba}_4\text{Mo}_{18}\text{O}_{28}$ stoichiometrically from BaMoO_4 , MoO_2 , and Mo in fused silica tubes at 1230°C for four to twenty-five days resulted in microcrystalline black powders that contained MoO_2 and the tetrameric oligomer, based on the Guinier powder diffraction patterns. Excess barium molybdate was added and fired under the same conditions as given above; no improvement was found. Thus BaCl_2 was deemed an essential ingredient necessary for the growth of larger crystals. Using the above stoichiometry, reactions with trace to 50 wt% anhydrous BaCl_2 were fired in fused silica tubes at 1230-1250°C for four to ten days. Generally, a larger quantity of BaCl_2 resulted in more, although badly twinned, crystals that were transported to the opposite end of the fused silica tube. Subsequently, it was determined that the BaCl_2 was not the necessary component, but rather, the presence of trace amounts of water, in the form of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. To ascertain that water was the transport agent, the same reaction with NH_4Cl , instead of BaCl_2 , was run. In this case, the transported product was MoO_2 , thus eliminating the possibility of HCl as the transport agent for the tetrameric oligomer.

Reactions to prepare $\text{Ba}_4\text{Mo}_{18}\text{O}_{28}$ from stoichiometric quantities of BaMoO_4 , MoO_2 , and Mo with 1.5 mg of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were fired in fused silica tubes at 1230°C for 5-15 days. One and a half milligrams of barium chloride dihydrate created a total vapor pressure of nearly one atmosphere at this firing temperature. All reactions resulted in the growth of numerous, large, chunk-like crystals on the far end of the tube, as viewed in Figure 1.1. A subsequent single crystal refinement was explored on a fragment of a crystal taken from a reaction run at 1230°C for 8.5 days in fused silica. This refinement indicated that the cation occupancy was only 75% of the possible cation sites. But again, the refinement was hindered by possible twinning and resulted in $R=6.0\%$.

Finally, better single crystals of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ were synthesized by loading a loose powder containing an intimate mixture in a 3:8:7 mole ratio of BaMoO_4 , MoO_2 , and Mo, with 1.5 mg of $\text{BaCl}_2 \cdot \text{H}_2\text{O}$ into a fused silica tube (4-6 cm in length). The evacuated, fused silica ampoule was fired at 1230°C for 15 days. All reactions were cooled at $-20^\circ\text{C}/20$ minutes to 1150°C , $-50^\circ\text{C}/20$ minutes to 800°C and then quenched to room temperature. In this case, the crystals were not only transported, but were also found dispersed in the loose, black bulk powder. Good single phase material of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$, based upon the Guinier powder diffraction patterns, could be prepared in fused silica vessels by omitting the dihydrate salt, firing the mixture at 1230°C for 8.5 days, and using the above cooling schedule. Good single phase material was only obtained when transport was eliminated. Precautions were taken to eliminate water and thus discourage transport. This was accomplished by firing unsealed, but evacuated, reagents at 200°C for one hour under dynamic vacuum.

Figure 1.1. SEM micrograph at 130X of transported $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. The small fragments on the crystal surfaces are quartz.

X-ray Powder Diffraction

The observed versus calculated d-spacings and relative intensities are given in Table 1.1 for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. The calculated d-spacings were derived from the lattice parameters determined by single crystal indexing. Figure 1.2 illustrates the observed diffraction pattern for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. All d-spacings are based on $\text{Cu K}\alpha_1$ radiation.

X-ray Single Crystal Data Collection

A large, black, chunk-like crystal with good faces was indexed and found to be twinned. The crystal was broken and a fragment having the dimensions $0.04 \times 0.07 \times 0.1 \text{ mm}^3$ was remounted on a glass fiber with Devcon five minute epoxy resin. A Rigaku AFC6R rotating anode diffractometer, equipped with graphite monochromated $\text{Mo K}\alpha$ radiation ($\lambda=0.71069\text{\AA}$) generated at 7 kW, was used. Lattice parameters and an orientation matrix for data collection were derived from 25 randomly located and centered reflections with a two theta range of $13\text{--}19^\circ$. The lattice was determined to belong to the monoclinic system with cell dimensions: $a=9.936(2)\text{\AA}$, $b=9.371(2)\text{\AA}$, $c=13.061(3)\text{\AA}$, $\beta=100.93(2)^\circ$, and volume= $1194.0(5)\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. A refinement on 19 reflections with strong intensity and two theta values near 40° gave an idealized cell with the following lattice parameters: $a=9.939(2)\text{\AA}$, $b=9.377(2)\text{\AA}$, $c=13.057(2)\text{\AA}$, $\beta=100.92(1)^\circ$, and volume= $1194.7(3)\text{\AA}^3$. Data were collected at room temperature from 0 to 50° in two theta in the hemisphere $(\pm h, k, \pm l)$, using an ω - 2θ scan mode. The number of reflections measured was 4587, of which 2599 were observed and 1284 were unique with $I > 3\sigma(I)$. The linear absorption coefficient for $\text{Mo K}\alpha$ was 138.45 cm^{-1} . An

Table 1.1. X-ray powder diffraction data for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
6.771	6.761	s	$\overline{110}$
6.440	6.410	w(sh)	$\overline{002}$
5.683	5.681	vw	$\overline{111}$
4.888	4.880	w	$\overline{200}$
4.672	4.688	m	$\overline{020}$
4.221	4.226	w	$\overline{120}$
3.672	3.669	vw	$\overline{122}$
3.562	3.567	vw	$\overline{203}$
3.379	3.381	w	$\overline{220}$ & $\overline{221}$
3.336	3.337	w	$\overline{212}$
3.307	3.306	vw	$\overline{301}$
3.114	3.118	s	$\overline{311}$
3.056	3.056	vw(sh)	$\overline{114}$
2.971	2.977	s	$\overline{130}$
2.815	2.814	vw	$\overline{213}$
2.699	2.702	m	$\overline{302}$ & $\overline{321}$
2.676	2.673	vw	$\overline{320}$
2.663	2.661	vw	$\overline{124}$
2.520	2.511	vw	$\overline{133}$
2.482	2.485	m	$\overline{401}$
2.399	2.402	s	$\overline{411}$
2.339	2.344	m	$\overline{040}$
2.301	2.300	m-w	$\overline{115}$
2.282	2.279	vw(sh)	$\overline{140}$
2.192	2.195	s	$\overline{421}$
2.171	2.172	vw	$\overline{331}$
2.135	2.137	vw	$\overline{006}$

^aIntensity: s=strong, m=medium, w=weak, v=very, and sh=shoulder

^bRefined monoclinic cell parameters obtained from single crystal measurements:
 $a=9.939(2)\text{Å}$, $b=9.377(2)\text{Å}$, $c=13.057(2)\text{Å}$, and $\beta=100.92(1)^\circ$

Table 1.1. (continued)

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
2.116	2.117	w	$\overline{125}$
2.106	2.111	w	$\overline{333}$
1.942	1.939	s	$\overline{234}$, $\overline{235}$, & $\overline{511}$
1.839	1.842	m	$\overline{150}$
1.827	1.829	m(sh)	$\overline{521}$
1.815	1.815	vw	$\overline{335}$
1.802	1.802	vw	$\overline{520}$
1.793	1.794	vw	$\overline{514}$
1.703	1.705	m	$\overline{441}$
1.581	1.581	w(sh)	$\overline{237}$
1.495	1.494	m	$\overline{254}$
1.434	1.433	m	$\overline{603}$
1.369	1.369	vw	$\overline{626}$
1.355	1.355	vw	$\overline{543}$
1.321	1.322	w	$\overline{724}$
1.240	1.240	w	$\overline{652}$, $\overline{651}$, & $\overline{634}$
1.227	1.227	w	$\overline{707}$
1.223	1.222	m	$\overline{643}$
1.170	1.171	m-w	$\overline{644}$
1.154	1.154	m-w	$\overline{626}$
1.097	1.097	w	$\overline{912}$
1.074	1.075	vw	$\overline{804}$ & $\overline{905}$
1.060	1.060	vw	$\overline{756}$
1.050	1.050	vw	$\overline{658}$
1.035	1.036	vw	$\overline{852}$
1.033	1.033	vw	$\overline{764}$
0.993	0.993	vw	$\overline{638}$
0.970	0.970	vw	$\overline{861}$, $\overline{737}$, & $\overline{863}$
0.960	0.960	vw	$\overline{857}$ & $\overline{718}$
0.959	0.959	vw	$\overline{578}$

Figure 1.2. X-ray powder diffraction pattern of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ using $\text{Cu K}\alpha_1$ radiation

empirical absorption correction³⁶ was applied based upon azimuthal scans of 3 reflections with an average transmission range of 0.763-1.000. The intensity data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The space group $P2_1/a$ (#14) was chosen based upon the systematic absences of $h0l$: $h \neq 2n$ and $0k0$: $k \neq 2n$, with violations for (100), (010), and $(\bar{5}06)$, all of which were located near intense reflections. The $(30\bar{3})$ was also in violation of the $h0l$: $h \neq 2n$ condition for the space group $P2_1/a$, however this reflection could be eliminated because the $(60\bar{6})$ was very intense. This violation most likely arises from $\lambda/2$ radiation. The structure was solved by direct methods using SHELXS³⁷ ($R=0.049$) and refined on $|F|$ by full matrix least squares techniques³⁸ with the TEXSAN³⁹ package. Since all atomic positions had been determined in previous refinements (as mentioned under Synthesis), positional parameters were entered and allowed to vary. The previous refinements also indicated that one of the cation sites was disordered about the special position at the origin. Therefore, this initial refinement allowed the barium to move positionally and have an occupancy of 50% on each of two sites located near the origin. These parameters converged at $R=11\%$. Refinement of the isotropic thermal parameters decreased R to 8.0%. Allowing the thermal parameters of the heavy atoms and those oxygens that would not go negative to refine anisotropically gave $R=5.5\%$. The barium occupancy and thermal parameters were varied simultaneously for both cations. Ba1 did not vary from full occupancy and was therefore fixed at that value. The final refined occupancy of Ba2 was 99.8(2)%. A secondary extinction correction was applied and refined to $3.6(2) \times 10^{-7}$. All molybdenum, barium, and 4 of 14 oxygen atom thermal parameters were refined anisotropically. The temperature factors for the

remaining ten oxygen atoms would only refine isotropically, with O12 having an unusually small thermal parameter. The refinement converged at $R=0.0427$ and $R_w=0.0509$ with a final electron difference map indicating the largest peak of $5.2 \text{ e}/\text{\AA}^3$ located at the center of the octahedra found at either end of the $n=4$ fragment and the smallest peak of $-1.6 \text{ e}/\text{\AA}^3$ located $0.7\text{\AA}$ from Mo5. Given the relatively large quantity of electron density remaining, the central position was refined as an oxygen (all distances were acceptable Mo-O bond lengths) with varying degrees of population. All refinements with this extra atom diverged. This residual electron density and the behavior of the thermal parameters of the oxygen atoms might be the result of the data to parameter ratio (7:1) and/or a poor absorption correction.

Details of the data collection and refinement for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ are given in Table 1.2. Final positional parameters and isotropic temperature parameters are given in Table 1.3. Anisotropic temperature factors are listed in Table 1.4. Selected metal-metal interatomic distances, metal-oxygen bond distances, and bond angles are found in Tables 1.5, 1.6, and 1.7, respectively.

Table 1.2. X-ray crystallographic data for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$

formula	$\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$
formula weight	2586.89
crystal system	monoclinic
space group	$P2_1/a$ (#14)
a, Å	9.939(2)
b, Å	9.377(2)
c, Å	13.057(2)
β , degrees	100.92(1)
volume, Å ³	1194.7(3)
Z	2
calculated density, g/cm ³	7.190
F000	2296
crystal size, mm ³	0.04 x 0.07 x 0.10
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	138.450
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.71069
temperature, °C	24
two theta range, degrees	0-50
scan mode	ω -2 θ
No. reflections collected	4587
No. observations ($I > 3\sigma(I)$), (unique)	2599 (1284)
No. variables	182
goodness of fit ^a	1.59
max. shift in final cycle	0.006
largest peaks in final diff. map, e/Å ³	+5.2, -1.6
transmission coefficient	0.763-1.000
R^b , R_w^c	0.0427, 0.0509

$$^a \text{Quality of fit} = [\sum \omega (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^c R_w = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}; \omega = 1/\sigma^2(|F_o|)$$

Table 1.3. Atomic coordinates for Ba₃Mo₁₈O₂₈

Atom ^a	X	Y	Z	B _{eq} ^b
Ba1	0.5747(1)	0.5079(2)	0.3434(1)	1.09(5)
Ba2 ^c	0.5162(3)	0.4989(3)	0.0627(2)	0.7(1)
Mo1	0.4165(2)	0.1103(2)	0.9989(1)	0.31(6)
Mo2	0.4648(2)	0.1204(2)	0.2151(1)	0.35(6)
Mo3	0.3559(2)	0.1179(2)	0.7823(1)	0.29(6)
Mo4	0.6248(2)	0.1276(2)	0.8783(1)	0.29(6)
Mo5	0.5726(2)	0.1222(2)	0.6756(1)	0.36(7)
Mo6	0.6847(2)	0.1307(2)	0.1211(1)	0.28(6)
Mo7	0.7360(2)	0.1319(2)	0.3229(1)	0.36(6)
Mo8	0.5320(2)	0.1261(2)	0.4270(1)	0.38(6)
Mo9	0.3032(2)	0.1135(2)	0.5710(1)	0.38(7)
O1	0.578(1)	0.249(1)	0.999(1)	0.4(2)
O2	0.753(1)	0.753(1)	0.334(1)	0.6(3)
O3	0.687(1)	0.258(1)	0.443(1)	0.6(3)
O4	0.490(1)	0.735(2)	0.224(1)	0.7(6)
O5	0.411(2)	0.247(2)	0.330(1)	0.7(3)
O6	0.620(1)	0.269(2)	0.220(1)	0.7(6)
O7	0.247(1)	0.482(1)	0.000(1)	0.3(2)
O8	0.352(1)	0.242(2)	0.109(1)	0.7(3)
O9	0.648(1)	0.508(2)	0.560(1)	0.8(5)
O10	0.317(1)	0.498(2)	0.221(1)	0.8(5)
O11	0.793(1)	0.504(2)	0.221(1)	0.5(2)
O12	0.298(1)	0.242(1)	0.888(1)	0.1(2)
O13	0.370(1)	0.996(2)	0.449(1)	0.3(5)
O14	0.536(1)	0.767(1)	0.450(1)	0.4(2)

^aAll atoms reside on the Wyckoff position 4e

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3 \sum_i \sum_j (U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j)$, where the summations of i and j range from 1 to 3

^cBa2 is split off the special position (2a) 1/2,1/2,0; each of the two positions with an occupancy of 49.9(1)%

Table 1.4. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1	8.5(7)	7.2(6)	24.9(8)	-0.1(6)	1.6(5)	3.3(6)
Ba2	8.(1)	6.(1)	14.(1)	2.(1)	2.(1)	1.(1)
Mo1	4.7(9)	3.3(9)	3.9(9)	-0.1(8)	1.5(7)	-0.9(7)
Mo2	4.8(9)	4.4(8)	4.(1)	0.4(8)	1.6(7)	-0.1(7)
Mo3	3.8(9)	4.0(8)	3.1(9)	-0.3(8)	0.2(7)	-0.3(7)
Mo4	3.6(9)	4.2(8)	3.3(9)	0.5(8)	1.0(7)	-0.7(8)
Mo5	6.(1)	4.0(9)	4.(1)	-1.4(8)	0.9(7)	0.6(7)
Mo6	5.0(9)	3.4(8)	2.2(9)	-0.4(8)	1.0(7)	-0.3(7)
Mo7	6.5(9)	2.9(8)	5.(1)	-0.0(8)	1.5(7)	-0.3(7)
Mo8	5.(1)	5.5(9)	4.(1)	-0.2(8)	0.0(7)	-0.1(7)
Mo9	5.8(9)	4.(1)	5.(1)	2.0(8)	1.9(7)	0.6(7)
O1	5.(3)					
O2	7.(3)					
O3	8.(3)					
O4	1.(8)	17.(8)	9.(8)	0.(7)	-1.(6)	-8.(7)
O5	9.(3)					
O6	13.(9)	7.(7)	7.(8)	5.(6)	6.(6)	1.(6)
O7	3.(3)					
O8	8.(3)					
O9	11.(7)	13.(8)	6.(7)	5.(7)	2.(6)	-2.(7)
O10	12.(7)	5.(7)	13.(8)	-6.(7)	2.(6)	-5.(7)
O11	6.(3)					
O12	2.(3)					
O13	3.(7)	4.(6)	4.(7)	1.(7)	-2.(5)	1.(6)
O14	5.(3)					

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$

^bThermal parameters for oxygens O1, O2, O3, O5, O7, O8, O11, O12, and O14 only refined isotropically

Table 1.5. Selected metal-metal interatomic distances (Å) for Ba₃Mo₁₈O₂₈^a

Mo1-Mo1'	2.650(4)	Mo1-Mo2	2.775(3)
Mo1-Mo3'	2.778(3)	Mo1-Mo4	2.833(3)
Mo1'-Mo4	2.822(3)	Mo1-Mo6	2.842(3)
Mo1'-Mo6	2.824(3)	Mo2-Mo3	2.854(3)
Mo2-Mo4	2.697(3)	Mo2-Mo5	2.747(3)
Mo2-Mo6	2.704(3)	Mo2-Mo7	2.796(3)
Mo2-Mo8	2.720(3)	Mo3-Mo4	2.730(3)
Mo3-Mo5	2.778(2)	Mo3-Mo6	2.716(3)
Mo3-Mo7	2.780(3)	Mo3-Mo9	2.710(3)
Mo4-Mo5	2.599(3) apical ^b	Mo4-Mo6'	3.113(2) apical
Mo5-Mo8	2.786(3)	Mo5-Mo8'	3.195(3) inter ^c
Mo5-Mo9	2.767(3)	Mo6-Mo7	2.587(3) apical
Mo7-Mo8	2.646(3)	Mo7-Mo9	2.752(3)
Mo8-Mo8'	3.176(4) inter	Mo8-Mo9	2.777(3)
Mo8-Mo9'	3.216(3) inter	Ba2...Ba2' ^d	1.607(5)
Ba1...Ba2	3.603(3)	Ba1...Ba1'	4.609(3)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

^bApical-apical Mo-Mo bond distances

^cIntercluster Mo-Mo bond distances

^dEach barium at 49.9% occupancy

Table 1.6. Selected metal-oxygen bond distances(Å) for Ba₃Mo₁₈O₂₈^a

Mo1-O1	2.06(1)	Mo1-O7'	2.03(1)
Mo1-O8'	2.08(1)	Mo1-O12'	2.09(1)
Mo2-O5'	2.07(2)	Mo2-O6	2.07(1)
Mo2-O8'	1.97(1)	Mo2-O11'	2.08(1)
Mo3-O2'	2.07(1)	Mo3-O4'	2.08(1)
Mo3-O10	2.05(2)	Mo3-O12'	1.97(1)
Mo4-O1'	2.07(1)	Mo4-O4'	2.04(1)
Mo4-O7'	2.08(1)	Mo4-O11'	2.02(1)
Mo4-O12'	2.10(1)	Mo5-O2'	2.15(1)
Mo5-O4'	2.05(1)	Mo5-O11'	2.03(1)
Mo5-O13'	2.13(1)	Mo5-O14'	2.07(1)
Mo6-O1	2.06(1)	Mo6-O6	2.02(1)
Mo6-O7	2.09(1)	Mo6-O8	2.08(1)
Mo6-O10	2.06(1)	Mo7-O3	2.09(1)
Mo7-O5	2.06(1)	Mo7-O6	2.04(1)
Mo7-O9	2.09(2)	Mo7-O10	2.07(2)
Mo8-O3	1.96(1)	Mo8-O5'	1.94(1)
Mo8-O13'	2.08(1) inter ^b	Mo8-O13'	2.07(1)
Mo8-O14'	2.11(1) inter	Mo9-O2'	1.92(1)
Mo9-O3'	2.20(1) inter	Mo9-O9	1.90(2)
Mo9-O13'	2.14(1)	Mo9-O14'	2.02(1)
Ba1-O2	2.92(1)	Ba1-O3	2.81(1)
Ba1-O4	2.68(2)	Ba1-O5	2.93(1)
Ba1-O6	2.85(1)	Ba1-O9'	2.78(1)
Ba1-O9	2.75(1)	Ba1-O10	2.75(1)
Ba1-O11	2.93(1)	Ba1-O13	3.00(1)
Ba1-O14	2.86(1)	Ba2-O1	2.60(1)
Ba2-O1'	2.62(1)	Ba2-O4	3.10(1)
Ba2-O6	3.03(1)	Ba2-O7'	2.65(1)
Ba2-O7	2.64(1)	Ba2-O8	3.04(1)
Ba2-O10	3.12(1)	Ba2-O11	3.12(1)
Ba2-O12	3.05(1)		

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

^bIntercluster Mo-O bond distances

Table 1.7. Selected bond angles (degrees) for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ ^a

Mo1-Mo1'-Mo2	91.7(1)	Mo1-Mo1'-Mo3	92.6(1)
Mo2-Mo1-Mo3'	175.7(1)	Mo4-Mo1-Mo6	87.63(9)
Mo4-Mo1-Mo6'	87.47(9)	Mo1-Mo2-Mo3	88.44(9)
Mo1-Mo2-Mo8	175.7(1)	Mo3-Mo2-Mo8	88.27(9)
Mo4-Mo2-Mo6	92.9(1)	Mo5-Mo2-Mo6	89.05(9)
Mo1'-Mo3-Mo2	87.26(9)	Mo1'-Mo3-Mo9	177.2(1)
Mo2-Mo3-Mo9	90.03(9)	Mo4-Mo3-Mo6	91.9(1)
Mo5-Mo3-Mo7	88.70(9)	Mo1'-Mo4-Mo2	89.34(9)
Mo1-Mo4-Mo3	90.0(1)	Mo5-Mo4-Mo6'	179.2(1)
Mo2-Mo5-Mo9	91.13(9)	Mo3-Mo5-Mo8	88.59(9)
Mo4-Mo5-Mo8'	175.4(1) inter ^b	Mo1-Mo6-Mo3	89.83(9)
Mo1'-Mo6-Mo2	89.40(9)	Mo4-Mo6'-Mo7'	179.7(1)
Mo2-Mo7-Mo9	90.3(1)	Mo3-Mo7-Mo8	91.4(1)
Mo2-Mo8-Mo5'	172.9(1) inter	Mo2-Mo8-Mo9	91.4(1)
Mo5-Mo8-Mo5'	116.30(9)	Mo5-Mo8-Mo7	91.3(1)
Mo3-Mo9-Mo8	90.16(9)	Mo5-Mo9-Mo7	89.46(9)
Mo4-O1'-Mo6'	99.(1)	Mo3-O2'-Mo9	85.3(7)
Ba1-O2'-Mo5	93.4(6)	Mo4-O4'-Mo5	78.7(7)
Ba1-O5-Mo7	89.9(7)	Mo2-O5'-Mo8	85.0(8)
Mo6-O6-Mo7	78.8(7)	Mo4-O7'-Mo6'	96.(1)
Ba2-O8-Mo6	91.2(6)	Mo1-O8'-Mo2	86.5(7)
Mo6-O10-Mo7	77.3(7)	Mo4-O11'-Mo5	80.6(7)
Ba2-O12'-Mo4	89.8(5)	Mo1-O12'-Mo3'	86.8(7)
Mo5-O13'-Mo8'	98.(1)	Mo5-O13'-Mo8	83.(1)
Mo5-O13'-Mo9'	177.(1) inter	Mo8-O13'-Mo8'	100.(1)
Mo8-O13'-Mo9'	100.(1) inter	Mo8-O13'-Mo9	82.(1)
Mo5-O14'-Mo8'	100.(1) inter	Mo5-O14'-Mo9	86.(1)
Mo8-O14'-Mo9'	102.(1) inter		

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

^bIntercluster angles

RESULTS AND DISCUSSION

Description of Structure

The basic building block, $\text{Mo}_{18}\text{O}_{42}$, of four trans edge-shared molybdenum octahedra in $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$, is shown in the ORTEP³⁹ drawing of Figure 1.3. The most notable feature of the structure is that the tetrameric unit has a short-long-short arrangement of apical-apical Mo-Mo bonds. The short apical-apical molybdenum bond distances, 2.599(3)Å for (Mo4-Mo5) and 2.587(3)Å for (Mo6-Mo7), are in the region typically considered single bonds, and constitute the strongest metal-metal bonds in $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. The pairing of the apical molybdenum atoms creates a central, long apical-apical distance of 3.113(2)Å for (Mo4-Mo6). Based upon the basal plane molybdenum bond angles of 175.7(1)° for (Mo8-Mo2-Mo1), 175.7(1)° for (Mo2-Mo1-Mo3'), and 177.2(1)° for (Mo1'-Mo3-Mo9), there is not only pairing of the apical molybdenum atoms but also a small contribution from tilting of the octahedra, similar to that encountered for $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$.¹⁴ The inequivalent apical-apical Mo-Mo bond distances are, in part, the result of this tilting. Perhaps the tilting is not so much due to electronic considerations as it is from packing considerations and the extended length of four edge-shared octahedra.

The formation of the four short apical-apical bonds can be thought of as arising from the condensation of two trans edge-shared bioctahedra, which also show strong apical-apical bonding ($\text{Ba}_2\text{Mo}_{10}\text{O}_{16}$, 2.621(2)Å).⁷ The short-long-short configuration of apical Mo-Mo bonds was first observed in the $n=4$ oligomeric cluster of Simon's $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ (2.651Å, 3.125Å, 2.651Å).²³ Formally, Simon's cluster has been assessed as having an anionic charge of $(\text{Mo}_{18}\text{O}_{28})^{7-}$, and the $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ metal oxide framework gives a formal charge of 6-. The

Figure 1.3. An ORTEP drawing of the tetrameric cluster unit, $\text{Mo}_{18}\text{O}_{42}$, of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ using 70% thermal ellipsoids. Note the short-long-short arrangement of apical-apical molybdenum bonds.

removal of one electron from Simon's framework, corresponding to the charge of 6^- , does not change the central, long apical-apical distance, but results in a decrease of the short apical-apical molybdenum distances by about $0.07\text{\AA}$. As reported by Wheeler and Hoffmann⁴¹, the observed apical-apical molybdenum bond distortions open a larger HOMO-LUMO gap. The positioning of this gap is more suitable for clusters formulated as $\text{Mo}_{18}\text{O}_{28}^{6-}$, as found in $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. A cluster with this electron count has the HOMO completely filled.

Many other similarities exist between the clusters in $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ and those in Simon's $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$. The average metal-metal bond distance of $2.761\text{\AA}$ found here is very similar to the $2.789\text{\AA}$ found in the $n=4$ cluster of $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$. Trans edge-shared molybdenum-molybdenum distances follow the opposite trend seen in the apical-apical molybdenum bond distances. If the apical-apical distance above the corresponding trans edge is very short, then the Mo-Mo bond distance of that trans edge will be longer than the average trans edge bond length, and vice versa. In $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$, the trans edges [and apical-apical] distances are $2.854(3)\text{\AA}$ for (Mo2-Mo3) [$2.599(3)\text{\AA}$ for (Mo4-Mo5)], and $2.650(4)\text{\AA}$ for (Mo1-Mo1') [$3.113(2)\text{\AA}$ for (Mo4-Mo6)]. This trend was also observed in $\text{In}_{11}\text{Mo}_{42}\text{O}_{62}$ ($2.676\text{\AA}$ [$3.125\text{\AA}$], $2.830\text{\AA}$ [$2.651\text{\AA}$]). Another interesting trend found in both compounds is the short-long-long-short arrangement of Mo-Mo octahedral edge bond distances parallel to the chain direction. The values for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ are reported first with the corresponding bond distance for $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ found within the square brackets. The edge Mo-Mo bond distances are: $2.720(3)\text{\AA}$ for (Mo8-Mo2) [$2.761\text{\AA}$], $2.775(3)\text{\AA}$ for (Mo2-Mo1) [$2.826\text{\AA}$], $2.778(3)\text{\AA}$ for (Mo1-Mo3') [$2.826\text{\AA}$], and $2.710(3)\text{\AA}$ for (Mo3'-Mo9') [$2.761\text{\AA}$].

The shortest intercluster Mo-Mo bond distances previously determined for oligomers with more than two trans edge-shared octahedra, namely $3.191(2)\text{\AA}$ for $\text{K}_3\text{Mo}_{14}\text{O}_{22}$ ⁷, $2.991(3)\text{\AA}$ for $\text{Ti}_{1.6}\text{Sn}_{1.2}\text{Mo}_{14}\text{O}_{22}$ ³⁰, and greater than $3.20\text{\AA}$ for the mixed oligomer $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$, indicate that there was little, if any, intercluster

metal-metal bonding. $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ also follows this trend with the three shortest intercluster metal-metal distances at 3.176(4)Å for (Mo8-Mo8'), 3.195(3)Å for (Mo5-Mo8'), and 3.216(3)Å for (Mo8-Mo9') as shown in Figure 1.4.

Within the Mo_{18} cluster, six molybdenums are only four-coordinate in oxygen (Mo1, Mo2, and Mo3) and the remaining twelve molybdenums are five-coordinate in oxygen (Mo4 to Mo9). The molybdenum-oxygen bond distances vary from 1.90(2)Å for (Mo9-O9) to 2.20(1)Å for (Mo9-O3). The average Mo-O bond distance is 2.06Å which compares to 2.07Å for the $n=4$ member in $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$. Both extreme molybdenum-oxygen distances occur within the region where intercluster bonding couples the chain fragments together through Mo-O-Mo bonding parallel to the c axis. The extreme Mo-O distances for $\text{In}_{11}\text{Mo}_{40}\text{O}_{62}$ occur at exactly the same atoms.

The stair-step fashion in which the tetrameric units are bonded to each other in the c axis direction is shown in Figure 1.4. This type of interconnection creates a void where cation coordination is irregular and therefore the barium-oxygen and molybdenum-oxygen bond distances vie for a suitable compromise, particularly at the ends of the cluster fragment. The coordination sphere of oxygen atoms around the bariums is shown in Figure 1.5. The cation located adjacent to the end octahedra in the tetrameric unit, Ba1, is eleven-coordinate in oxygen. The barium-oxygen bond distances range from 2.68(2)Å for (Ba1-O4) to 3.00(1)Å for (Ba1-O13). The second barium is ten-coordinate in oxygen and the barium-oxygen bond distances range from 2.60(1)Å for (Ba2-O1) to 3.12(1)Å for (Ba2-O10 and Ba2-O11). Oxygen atoms O1 and O7 are shared between the statistically occupied Ba2 and oxygen atoms O4, O6, O10, and O11 are shared between Ba1 and Ba2. Ba2 resides on one of two sites at any given time, disordered about the special position at the origin. These two sites are separated by 1.607(5)Å for (Ba2-Ba2'). Ba2 probably does not reside at the origin because this would require the cation to be in square planar coordination by oxygen.

Figure 1.4. An ORTEP representation (70% thermal ellipsoids) of the tetrameric cluster unit emphasizing Mo-O intercluster connections in a stair-step manner

Figure 1.5. An ORTEP drawing (70% thermal ellipsoids) of the coordination environment surrounding bariums in $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. Ba2 and Ba2' are each 50% occupied.

Based upon the structural systematics and the general formulation, $M_nMo_{4n+2}O_{6n+4}$, there should be four cation sites available, separated on average by the repeat distance along the molybdenum octahedra, $\sim 2.75\text{\AA}$. This distance would be shorter than twice the ionic radius for Ba^{+2} reported by Shannon.⁴² The distance between Ba1 and Ba2 of $3.603(3)\text{\AA}$, is reasonable based upon the Shannon ionic radius of $1.52\text{\AA}$ for ten-coordinate Ba^{+2} or $1.57\text{\AA}$ for eleven-coordinate Ba^{+2} . This cation separation is larger than the $3.524(2)\text{\AA}$ reported for $Ba_2Mo_{10}O_{16}$. $Ba_2Mo_{10}O_{16}$ incorporates the maximum number of barium cations into the pockets created by the molybdenum-oxide framework. $Ba_3Mo_{18}O_{28}$ uses only 75% of the possible cation sites. Therefore it is reasonable that the cations are located further apart in the $n=4$ oligomer.

The statistical occupation of Ba2 raises two questions: 1) can the cation population be verified by an alternate method, and 2) is there any superstructural ordering due to the partial occupation of barium? Confirmation of the composition was carried out by electron microprobe analyses. Data collected on three different crystals indicated that the composition was $Ba_{3.01(2)}Mo_{18}O_{28}$, in excellent agreement with the value determined by crystallographic methods. Based upon single crystal lattice parameters, electron diffraction patterns were indexed as the $[\bar{1}00]$, $[\bar{1}10]$, and the $[\bar{2}01]$ zone axes. No superstructure reflections were observed in any of the micrographs, furthermore the $[\bar{1}00]$ and $[\bar{1}10]$ diffraction patterns explicitly indicated no superstructure parallel to the c-axis, the expected direction if there was any ordering of the cations. The $[\bar{1}00]$ and $[\bar{2}01]$ diffraction patterns also indicated that no ordering occurred parallel to the b axis. Thus Ba2 must be randomly distributed over the two sites located near the special position at the origin.

Figure 1.6 is an ORTEP drawing of the unit cell of $Ba_3Mo_{18}O_{28}$ as viewed down the c axis. From this perspective, the interconnection among Mo_{18} units in the a and b directions through bridging oxygens can be seen. This cross-linking

Figure 1.6. A view down the c axis of Ba₃Mo₁₈O₂₈, parallel to the Mo octahedral chains. Barium-oxygen bonds have been omitted for clarity. Thermal ellipsoids are at 70% probability for this ORTEP drawing.

creates pockets in which the barium cations reside. This view is reminiscent of the infinite chain compounds, such as $\text{NaMo}_4\text{O}_6^1$, and shows that the couplings in the a-b plane are quite similar.

$\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ can be described by the following connectivity formula, $\text{Ba}_3^{6+}[(\text{Mo}_{18}\text{O}_{14}^{\text{i}}\text{O}_{4/2}^{\text{i-i}}\text{O}_{12/2}^{\text{i-a}})\text{O}_{12/2}^{\text{a-i}}]^{6-}$. Oxygen atoms O1, O4, O6, O7, O9, O10, and O11 are edge-bridging only within the cluster unit and are labelled O^{i} . The oxygen atoms corresponding to $\text{O}^{\text{i-i}}$ are edge-sharing between neighboring clusters, these are labelled O13. Oxygens considered $\text{O}^{\text{i-a}}$ (or $\text{O}^{\text{a-i}}$) are edge-bridging between molybdenum atoms of one cluster and terminal to another molybdenum in a neighboring cluster (or vice versa), these include O2, O3, O5, O8, O12, and O14.

Discussion of Properties

Bond length-bond strength relationships

The application of bond length-bond strength relationships has provided valuable insights into the structure, bonding, and oxidation states of reduced molybdenum oxides that have been synthesized in this laboratory.⁴³ The bond order for metal-metal bonds can be determined using Pauling's bond order equation⁴⁴ found in Equation 1,

$$d(n) = d(1) - 0.61\log(n) \quad (1)$$

where $d(n)$ is the bond distance for a metal-metal bond in question and n is the bond order for that metal-metal bond. $d(1)$ is the metal-metal distance considered a single bond; for molybdenum this value is $2.614\text{\AA}$, derived from the distance to nearest and next-nearest neighbors in bcc molybdenum metal. Bond strengths

for Mo-O bonds are calculated from the empirical relationship developed by Brown and Wu⁴⁵ and given in Equation 2.

$$s(\text{Mo-O}) = [d(\text{Mo-O})/1.882]^{-6.0} \quad (2)$$

The bond length, in valence units (v.u), is given by $s(\text{Mo-O})$ and $d(\text{Mo-O})$ is the observed Mo-O bond distance in angstroms. Since $s(\text{Mo-O})$ is given in valence units, the sum of all Mo-O bond valences about a given Mo atom will give the valence (oxidation state) of that atom.

The numerical values of these calculations are found in Table 1.8.

$\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ follows the same general trends for valence as has been found for the other oligomers discovered in this laboratory, namely $\text{Ba}_2\text{Mo}_{10}\text{O}_{16}$ and $\text{K}_3\text{Mo}_{14}\text{O}_{22}$. The molybdenums in the basal plane (Mo1, Mo2, and Mo3), but not at the end of cluster unit, have the highest coordination by other molybdenum and therefore the most electrons available for metal-metal bonding. Apical molybdenums (Mo4, Mo5, Mo6, and Mo7) are five-coordinate in molybdenum (or six if there is apical-apical bonding) and exhibit intermediate metal-centered electron counts. And molybdenums (Mo8 and Mo9), located at the end of the cluster unit, are four-coordinate in molybdenum (or more depending on intercluster bonding) and have the fewest electrons per molybdenum available for metal-metal bonding.

The number of metal-centered electrons (MCE) per $\text{Mo}_{18}\text{O}_{28}^{6-}$ cluster can be estimated from the sum of the metal-metal bond orders (n), and results in $\text{MCE}(2\sum n)=62.8(7)e^-$ if all bonds are included, or $61.7(6)e^-$ if intercluster bonds are excluded. The total valence of the tetrameric unit based upon the summation of the individual valences of the molybdenum atoms derived from Mo-O bonds is $2\sum s=50(2)e^-$. The number of electrons available for metal-metal bonding can also be calculated by subtraction of $50(2)$ from 108 (6×18), the maximum number of

Table 1.8. Bond length-bond strength relationships for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo1	2.650(4)	0.873(13)	2.06(1)	0.581(16)
	2.775(3)	0.545(7)	2.03(1)	0.635(18)
	2.778(3)	0.538(6)	2.08(1)	0.549(16)
	2.833(3)	0.438(5)	2.09(1)	<u>0.533(15)</u>
	2.822(3)	0.456(5)		$\Sigma s = 2.30(7)$
	2.842(3)	0.423(5)		
	2.824(3)	<u>0.453(5)</u>		
		$\Sigma n = 3.73(5)$		
Mo2	2.775(3)	0.545(7)	2.07(2)	0.565(32)
	2.854(3)	0.404(4)	2.07(1)	0.565(16)
	2.697(3)	0.731(8)	1.97(1)	0.760(23)
	2.747(3)	0.605(7)	2.08(1)	<u>0.549(16)</u>
	2.704(3)	0.712(8)		$\Sigma s = 2.44(9)$
	2.796(3)	0.503(6)		
	2.720(3)	<u>0.670(7)</u>		
		$\Sigma n = 4.17(5)$		
Mo3	2.778(3)	0.538(6)	2.07(1)	0.565(16)
	2.854(3)	0.404(4)	2.08(1)	0.549(16)
	2.730(3)	0.645(7)	2.05(2)	0.599(18)
	2.778(2)	0.538(4)	1.97(1)	<u>0.760(23)</u>
	2.716(3)	0.680(8)		$\Sigma s = 2.44(7)$
	2.780(3)	0.534(6)		
	2.710(3)	<u>0.696(8)</u>		
		$\Sigma n = 4.04(5)$		
Mo4	2.833(3)	0.438(5)	2.07(1)	0.565(16)
	2.822(3)	0.456(5)	2.04(1)	0.617(18)
	2.697(3)	0.731(8)	2.08(1)	0.549(16)
	2.730(3)	0.645(7)	2.02(1)	0.654(19)
	2.599(3)	1.058(12)	2.10(1)	<u>0.519(15)</u>
	3.113(2)	<u>0.152(1)</u>		$\Sigma s = 2.90(8)$
		$\Sigma n = 3.48(4)$		

Table 1.8. (continued)

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo5	2.747(3)	0.605(7)	2.15(1)	0.450(12)
	2.778(2)	0.538(4)	2.05(1)	0.599(18)
	2.599(3)	1.058(12)	2.03(1)	0.635(18)
	2.786(3)	0.522(5)	2.13(1)	0.476(13)
	3.195(3) ^a	0.112(2)	2.07(1)	<u>0.565(16)</u>
	2.767(3)	<u>0.561(6)</u>		$\Sigma s = 2.73(8)$
		$\Sigma n = 3.40(4)$		
Mo6	2.842(3)	0.423(5)	2.06(1)	0.581(16)
	2.824(3)	0.453(5)	2.02(1)	0.654(19)
	2.704(3)	0.712(8)	2.09(1)	0.533(15)
	2.716(3)	0.680(8)	2.08(1)	0.549(16)
	3.113(2)	0.152(1)	2.06(1)	<u>0.581(16)</u>
	2.587(3)	<u>1.107(12)</u>		$\Sigma s = 2.90(8)$
		$\Sigma n = 3.53(4)$		
Mo7	2.796(3)	0.503(6)	2.09(1)	0.533(15)
	2.780(3)	0.534(6)	2.06(1)	0.581(16)
	2.587(3)	1.107(12)	2.04(1)	0.617(18)
	2.646(3)	0.886(10)	2.09(2)	0.533(29)
	2.752(3)	<u>0.594(7)</u>	2.07(2)	<u>0.565(32)</u>
		$\Sigma n = 3.62(4)$		$\Sigma s = 2.83(11)$
Mo8	2.720(3)	0.670(7)	1.96(1)	0.784(24)
	2.786(3)	0.522(5)	1.94(1)	0.834(26)
	3.195(3) ^a	0.112(2)	2.08(1)	0.549(16)
	2.646(3)	0.886(10)	2.07(1)	0.565(16)
	3.176(4) ^a	0.120(2)	2.11(1)	<u>0.504(15)</u>
	2.777(3)	0.540(6)		$\Sigma s = 3.24(10)$
	3.216(3) ^a	<u>0.103(1)</u>		
		$\Sigma n = 2.95(3)$		
Mo9	2.710(3)	0.696(8)	1.92(1)	0.887(17)
	2.767(3)	0.561(6)	2.20(1)	0.392(11)
	2.752(3)	0.594(7)	1.90(2)	0.944(57)
	2.777(3)	0.540(6)	2.14(1)	0.463(13)
	3.216(3) ^a	<u>0.103(1)</u>	2.02(1)	<u>0.654(19)</u>
		$\Sigma n = 2.49(2)$		$\Sigma s = 3.34(13)$

^aIntercluster metal-metal bond distance

valence electrons available from eighteen molybdenum atoms. The resulting MCE, based on the bond valences calculated in valence units, is $58(2)e^-$. This value is in excellent agreement with the $58e^-$ expected, based on the formula and formal oxidation states for barium and oxygen.

The value, based on Equation 1, of 61.7 electrons is obviously too high. Perhaps the value derived from Pauling's equation is high due to the length used for a Mo-Mo single bond. The Pauling's $d(1)$ was derived from interatomic distances in molybdenum metal. In molybdenum metal, which is body-centered cubic, the environment around each metal is identical. Likewise, each molybdenum atom in the infinite chain compounds, $M_xMo_4O_6$, also have a quite regular environment. Thus Pauling's formulation worked well. However, this scenario is not the case for a number of members of the oligomeric series⁷, $M_xMo_{4n+2}O_{6n+4}$. Metal-metal bonding of apical molybdenums and varying degrees of intercluster Mo-Mo bonding in the oligomers create disparate environments, where the coordination number of surrounding metal atoms for any given molybdenum will range from four to seven. The larger than expected number of electrons available for metal-metal bonding may be the result of such varying environments for the molybdenum atoms in the oligomeric series.

Using Equation 2 to determine the valence of the barium cations, where $d(Ba-O) = 2.297$ and the exponent is -7.0 , gives a value of $2.56(8)$ for Ba1 and $2.34(5)$ for Ba2. Both values are above the expected $+2$, however, similar results were obtained for the $n=1$ cluster, $BaMo_6O_{10}$ ²⁴, and $n=2$ cluster, $Ba_2Mo_{10}O_{16}$, with the calculated valences at $2.6(1)$ and $2.78(9)$, respectively.

Magnetic and resistivity properties

The magnetic susceptibility of $Ba_3Mo_{18}O_{28}$ was measured on selected crystals over the temperature range of 6-356 K. The data have been corrected for diamagnetic core contributions based on values reported by Selwood.⁴⁶

Figure 1.7 displays both the molar and inverse molar susceptibilities for the tetrameric compound. The tail from 6-100 K most likely arises from paramagnetic impurities. Interestingly, the susceptibility nearly levels off at -4500×10^{-6} emu/mol from 100-356 K with a slight increase in the slope. This value would imply that the compound is either Pauli paramagnetic or that the cluster has a residual moment (due to temperature independent paramagnetism, χ_{TIP}) of about 250×10^{-6} emu/Mo, which is not too unreasonable. The relative flatness of the data above 100 K indicates that the material is essentially diamagnetic, in agreement with the calculated even electron count based upon formal oxidation states.

If $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ were Pauli paramagnetic, it would imply that the compound should be metallic. Attempts to attach leads to large crystals failed, due in part to the chunk-like nature in which the crystals grow. Most crystals were no larger than 0.5mm in the longest dimension. Therefore, a sintered, pressed pellet of the tetramer was subjected to resistivity studies. The sample was measured from liquid nitrogen (77 K) to room temperature (295 K), as the system slowly warmed up with evaporation of the coolant. The resistivity of this sample at 295 K was ~ 8.8 ohms, or ~ 2.6 ohm-cm. A plot of the resistivity ratio ($\rho(T)/\rho(295)$) versus temperature and the natural log of the resistivity ratio versus temperature⁻¹ (inset) are shown in Figure 1.8. The increasing resistivity with decreasing temperature clearly indicate the semiconducting behavior of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. As can be observed from the inset, the data can not be linearly fit (as would be expected for a strictly semiconducting material). The changing slope would imply a changing size in the band gap, most likely due to impurities in the sample. Nonetheless, the semiconducting behavior excludes the possibility that the material is Pauli paramagnetic.

Figure 1.7. Molar and inverse molar susceptibility versus temperature of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$

Figure 1.8. Resistivity ratio of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ plotted versus temperature. The inset shows the nearly linear relationship between the natural logarithm versus $1/T$, indicating semiconducting behavior.

CONCLUSIONS

The structural aspects of the pure $n=4$ oligomeric compound, $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$, are very similar to those reported by Simon²³ for the analogous cluster in $\text{In}_{11}\text{Mo}_{40}\text{O}_{26}$. Apical-apical molybdenum bond distances follow a short-long-short arrangement and the average metal-metal and metal-oxygen bond distances are comparable. As the chain length increases, the cluster units tend to be interconnected via Mo-O bonds only, such is also the case for $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$. Perhaps the greatest benefit from the analysis of $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ can be the certainty that the barium cations are isolated (i.e. no metal-metal bonding) and that the cluster unit can be considered a $\text{Mo}_{18}\text{O}_{28}^{6-}$ fragment from an electronic point of view. Bond order sums around the molybdenums result in a larger than expected number of MCE, most likely due to the choice of $d(1)$, the length of a molybdenum-molybdenum single bond. The summation of the individual molybdenum valences predicts $58(2)e^-$ available for metal-metal bonding, this value coincides with calculations using formal oxidation states.

Magnetic susceptibility measurements indicate that the tetrameric oligomer is diamagnetic, but does have a substantial temperature independent paramagnetic susceptibility. The diamagnetic character is in agreement with the even electron count and the arrangement of the molecular orbitals calculated by Wheeler and Hoffmann.⁴¹ Pressed pellet resistivity measurements confirm that the material is not Pauli paramagnetic, but actually a small band gap semiconductor.

SECTION 2

SYNTHESIS AND CHARACTERIZATION OF $K_xM_yMo_{14}O_{22}$ ($M=Sn,Pb,Sr$): OLIGOMERS WITH THREE TRANS EDGE-SHARING Mo OCTAHEDRA

INTRODUCTION

New compounds, in which the condensation of trans edge-sharing molybdenum octahedra has been limited to finite segments, have been fittingly called oligomers. These materials have clusters of metal-metal bonded octahedra that are similar to those in the infinite chain compounds, $M_x Mo_4 O_6$.^{1,3-12} However, various structural distortions abound in the oligomeric members. The quest for new materials with three edge-sharing molybdenum octahedra is fueled, in part, by the desire to learn more about the relationships that exist between these structural distortions and the number of electrons available for metal-metal bonding. Promoting the growth of crystals containing any given oligomer requires an intricate and interdependent set of variables, including reaction temperature and time, transport agents, cationic size, and number of electrons donated by the cations. Members of the oligomeric series can be derived from the general formulation, $M_{n-x} Mo_{4n+2} O_{6n+4}$, where n equals the number of trans edge-sharing molybdenum octahedra. A brief communication on the first $n=3$ member, $Tl_{1.6} Sn_{1.2} Mo_{14} O_{22}$, was reported by Simon in 1989.^{26a} A more detailed study followed in 1991.³⁰ Also in 1991, $K_3 Mo_{14} O_{22}$ was prepared and characterized by Chen.⁷ Two analogous compounds with intermediate electron counts, $K_{1.3} Sn_{1.7} Mo_{14} O_{22}$ and $K_{1.7} Pb_{1.3} Mo_{14} O_{22}$ have been synthesized, structured, and their magnetic properties investigated. A third new member, $K_{2.6} Sr_{0.4} Mo_{14} O_{22}$, has also been identified. These new members will be compared and contrasted with the two previously reported compounds via their structural distortions and the electron counts available for metal-metal bonding.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically.

Therefore, all reactions were carried out in evacuated vessels made of fused silica ($\sim 1 \times 10^{-4}$ torr) or molybdenum metal ($\sim 2 \times 10^{-5}$ torr). All reactants were thoroughly ground to produce a homogeneous mixture before being used as loose powders or pressed pellets. Mixed starting materials were subsequently stored in a desiccator.

The starting reagents included K_2MoO_4 , $SrMoO_4$, SnO , Sn , PbO , MoO_3 , MoO_2 , and Mo . Potassium molybdate was prepared by reacting KOH (Fisher Certified A.C.S.) with a stoichiometric quantity of MoO_3 in deionized water. The molybdate solution was filtered, the volume reduced by heating, and the product collected on a glass frit. The wet molybdate was dried at $120^\circ C$ overnight. Strontium molybdate was prepared by reacting $SrCO_3$ (Baker Analyzed, 99.6%) with a stoichiometric quantity of MoO_3 at $550^\circ C$ for three days in an open crucible. The resulting product was air cooled to room temperature. Tin (II) oxide was prepared by the method of Weiser and Milligan.⁴⁷ Molybdenum dioxide (Alfa, 99%) was cleaned and dried as discussed previously in Section 1. Lead(II) oxide (Aldrich, 99.9%) was used directly from the bottle. Molybdenum trioxide was fired at $520^\circ C$ overnight in an open crucible and then cooled over desiccant. Molybdenum and tin powders (Aldrich, 99.99% and Fisher, respectively) were dried under dynamic vacuum at $120^\circ C$ overnight. All reagents were stored in a desiccator. In some reactions, molybdenum tubing (Thermoelectron Corp., 99.97%) was used as a reactant vessel. The tubing was cleaned by heating at

950°C for five hours under a flowing hydrogen atmosphere. After cooling to room temperature under hydrogen, the tubing was also stored over desiccant.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with Cu $K\alpha_1$ radiation ($\lambda = 1.540562\text{\AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard.

Magnetic susceptibility

The magnetic properties were examined on samples of selected crystals with a Quantum Design SQUID magnetosusceptometer. The samples were loaded into a 3mm inner diameter quartz tube that had been sealed on the bottom half with a 3mm outer diameter quartz rod. A quartz rod also was placed in the top half of the loaded sample tube, which was then mounted in an apparatus that allowed the evacuation of the sample tube and purging with helium gas. To eliminate water, the system was heated to 120°C for an hour under dynamic vacuum. After cooling, the system was pumped and purged with helium three more times. The upper quartz tube was pushed into place under a partial pressure of helium (to facilitate temperature equilibration during measurements), sandwiching the sample between "solid" quartz, and sealed off. This procedure was used to eliminate oxygen contamination, which has an antiferromagnetic transition at ~50 K. The experimental data were corrected for the diamagnetic contribution from the quartz. Measurements on empty quartz tube/rod assemblies, with varying gap sizes, indicated that the diamagnetic contribution from the quartz was related to the size of the gap. Since the signal versus gap

size data could be fit by a line, a correction was employed by measuring the length of the gap containing the sample.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Samples were loaded onto a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Microprobe analysis

Elemental analyses were completed by Dr. Alfred Kracher (Department of Geological and Atmospheric Sciences) on an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers (WDS) and operated at 15 kV and 25 nA. Samples were mounted in an epoxy resin, dried, and polished to produce a flat surface. Prior to examination, the samples were sputtered with carbon to insure conductivity. Peak profiles and backgrounds were measured for KAlSi_3O_8 , PbS, Sn metal, and Mo metal standards. Data were analyzed using Probe³⁵ software.

Electron spin resonance

X-band electron spin resonance (ESR) spectra were recorded on a powdered sample of $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$ with a Bruker ER200-SRC instrument equipped with an Oxford Instruments ESR 900 flow through cryostat and a DTC-2 digital temperature controller. A Hewlett-Packard 5342 microwave frequency recorder was used to measure the exact frequency of the microwave radiation. Data were averaged over five scans and collected at a modulation frequency of 100 kHz and a power setting of 3.2 Gpp. The instrument was calibrated against weak pitchblende prior to use.

Synthesis

Crystals of the compound $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ were first discovered in a reaction to prepare the quaternary $K_2Sn_2Mo_{18}O_{28}$, an $n=4$ oligomer. A pressed pellet with the correct stoichiometric ratio of K_2MoO_4 , SnO, MoO_2 , and Mo for the tetramer was loaded into a molybdenum tube, that was subsequently sealed under vacuum by electron beam welding. The sample was fired at 1500°C for 94 hours in a vacuum furnace and cooled to 1200°C over three hours, to 800°C over one hour, and finally furnace cooled (to 100°C in approximately one hour). Upon opening the tube, many large, black crystals with chunk-like morphology were found on the upper molybdenum cap, along with silvery beads of tin metal. The upper twenty percent of the tube walls also contained a multitude of crystals, all of which had well defined faces. The remains of the pellet were a porous matrix of molybdenum metal. The elemental components of the matrix, silvery beads, and crystals were verified by SEM EDS.

Based upon the composition determined through a single crystal structure refinement, preparation of single phase $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ was undertaken. A loose powder containing an intimate mixture of K_2MoO_4 , Sn, MoO_3 , and Mo in the proper mole ratio was loaded into a fused silica tube with a one-fold excess of K_2MoO_4 . The system was evacuated and heated to 300°C for one hour to remove adventitious water. The reaction tube was then sealed and loaded into an outer fused silica tube, which was subsequently evacuated before being sealed. This outer jacket was used to protect the reaction from oxygen contamination. The reaction was fired at 1250°C for nine days. After firing, the inner tube was found to be badly devitrified, but the contents looked unaffected, and the outer fused silica jacket was intact. The product contained the same chunk-like crystals, as described above, embedded in a loose black powder. The reaction appeared to be single phase, except for a few needles of molybdenum dioxide that were found transported to the tube walls. A Guinier powder pattern

of a mixture of bulk powder and crystals indicated the presence of only the $n=3$ oligomer. No K_2MoO_4 was detected visually, or by x-ray powder diffraction. The degradation of the fused silica tube indicates that the excess molybdate had reacted with the container. Reactions in which a stoichiometric quantity of potassium molybdate was used resulted in the formation of the correct oligomer, but a significant amount of tin metal also remained. Microprobe analyses indicated that the potassium and tin content are be variable. The range of composition observed will discussed later with reference to the cation coordination environment.

Large crystals, up to 0.4 mm, of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ were first discovered in a reaction to prepare $K_2PbMo_{14}O_{22}$. A pressed pellet with the correct stoichiometry for $K_2PbMo_{14}O_{22}$ was loaded into a molybdenum tube, evacuated, and fired at 400°C for two hours under dynamic vacuum before being sealed by electron beam welding. The sample was fired at 1500°C for 93 hours in a vacuum furnace and cooled to 700°C at 3°C/min and then furnace cooled (to 100°C in approximately one hour). The products of this reaction were located in the tube as described for $K_{1.3}Sn_{1.7}Mo_{14}O_{22}$: black, chunk-like crystals deposited on the upper molybdenum cap and walls, with beads of lead metal, and the remains of the pellet as a matrix of molybdenum metal. The constituents of the crystals could not be verified by SEM EDS because molybdenum and lead peaks reside at nearly the same energies, however, the identity of the metal beads and pellet matrix were ascertained. Single phase material of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ was not prepared. Microprobe analyses on the K-Pb member indicated that composition was variable. These results will be discussed with reference to the cation coordination.

Chunk-like crystals of $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$ were first discovered in a reaction prepared to synthesize $K_2SrMo_{14}O_{22}$. The starting materials included a stoichiometric ratio of $SrMoO_4$, K_2MoO_4 , MoO_3 , and Mo which were fired in an

evacuated quartz tube at 1250°C for nine days. The reaction was cooled at about 100°C/hour to 800°C and then quenched to room temperature. The bulk product contained clusters of black chunk crystals. Single phase preparation of this material was not attempted.

X-ray Powder Diffraction

The diffraction patterns of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$ could be indexed based on the monoclinic cell parameters determined from the single crystal refinements. The observed versus calculated d-spacings are reported in Tables 2.1 and 2.2, respectively. The sample of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ was highly crystalline, with 142 measured and indexed d-spacings. Table 2.1 is only a partial listing which includes all observed reflections out to 35° in two theta ($d=2.6\text{\AA}$) and those reflections with two theta between 35° and 85° ($d=1.2\text{\AA}$) having intensities considered as strong, medium, or weak. In Table 2.2 the d-spacings for $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$ are listed, this material was not single phase, therefore impurity reflections, which included Mo and MoO_2 were excluded. All d-spacings were derived from Cu $K\alpha_1$ radiation.

X-ray Single Crystal Data Collection

A black, chunk-like crystal of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ with good faces and measuring $0.06 \times 0.08 \times 0.10 \text{ mm}^3$ was mounted with epoxy cement on a glass fiber for data collection. A Rigaku AFC6R rotating anode diffractometer was used with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069\text{\AA}$) generated at 7 kW. Lattice parameters and an orientation matrix for data collection were derived from 22 randomly located and centered reflections with a two theta range of 12-17°.

Table 2.1. X-ray powder diffraction data for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
6.740	6.687	s	$\overline{1}10$
6.104	6.057	m	111
5.206	5.173	vw	$\overline{1}11$
4.840	4.824	w	201
4.673	4.647	w	002
4.404	4.383	w	112
4.229	4.216	vw	021
4.206	4.185	w	$\overline{1}20$
4.042	4.027	w	121
3.990	3.978	vw	201
3.736	3.724	w	$\overline{1}21$
3.405	3.395	vw	122
3.359	3.344 & 3.342	m	$\overline{2}20$ & 003
3.230	3.215	w	$\overline{1}13$
3.140	3.126	w	$\overline{2}03$
3.121	3.110	s	311
3.069	3.057	w	122
3.043	3.057	m	$\overline{3}10$
2.976	2.963 & 2.960	w	213 & 031
2.960	2.949	s	$\overline{1}30$
2.920	2.910	vw	$\overline{3}12$
2.899	2.888	w	131
2.816	2.805	s	113
2.783	2.774	w	$\overline{1}31$
2.770	2.758	w	123
2.743	2.734	w	311
2.709	2.713	vw	$\overline{0}23$
2.699	2.690	s	$\overline{3}21$
2.638	2.629	vw	$\overline{1}32$
2.603	2.594	vw	$\overline{2}23$
2.567	2.559 & 2.558	w	$\overline{3}13$ & $\overline{3}22$
2.515	2.506	w	004

^aIntensity: s=strong, m=medium, w=weak, b=broad, and v=very

^bRefined monoclinic cell parameters obtained from single crystal measurements:
a=9.929(2)Å, b=9.294(1)Å, c=10.338(2)Å, and $\beta=104.13(2)^\circ$

Table 2.1. (continued)

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
2.469	2.463	w	132
2.445	2.436	w	<u>3</u> 21
2.429	2.419	w	<u>4</u> 02
2.411	2.401 & 2.398	s	214 & $\bar{4}$ 11
2.401	2.393	s	213
2.372	2.365	w	312
2.332	2.323	m	<u>0</u> 40
2.318	2.310	w	<u>3</u> 23
2.306	2.298	w	<u>1</u> 33
2.266	2.259 & 2.258	s	<u>3</u> 31 & $\bar{1}$ 24
2.206	2.197	w	314
2.192	2.186	w	223
2.062	2.056	w	<u>1</u> 24
2.040	2.033	m	324
2.031	2.026	w	<u>3</u> 13
1.946	1.939	s	<u>5</u> 11 & 234
1.940	1.937 & 1.934	s	431 & 233
1.900	1.895	m	323
1.828	1.825 & 1.824	s	<u>1</u> 50 & <u>5</u> 21
1.815	1.810	w	<u>1</u> 51 & 522
1.784	1.778	w	<u>3</u> 25
1.700	1.697 & 1.696	s	244 & 441
1.700	1.695	s	<u>2</u> 43
1.640	1.635 & 1.634	w	<u>5</u> 24 & $\bar{3}$ 35 & $\bar{1}$ 53
1.579	1.574	m-b	<u>5</u> 15
1.491	1.489 & 1.488	s	254 & 451
"	1.487	s	253
1.471	1.468	w	<u>5</u> 32
1.466	1.461	w	<u>3</u> 36 & $\bar{5}$ 43
1.456	1.452	w	<u>1</u> 17
1.440	1.436	m	605
1.437	1.432	m	007
1.434	1.430	m	<u>6</u> 02
1.406	1.402	w	<u>3</u> 61
1.375	1.373	w	<u>2</u> 55
1.359	1.356	m	722
1.358	1.354	m	117

Table 2.2. X-ray powder diffraction data for $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
6.661	6.672	s	$\overline{110}$
6.041	6.039	m-b	$\overline{111}$
4.175	4.170	w	$\overline{120}$
3.396	3.386	w	$\overline{122}$
3.102	3.104	s	$\overline{311}$
3.030	3.033	m-b	$\overline{310}$
2.942	2.937	s-b	$\overline{130}$
2.815	2.814	w/m	$\overline{113}$
2.685	2.684	s	$\overline{321}$
2.495	2.489	s	$\overline{123}$
2.481	2.485 & 2.479	s	$\overline{204}$ & $\overline{401}$
2.407	2.401 & 2.400	s	$\overline{213}$ & $\overline{214}$
2.397	2.395	s	$\overline{411}$
2.314	2.313	w-b	$\overline{040}$
2.265	2.258	m-b	$\overline{124}$ & $\overline{304}$
2.194	2.194	m	$\overline{314}$
2.188	2.190 & 2.189	m/w	$\overline{223}$ & $\overline{224}$
"	2.185	"	$\overline{421}$
2.034	2.029	s-b	$\overline{324}$
1.942	1.935	vs	$\overline{233}$ & $\overline{234}$
1.935	1.932	vs	$\overline{431}$
1.902	1.899	m	$\overline{323}$
1.823	1.821	s-b	$\overline{521}$ & $\overline{143}$
1.699	1.693	vs	$\overline{243}$, $\overline{244}$, & $\overline{116}$
1.696	1.691	vs	$\overline{441}$
1.487	1.484 & 1.483	m-b	$\overline{253}$, $\overline{254}$, & $\overline{451}$
1.441	1.442	m-b	$\overline{154}$
1.434	1.436 & 1.433	m-b	$\overline{007}$, $\overline{602}$, $\overline{605}$

^aIntensity: s=strong, m=medium, w=weak, b=broad, and v=very

^bRefined monoclinic cell parameters: $a=9.918(2)\text{\AA}$, $b=9.252(2)\text{\AA}$, $c=10.354(2)\text{\AA}$, and $\beta=103.83(1)^\circ$

The monoclinic lattice had cell dimensions of $a=9.929(3)\text{\AA}$, $b=9.286(3)\text{\AA}$, $c=10.337(3)\text{\AA}$, $\beta=104.14(2)^\circ$, and volume= $924.2(5)\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. A refinement on 25 reflections with strong intensity and two theta values near 40° gave an idealized cell with the following lattice parameters: $a=9.929(2)\text{\AA}$, $b=9.294(1)\text{\AA}$, $c=10.338(2)\text{\AA}$, $\beta=104.13(2)^\circ$, and volume= $925.1(3)\text{\AA}^3$. Data were collected at room temperature from 0 to 50° in two theta in the hemisphere ($h, k, \pm l$), using an ω - 2θ scan mode. The number of reflections measured was 3417, of which 2066 were observed and 1015 were unique with $I > 3\sigma(I)$. The linear absorption coefficient for Mo $K\alpha$ was 115.170 cm^{-1} . An empirical absorption correction³⁶ was applied based upon one azimuthal scan of a reflection with an average transmission range of 0.763-1.000. The intensity data were corrected for Lorentz and polarization effects.

A large, black crystal of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ measuring $0.15 \times 0.20 \times 0.28\text{ mm}^3$ was mounted on a glass fiber. A Rigaku AFC6R rotating anode diffractometer was used with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069\text{\AA}$) generated at 7 kW. Lattice parameters and an orientation matrix for data collection were derived from 14 randomly located and centered reflections with a two theta range of 13 - 16° . The monoclinic lattice had cell dimensions of $a=9.928(3)\text{\AA}$, $b=9.285(3)\text{\AA}$, $c=10.359(3)\text{\AA}$, $\beta=103.79(2)^\circ$, and volume= $927.4(5)\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. A refinement on 25 reflections with strong intensity and two theta values ranging from 39 to 41° gave an idealized cell with the following lattice parameters: $a=9.917(1)\text{\AA}$, $b=9.276(1)\text{\AA}$, $c=10.3560(9)\text{\AA}$, $\beta=103.827(7)^\circ$, and volume= $925.1(2)\text{\AA}^3$. Data were collected at room temperature from 0 to 55° in two theta in the octants ($h, k, \pm l$), using an ω - 2θ scan mode. The number of reflections measured was 2403, of which 2009 were observed and 1830 were

unique with $I > 3\sigma(I)$. The linear absorption coefficient for Mo K α was 229.19 cm⁻¹. A spherical absorption correction⁴⁸ was applied based upon an average radius of 0.1 mm and three azimuthal scans of reflections with an average transmission range of 0.563-1.000. The intensity data were corrected for Lorentz and polarization effects.

A small, black crystal of K_{2.6}Sr_{0.4}Mo₁₄O₂₂ measuring 0.03 x 0.04 x 0.05 mm³ was mounted on a glass fiber. A Rigaku AFC6R rotating anode diffractometer was used with graphite monochromated Mo K α radiation ($\lambda=0.71069\text{\AA}$) generated at 7 kW. Lattice parameters and an orientation matrix for data collection were derived from 25 randomly located and centered reflections with a two theta range of 13-29°. The monoclinic lattice had cell dimensions of $a=9.917(2)\text{\AA}$, $b=9.253(2)\text{\AA}$, $c=10.355(2)\text{\AA}$, $\beta=103.83(2)^\circ$, and volume= $922.7(3)\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. The final idealized cell gave the following lattice parameters: $a=9.918(2)\text{\AA}$, $b=9.252(2)\text{\AA}$, $c=10.354(2)\text{\AA}$, $\beta=103.83(1)^\circ$, and volume= $925.5(3)\text{\AA}^3$. Data were collected at room temperature from 0 to 50° in two theta in the octants (h,k, $\pm$ l), using an ω -2 θ scan mode. The number of reflections measured was 1839, of which 623 were observed and unique with $I > 3\sigma(I)$. The intensity data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The space group P2₁/a (#14) was chosen for K_{1.29}Sn_{1.71}Mo₁₄O₂₂, based upon the systematic absences of $h0l$: $h \neq 2n$ and $0k0$: $k \neq 2n$, with no violations. The structure was solved by direct methods using SHELXS³⁷ ($R=0.037$) and refined on $|F|$ by full matrix least squares techniques³⁸ with the TEXSAN³⁹

package. Based upon lattice parameters and systematic absences, the molybdenum oxide framework was presumed to be isostructural to $K_3Mo_{14}O_{22}$.⁷ Therefore, atomic positions for the molybdenum and oxygen atoms were entered based upon the $K_3Mo_{14}O_{22}$ member. These parameters converged at R=24%. Two cation positions were located from electron density difference maps, one at the origin and one at approximately 0,0,0.35. These two positions were entered as K1 and Sn2, respectively. With these atoms included, the refinement converged at 17%. All the atomic thermal parameters were refined isotropically. Cation occupancies that combined potassium and tin on the origin and only tin on the second cation site were refined. All molybdenum atom thermal parameters were then refined anisotropically. The refinement converged at R=5.9%. At this point, a Fourier difference map revealed two more cation sites, one located near the origin ($\sim 0.5\text{\AA}$ away) and the second about $0.7\text{\AA}$ from the cation at the general position. Neither peak was accounted for by the thermal parameters of the cations already refined. Both peaks were entered, Sn1A and K2A, and positionally refined with very low occupancies, to prevent the refinement from diverging. After convergence, the origin satellite cation atom and its multiplicity were refined solely as tin, due to two short cation-oxygen bond distances that could not reasonably be accepted as potassium-oxygen distances. The origin and its satellite were determined to be fully occupied and both of their thermal parameters were refined anisotropically. The satellite related to Sn2 was refined as potassium. Based upon bond valence sums, potassium or tin could occupy the satellite position, but microprobe analyses indicated that no more tin should be present, therefore potassium was chosen to reside in this site. This second cation and its satellite also refined to full occupancy. In this case the thermal parameter of the major site, Sn2, was refined anisotropically, however, the corresponding thermal parameters for the potassium satellite would only refine isotropically. This thermal behavior was most likely due to the proximity of large electron density from the majority site, Sn2. The thermal parameters for the

oxygen atoms that could be refined anisotropically, without going negative, were varied. A secondary extinction correction was applied and refined to $3.1(2) \times 10^{-7}$, the residual decreased to $R=2.45\%$.

The final occupancy for the potassium at the origin was determined to be 59(1)%. The satellite tin atom, Sn1A, had an occupancy of 41(1)%. Thus, an atom always resides on or near the origin. Sn2 was refined with an occupancy of 64.8(6)% with the satellite, K2A, at 35.2(6)% occupancy. Again, this site was also determined to be fully occupied. This cation assessment results in the following formulation, $K_{1.29(1)}Sn_{1.71(1)}Mo_4O_{22}$, in good agreement with microprobe analyses, which will be discussed after the analysis of the cation coordination environment. The final refinement converged at $R=0.0245$ and $R_w=0.0299$ with all seven molybdenums, nine of the eleven oxygens, and three of the four unique cations having their thermal parameters refined anisotropically. A final Fourier electron difference map indicated that the largest peak of $1.07 \text{ e}/\text{\AA}^3$ was located $1.4\text{\AA}$ from Mo4 and the smallest peak of $-1.09 \text{ e}/\text{\AA}^3$ was located $2.3\text{\AA}$ from Mo6.

Details of the data collection and refinement for $K_{1.29}Sn_{1.71}Mo_4O_{22}$ are given in Table 2.3. Final positional parameters and isotropic temperature parameters are given in Table 2.4. Anisotropic temperature factors are listed in Table 2.5. Selected metal-metal and metal-oxygen interatomic distances are given in Table 2.6. Selected bond angles are found in Table 2.7.

The space group $P2_1/a$ (#14) was also chosen for $K_{1.66}Pb_{1.34}Mo_4O_{22}$ based upon the systematic absences of $h0l$: $h \neq 2n$ and $0k0$: $k \neq 2n$. However, there were fifteen violations of the former condition and one violation of the latter. Some, although not all, of the violations could be interpreted as shoulders to very large neighboring peaks. The data were processed in three space groups: $P2_1$, Pa , and $P2_1/a$; and the predicted refinement based on SHELXS³⁷ direct methods was 0.022, 0.027, and 0.032, respectively. The structure was subsequently

Table 2.3. X-ray crystallographic data for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$

formula	$K_{1.29}Sn_{1.71}Mo_{14}O_{22}$
formula weight	1948.54
crystal system	monoclinic
space group	$P2_1/a$ (#14)
a, Å	9.929(2)
b, Å	9.294(1)
c, Å	10.338(2)
β , degrees	104.13(2)
volume, Å ³	925.1(3)
Z	2
calculated density, g/cm ³	6.975
F000	1666
crystal size, mm ³	0.06 x 0.08 x 0.10
μ (Mo K α), cm ⁻¹	115.170
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.709580
temperature, °C	24
two theta range, degrees	0-50
scan mode	ω -2 θ
No. reflections collected	3471
No. observations ($I > 3\sigma(I)$), (unique)	2066 (1015)
No. variables	182
goodness of fit ^a	0.925
max. shift in final cycle	0.099
largest peaks in final diff. map, e/Å ³	+1.07, -1.09
transmission coefficient	0.827-1.000
R^b , R_w^c	0.0245, 0.0299

$$^a \text{Quality of fit} = [\sum \omega (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^c R_w = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}; \omega = 1/\sigma^2(|F_o|)$$

Table 2.4. Atomic coordinates for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$

Atom ^a	X	Y	Z	B _{eq} ^b
K1 ^c	0.0	0.0	0.0	3.(1)
Sn1A ^c	0.036(2)	0.990(3)	0.039(2)	3.0(5)
Sn2 ^d	0.0449(1)	0.0281(1)	0.3528(1)	1.30(5)
K2A ^d	0.0633(9)	0.005(1)	0.2994(9)	1.6(2)
Mo1	0.11946(8)	0.3850(1)	0.13931(8)	0.40(3)
Mo2	0.91251(8)	0.3799(1)	0.28156(9)	0.61(3)
Mo3	0.22609(9)	0.6317(1)	0.2828(1)	0.73(4)
Mo4	0.84360(9)	0.3717(1)	0.0004(1)	0.92(4)
Mo5	0.19152(9)	0.3842(1)	0.41321(8)	0.42(3)
Mo6	0.05033(8)	0.3819(1)	0.86318(8)	0.46(3)
Mo7	0.9750(1)	0.3783(1)	0.5831(1)	0.85(4)
O1	0.1733(7)	0.2576(8)	0.0033(7)	0.7(3)
O2	0.4004(7)	0.7579(8)	0.2844(6)	0.6(3)
O3	0.1839(7)	0.7544(8)	0.4295(6)	0.8(3)
O4	0.8486(7)	0.4994(9)	0.4286(7)	1.1(1)
O5	0.7794(7)	0.4926(8)	0.1398(6)	0.9(3)
O6	0.2889(7)	0.5105(8)	0.1441(6)	0.9(1)
O7	0.1079(8)	0.7600(8)	0.1425(7)	1.0(3)
O8	0.3553(6)	0.5066(7)	0.4255(7)	0.6(2)
O9	0.0309(7)	0.2564(8)	0.4299(7)	0.8(3)
O10	0.2432(7)	0.2555(7)	0.2879(6)	0.8(3)
O11	0.9620(8)	0.2432(8)	0.1462(7)	1.0(3)

^aAll atoms reside on the Wyckoff position 4e, except K1, which resides on 2a

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3 \{ \sum_i \sum_j (U_{ij} a_i^* a_j^* a_i \cdot a_j) \}$, where the summations of i and j range from 1 to 3

^cSn1A is a satellite of K1, with occupancies of 41(1)% and 59(1)%, respectively

^dSn2 has an occupancy of 64.8(6)% with a satellite labelled K2A that has an occupancy of 35.2(6)%

Table 2.5. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
K1	60.(3)	40.(1)	10.(1)	-30.(2)	-10.(1)	10.(1)
Sn1A	35.(6)	26.(5)	50.(1)	-3.(4)	-2.(8)	-3.(8)
Sn2	11.4(6)	15.8(7)	21.7(8)	0.3(5)	3.3(6)	-2.1(6)
K2A	20.(2)					
Mo1	6.2(4)	4.9(5)	4.2(4)	-1.4(4)	1.5(3)	-0.8(4)
Mo2	5.4(4)	5.3(5)	12.6(5)	0.3(4)	2.6(4)	0.9(4)
Mo3	5.6(4)	4.9(5)	15.4(5)	0.5(4)	-1.3(4)	-3.5(4)
Mo4	5.7(5)	5.6(5)	24.6(5)	0.5(4)	5.6(4)	3.0(4)
Mo5	5.7(4)	5.5(5)	4.9(4)	0.0(4)	1.3(3)	-0.4(4)
Mo6	5.5(4)	7.4(5)	4.2(4)	-1.3(4)	0.8(3)	-0.7(4)
Mo7	5.4(4)	7.4(5)	17.9(5)	0.9(4)	-0.6(4)	-6.4(4)
O1	5.(4)	10.(4)	10.(3)	-3.(3)	1.(3)	-4.(3)
O2	5.(4)	13.(4)	2.(3)	0.(3)	-0.(3)	-1.(3)
O3	14.(4)	9.(4)	7.(4)	-3.(3)	4.(3)	2.(3)
O4	14.(2)					
O5	14.(4)	11.(4)	12.(4)	-6.(3)	6.(3)	4.(3)
O6	11.(2)					
O7	15.(4)	11.(4)	10.(4)	-5.(3)	4.(3)	-2.(3)
O8	8.(3)	5.(4)	11.(3)	-1.(3)	3.(3)	-4.(3)
O9	7.(4)	10.(4)	12.(4)	-2.(3)	1.(3)	-0.(3)
O10	10.(4)	6.(4)	14.(4)	1.(3)	4.(3)	-0.(3)
O11	13.(4)	17.(4)	9.(3)	-3.(3)	3.(3)	-1.(3)

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a*b*U_{12}hk+2a*c*U_{13}hl+2b*c*U_{23}kl))$

^bThe thermal parameters of K2A, O4, and O6 only refined isotropically

Table 2.6. Selected interatomic distances (Å) for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ ^a

Mo1-Mo2'	2.804(1)	Mo1-Mo3	2.795(1)
Mo1-Mo4	2.767(1)	Mo1-Mo4'	2.755(1)
Mo1-Mo5	2.746(1)	Mo1-Mo6	2.768(1)
Mo1-Mo6'	2.741(1)	Mo2-Mo4 apical ^b	2.820(1)
Mo2-Mo5'	2.773(1)	Mo2-Mo6	2.747(1)
Mo2-Mo7	2.736(1)	Mo2-Mo7' inter ^c	3.026(1)
Mo3-Mo4 apical	2.839(1)	Mo3-Mo5	2.730(1)
Mo3-Mo6'	2.794(1)	Mo3-Mo7'	2.696(1)
Mo4-Mo6	2.759(1)	Mo4-Mo6'	2.767(1)
Mo5-Mo7'	2.764(1)	Mo5-Mo7' inter	3.091(1)
Mo6-Mo7	2.808(1)	Mo7-Mo7' inter	2.955(2)
Sn2...K2A ^d	0.660(8)	Sn2...Sn2 ^d inter	3.414(3)
Sn2...Sn1A ^d	3.303(8)	K2A...Sn1A ^d	2.70(1)
K2A...K1 ^d	3.004(9)	Sn1A...Sn1A ^d	0.93(2)
Sn1A...K1 ^d	0.464(9)	Mo1-O1	2.009(7)
Mo1-O6	2.036(7)	Mo1-O10	2.097(7)
Mo1-O11'	2.058(8)	Mo2-O4	2.101(7)
Mo2-O5	2.011(7)	Mo2-O9	2.041(7)
Mo2-O10	2.113(7)	Mo2-O11	2.037(7)
Mo3-O2	2.086(7)	Mo3-O3	2.021(7)
Mo3-O6	2.038(7)	Mo3-O7	2.017(8)
Mo3-O8	2.061(7)	Mo4-O1	2.080(7)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

^bApical-apical Mo-Mo bond distances

^cIntercluster Mo-Mo bond distances

^dPartially occupied positions

Table 2.6. (continued)

Mo4-O5	2.048(7)	Mo4-O6	2.050(7)
Mo4-O7	2.064(7)	Mo4-O11	2.053(8)
Mo5-O3'	2.156(7)	Mo5-O4'	2.080(7)
Mo5-O8	1.963(7)	Mo5-O9'	2.029(8)
Mo5-O10	1.925(7)	Mo6-O1	2.015(7)
Mo6-O2	2.064(7)	Mo6-O5	2.060(7)
Mo6-O7'	2.041(7)	Mo7-O2	1.959(7)
Mo7'-O3'	1.981(7)	Mo7-O4	2.102(7)
Mo7-O4'	2.115(7)	Mo7-O9'	2.129(7)
Sn1A-O1	2.887(9)	Sn1A-O1'	3.069(9)
Sn1A-O5	2.38(1)	Sn1A-O5'	3.23(1)
Sn1A-O6	2.972(9)	Sn1A-O6'	2.811(9)
Sn1A-O7	2.42(1)	Sn1A-O7'	3.10(1)
Sn1A-O11	2.82(1)	Sn1A-O11'	2.85(1)
K1-O1 (x2)	2.943(7)	K1-O5 (x2)	2.798(7)
K1-O6 (x2)	2.855(6)	K1-O7 (x2)	2.743(8)
K1-O11 (x2)	2.795(7)	Sn2-O2	3.020(7)
Sn2-O3	2.910(7)	Sn2-O4	2.936(7)
Sn2-O6	2.927(7)	Sn2-O8	2.215(6)
Sn2-O8'	2.272(7)	Sn2-O9	2.283(7)
Sn2-O10	3.072(7)	Sn2-O11	2.895(8)
K2A-O2	2.91(1)	K2A-O3	2.80(1)
K2A-O4	2.82(1)	K2A-O5	3.01(1)
K2A-O6	2.81(1)	K2A-O7	2.89(1)
K2A-O8	2.70(1)	K2A-O8'	2.76(1)
K2A-O9	2.76(1)	K2A-O10	2.95(1)
K2A-O11	2.77(1)		

Table 2.7. Selected bond angles (degrees) for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ ^a

Mo2'-Mo1-Mo3	88.09(4)	Mo4-Mo1-Mo4'	90.37(4)
Mo5-Mo1-Mo6	178.93(5)	Mo5-Mo1-Mo6'	90.96(4)
Mo6-Mo1-Mo6'	90.10(4)	Mo5-Mo1-O6	88.3(2)
Mo5-Mo1-O11'	88.4(2)	Mo6-Mo1-O11'	91.7(2)
O6-Mo1-O11'	174.1(3)	Mo1'-Mo2-Mo7	89.68(4)
Mo4-Mo2-Mo7'	177.18(4)	Mo5'-Mo2-Mo6	90.28(4)
Mo4-Mo2-O10	91.2(2)	O4-Mo2-O11	173.0(3)
O5-Mo2-O9	174.3(3)	O5-Mo2-O11	92.9(3)
Mo1-Mo3-Mo7'	90.70(4)	Mo5-Mo3-Mo6'	90.19(4)
Mo4-Mo3-O2	90.4(2)	O3-Mo3-O6	174.4(3)
O6-Mo3-O7	92.6(3)	O7-Mo3-O8	177.2(3)
Mo1-Mo4-Mo1'	89.63(4)	Mo2-Mo4-Mo3	179.10(5)
Mo6-Mo4-Mo6'	89.73(4)	Mo2-Mo4-O1	89.7(2)
Mo3-Mo4-O1	90.8(2)	O5-Mo4-O7	175.0(3)
O5-Mo4-O11	91.4(3)	O6-Mo4-O7	90.9(3)
O6-Mo4-O11	175.2(3)	Mo1-Mo5-Mo7'	90.31(4)
Mo2'-Mo5-Mo3	90.04(4)	Mo1-Mo5-O8	93.9(2)
Mo1-Mo5-O9'	94.4(2)	O8-Mo5-O9'	171.7(3)
Mo1-Mo6-Mo1'	89.90(4)	Mo1'-Mo6-Mo7	89.51(4)
Mo1-Mo6-Mo7	178.94(4)	Mo2-Mo6-Mo3'	89.26(4)
Mo1-Mo6-O5	90.7(2)	Mo1-Mo6-O7'	91.8(2)
O5-Mo6-O7'	173.7(3)	Mo2-Mo7-Mo3'	91.53(4)
Mo2'-Mo7-Mo6	176.38(4)	Mo5'-Mo7-Mo6	89.20(4)
Mo6-Mo7-O3'	94.7(2)	Mo6-Mo7-O4	92.1(2)
O3'-Mo7-O4	170.9(3)	Mo1-O1-Mo6	86.9(3)
K1-O1-Mo4	90.3(2)	Sn1A-O1-Mo4	84.4(3)
Mo6-O2-Mo7	88.5(3)	Sn2-O2-Mo3	81.6(2)
K2A-O2-Mo3	88.8(3)	Mo5-O4-Mo7'	94.9(3)
Mo1-O10-Mo5	86.0(3)	Sn2-O10-Mo2	98.9(3)
K2A-O10-Mo2	91.5(3)	K2A-Sn1A-K1	127.4(9)
Sn2-K2A-Sn1A	153.(1)		

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

solved in $P2_1$ and $P2_1/a$. The refinement in $P2_1$ converged at $R=5.58\%$ and $R_w=7.49\%$, however, only the thermal parameters of the heavy atoms would refine isotropically and the oxygen atom thermal parameters could not be varied. This solution was not data limited (13:1 data to parameter ratio) even though all atoms become unique in $P2_1$. The general structural features were essentially identical to the refinement in $P2_1/a$, with only small distortions. The violations observed for $P2_1/a$ would seem to imply that the cluster is distorting slightly, but not enough to give adequate intensity information to solve the structure in $P2_1$.

The structure was therefore solved in $P2_1/a$ by direct methods using SHELXS³⁷ ($R=0.032$) and refined on $|F|$ by full matrix least squares techniques³⁸ with the TEXSAN³⁹ package. The lattice parameters and systematic absences indicated that this phase should be isostructural to $K_3Mo_{14}O_{22}$.⁷ Therefore, atomic positions for the molybdenum and oxygen atoms were entered based upon the $K_3Mo_{14}O_{22}$ member. A refinement on these positional parameters converged at 31%. The two major cation positions were then easily located from a Fourier difference map. With these two cation positions refined and their occupancy varied with a combination of potassium and lead, the R factor was 13%. Appropriate isotropic and anisotropic thermal parameters were varied and converged at $R=7.9\%$ and $R_w=10\%$, although only the cation and three molybdenum thermal parameters would refine anisotropically. The significant absorption of this phase, due in large part to the lead content, and the high R factor implied that an appropriate absorption correction was not being applied. When a secondary empirical DIFABS⁴⁹ correction (0.829-1.087) was subsequently applied to the isotropically refined data, the refinement converged at $R=5.49\%$ and $R_w=8.12\%$. Thermal parameters on all the atoms were unusually small. The final formulation was $K_{0.76(4)}Pb_{1.52(4)}Mo_{14}O_{22}$.

Because this solution was not very satisfactory, the structure was resolved by a second approach using the same data. In this case, the data were corrected

for absorption by an alternate route. A spherical absorption correction, in tandem with the azimuthal scans, was applied.⁴⁸ In this case, all the heavy atoms and two oxygen atom thermal parameters could be refined anisotropically and the remaining nine oxygen atom temperature factors were treated isotropically. Unlike the $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$, this compound had only the two unique cation positions, similar to that of $K_3Mo_{14}O_{22}$. Because microprobe analyses indicated full cation occupancy, potassium and lead were allowed to refine on both sites, with the only restriction being full occupancy. This refinement converged at $R=7.91\%$ and $R_w=6.43\%$. Again the DIFABS⁴⁹ correction (0.876-1.136) was applied was applied after isotropic refinement. Cation occupancies and thermal parameters were allowed to vary. This set of conditions converged at $R=6.00\%$ and $R_w=4.81\%$ with the origin fully occupied (76.0(6)% K and 24.0(6)% Pb) and the second cation position 45.0(8)% K and 55.0(8)% Pb. The final formulation for this compound was $K_{1.66(1)}Pb_{1.34(1)}Mo_{14}O_{22}$. The final electron difference map indicated that the largest peak of $+4.53e/\text{\AA}^3$ was located 1.63\AA from Pb2 and 2.09\AA from O8 (the region of inter-cluster bonding) and the smallest peak of $-4.11e/\text{\AA}^3$ was located 0.80\AA from Pb2.

Details of the data collection and refinement for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ are given in Table 2.8. Final positional and isotropic temperature parameters are found in Table 2.9. Anisotropic temperature factors are listed in Table 2.10. Selected metal-metal and metal-oxygen bond distances are given in Table 2.11. Selected bond angles can be found in Table 2.12.

The space $P2_1/a$ (#14) also was chosen for $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$ based upon the systematic absences of $h0l$: $h \neq 2n$ and $0k0$: $k \neq 2n$. There were no violations of these two conditions. Unfortunately, the data collected was quite limited, with only 600 unique reflections observed. The small crystal size might reasonable be the problem for the limited data. This phase was presumed to be isostructural to the other known $n=3$ oligomeric members, thus approximate atomic positions

Table 2.8. X-ray crystallographic data for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$

formula	$K_{1.66}Pb_{1.34}Mo_{14}O_{22}$
formula weight	2037.70
crystal system	monoclinic
space group	$P2_1/a$ (#14)
a, Å	9.917(1)
b, Å	9.276(1)
c, Å	10.3560(9)
β , degrees	103.827(7)
volume, Å ³	925.1(2)
Z	2
calculated density, g/cm ³	7.313
F000	1692
crystal size, mm ³	0.15 x 0.20 x 0.28
μ (Mo K α), cm ⁻¹	229.190
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.709580
temperature, °C	24
two theta range, degrees	0-55
scan mode	ω -2 θ
No. reflections collected	2403
No. observations ($I > 3\sigma(I)$), (unique)	2009 (1830)
No. variables	135
goodness of fit ^a	5.414
max. shift in final cycle	0.010
largest peaks in final diff. map, e/Å ³	+4.53, -4.11
transmission coefficient	0.563-1.000
R^b , R_w^c	0.0600, 0.0481

$$^a \text{Quality of fit} = [\sum \omega (F_o - F_c)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum (F_o - F_c) / \sum F_o$$

$$^c R_w = [\sum \omega (F_o - F_c)^2 / \sum \omega F_o^2]^{1/2}; \omega = 1/\sigma^2(F_o)$$

Table 2.9. Atomic coordinates for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$

Atom ^a	X	Y	Z	B _{eq} ^b
K1/Pb1 ^c	0.0	0.0	0.0	2.0(2)
K2/Pb2 ^d	0.0552(2)	0.0099(2)	0.3349(1)	1.50(6)
Mo1	0.1213(2)	0.3876(2)	0.1391(2)	0.31(5)
Mo2	0.9108(2)	0.3763(2)	0.2735(2)	0.40(6)
Mo3	0.2261(2)	0.6305(2)	0.2888(1)	0.38(6)
Mo4	0.8466(2)	0.3706(2)	0.0116(2)	0.40(6)
Mo5	0.1892(2)	0.3837(2)	0.4123(1)	0.33(6)
Mo6	0.0483(2)	0.3794(2)	0.8601(1)	0.32(6)
Mo7	0.9774(2)	0.3841(2)	0.5818(2)	0.47(6)
O1	0.174(1)	0.245(1)	0.003(1)	0.3(2)
O2	0.402(1)	0.755(1)	0.287(1)	0.5(2)
O3	0.185(1)	0.744(1)	0.428(1)	0.4(2)
O4	0.845(1)	0.495(1)	0.423(1)	0.3(2)
O5	0.776(1)	0.499(1)	0.139(1)	0.5(2)
O6	0.287(1)	0.519(1)	0.146(1)	0.5(2)
O7	0.113(1)	0.743(1)	0.143(1)	0.4(2)
O8	0.349(1)	0.507(2)	0.424(1)	0.6(2)
O9	0.029(2)	0.260(1)	0.431(1)	0.8(2)
O10	0.257(2)	0.243(2)	0.285(1)	0.9(5)
O11	0.970(2)	0.236(1)	0.147(1)	0.7(5)

^aAll atoms reside on the Wyckoff position 4e, except K1/Pb1 which resides on 2a

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3 \sum_i \sum_j (U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j)$, where the summations of i and j range from 1 to 3

^cK1 and Pb1 have occupancies of 76.0(6)% and 24.0(6)%, respectively

^dK2 and Pb2 have occupancies of 45.0(8)% and 55.0(8)%, respectively

Table 2.10. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{K}_{1.66}\text{Pb}_{1.34}\text{Mo}_{14}\text{O}_{22}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb1/K1	38.(3)	23.(2)	19.(2)	-6.(3)	14.(2)	-5.(2)
Pb2/K2	14.2(8)	18.3(7)	21.8(8)	-1.1(6)	-1.0(5)	2.4(6)
Mo1	2.8(8)	4.3(7)	3.7(7)	0.4(7)	-0.9(6)	-0.0(6)
Mo2	4.9(9)	4.6(8)	5.5(7)	0.1(7)	0.6(6)	-0.0(6)
Mo3	3.8(9)	4.4(8)	5.5(7)	-0.6(7)	-0.5(6)	-0.5(6)
Mo4	3.2(9)	5.2(8)	6.2(7)	-0.1(7)	0.1(6)	-0.1(6)
Mo5	4.1(9)	4.4(7)	3.4(7)	0.4(7)	0.1(6)	-0.1(6)
Mo6	2.7(9)	4.3(7)	4.3(7)	0.1(7)	-0.8(6)	-0.2(6)
Mo7	3.3(9)	7.7(8)	6.0(7)	1.2(7)	-0.5(6)	-2.9(6)
O1	4.(3)					
O2	7.(3)					
O3	6.(3)					
O4	4.(3)					
O5	6.(3)					
O6	6.(3)					
O7	5.(3)					
O8	8.(3)					
O9	11.(3)					
O10	9.(8)	16.(7)	6.(6)	-10.(6)	-1.(5)	-3.(6)
O11	14.(8)	9.(7)	2.(6)	5.(6)	-0.(5)	-1.(5)

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a*b*U_{12}hk+2a*c*U_{13}hl+2b*c*U_{23}kl))$

^bThe thermal parameters of K1 and K2 were fixed to the anisotropic values of Pb1 and Pb2, respectively. The thermal parameters of oxygens O1 to O9 were only refined isotropically.

Table 2.11. Selected bond distances (Å) for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ ^a

Mo1-Mo2'	2.774(2)	Mo1-Mo3	2.792(2)
Mo1-Mo4	2.794(2)	Mo1-Mo4'	2.734(2)
Mo1-Mo5	2.748(2)	Mo1-Mo6	2.806(2)
Mo1-Mo6'	2.740(2)	Mo2-Mo4 apical ^b	2.634(2)
Mo2-Mo5'	2.793(2)	Mo2-Mo6	2.735(2)
Mo2-Mo7	2.761(2)	Mo2-Mo7' inter ^c	3.103(2)
Mo3-Mo4 apical	3.021(2)	Mo3-Mo5	2.689(2)
Mo3-Mo6'	2.790(3)	Mo3-Mo7'	2.680(2)
Mo4-Mo6	2.750(2)	Mo4-Mo6'	2.823(2)
Mo5-Mo7'	2.725(2)	Mo5-Mo7' inter	3.042(2)
Mo6-Mo7	2.800(2)	Mo7-Mo7' inter	2.838(4)
Pb1...Pb2 ^d	3.380(1)	Pb2...Pb2 ^d inter	3.836(3)
Mo1-O1	2.03(1)	Mo1-O6	2.03(1)
Mo1-O10	2.08(1)	Mo1-O11'	2.07(1)
Mo2-O4	2.13(1)	Mo2-O5	2.03(1)
Mo2-O9	2.07(1)	Mo2-O10	2.10(1)
Mo2-O11	2.03(1)	Mo3-O2	2.10(1)
Mo3-O3	1.97(1)	Mo3-O6	2.01(1)
Mo3-O7	2.03(1)	Mo3-O8	1.99(1)
Mo4-O1	2.05(1)	Mo4-O5	2.02(1)
Mo4-O6	2.10(1)	Mo4-O7	2.11(1)
Mo4-O11	2.05(1)	Mo5-O3'	2.17(1)
Mo5-O4'	2.14(1)	Mo5-O8	1.93(1)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

^bApical-apical Mo-Mo bond distances

^cIntercluster Mo-Mo bond distances

^dPb1 and K1 both reside at the origin

Table 2.11. (continued)

Mo5-O9'	2.01(1)	Mo5-O10	1.93(1)
Mo6-O1	2.05(1)	Mo6-O2	2.07(1)
Mo6-O5	2.07(1)	Mo6-O7'	2.04(1)
Mo7-O2	1.98(1)	Mo7'-O3'	2.05(1)
Mo7-O4	2.10(1)	Mo7-O4'	2.11(1)
Mo7-O9'	2.10(1)	Pb1-O1 (x2)	2.93(1)
Pb1-O5 (x2)	2.77(1)	Pb1-O6 (x2)	2.88(1)
Pb1-O7 (x2)	2.78(1)	Pb1-O11 (x2)	2.72(1)
Pb2-O2	2.86(1)	Pb2-O3	2.75(1)
Pb2-O4	2.80(1)	Pb2-O6	2.91(1)
Pb2-O7	3.21(1)	Pb2-O8	2.45(1)
Pb2-O8'	2.44(1)	Pb2-O9	2.56(1)
Pb2-O10	3.08(2)	Pb2-O11	2.85(1)

were initially refined based on the $K_3Mo_{14}O_{22}$ member.⁷ The limited data would only allow the positional parameters for all the atoms and the occupancy of the cations to be varied. This set of conditions converged at approximately 23%, therefore, no detailed crystallographic information will be given. However, throughout the discussion of the other trimeric members, brief comments on $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$ might be included. Perhaps, the poor refinement might also be a consequence of poor crystal quality due to intergrowth of other oligomeric members.

2 of 4

Table 2.12. Selected bond angles (degrees) for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ ^a

Mo2'-Mo1-Mo3	88.65(7)	Mo4-Mo1-Mo4'	90.57(7)
Mo5-Mo1-Mo6	177.59(9)	Mo5-Mo1-Mo6'	90.39(7)
Mo6-Mo1-Mo6'	90.95(7)	Mo5-Mo1-O6	88.6(3)
Mo5-Mo1-O11'	87.2(3)	Mo6-Mo1-O11'	94.9(4)
O6-Mo1-O11'	172.8(5)	Mo1'-Mo2-Mo7	89.41(7)
Mo4-Mo2-Mo7'	178.33(9)	Mo5'-Mo2-Mo6	89.56(7)
Mo4-Mo2-O10	92.6(3)	O4-Mo2-O11	171.3(5)
O5-Mo2-O9	170.9(5)	O5-Mo2-O11	99.3(5)
Mo1-Mo3-Mo7'	90.70(7)	Mo5-Mo3-Mo6'	90.54(7)
Mo4-Mo3-O2	89.3(3)	O3-Mo3-O6	173.1(6)
O6-Mo3-O7	87.6(5)	O7-Mo3-O8	175.5(5)
Mo1-Mo4-Mo1'	89.43(7)	Mo2-Mo4-Mo3	179.03(9)
Mo6-Mo4-Mo6'	90.38(7)	Mo2-Mo4-O1	92.8(3)
Mo3-Mo4-O1	87.9(3)	O5-Mo4-O7	170.3(5)
O5-Mo4-O11	99.0(5)	O6-Mo4-O7	83.3(5)
O6-Mo4-O11	171.3(5)	Mo1-Mo5-Mo7'	90.70(7)
Mo2'-Mo5-Mo3	90.35(7)	Mo1-Mo5-O8	93.1(4)
Mo1-Mo5-O9'	95.9(4)	O8-Mo5-O9'	170.9(5)
Mo1-Mo6-Mo1'	89.05(7)	Mo1'-Mo6-Mo7	89.30(7)
Mo1-Mo6-Mo7	177.54(9)	Mo2-Mo6-Mo3'	89.46(7)
Mo1-Mo6-O5	88.3(3)	Mo1-Mo6-O7'	92.4(4)
O5-Mo6-O7'	174.4(5)	Mo2-Mo7-Mo3'	91.24(7)
Mo2'-Mo7-Mo6	176.90(9)	Mo5'-Mo7-Mo6	89.62(7)
Mo6-Mo7-O3'	92.5(3)	Mo6-Mo7-O4	91.5(3)
O3'-Mo7-O4	171.8(5)	Mo1-O1-Mo6	87.0(5)
Pb1-O1-Mo4	91.3(4)	Mo6-O2-Mo7	87.5(5)
Pb2-O2-Mo3	86.3(4)	Mo5-O4-Mo7'	91.9(5)
Mo1-O10-Mo5	86.4(5)	Pb2-O10-Mo2	95.1(5)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

RESULTS AND DISCUSSION

Description of Structure

$K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ have a molybdenum-oxygen framework built up from clusters consisting of three trans edge-shared molybdenum octahedra. All exterior edges of the trimeric cluster are bridged by oxygen atoms and all apical molybdenums are also capped by oxygen atoms. Figures 2.1 and 2.2 are ORTEP⁴⁰ representations of the basic building block, the $Mo_{14}O_{34}$ cluster, found in the K-Sn and K-Pb members, respectively. The number of electrons formally available for metal-metal bonding is $44.7e^-$ in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $44.3e^-$ for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$, given K^+ , Sn^{2+} , Pb^{2+} , O^{2-} , and six electrons per molybdenum. These electron counts are intermediate members to the two previously reported $n=3$ oligomers: Simon's $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}^{30}$ ($45.6e^-$) and Chen's $K_3Mo_{14}O_{22}^7$ ($43.0e^-$). The variability in electron count can be observed via changes in the apical-apical and intercluster molybdenum bond distances, as summarized in Table 2.13.

From Table 2.13 a few generalizations can be extracted. When only $43e^-$ are available for metal-metal bonding, as with $K_3Mo_{14}O_{22}$, the clusters are interconnected primarily by metal-oxygen bonding; also two strong apical-apical Mo-Mo interactions are observed. When the system accepts up to approximately one more electron, it appears to be utilized in orbitals for intercluster metal-metal bonding, as exhibited in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. When the system contains greater than 44.5 and less than $46e^-$, as calculated for $K_{1.3}Sn_{1.7}Mo_{14}O_{22}$ and $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}$, the electrons might be entering nonbonding, or more likely, antibonding orbitals since the apical-apical bond order sums total $1.35e^-$ for the K-Sn member versus $2.28e^-$ for the K-Pb member. The intercluster bonding is also

Figure 2.1. An ORTEP representation (70% thermal ellipsoids) of the $\text{Mo}_{14}\text{O}_{34}$ cluster observed in $\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$. Note the four nearly equivalent apical-apical bond distances.

Figure 2.2. An ORTEP representation (70% thermal ellipsoids) of the $\text{Mo}_{14}\text{O}_{34}$ cluster observed in $\text{K}_{1.66}\text{Pb}_{1.34}\text{Mo}_{14}\text{O}_{22}$. Note the short-long arrangement of apical-apical bond distances.

Table 2.13. Bond distance-electron counting relationships in $M_xMo_{14}O_{22}$

$M_xMo_{14}O_{22}$	Apical ^a (Å)	Intercluster ^b (Å)	MCE(Σn) ^c	MCE(Σs) ^d	Formal ^e
$Tl_{1.6}Sn_{1.2}$	2.824(2) 2.856(2)	2.991(3), 3.040(2) 3.116(2)	43.4	45.4	45.6
$K_{1.29}Sn_{1.71}$	2.820(1) 2.839(1)	2.955(2), 3.026(1) 3.091(1)	42.7(2)	43.9(8)	44.7
$K_{1.66}Pb_{1.34}$	2.634(2) 3.021(2)	2.838(4), 3.042(2) 3.103(2)	44.1(3)	44.(1)	44.3
$K_{2.6}Sr_{0.4}$ ^f	2.68/3.04	2.84, 3.04, 3.06	-----	-----	43.4
K_3	2.639(2) 3.060(2)	3.191(2), 3.194(2) 3.234(2)	45.0(4)	42.(1)	43.0

^aApical-apical Mo-Mo bond distances^bIntercluster Mo-Mo bond distances^cNumber of electrons available for Mo-Mo bonding within the cluster unit, based upon Pauling's bond order equation⁴⁴^dNumber of electrons available for Mo-Mo bonding within the cluster unit, based upon an empirical bond valence equation⁴⁵^eFormal number of electrons available for Mo-Mo bonding, based upon six electrons from each Mo and the following oxidation states: Tl_2^{4+} , Sn^{2+} , Pb^{2+} , Sr^{2+} , K^+ , and O^{2-} ^fRefinement on a data limited structure, $R \sim 23\%$: $P2_1/a$, $a=9.918(2)\text{\AA}$, $b=9.252(2)\text{\AA}$, $c=10.354(2)\text{\AA}$, and $\beta=103.83(1)^\circ$

drastically weakened in the K-Sn member. If a material with at least $46e^-$ available for metal-metal bonding could be synthesized, the electrons would most certainly enter anti-bonding orbitals.

The angular relationships of the waist molybdenum atoms in the octahedra are quite regular for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. The interior

bond angles in the basal planes average $90.0 \pm 0.6^\circ$ for the former and $90.1 \pm 0.7^\circ$ for the latter. Bond angles along the basal edges are nearly linear for the K-Sn and K-Pb members at $178.93(5)^\circ$ and $177.59(9)^\circ$ for Mo5-Mo1-Mo6 and $178.94(4)^\circ$ and $177.54(9)^\circ$ for Mo1-Mo6-Mo7, respectively. The trans edge-shared molybdenum bond distances, perpendicular to the chain direction, are nearly identical ($2.764(1)\text{\AA}$ for Mo5-Mo7 and $2.768(1)\text{\AA}$ for Mo1-Mo6'), supporting the view of a condensation along trans edges of three nearly regular octahedra for $K_{1.3}Sn_{1.7}Mo_{14}O_{22}$. This arrangement is also seen in the $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ member ($2.725(2)\text{\AA}$ for Mo5-Mo7 and $2.740(2)\text{\AA}$ for Mo1-Mo6').

The average intracluster metal-metal bond distances are $2.769\text{\AA}$ for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $2.768\text{\AA}$ for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$, slightly shorter than the $2.78\text{\AA}$ reported for $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}$ and nearly identical to the $2.764\text{\AA}$ found in $K_3Mo_{14}O_{22}$. This similarity is rather striking; however, the best measure of the utilization of electrons in metal-metal bonding is through bond order sums.⁴³ Excluding the apical-apical bonds, the shortest metal-metal bond distances in all of the $n=3$ oligomers are the (Mo3-Mo7') distance, an exterior edge of the outer octahedron. There seems to be no logical explanation for this behavior.

Figures 2.3 and 2.4 illustrate the manner in which the trimeric cluster units connect in a stair-step fashion for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$, respectively. The K, K-Sn, and Tl-Sn members are essentially held together via molybdenum-oxygen bridges. The K-Pb and K-Sr members have significant intercluster metal-metal bonding. The details of the intercluster bond distances also are found in Table 2.13.

The molybdenum-oxygen bond distances in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ range from $1.925(7)\text{\AA}$ for (Mo5-O10) to $2.156(7)\text{\AA}$ for (Mo5-O3'). Similar results are observed for the same Mo-O bonds in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ ($1.93(1)\text{\AA}$ and $2.17(1)\text{\AA}$, respectively). The average Mo-O bond distance for both the K-Sn and the K-Pb

Figure 2.3. An ORTEP view (70% thermal ellipsoids) perpendicular to the c axis of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ with fragments of neighboring clusters included to indicate the stair-step manner in which the oligomeric units interconnect. Note the absence of intercluster metal-metal bonding.

Figure 2.4. An ORTEP view (70% thermal ellipsoids) perpendicular to the c axis of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ with fragments of neighboring clusters included to indicate the stair-step manner in which the oligomeric units interconnect, and the intercluster metal-metal bond.

members is 2.050Å, identical to $K_3Mo_{14}O_{22}$ and very similar to the 2.06Å distance reported for Simon's trimer, $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}$. The oxygen in the longest Mo-O bond, O3, is coordinated to only one molybdenum at the end of the cluster and one tin/potassium or lead cation in the pocket. The (Sn2-O3), (K2A-O3) or (Pb2-O3) bond distances at ~2.91, 2.80Å, or 2.75Å, respectively, indicate that O3 is not strongly coordinated to any metal atom in this cluster. However, O3 does show significant bonding to a molybdenum in a neighboring cluster of the K-Sn and K-Pb members, 1.981(7)Å or 2.05(1)Å for (Mo7'-O3'), respectively. The shortest Mo-O bond occurs on a basal edge-bridging position. This particular oxygen, O10, exhibits a rather long bond distance (~3.08Å for (Sn2- or Pb2-O10) or 2.95Å for (K2A-O10)) to either the tin/potassium or the lead cation. Neither the long nor the short Mo-O bond distances seem to correlate to any structural distortion; perhaps, they compensate for other subliminal inter- or intra-cluster distortions that must occur when two of these trimers are fused in a stair-step fashion. Once again, these two extreme distances are found in identical positions to those observed in the other two previously reported trimeric oligomers.

Within the Mo_{14} cluster, four molybdenums are four-coordinate in oxygen (Mo1 and Mo6) and the remaining ten molybdenums are all five-coordinate in oxygen (Mo2, Mo3, Mo4, Mo5, and Mo7). The connectivity of $K_{1.3}Sn_{1.7}Mo_{14}O_{22}$ or $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ can be expressed by the following formulation, $[M_3]^{y+} [(Mo_{14}O_{10}^i O_{4/2}^{i-i} O_{10/2}^{i-a}) O_{10/2}^{a-i}]^{y-}$. Oxygen atoms O5, O6, O7, O8, and O11 constitute the group labelled O^i , and are edge-bridging within the cluster unit. Oxygen 4 is defined as O^{i-i} , and is edge-sharing between neighboring clusters. Oxygen atoms labelled as O^{i-a} and O^{a-i} are edge-bridging between molybdenum atoms of one cluster and terminal to another molybdenum in a neighboring cluster (or vice versa); oxygen atoms O1, O2, O3, O9, and O10 define this class. This interconnectivity can be further observed in Figure 2.5 for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$.

Figure 2.5. An ORTEP view (70% thermal ellipsoids) of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ nearly parallel to the c axis, indicating the manner in which the chains interconnect, thus creating pockets for the cations. Cation-oxygen bonds omitted for clarity.

The voids where the cations reside are not channels, but rather, pockets in which both ends are partially closed by the neighboring Mo-O cluster fragments. This pocket is formed as a result of the stair-step interconnection between clusters. Figure 2.6 is a view nearly parallel to the c axis where the adjacent clusters have been included for the K-Sn member. The partial closure essentially traps the cations inside. From this arrangement of framework and cations, one could speculate that the growth of these types of compounds is not only driven by the formation of a strongly metal-metal bonded framework, but also, by the simultaneous formation of suitable cation-oxygen interactions.

Each pocket within a trimeric oligomer has space for three fully occupied cations, with each position located adjacent to a molybdenum octahedron. The compound, $K_{1.3}Sn_{1.7}Mo_{14}O_{22}$, has seven partially occupied cation positions, four unique, and total three cations per formula unit. Potassium was refined at the origin with an occupancy of 59%. The off-origin satellite position has a coordination environment better suited to accommodate tin. This tin position (Sn1A) resides 0.464(9)Å on either side of the origin and accounts for the remaining occupancy available to this position, 41%. The origin and its two satellite positions account for three of the seven positions. The outer cation positions were determined to be suitable only for tin and the satellites located to the interior side of the pocket were best refined as potassium (K2A). The major tin site (Sn2A) was found to be 65% occupied. The satellite potassium atom, 0.660(8)Å away from the major tin position utilizes the remaining 35% occupancy. These two cations, plus inversion, account for the four remaining cation sites within one pocket. The seven cation sites occupied by potassium and tin in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ do not reside in a linear fashion, but rather their positions are skewed in such a manner to create favorable coordination by oxygen atoms. This behavior can be seen in the cation angles, (K1-Sn1A-K2A) at 127.4(9)° and (Sn2-K2A-Sn1A) at 153.(1)°. The cation arrangement is much more clear and

Figure 2.6. An ORTEP view (70% thermal ellipsoids) of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ nearly parallel to the c axis. One adjacent set of trimeric cluster units is included in the c direction to indicate the cation pocket. Cation-oxygen bonds are omitted for clarity.

simple in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. Only the three main cation positions were occupied, with the origin containing potassium 76% and lead 24% and the second position refined as 45% potassium and 55% lead.

The coordination at the origin for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ is quite regular, as shown in Figure 2.7, with ten oxygens ranging from 2.743(8)Å for (K1-O7) to 2.943(7)Å for (K1-O1). The eight closest oxygens, which have cation-oxygen bond valence sums greater than 0.1 valence units, form a nearly regular cube around the potassium. The origin satellites of tin are nine-coordinate in oxygen, using the same criterion as K1, but are arranged irregularly, with no definitive coordination geometry, from 2.38(1)Å for (Sn1A-O5) to 3.10(1)Å for (Sn1A-O7'). As viewed in Figure 2.8, the other major cation site, Sn2, is nine coordinate in oxygen, however, three of these oxygens are strongly bonded: (Sn2-O9) at 2.283(7)Å, (Sn2-O8) at 2.215(6)Å, and (Sn2-O8') at 2.272(7)Å. These three oxygens and the tin (Sn2) have a trigonal prismatic geometry. The remaining six oxygens are weakly coordinated, ranging from 2.895(8)Å for (Sn2-O11) to 2.936(7)Å for (Sn2-O4). The satellite of this tin cation is eleven-coordinate in oxygen, varying from 2.70(1)Å for (K2A-O8) to 3.01(1)Å for (K2A-O5).

The tendency of the cations in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ to move off the "ideal" positions may be promoted by the opportunity for tin to obtain significant metal-oxygen interactions, i.e., interactions that are not suitable for a large cation such as potassium. The synthesis of such a quaternary phase, in which a hard cation, potassium, and a soft cation, tin, cooperatively mix, results in multiple, partially occupied cation sites. All, but one, cation-cation distances are nonbonding, even the interpocket (Sn2-Sn2') distance at 3.414(3)Å. The one exception occurs for (Sn1-K2A) at 2.70(1)Å. However, the probability of occupying both of these satellite atom positions simultaneously is approximately one in ten; and from a chemical viewpoint, this possibility is highly unlikely and would probably result in a repulsive interaction. Perhaps, a more intriguing question arises as to whether or

Figure 2.7. Oxygen coordination around the potassium at the origin and the tin satellites located on either side of the origin in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$. This ORTEP view is shown with 70% thermal ellipsoids.

Figure 2.8. Cation coordination environment of the second major cation site, Sn2, and its satellite, K2A, in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$. Note the three dark bonds which represent short Sn2-O distances. This ORTEP was drawn with 70% thermal ellipsoids.

not an ordering of the cations exists such that isolated pure potassium, tin, or mixed cation regions are intergrown. Or is the cation distribution based on initial composition and entropy?

If the cations were ordered in some manner, a superstructure should be observed. Based upon previous work with superstructures generated by cation ordering, TEM should give the best possibility for observing such phenomena, although HREM may be able to discern regions containing a greater abundance of tin versus potassium cation sites.

Microprobe analyses were completed on crystals taken from the original reaction of the K-Sn member where the mole ratio of K/Sn was prepared to be one. The analyses of two crystals, with seven data points each, indicated the average K/Sn mole ratios were 0.83 and 0.86. Microprobe analyses of single crystals taken from a reaction to prepare $K_{0.59}Sn_2Mo_{14}O_{22}$ also indicated that the cation occupancy may be widely variable. Analyses of four large crystals, with two or three data points per crystal, gave average K/Sn cation mole ratios of 0.61, 0.54, 0.46, and 0.41. These values are significantly smaller than the 0.75 mole ratio determined by single crystal refinement and bond valence sums. The above result may indicate that K_2MoO_4 or its decomposition products acts as a good flux, since potassium molybdate's melting point is 919°C and it decomposes at ~1400°C. The actual potassium content incorporated into the crystal lattice may be dependent upon the partial vapor pressure of the potassium containing flux, since most crystals were grown by transport. As the reaction progresses, the partial pressure due to the potassium component will decrease, because it is utilized in the lattice. Therefore, crystal growth at later times should be deficient in potassium relative to earlier crystal growth. This argument may also hold true for tin metal (mp=232°C). However, based on the quantity of tin remaining from stoichiometric reactions, it appears to be present in excess. Since analyses of various crystals of the K-Sn oligomer gave variable results, the single crystal that

was used for data collection was mounted for microprobe analyses. The results from this analysis were more fruitful. Five data points gave an average K:Sn mole ratio of 0.77 (or the molar composition of $K_{1.31(2)}Sn_{1.71(5)}Mo_{14}O_{22}$). This value was in good agreement with the single crystal refinement.

The coordination at the origin for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ is quite regular and forms a bicapped cube, as shown in Figure 2.9, with ten oxygens ranging from 2.72(1)Å for (K1/Pb1-O11) to 2.93(1)Å for (K1/Pb1-O1). As viewed in Figure 2.10, the other major cation site, Pb2/K2, is also ten-coordinate in oxygen, but three of these oxygens are strongly bonded: (Pb2/K2-O9) at 2.56(1)Å, (Pb2/K2-O8) at 2.45(1)Å, and (Pb2/K2-O8') at 2.44(1)Å in trigonal prismatic geometry. Six oxygens are weakly coordinated, ranging from 2.75(1)Å for (Pb2/K2-O3) to 3.07(2)Å for (Pb2/K2-O10). The coordination sphere also contains one very long (Pb2/K2-O7) distance at 3.21(1)Å. Unlike the cation situation found in the $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$, the mixed lead/potassium atoms are well defined within the cation pockets of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. The cations are also well separated, at 3.380(1)Å for (Pb1-Pb2) and the interpocket (Pb2-Pb2) distance is even greater at 3.836(3)Å. Once again, this phase is a mixture of hard and soft cations, and one might expect satellite cation positions. Perhaps, they are not observed in this system for two reasons: 1) the potassium and lead content may be balanced in such a manner that the optimal cation-oxygen bonding dominates the cation choice for a given position or 2) the quality of the data set and the refinement are limited, thus not allowing the nuances of the systems to be made apparent. In either case, TEM may elucidate the presence or absence of a superstructure.

Microprobe analyses on K/Pb crystals was completed. The selected crystals were taken from the same reaction product as the crystal for x-ray data collection indicated a wide compositional variation. Approximately twenty-six different grains were analyzed. Three distinct compositions were observed. Twenty data

Figure 2.9. Oxygen coordination around the potassium/lead at the origin in $\text{K}_{1.66}\text{Pb}_{1.34}\text{Mo}_{14}\text{O}_{22}$. This ORTEP view is shown with 70% thermal ellipsoids.

Figure 2.10. Oxygen coordination environment of the second cation site, Pb2/K2, in $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. The dark bonds represent short cation-oxygen bonds. This ORTEP was drawn with 70% thermal ellipsoids.

points gave an average composition of $K_{1.99(7)}Pb_{1.00(7)}Mo_{14}O_{22}$, twenty-nine points averaged to $K_{1.55(3)}Pb_{1.45(5)}Mo_{14}O_{22}$, and sixteen data points averaged $K_{1.74(4)}Pb_{1.26(5)}Mo_{14}O_{22}$. The composition determined by the single crystal refinement clearly is within the scope of the data calculated from microprobe analyses and all cation pockets appear to be fully occupied.

Discussion of Properties

Bond length-bond strength relationships

The implications of bond length-bond strength calculations as related to cation coordination and placement have been previously discussed in the **RESULTS** and **EXPERIMENTAL** sections. The empirical bond valence equation (Equation 1) developed by Brown and Wu⁴⁵ was used with values of $R(1)$ and (N) , for K^+ , Sn^{2+} , and Pb^{2+} respectively, of 2.276Å (9.1), 1.860Å (4.5), and

$$s(\text{cation-O}) = [R(\text{cation-O})/R(1)]^{-N} \quad (1)$$

2.044Å (5.5). Based upon Equation 1, the final bond valence sums were calculated for each of the cations in the K-Sn member: Sn2, 2.01(3); K2A, 1.56(5); Sn1A, 1.64(3); and K1, 1.43(4). The final bond valence sums calculated for the K-Pb member were: K1, 1.49(5); Pb1, 1.74(3); K2, 2.08(7); and Pb2, 2.07(5). Bond valence sums for the two unique potassiums in $K_3Mo_{14}O_{22}$ were reported as 1.32 and 1.45. In general, the bond valence sums calculated for potassium have been high and tin and lead have been low when residing on or near a site with potassium. When a given position contains a mixture of cations, the cation-oxygen distances are some average over the whole crystal. Therefore, bond valence sums do not work as well. However, the values generally reflect the ability to distinguish between mono- and di-valent cations.

The numerical values resulting from bond length-bond order calculations, as discussed previously in Section 1, are found in Table 2.14 for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and Table 2.15 for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. The summations for the metal-centered electrons (MCE) include apical-apical bond distances. Metal-metal interactions were tabulated and summed with and without inclusion of the intercluster metal-metal interactions at the end of the tables. The number of electrons available for metal-metal bonding ($2\Sigma(\Sigma n)$) was $42.7(2)e^-$ for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $44.1(3)e^-$ for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ when intercluster interactions were not included. The total Mo-O valence for the $Mo_{14}O_{22}^{4.7-}$ cluster, in the K-Sn member, was $40.1(8)$ v.u., calculated from the summation of individual Mo-O valences on each Mo atom within the cluster. The Mo_{14} cluster has $84 (6 \times 14) e^-$ less $40.1(8)e^-$, or $43.9(8)e^-$ available for metal-metal bonding in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$. The bond valence calculations for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ are in much better agreement with the $44.7e^-$ calculated using formalized oxidation states, as noted at the bottom of Table 2.14. The total Mo-O valence for the $Mo_{14}O_{22}^{4.3-}$ cluster from $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ was $40.(1)$ valence units. The Mo_{14} cluster has $84 (6 \times 14) e^-$ less $40.(1)e^-$, or $44.(1)e^-$ available for metal-metal bonding. In the K-Pb member, bond order sums and bond valence calculations are both in reasonable agreement with the formal electron count based on oxidation states. These values are located at the end of Table 2.15.

The trends observed in the known oligomeric members, $Ba_2Mo_{10}O_{16}^{7-}$, $K_3Mo_{14}O_{22}^{7-}$, and $Ba_3Mo_{18}O_{28}^{19b}$, also are followed by $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ and $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$. The metal atoms with about four electrons per molybdenum have the greatest number of metal-metal bonds (Mo1 and Mo6). Molybdenums with an intermediate number of metal-metal bonds (Mo2, Mo3, and Mo4, apical) have about one electron per molybdenum less than the former group. Molybdenums at the ends of the cluster (Mo5 and Mo7) average less than three electrons per molybdenum available for metal-metal bonding.

Table 2.14. Bond length-bond strength relationships for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo1	2.804(1)	0.488(2)	2.009(7)	0.676(14)
	2.795(1)	0.505(2)	2.058(8)	0.585(14)
	2.767(1)	0.561(2)	2.097(7)	0.523(11)
	2.755(1)	0.587(2)	2.036(7)	<u>0.624(13)</u>
	2.746(1)	0.608(3)	$\Sigma s = 2.41(5)$	
	2.768(1)	0.559(2)		
	2.741(1)	<u>0.619(2)</u>		
	$\Sigma n = 3.93(2)$			
Mo2	2.804(1)	0.488(2)	2.041(7)	0.615(13)
	2.820(1)	0.460(2)	2.037(7)	0.622(13)
	2.773(1)	0.549(2)	2.113(7)	0.499(10)
	2.747(1)	0.605(2)	2.011(7)	0.672(14)
	3.026(1) ^a	0.2111(7)	2.101(7)	<u>0.517(11)</u>
	2.736(1)	<u>0.631(2)</u>	$\Sigma s = 2.93(6)$	
	$\Sigma n = 2.94(1)$			
Mo3	2.795(1)	0.505(2)	2.086(7)	0.539(10)
	2.839(1)	0.428(2)	2.017(8)	0.660(15)
	2.730(1)	0.645(2)	2.021(7)	0.652(13)
	2.794(1)	0.507(2)	2.061(7)	0.580(12)
	2.696(1)	<u>0.734(3)</u>	2.038(7)	<u>0.620(12)</u>
	$\Sigma n = 2.82(1)$		$\Sigma s = 3.05(6)$	
Mo4	2.767(1)	0.561(2)	2.080(7)	0.549(11)
	2.755(1)	0.587(2)	2.053(8)	0.593(13)
	2.820(1)	0.460(2)	2.064(7)	0.575(12)
	2.839(1)	0.428(2)	2.048(7)	0.602(12)
	2.767(1)	0.561(2)	2.050(7)	<u>0.599(12)</u>
	2.759(1)	<u>0.578(2)</u>	$\Sigma s = 2.92(6)$	
	$\Sigma n = 3.18(1)$			
Mo5	2.746(1)	0.608(3)	2.029(8)	0.637(15)
	2.773(1)	0.549(2)	1.925(7)	0.873(19)
	2.730(1)	0.645(2)	2.156(7)	0.442(8)
	3.091(1) ^a	0.1652(6)	1.963(7)	0.777(17)
	2.764(1)	<u>0.568(2)</u>	2.080(7)	<u>0.549(11)</u>
	$\Sigma n = 2.54(1)$		$\Sigma s = 3.28(7)$	

^aIntercluster Mo-Mo bond distances

Table 2.14. (continued)

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo6	2.768(1)	0.559(2)	2.064(7)	0.575(12)
	2.741(1)	0.619(2)	2.015(7)	0.664(14)
	2.747(1)	0.605(2)	2.041(7)	0.615(13)
	2.794(1)	0.507(2)	2.060(7)	<u>0.581(11)</u>
	2.767(1)	0.561(2)		$\Sigma s = 2.44(5)$
	2.759(1)	0.578(2)		
	2.808(1)	<u>0.481(2)</u>		
		$\Sigma n = 3.91(2)$		
Mo7	3.026(1) ^a	0.2111(7)	1.959(7)	0.786(16)
	2.736(1)	0.631(2)	2.129(7)	0.477(9)
	2.696(1)	0.734(3)	1.981(7)	0.735(15)
	3.091(1) ^a	0.1652(6)	2.102(7)	0.515(10)
	2.764(1)	0.568(2)	2.115(7)	<u>0.496(9)</u>
	2.808(1)	0.481(2)		$\Sigma s = 3.01(6)$
	2.955(2) ^a	<u>0.276(1)</u>		
		$\Sigma n = 3.06(1)$		

Metal-Metal MCE(Σn) = $2\Sigma(\Sigma n) = 42.7(2)e^-$ (w/o intercluster bonds)

Metal-Metal MCE(Σn) = $2\Sigma(\Sigma n) = 44.8(2)e^-$ (with intercluster bonds)

Total valence of Mo_{14} unit = $2\Sigma(\Sigma s) = 40.1(8)$ v.u.

MCE = $(6 \times 14) - 40.1(8) = 43.9(8)e^-$

Formalized oxidation states^b: $(6 \times 14) - (22 \times 2) + (1 \times 1.29) + (2 \times 1.71) = 44.7e^-$

^bSix electrons from each Mo and using the following oxidation states: O^{-2} , K^+ , and Sn^{+2}

Table 2.15. Bond length-bond strength relationships for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo1	2.774(2)	0.547(4)	2.03(1)	0.635(18)
	2.792(2)	0.511(4)	2.03(1)	0.635(18)
	2.734(2)	0.636(5)	2.08(1)	0.549(16)
	2.794(2)	0.507(4)	2.07(1)	<u>0.565(16)</u>
	2.748(2)	0.603(4)	$\Sigma s = 2.38(7)$	
	2.806(2)	0.484(3)		
	2.740(2)	<u>0.622(5)</u>		
	$\Sigma n = 3.91(3)$			
Mo2	2.774(2)	0.547(4)	2.13(1)	0.476(13)
	2.634(2)	0.927(7)	2.03(1)	0.635(18)
	2.793(2)	0.509(4)	2.07(1)	0.565(16)
	2.735(2)	0.633(4)	2.10(1)	0.518(14)
	3.103(2) ^a	0.158(1)	2.03(1)	<u>0.635(13)</u>
	2.761(2)	<u>0.574(5)</u>	$\Sigma s = 2.83(8)$	
	$\Sigma n = 3.35(2)$			
Mo3	2.792(2)	0.511(4)	2.10(1)	0.518(14)
	3.021(2)	0.215(1)	1.97(1)	0.760(23)
	2.689(2)	0.753(5)	2.01(1)	0.674(20)
	2.790(3)	0.515(6)	2.03(1)	0.635(18)
	2.680(2)	<u>0.780(6)</u>	1.99(1)	<u>0.716(22)</u>
	$\Sigma n = 2.77(2)$		$\Sigma s = 3.30(9)$	
Mo4	2.734(2)	0.636(5)	2.05(1)	0.599(17)
	2.794(2)	0.507(4)	2.03(1)	0.654(19)
	2.634(2)	0.927(7)	2.10(1)	0.528(14)
	3.021(2)	0.215(1)	2.11(1)	0.504(15)
	2.823(2)	0.454(3)	2.05(1)	<u>0.599(17)</u>
	2.750(2)	<u>0.599(5)</u>	$\Sigma s = 2.87(8)$	
	$\Sigma n = 3.34(3)$			
Mo5	2.748(2)	0.603(4)	2.17(1)	0.426(12)
	2.793(2)	0.509(4)	2.13(1)	0.463(13)
	2.689(2)	0.753(5)	1.93(1)	0.860(26)
	3.042(2) ^a	0.199(2)	2.01(1)	0.674(20)
	2.725(2)	<u>0.658(5)</u>	1.93(1)	<u>0.860(26)</u>
	$\Sigma n = 2.72(2)$		$\Sigma s = 3.28(9)$	

^aIntercluster Mo-Mo bond distances

Table 2.15. (continued)

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo6	2.806(2)	0.484(3)	2.05(1)	0.599(17)
	2.740(2)	0.622(5)	2.07(1)	0.565(16)
	2.735(2)	0.633(4)	2.07(1)	0.565(16)
	2.790(3)	0.515(6)	2.04(1)	<u>0.617(18)</u>
	2.823(2)	0.454(3)		$\Sigma s = 2.35(7)$
	2.750(2)	0.599(5)		
	2.800(2)	<u>0.496(4)</u>		
		$\Sigma n = 3.80(3)$		
Mo7	3.103(2) ^a	0.158(1)	1.98(1)	0.737(21)
	2.761(2)	0.574(4)	2.05(1)	0.599(17)
	2.680(2)	0.780(6)	2.10(1)	0.518(14)
	3.042(2) ^a	0.199(2)	2.11(1)	0.504(15)
	2.725(2)	0.658(4)	2.10(1)	<u>0.516(14)</u>
	2.800(2)	0.496(4)		$\Sigma s = 2.88(9)$
	2.838(4) ^a	<u>0.428(7)</u>		
		$\Sigma n = 3.29(3)$		

Metal-Metal MCE(Σn) = $2\Sigma(\Sigma n) = 44.1(3)e^-$ (w/o intercluster bonds)

Metal-Metal MCE(Σn) = $2\Sigma(\Sigma n) = 46.4(4)e^-$ (with intercluster bonds)

Total valence of Mo₁₄ unit = $2\Sigma(\Sigma s) = 40(1)$ v.u.

$$\text{MCE} = (6 \times 14) - 40.(1) = 44(1)e^-$$

Formalized oxidation states^b: $(6 \times 14) - (22 \times 2) + (1 \times 1.66) + (2 \times 1.34) = 44.3e^-$

^bSix electrons from each Mo and using the following oxidation states: O⁻², K⁺, and Pb⁺²

Magnetic properties

The magnetic susceptibility of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ was measured on selected crystals over the temperature range of 6-346 K. Based upon microprobe analysis, there may be a variable composition range for this K-Sn phase, thus its purity is suspect. The data were corrected for diamagnetic core contributions, based upon the composition determined by microprobe analyses and the single crystal refinement, using values for individual ions reported by Selwood.⁴⁶ Figure 2.11 displays both the molar and inverse molar susceptibilities for this trimeric oligomer. The susceptibility levels off above 150 K at $\sim 1500 \times 10^{-6}$ emu/mol and shows a slight increase above 300 K. This results in a residual susceptibility, due to temperature independent paramagnetism, χ_{TIP} , of about 102×10^{-6} emu/Mo. The tail from 6-106 K can be fit by the Curie-Weiss relationship and corresponds to a moment of $0.45 \mu_B$. If this paramagnetic tail was due to high spin Fe(II), the impurity level would be ~ 0.2 weight percent. Microprobe analyses on crystals from the same sample indicated no iron down to the 0.05 weight percent level. A hysteresis loop, using the SQUID magnetosusceptometer, in which the temperature was held constant and the field was varied, also indicated that no such ferromagnetic impurity was present.

The measured moment is too low for the expected 0.7 unpaired electrons per formula unit. However, if one electron was trapped on a $Mo_{14}O_{34}$ unit for every fourteen clusters that were diamagnetic, then the effective moment would be valid. Interestingly, the moment measured for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ is very similar to that of $K_3Mo_{14}O_{22}$ ($0.54 \mu_B$).

The magnetic susceptibility of $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ was measured on selected crystals over the temperature range of 6-356 K. The data were corrected for diamagnetic core contributions based upon the individual ion values reported by Selwood.⁴⁶ The molar and inverse molar susceptibilities for the K-Pb trimeric oligomer are shown in Figure 2.12. From this graph, the relatively small

Figure 2.11. Molar and inverse molar susceptibilities versus temperature for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$

Figure 2.12. Molar and inverse molar susceptibilities versus temperature for $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$

signal is quite noisy; this result may be the consequence of the small sample size or that the material is diamagnetic. The tail from 6-86 K can be fit by the Curie-Weiss relationship, however, the apparent moment is very small ($0.04 \mu_B$) and can most likely be attributed to a low concentration of paramagnetic impurities. Again, variable composition, as indicated by microprobe analyses, could result in an invalid measurement.

Electron spin resonance

In an attempt to clarify the magnetic results, ESR experiments were undertaken for the K-Sn member. A ground, powder sample of $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ was loaded into a quartz tube suitable for the resonance cavity of the ESR unit. The sample was measured at 395 K, 112 K, and 7 K. All spectra exhibited the same features. Figure 2.13 displays the first derivative spectrum of five averaged scans at 112 K. There are two features of interest in this spectrum. The central resonance is particularly symmetric and has a g value of 1.91. The second feature is the hyperfine splitting of ^{95}Mo and ^{97}Mo , which both have $I=5/2$. With spin 5/2, there should be six resonances visible, two are easily detected at lower field than the main peak, two are not visible since they fall under the main resonance, and two are at higher field, although much weaker in intensity. The g value of the central resonance corresponds to a moment of $1.66 \mu_B$, which is larger than the observed moment determined via magnetic susceptibility measurements. This low value may indicate that it arises from an impurity in the sample or that one unpaired electron is trapped on one of every fourteen clusters, based upon the magnetic data. The g value and the hyperfine coupling also indicate that the unpaired electron is residing on a Mo containing impurity, or a Mo that is isolated within a cation pocket.

Figure 2.13. ESR spectrum for $K_{1.29}Sn_{1.29}Mo_{14}O_{22}$ taken at 112 K

CONCLUSIONS

The three trimeric oligomers, $K_xM_yMo_{14}O_{22}$ ($M = Sn, Pb, \text{ or } Sr$), reported here and the two previously reported members begin to show the electronic flexibility that can be realized in a finite chain of edge-sharing molybdenum octahedra. In particular, the electron count available for metal-metal bonding has a significant impact on the magnitude of apical-apical and intercluster metal-metal bonding. Both the K-Sn and K-Pb members have bond valence sums around the molybdenums that correlate reasonably well with the electron count derived from the formal oxidation states. Bond order sums did not fit the formal electron counts for $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$, in contrast to $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$, whose bond order sums were nearly equivalent to the formal electron counts. This observation is most likely the result of electrons entering non- or anti-bonding states in the K-Sn member, while all the electrons available for metal-metal bonding are utilized as such in the K-Pb member. The nearly equivalent apical-apical bonds and relatively long intercluster interaction in $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ is similar to Simon's $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}$. The $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ and $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$ members constitute a new arrangement, with short-long apical-apical molybdenum bonds and a significant intercluster metal-metal bond.

Unfortunately, the magnetic properties of the K-Sn and K-Pb members are not easily interpreted with respect to their formal electron counts. $K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ has a calculated effective moment of $0.45\mu_B$ and $K_{1.66}Pb_{1.34}Mo_{14}O_{22}$ is diamagnetic. Perhaps, these values imply a greater underlying structural meaning. A complicated superstructure may exist, however, its origin can be questioned; it may be the resultant of ordered cations or an electronic effect, such as ordering of differently charged molybdenum oxide cluster units. Regrettably, ESR did not add any more decisive information.

SECTION 3

**SYNTHESIS AND CHARACTERIZATION OF $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$:
AN OLIGOMER WITH FIVE TRANS EDGE-SHARING Mo OCTAHEDRA**

INTRODUCTION

The synthesis of compounds containing chain-segment oligomers, $M_{n-x}Mo_{4n+2}O_{6n+4}$, appears to become increasingly more difficult as n , the number of trans edge-shared molybdenum octahedra, becomes larger. The thermodynamic stability of large oligomeric members, with respect to smaller members, or the $n=\infty$ (infinite chain) $M_xMo_4O_6$ members, must then necessarily be small. The preparation of such materials becomes increasingly sensitive to such factors as cation choice (or optimal electron count), starting reagents, and reaction temperatures. To date, no synthesis or single crystal x-ray structure refinement has been reported for an oligomer with five trans edge-shared Mo octahedra. Simon's study of the In-Mo-O system has shown that the mixed $n=4$ and 5 member, $In_{11}Mo_{40}O_{62}$,²³ can be prepared. A structural refinement of $In_6Mo_{22}O_{34}$ has also been completed; however, the quality of the results has not been reported.³¹ In this section, the synthesis and characterization of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ will be discussed. This $n=5$ oligomer was studied by x-ray powder diffraction, single crystal x-ray structure refinements, microprobe analyses, magnetic susceptibility, and electron spin resonance.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated ($\sim 2 \times 10^{-5}$ torr) molybdenum tubes.

The starting reagents included K_2MoO_4 , $BaMoO_4$, MoO_3 , and Mo. Potassium molybdate was prepared by reacting KOH (Fisher Certified A.C.S.) with a stoichiometric quantity of MoO_3 in deionized water. The molybdate solution was filtered, the volume reduced by heating, and the product collected on a glass frit. The wet molybdate was dried at $120^\circ C$ overnight. Barium molybdate was prepared by mixing an aqueous solution of $BaCl_2 \cdot 2H_2O$ (Baker Analyzed Reagent, 99.6%) with an aqueous solution containing a stoichiometric quantity of sodium molybdate dihydrate (Fisher Certified). The white precipitate was filtered, washed with copious amounts of distilled water, and then dried overnight at $130^\circ C$ under dynamic vacuum. Molybdenum trioxide was fired at $520^\circ C$ overnight in an open crucible and then cooled over desiccant. Molybdenum powder (Aldrich, 99.99%) was dried under dynamic vacuum at $120^\circ C$ overnight. All the starting reagents were stored in a desiccator. These materials were thoroughly ground to produce a homogeneous mixture which was also stored in a desiccator. Molybdenum tubing (Thermoelectron Corp., 99.97%) was cleaned by heating at $950^\circ C$ for five hours under a flowing hydrogen atmosphere. After cooling to room temperature under hydrogen, the tubing also was stored over desiccant.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with Cu $K\alpha_1$ radiation ($\lambda = 1.540562\text{\AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard.

Magnetic susceptibility

The magnetic properties were examined on selected crystals with a Quantum Design SQUID magnetosusceptometer. The sample was loaded into a 3mm inner diameter quartz tube that had been sealed on the bottom half with a 3mm outer diameter quartz rod. A quartz rod also was placed in the top half of the loaded sample tube, which was then mounted in an apparatus that allowed the evacuation of the sample tube and purging with helium gas. To eliminate water, the system was heated to 120°C for an hour under dynamic vacuum. After cooling, the system was pumped and purged with helium three more times. The upper quartz tube was pushed into place under a partial pressure of helium (to facilitate temperature equilibration during measurements), sandwiching the sample between "solid" quartz, and sealed off. This procedure was used to eliminate oxygen contamination, which has an antiferromagnetic transition at ~50 K. The experimental data were corrected for the diamagnetic contribution from the quartz. Measurements on empty quartz tube/rod assemblies, with varying gap sizes, indicated that the diamagnetic contribution from the quartz was related to the size of the gap (the area normally reserved for the sample material). Since the signal versus gap size data could be fit by a line, a correction was employed by measuring the length of the gap containing the sample.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Powdered samples and/or crystals were loaded onto a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Microprobe analysis

Elemental analyses were completed by Dr. Alfred Kracher (Department of Geological and Atmospheric Sciences) on an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers (WDS) and operated at 15 kV and 25 nA. Samples were mounted in Epo-Tek 301-2 epoxy resin, dried, and polished to produce a flat surface. Prior to examination, the samples were sputtered with carbon to insure conductivity. Peak profiles and backgrounds were measured for the standards, which included KAlSi_3O_8 , BaSO_4 , and MoO_2 . Data were analyzed using Probe³⁵ software.

Electron spin resonance

X-band electron spin resonance (ESR) spectra were recorded on powdered samples of $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$ with a Bruker ER200-SRC instrument equipped with an Oxford Instruments ESR 900 flow through cryostat and a DTC-2 digital temperature controller. A Hewlett-Packard 5342 microwave frequency recorder was used to measure the exact frequency of the microwave radiation. The data to be described was averaged over five scans and collected at a modulation frequency of 100 kHz and a power of 3.2 Gpp. The instrument was calibrated against weak pitchblende prior to use.

Synthesis

Attempts to prepare the quaternary $K_2Ba_2Mo_{18}O_{28}$ resulted in the formation of another oligomeric member, the $n=5$, $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$. The correct stoichiometric mole ratios of K_2MoO_4 , $BaMoO_4$, MoO_3 , and Mo necessary to prepare the tetramer were thoroughly ground, pressed into a pellet, and loaded into a molybdenum tube. The tube and contents were evacuated, fired at 150°C for 20 minutes, and left under dynamic vacuum overnight before being sealed by electron beam welding. The sample was fired at 1400°C in a high temperature vacuum furnace overnight and then further reacted at 1500°C for 119 hours. The furnace was cooled at an average of $1^\circ\text{C}/\text{min}$ down to 1240°C , $2^\circ\text{C}/\text{min}$ to 1000°C , $5^\circ\text{C}/\text{min}$ to 800°C , and then furnace cooled to 100°C in approximately one hour. Upon opening, the interior tube walls were found to be clean. The pellet was a coarse mixture of black crystals (oligomer), black powder (MoO_2), and silver beads (Mo).

Unfortunately, single phase preparation of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ has not been achieved. As observed in the previous synthetic routes to oligomeric members, $M_xMo_{4n+2}O_{6n+4}$, in which potassium was utilized, preparation of these phases appears to be promoted in the presence of excess K_2MoO_4 . The potassium molybdate, or its decomposition products, act as a good flux. Over the course of the reaction, potassium may be incorporated into the structure with a wide range of concentrations. In this case, the pentameric oligomer only includes a small amount of potassium. The overall composition, $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$, was determined by the single crystal structure refinement, to be discussed later, and was essentially verified by microprobe analyses. Quantitative analyses of four small crystals with a total of five data points resulted in a net composition of $K_{0.09(2)}Ba_{3.6(2)}Mo_{22}O_{33.9(1)}$. This stoichiometry is derived from a fixed number of molybdenums and the oxygen content was then calculated by difference.

Prior to the investigation of the K-Ba-Mo₂₂O₃₄ system, the compound Ba_{4.2}Mo₂₂O₃₄ was identified by a single crystal structure refinement. This phase was found in a reaction intended to prepare Ba₄Mo₁₈O₂₈. BaMoO₄, MoO₂, and Mo (4:6:8 mole ratio) were thoroughly ground, loaded into fused silica tubing, evacuated, and heated to 200°C for two hours before sealing. The reaction mixture was fired at 1250°C for 3 days, then 1230°C for 2 days, and finally cooled to 800°C at about 100°C/hour before quenching to room temperature. The product was reground and loaded back into fused silica tubing. This mixture was fired at 1220°C for 15 more days. Many crystals were transported to the cool end of the tube. Most of these indexed as the tetrameric oligomer, although highly twinned. One single crystal was indexed in an orthorhombic cell with $a=9.909(18)\text{\AA}$, $b=31.526(9)\text{\AA}$, and $c=9.353(9)\text{\AA}$. From the 5861 reflections collected, 3261 had $I>3\sigma(I)$, and 1574 were unique. Unfortunately, a definite space group could not be assigned. However, using $P2_12_12_1$, the final refinement converged at $R=24\%$. Based upon the axial lengths, this phase might be isostructural to Simon's briefly mentioned $\text{In}_6\text{Mo}_{22}\text{O}_{34}$.³¹ The main structural difference between Ba_{4.2}Mo₂₂O₃₄ and $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$ is that the clusters interconnect in a zig-zag fashion in the former, similar to BaMo₆O₁₀²⁴; and they interconnect in a stair-step manner in the latter, like all the known oligomers with $n=2$ and 3.^{19b} Regrettably, the synthesis of more Ba_{5-x}Mo₂₂O₃₄ with zig-zag interconnected chain segments was unsuccessful.

X-ray Powder Diffraction

The observed versus calculated d-spacings and relative intensities are given in Table 3.1 for $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$. Table 3.1 is only a partial listing, reflections that were very weak or broad have been excluded. The calculated d-spacings

Table 3.1. X-ray powder diffraction data for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
6.790	6.763	s	110
4.884	4.896, 4.892	w-b	200, $\bar{2}01$
4.884	4.885	"	112
4.700	4.677	w-b	020
4.301	4.338 & 4.335	w-b	210 & 211
4.235	4.220	w-b	$\bar{1}20$
3.574	3.573	w-b	$\bar{1}14$
3.425	3.401	w-b	$\bar{1}23$
3.387	3.382 & 3.380	w-b	$\bar{2}20$ & $\bar{2}21$
3.120	3.110	m-b	311
3.080	3.082	w	310
2.982	2.970	s	130
2.763	2.790	w-b	$\bar{1}24$
2.705	2.695	m	$\bar{3}21$
2.517	2.516 & 2.505	w-b	322 & 313
2.490	2.484	w	$\bar{2}05$
2.478	2.478 & 2.477	w	206 & $\bar{4}01$
2.463	2.450	m	$\bar{1}25$
2.405	2.401	m	$\bar{2}15$
2.397	2.395	s	$\bar{2}16$
2.281	2.299	m	126
2.198	2.194	m	$\bar{2}25$
2.192	2.189	m	$\bar{2}26$
2.172	2.188	w	421
2.047	2.060	w	$\bar{3}15$
2.017	2.005	w	326
1.948	1.943 & 1.940	m	$\bar{2}35$ & $\bar{2}36$
1.942	1.939 & 1.938	s	$\bar{4}31$ & 511
1.915	1.925	w	$\bar{3}25$
1.712	1.703 & 1.701	m	$\bar{2}45$ & $\bar{2}46$
1.703	1.700	m	441

^aIntensity: s=strong, m=medium, w=weak, and b=broad

^bRefined monoclinic cell parameters determined from single crystal indexing:
 $a=9.908(2)\text{\AA}$, $b=9.353(2)\text{\AA}$, $c=15.951(3)\text{\AA}$, and $\beta=98.78(2)^\circ$

were derived from the lattice parameters determined by single crystal indexing. All d-spacings are based on Cu $K\alpha_1$ radiation.

X-ray Single Crystal Data Collection

A black, chunk-like crystal of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ measuring $0.07 \times 0.12 \times 0.12 \text{ mm}^3$ was mounted with epoxy cement on a glass fiber for data collection. A Rigaku AFC6R rotating anode diffractometer was used with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069\text{\AA}$) generated at 7 kW. Lattice parameters and an orientation matrix for data collection were derived from 13 randomly located and centered reflections with a two theta range of $13\text{--}16^\circ$. The monoclinic lattice had cell dimensions of $a=9.912(4)\text{\AA}$, $b=9.356(4)\text{\AA}$, $c=15.958(8)\text{\AA}$, $\beta=98.75(4)^\circ$, and volume= $1463.1\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. A refinement on 25 reflections with strong intensity and two theta values near 40° gave a final idealized cell with the following lattice parameters: $a=9.908(2)\text{\AA}$, $b=9.353(2)\text{\AA}$, $c=15.951(3)\text{\AA}$, $\beta=98.78(2)^\circ$, and volume= $1460.8(4)\text{\AA}^3$. Data were collected at room temperature from 0 to 60° in two theta in the hemisphere ($\pm h, k, \pm l$), using an ω - 2θ scan mode. The number of reflections measured was 9042, of which 6212 were observed ($I > 3\sigma(I)$) and 2768 were unique with $I > 3.5\sigma(I)$. The linear absorption coefficient for Mo $K\alpha$ was 136.910 cm^{-1} . An empirical absorption correction³⁶ was applied based upon five azimuthal scans of reflections with an average transmission range of $0.942\text{--}1.000$. The intensity data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The space group $P2_1/a$ (#14) was chosen based on the systematic absences of $h0l$: $h \neq 2n$ and $0k0$: $k \neq 2n$, however, there was one violation of the latter condition which could be attributed to a very intense neighboring reflection and 49 violations of the former condition, none of which could be validly excluded. Therefore the structure was solved by direct methods using SHELXS³⁷ in three space groups: $P2_1/a$ (0.055), $P2_1$ (0.041), and Pa (0.034). The structure was refined in $P2_1/a$ and Pa on $|F|$ by full matrix least squares techniques³⁸ with the TEXSAN³⁹ package. The refinement in Pa converged at $R=7.3\%$. In this space group, all the atoms in the formula unit are unique, thereby allowing distortions to occur that do not necessitate an inversion related contribution to another part of the same cluster. The distortions that occur within the cluster are only slightly different than the more symmetrical solution in $P2_1/a$. Thus the centrosymmetric space group, $P2_1/a$, was chosen to be a more valid model, with the realization that small distortions presumably do occur, but do not contribute significantly to the intensity of the measured data.

Using $P2_1/a$ as the space group, about half of the molybdenum atoms were located in the initial output from direct methods. After refining on these positions, the remaining molybdenum atom positions were found in a Fourier electron difference map. The molybdenum atom positions refined to $R=41\%$. Two very large peaks remained in the difference map and these were assigned as barium cations. Inclusion of these two atoms resulted in a refinement at 18% . The two cations were allowed to refine as a combination of potassium and barium, since SEM EDS indicated that both cations were present in other crystals from the same reaction product. These conditions converged at $R=12\%$. All the thermal parameters of the heavy atoms were then allowed to refine isotropically; this resulted in $R=8.1\%$. After refining the oxygen atom thermal parameters

isotropically, the R factor was 7.0%. Anisotropic refinement of the thermal parameters for the heavy atoms and eight of the oxygen atoms converged at $R=6.2\%$. A secondary extinction correction was applied ($5.6(9)\times 10^{-8}$) and cation occupancies were rechecked. The final cycle converged at $R=4.93\%$ and $R_w=6.03\%$. The final occupancies indicated that the two cation sites were fully occupied, with Ba1/K1 at 95.1/4.9(7)% and Ba2/K2 at 95.6/4.4(7)%. However, the site at the origin, the central available cation position, was determined to be completely vacant. The thermal parameters of the potassium atoms were fixed to the anisotropic values derived for the respective barium cations. All the thermal parameters for the molybdenum, barium, and eight of seventeen oxygen atoms were refined anisotropically. A final electron difference map was not void of electron density, since there were ten peaks with electron density between 10.1 and 7.4 e/Å³. All peaks were located within the cation pockets and had cation to peak distances ranging from 1.7 to 2.2 Å. No strongly convincing arguments can be made to explain the considerable quantity of electron density remaining. Perhaps, the correct space group, Pa, would alleviate this problem. Absorption does not seem to be the problem, and when a cylindrical absorption correction was made, the resulting refinement was even poorer, $R=9.8\%$. Another possibility is that the current assessment of the cation locations in the pockets is not correct. It is peculiar that the central cation site, which should be ideal for potassium, is left vacant. A fourth scenario, and perhaps the most realistic possibility, is that the crystal is actually composed of domains of oligomers with varying chain lengths or modes of interconnection. This behavior was observed in the In-Mo-O system studied by Simon.³¹ Given the quality of the refinement, the crystal used for data collection is probably composed of essentially, although not all, Mo₂₂ units connected in a stair-step fashion.

Details of the data collection and refinement for $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$ are given in Table 3.2. Final positional parameters and isotropic temperature factors are given in Table 3.3. Anisotropic temperature factors are listed in Table 3.4. Selected interatomic metal-metal bond distances, metal-oxygen bond distances, and bond angles are found in Tables 3.5, 3.6, and 3.7, respectively.

Table 3.2. X-ray crystallographic data for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$

formula	$K_{0.19}Ba_{3.81}Mo_{22}O_{34}$
formula weight	3185.32
crystal system	monoclinic
space group	$P2_1/a$ (#14)
a, Å	9.908(2)
b, Å	9.353(2)
c, Å	15.951(3)
β , degrees	98.78(2)
volume, Å ³	1460.8(4)
Z	2
calculated density, g/cm ³	7.172
F000	2826
crystal size, mm ³	0.07 x 0.12 x 0.12
μ (Mo K α), cm ⁻¹	136.910
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.71069
temperature, °C	24
two theta range, degrees	0-60
scan mode	ω -2 θ
No. reflections collected	9042
No. observations ($I > 3\sigma(I)$), (unique, $I > 3.5\sigma(I)$)	6212 (2768)
No. variables	229
goodness of fit ^a	2.138
max. shift in final cycle	0.002
largest peaks in final diff. map, e/Å ³	+10.1, -3.9
transmission coefficient	0.942-1.000
R^b , R_w^c	0.0493, 0.0603

$$^a \text{Quality of fit} = [\sum \omega (F_o - F_c)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o - F_c| / \sum F_o$$

$$^c R_w = [\sum \omega (F_o - F_c)^2 / \sum \omega F_o^2]^{1/2}; \omega = 1/\sigma^2(F_o)$$

Table 3.3. Atomic coordinates for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$

Atom ^a	X	Y	Z	B _{eq} ^b
Ba1/K1 ^c	0.91910(8)	0.0072(1)	0.11851(5)	0.58(3)
Ba2/K2 ^d	0.96132(8)	0.0005(1)	0.34553(6)	0.63(3)
Mo1	0.6072(1)	0.1280(1)	0.30985(7)	0.24(4)
Mo2	0.5635(1)	0.8879(1)	0.41055(7)	0.24(4)
Mo3	0.5221(1)	0.8798(1)	0.23092(7)	0.23(4)
Mo4	0.3001(1)	0.8690(1)	0.31198(8)	0.43(4)
Mo5	0.3438(1)	0.1165(1)	0.23082(7)	0.21(4)
Mo6	0.5663(1)	0.1233(1)	0.14431(7)	0.21(4)
Mo7	0.3928(1)	0.1128(1)	0.41011(7)	0.19(4)
Mo8	0.4673(1)	0.8797(1)	0.05567(8)	0.52(4)
Mo9	0.6543(1)	0.1290(1)	0.50139(8)	0.28(4)
Mo10	0.2570(1)	0.8679(1)	0.14266(8)	0.33(4)
Mo11	0.3014(1)	0.1148(1)	0.05765(7)	0.22(4)
O1	0.675(1)	0.765(1)	0.5012(6)	0.4(1)
O2	0.465(1)	0.238(1)	0.0420(6)	0.5(3)
O3	0.1730(9)	0.994(1)	0.2288(6)	0.4(1)
O4	0.639(1)	0.005(1)	0.0451(6)	0.4(1)
O5	0.310(1)	0.743(1)	0.0468(6)	0.6(1)
O6	0.497(1)	0.269(1)	0.2246(6)	0.4(3)
O7	0.368(1)	0.730(1)	0.2290(7)	0.8(3)
O8	0.631(1)	0.757(1)	0.3218(6)	0.5(1)
O9	0.7290(9)	0.018(1)	0.4102(6)	0.3(3)
O10	0.6955(9)	0.004(1)	0.2288(6)	0.3(1)
O11	0.555(1)	0.251(1)	0.4080(6)	0.5(1)
O12	0.237(1)	0.247(1)	0.1352(6)	0.6(3)
O13	0.403(1)	0.746(1)	0.4108(6)	0.7(3)
O14	0.781(1)	0.258(1)	0.3163(6)	0.4(1)
O15	0.582(1)	0.754(1)	0.1382(6)	0.5(3)
O16	0.226(1)	0.984(1)	0.4083(7)	0.9(4)
O17	0.147(1)	0.991(1)	0.0488(6)	0.6(1)

^aAll atoms reside on the Wyckoff position 4e

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3[\sum_i \sum_j (U_{ij} a_i^* a_j^* \vec{a}_i \cdot \vec{a}_j)]$, where the summations of i and j range from 1 to 3

^cBa1 and K1 reside on the same site with 95.1(7)% and 4.9(7)% occupancies, respectively

^dBa2 and K2 reside on the same site with 95.6(7)% and 4.4(7)% occupancies, respectively

Table 3.4. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ba1/K1	6.5(4)	6.6(4)	8.7(4)	0.7(3)	-0.1(3)	-0.3(3)
Ba2/K2	5.7(4)	5.9(4)	12.3(5)	-0.2(3)	1.8(3)	-0.4(3)
Mo1	2.7(5)	2.6(5)	3.8(5)	0.2(4)	0.2(4)	-0.2(4)
Mo2	2.9(5)	2.1(5)	4.2(5)	0.9(4)	1.2(4)	0.3(4)
Mo3	2.6(5)	1.9(5)	4.0(5)	0.0(4)	0.4(4)	-0.5(4)
Mo4	1.2(5)	3.1(5)	11.8(6)	-0.5(4)	0.5(4)	0.3(4)
Mo5	1.1(5)	2.7(5)	3.9(5)	0.6(4)	-0.4(4)	-0.3(4)
Mo6	1.8(5)	2.4(5)	3.4(5)	-0.2(4)	-0.1(4)	-0.5(4)
Mo7	1.2(5)	2.6(5)	3.5(5)	-0.2(4)	0.1(4)	0.3(4)
Mo8	3.5(5)	7.1(5)	8.5(6)	1.7(4)	-1.4(4)	-5.7(4)
Mo9	1.4(5)	3.1(5)	6.4(5)	0.1(4)	1.2(4)	-0.2(4)
Mo10	2.2(5)	3.3(5)	6.7(5)	-0.4(4)	-0.5(4)	-1.9(4)
Mo11	2.0(5)	2.3(5)	3.6(5)	0.6(4)	-0.5(4)	-0.4(4)
O1	5.(2)					
O2	2.(4)	12.(5)	7.(5)	-1.(4)	3.(3)	-5.(4)
O3	5.(2)					
O4	6.(2)					
O5	8.(2)					
O6	5.(4)	4.(4)	7.(4)	-1.(3)	0.(3)	4.(3)
O7	8.(5)	16.(5)	5.(5)	3.(4)	-0.(4)	6.(4)
O8	6.(2)					
O9	3.(4)	9.(4)	2.(4)	0.(3)	1.(3)	-2.(3)
O10	4.(2)					
O11	6.(2)					
O12	6.(4)	13.(5)	6.(5)	2.(4)	1.(4)	3.(4)
O13	8.(5)	14.(5)	6.(5)	2.(4)	3.(4)	6.(4)
O14	5.(2)					
O15	3.(4)	11.(5)	4.(5)	2.(4)	-0.(3)	-5.(4)
O16	11.(5)	12.(5)	12.(5)	-5.(4)	2.(4)	-2.(4)
O17	7.(2)					

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a*b*U_{12}hk+2a*c*U_{13}hl+2b*c*U_{23}kl))$

^bThe thermal parameters for oxygens O1, O3, O4, O5, O8, O10, O11, O14, and O17 only refined isotropically

Table 3.5. Selected metal-metal interatomic distances (Å) for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$

Mo1-Mo2	2.832(2)	Mo1-Mo3	2.713(2)
Mo1-Mo5'	2.722(2)	Mo1-Mo6	2.610(2) apical ^b
Mo1-Mo7'	2.851(2)	Mo1-Mo9	3.019(2) apical
Mo2-Mo3	2.833(2)	Mo2-Mo4'	2.839(2)
Mo2-Mo7'	2.698(2)	Mo2-Mo7	2.827(2)
Mo2-Mo9	2.753(2)	Mo2-Mo9'	2.756(2)
Mo3-Mo4'	2.718(2)	Mo3-Mo5'	2.832(2)
Mo3-Mo6	2.734(2)	Mo3-Mo8	2.765(2)
Mo3-Mo10'	2.786(2)	Mo4-Mo5	2.720(2)
Mo4-Mo7	2.838(2)	Mo4-Mo9	2.942(2) apical
Mo4-Mo10	2.669(2) apical	Mo5-Mo6'	2.774(2)
Mo5-Mo7	2.827(2)	Mo5-Mo10	2.785(2)
Mo5-Mo11	2.730(2)	Mo6-Mo8	2.780(2)
Mo6-Mo8'	3.156(2) inter ^c	Mo6-Mo11'	2.774(2)
Mo7-Mo9'	2.743(2)	Mo7-Mo9	2.775(2)
Mo8-Mo8'	2.998(3) inter	Mo8-Mo10'	2.676(2)
Mo8-Mo11'	2.748(2)	Mo8-Mo11'	3.128(2) inter
Mo10-Mo11	2.747(2)	Ba1...Ba1 ^d	4.328(1) inter
Ba1...Ba2 ^d	3.582(1)	Ba2...Ba2 ^d	4.870(2)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center.

^bApical-apical Mo-Mo bond distances

^cIntercluster Mo-Mo bond distances

^dOccupancy of these cation positions combines both potassium and barium

Table 3.6. Selected metal-oxygen bond distances (Å) for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ ^a

Mo1-O6	2.081(9)	Mo1-O9	2.117(9)
Mo1-O10	2.031(9)	Mo1-O11	2.07(1)
Mo1-O14	2.097(9)	Mo2-O1'	2.03(1)
Mo2-O8'	2.06(1)	Mo2-O9	2.045(9)
Mo2-O13'	2.07(1)	Mo3-O7'	2.07(1)
Mo3-O8'	2.03(1)	Mo3-O10	2.078(9)
Mo3-O15'	2.049(9)	Mo4-O3	2.048(9)
Mo4-O7	2.04(1)	Mo4-O8	2.07(1)
Mo4-O13	2.09(1)	Mo4-O16	2.10(1)
Mo5-O3	2.042(9)	Mo5-O6'	2.091(9)
Mo5-O12'	2.10(1)	Mo5-O14'	1.97(1)
Mo6-O2	2.08(1)	Mo6-O4	2.15(1)
Mo6-O δ	2.06(1)	Mo6-O10	2.044(9)
Mo6-O12	2.11(1)	Mo7-O1'	2.01(1)
Mo7-O11'	2.07(1)	Mo7-O14'	2.10(1)
Mo7-O16	2.05(1)	Mo8-O2'	2.10(1)
Mo8-O4'	2.09(1)	Mo8-O4'	2.08(1)
Mo8-O5'	2.00(1)	Mo8-O15'	1.99(1)
Mo9-O1	2.125(9)	Mo9-O9	2.015(9)
Mo9-O11	2.01(1)	Mo9-O13	1.97(1)
Mo9-O16	2.02(1)	Mo10-O3	2.077(9)
Mo10-O5	2.05(1)	Mo10-O7	2.08(1)
Mo10-O15	2.065(9)	Mo10-O17	2.06(1)
Mo11-O2'	2.03(1)	Mo11-O4'	2.14(1)
Mo11-O5'	2.21(1)	Mo11-O12'	1.92(1)
Mo11-O17	1.91(1)	Ba1-O2	2.75(1)
Ba1-O3	2.844(9)	Ba1-O4	2.842(9)
Ba1-O5	2.76(1)	Ba1-O6	2.729(9)
Ba1-O7	2.92(1)	Ba1-O10	3.032(9)
Ba1-O12	2.96(1)	Ba1-O15	2.92(1)
Ba1-O17	2.65(1)	Ba1-O17'	2.67(1)
Ba2-O3	3.010(9)	Ba2-O6	2.95(1)
Ba2-O7	2.90(1)	Ba2-O8	2.99(1)
Ba2-O9	2.668(9)	Ba2-O10	2.984(9)
Ba2-O11	2.64(1)	Ba2-O13	2.63(1)
Ba2-O14	2.99(1)	Ba2-O16	2.66(1)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center. Cationic bond distances reported using barium, although the cation position is partially occupied by potassium.

Table 3.7. Selected bond angles (degrees) for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ ^a

Mo2-Mo1-Mo5'	90.72(5)	Mo3-Mo1-Mo7'	90.69(5)
Mo6-Mo1-Mo9	179.21(6)	Mo1-Mo2-Mo4'	86.71(5)
Mo3-Mo2-Mo7'	91.39(5)	Mo3-Mo2-Mo7	178.27(6)
Mo9-Mo2-Mo9'	89.82(5)	Mo7-Mo2-Mo7'	90.21(5)
Mo1-Mo3-Mo4'	91.61(5)	Mo5'-Mo3-Mo8	88.48(5)
Mo6-Mo3-Mo10'	89.40(5)	Mo2-Mo3-Mo5'	88.49(5)
Mo2-Mo3-Mo8	176.68(5)	Mo2-Mo4'-Mo5'	90.62(5)
Mo9-Mo4-Mo10	179.62(5)	Mo3-Mo4'-Mo7'	90.87(5)
Mo1-Mo5'-Mo4'	91.38(5)	Mo6-Mo5'-Mo10'	88.59(5)
Mo7-Mo5-Mo11	178.52(5)	Mo3-Mo5'-Mo7'	88.79(5)
Mo3-Mo5'-Mo11'	89.74(5)	Mo5'-Mo6-Mo8	89.35(5)
Mo1-Mo6-Mo8'	177.11(5)	Mo3-Mo6-Mo11'	90.88(5)
Mo2-Mo7-Mo5	178.79(5)	Mo1-Mo7'-Mo4'	86.38(5)
Mo2-Mo7-Mo2'	89.79(5)	Mo2-Mo7'-Mo5'	91.33(5)
Mo9-Mo7-Mo9'	89.62(5)	Mo6-Mo8-Mo10'	90.71(5)
Mo3-Mo8-Mo6'	174.77(5)	Mo3-Mo8-Mo11'	90.78(5)
Mo1-Mo9-Mo4	179.79(5)	Mo2-Mo9-Mo2'	90.18(5)
Mo3-Mo10'-Mo11'	90.35(5)	Mo7-Mo9-Mo7'	90.38(5)
Mo5-Mo10-Mo8'	91.29(5)	Mo6-Mo11'-Mo10'	89.36(5)
Mo5'-Mo11'-Mo8	90.95(5)		

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center

RESULTS AND DISCUSSION

Description of Structure

$K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ can be described as a framework of molybdenum oxide cluster units in which five trans edge-shared molybdenum octahedra have all edges bridged by oxygen and all apical Mo atoms also capped by oxygen. This building block, the $Mo_{22}O_{50}$ unit, is shown in Figure 3.1 using ORTEP.⁴⁰ A prominent feature of this unit, within the metal-metal framework, is the pairwise distortion of the apical molybdenum atoms to give a short-long-long-short arrangement of Mo-Mo bond distances: 2.610(2)Å for (Mo1-Mo6), 3.019(2)Å for (Mo1-Mo9), 2.942(2)Å for (Mo4-Mo9), and 2.669(2)Å for (Mo4-Mo10). These values are similar to the apical-apical bond distances of 2.749Å, 2.938Å, 2.938Å, 2.749Å reported by Simon²³ for the Mo_{22} cluster found in $In_{11}Mo_{40}O_{62}$. Extended Hückel calculations by Hoffmann and Wheeler⁴¹ on the clusters that make up $In_{11}Mo_{40}O_{62}$ indicate that such a pairwise distortion on the apical molybdenum bond distances in the Mo_{22} unit does not change the HOMO-LUMO gap. However, two molecular orbitals that contribute significantly to apical-apical bonding are lowered in energy by approximately 0.1 eV. The angles between adjacent basal plane molybdenum atoms running parallel to the c axis (the chain direction) indicate only a small component of tilting: (Mo2-Mo7-Mo5) at 176.68(5)°, (Mo3-Mo2-Mo7) at 178.27(6)°, (Mo2-Mo7-Mo5) at 178.79(5)°, and (Mo7-Mo5-Mo11) at 178.52(5)°. Therefore, the apical-apical interactions observed are basically pairwise distortions of the apical molybdenum atoms formed by displacement of these atoms along the c direction.

The variation of the bond distances between the trans edge-shared molybdenums follows the trend observed in $Ba_3Mo_{18}O_{28}$ and $In_{11}Mo_{40}O_{62}$.

Figure 3.1. An ORTEP drawing (70% thermal ellipsoids) of the $n=5$ metal oxide cluster unit in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ as they are found parallel to the c axis

This trend indicates that the trans edge above and below an apical-apical bond will be short if the apical-apical distance is long, and vice versa. For $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$, the trans edge-shared molybdenum bond distances [and apical bond distances] are 2.832(2)Å for (Mo3-Mo5') [2.610(2)Å & 2.669(2)Å] and 2.698(2)Å for (Mo2-Mo7') [3.019(2)Å & 2.942(2)Å]. The basal edges of the molybdenum octahedra that run parallel to the chain also follow the general trend observed in the oligomeric series, $M_{n-x}Mo_{4n+2}O_{6n+4}$, that is, shorter metal-metal bond distances at the ends of the cluster (2.730(2)Å for (Mo5-Mo11) and 2.765(2)Å for (Mo3-Mo8)) and longer bond distances toward the center of the cluster (2.827(2)Å for (Mo5-Mo7) & (Mo2-Mo7) and 2.833(2)Å for (Mo2-Mo3)).

The clusters in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ are interconnected along the chains in the same stair-step fashion observed for all the oligomeric members with two or three edge-sharing octahedra. This can be observed in the ORTEP drawing shown in Figure 3.2. The intercluster bond distances for this pentameric oligomer are indicative of clusters that have only a small metal-metal interaction, 2.998(3)Å for (Mo8-Mo8'), 3.128(2)Å for (Mo8-Mo11'), and 3.156(2)Å for (Mo6-Mo8'). Thus the clusters tend to be isolated units connected via Mo-O bonds. Table 3.8 lists all the intercluster metal-metal bond distances for the oligomeric members with at least three trans edge-sharing molybdenum octahedra. Regrettably, this short list does not indicate an emerging trend with respect to the number of electrons available for metal-metal bonding per molybdenum atom as has been observed for the $n=2$ oligomers.^{19b} One member missing from Table 3.8 which would help compare and contrast the K-Ba pentameric oligomer, $In_6Mo_{22}O_{34}$, has only received a brief mention,³¹ and thus no bond distances are available.

The average intracluster Mo-Mo bond distance is 2.776Å, quite comparable to the 2.798Å found in Simon's Mo_{22} cluster. This result appears to be consistent with the apparent charges on the cluster frameworks, and therefore, also similar to the number of electrons available for metal-metal bonding. The $Mo_{22}O_{34}$

Table 3.8. Intercluster Mo-Mo bond distances and electron counts for selected oligomeric members of the series, $M_x\text{Mo}_{4n+2}\text{O}_{6n+4}$

Compound	n^a	Intercluster bond distances	MCE/Mo ^b	
			(Σ s)	Formal
$\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$	5	2.998(3), 3.128(2), 3.156(2)	3.25	3.26
$\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$	4	3.176(4), 3.195(3), 3.216(3)	3.22	3.22
$\text{Ti}_{1.6}\text{Sn}_{1.2}\text{Mo}_{14}\text{O}_{22}$	3	2.991(3), 3.040(2), 3.116(2)	3.24	3.26
$\text{K}_{1.29}\text{Sn}_{1.71}\text{Mo}_{14}\text{O}_{22}$	3	2.955(2), 3.026(1), 3.091(1)	3.14	3.19
$\text{K}_{1.66}\text{Pb}_{1.34}\text{Mo}_{14}\text{O}_{22}$	3	2.838(4), 3.042(2), 3.103(2)	3.14	3.17
$\text{K}_{2.6}\text{Sr}_{0.4}\text{Mo}_{14}\text{O}_{22}$	3	2.84, 3.04, 3.06	na	3.10
$\text{K}_3\text{Mo}_{14}\text{O}_{22}$	3	3.191(1), 3.194(2), 3.234(2)	3.00	3.07

^aNumber of Mo octahedra sharing trans edges

^bNumber of metal-centered electrons per Mo atom, based on bond valence sums⁴⁵ and formal oxidation states.

framework is formally 7.81- in the K-Ba member and reported as 8- in Simon's cluster. Similar to all the oligomeric members reported, the K-Ba pentameric member also contains the anomalously short metal-metal bond distance, 2.676(2) for (Mo8-Mo10'), for the outer octahedral basal to apical edge.

The average Mo-O bond distance in the Mo_{22} units for K-Ba and the In members are nearly identical, at 2.059Å and 2.060Å, respectively.

$\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$ does contain two short Mo-O bonds, (Mo11-O17) at 1.91(1)Å and (Mo11-O12') at 1.92(1)Å. The former Mo-O bond is on the outer octahedron on the side of the cluster not involved in intercluster Mo-O bonding and the latter Mo-O bond is on the same octahedron in a basal edge-bridging position. These short Mo-O bonds also occur in Simon's Mo_{22} cluster. The two longest Mo-O bond distances, 2.14(1)Å for (Mo11-O4') and 2.15(1)Å for (Mo6-O4), occur in the region of intercluster bonding.

The coordination environment for the cations is shown in Figure 3.3. Note that O1 in the waist-bridging position of the central molybdenum octahedron, does not partake in any other bonding since the central cation site is vacant. The outer cation site, Ba1/K1, is coordinated by eleven oxygens ranging from 2.65(1)Å for (Ba1/K1-O17) to 3.032(9)Å for (Ba1/K1-O10), although five of these cation-oxygen bonds are much shorter than the others. The arrangement of these five oxygens is irregular and does not constitute a simple geometric coordination sphere. Ba2/K2, the inner cation site, is ten coordinate in oxygen, ranging from 2.63(1)Å for (Ba2/K2-O13) to 3.010(9)Å for (Ba2/K2-O3). However, four of these bonds are under 2.7Å, giving a coordination environment in which the cation resides at the top of a square pyramid. The four short Ba2/K2-O bonds are all located towards the center of the cation pocket; this location is where the central cation vacancy is located, and thus this arrangement is not unexpected.

$K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ can be described by the following connectivity formula, $[M_{5-x}]^{y+}[(Mo_{22}O_{18}^i O_{4/2}^{i-i} O_{14/2}^{i-a})O_{14/2}^{a-i}]^{y-}$. Oxygen atoms O3, O6, O7, O9, O10, O11, O13, O16, and O17 are edge-bridging only within the cluster unit and are labelled O^i . The oxygen atoms corresponding to O^{i-i} are edge-sharing between neighboring clusters, these are labelled O4. Oxygens considered O^{i-a} (or O^{a-i}) are edge-bridging between molybdenum atoms of one cluster and terminal to another molybdenum in a neighboring cluster (or vice versa), these include O1, O2, O5, O8, O12, O14, and O15. Some of the connectivity can be seen in Figures 3.2 and 3.4.

Figure 3.3. An ORTEP drawing (70% thermal ellipsoids) of the coordination environment surrounding barium/potassiums in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$.

Figure 3.4. An ORTEP drawing (70% thermal ellipsoids), as viewed down the c axis, emphasizing the interconnected metal oxide cluster units found in $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$. Cation-oxygen bonds are omitted for clarity.

Discussion of Properties

Bond length-bond strength relationships

The application of bond length-bond strength relationships has provided valuable insights into the structure, bonding, and oxidation states of reduced molybdenum oxides that have been synthesized in this laboratory.⁴³ The bond order for metal-metal bonds can be determined using Pauling's bond order equation⁴⁴ found in Equation 1, where $d(n)$ is the bond distance for a metal-metal

$$d(n) = d(1) - 0.61 \log(n) \quad (1)$$

bond in question and n is the bond order for that metal-metal bond. $d(1)$ is the metal-metal distance considered a single bond; for molybdenum this value is 2.614 Å, derived from the distance to nearest and next-nearest neighbors in bcc molybdenum metal. Bond strengths for Mo-O bonds are calculated from the empirical relationship developed by Brown and Wu⁴⁵ and given in Equation 2.

$$s(\text{Mo-O}) = [d(\text{Mo-O})/1.882]^{-6.0} \quad (2)$$

The bond length, in valence units (v.u), is given by $s(\text{Mo-O})$ and $d(\text{Mo-O})$ is the observed Mo-O bond distance in Ångströms. Since $s(\text{Mo-O})$ is given in valence units, the sum of all Mo-O bond valences about a given Mo atom will result in the valence (oxidation state) of that atom.

The numerical values of these calculations are found in Table 3.9. The number of metal-centered electrons (MCE) per $\text{Mo}_{22}\text{O}_{34}$ cluster can be estimated from the sum of the metal-metal bond orders (n), and results in $\text{MCE}(2\sum(\sum n)) = 74.4(5)e^-$ if all bonds are included, or $72.8(5)e^-$ if the intercluster bonds are excluded. The total valence of the pentameric unit, based upon the

Table 3.9. Bond length-bond strength relationships for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$

Atom	d(Mo-Mo)	n	d(M-O)	s
Mo1	2.832(2)	0.439(3)	2.081(9)	0.547(14)
	2.713(2)	0.688(5)	2.117(9)	0.494(13)
	2.722(2)	0.665(5)	2.031(9)	0.633(16)
	2.610(2)	1.015(7)	2.07(1)	0.565(16)
	2.851(2)	0.409(3)	2.097(9)	<u>0.523(14)</u>
	3.019(2)	<u>0.219(2)</u>		$\Sigma s = 2.76(7)$
		$\Sigma n = 3.43(2)$		
Mo2	2.832(2)	0.439(3)	2.03(1)	0.635(18)
	2.833(2)	0.438(4)	2.06(1)	0.582(17)
	2.839(2)	0.428(3)	2.045(9)	0.608(16)
	2.698(2)	0.728(5)	2.07(1)	<u>0.565(16)</u>
	2.827(2)	0.448(4)		$\Sigma s = 2.39(7)$
	2.753(2)	0.592(5)		
	2.756(2)	<u>0.585(4)</u>		
		$\Sigma n = 3.66(3)$		
Mo3	2.713(2)	0.688(5)	2.07(1)	0.565(16)
	2.833(2)	0.438(4)	2.03(1)	0.635(18)
	2.718(2)	0.675(5)	2.078(9)	0.552(14)
	2.832(2)	0.439(3)	2.049(9)	<u>0.600(15)</u>
	2.734(2)	0.636(5)		$\Sigma s = 2.35(6)$
	2.765(2)	0.566(5)		
	2.786(2)	<u>0.522(3)</u>		
		$\Sigma n = 3.96(3)$		
Mo4	2.839(2)	0.428(2)	2.048(9)	0.602(15)
	2.718(2)	0.675(5)	2.04(1)	0.617(18)
	2.720(2)	0.670(5)	2.07(1)	0.565(16)
	2.838(2)	0.429(3)	2.09(1)	0.533(15)
	2.942(2)	0.290(2)	2.10(1)	<u>0.518(14)</u>
	2.669(2)	<u>0.813(7)</u>		$\Sigma s = 2.83(7)$
		$\Sigma n = 3.30(2)$		

Table 3.9. (continued)

Atom	d(Mo-Mo)	n	d(M-O)	s
Mo5	2.722(2)	0.665(5)	2.042(9)	0.613(16)
	2.832(2)	0.439(3)	2.091(9)	0.532(14)
	2.720(2)	0.670(5)	2.10(1)	0.518(14)
	2.744(2)	0.547(4)	1.97(1)	<u>0.760(23)</u>
	2.827(2)	0.448(4)		$\Sigma s = 2.42(7)$
	2.785(2)	0.524(3)		
	2.730(2)	<u>0.645(4)</u>		
		$\Sigma n = 3.94(3)$		
Mo6	2.610(2)	1.015(7)	2.08(1)	0.549(16)
	2.734(2)	0.636(5)	2.15(1)	0.450(12)
	2.774(2)	0.547(4)	2.06(1)	0.582(17)
	2.780(2)	0.534(4)	2.044(9)	0.609(16)
	3.156(2) ^a	0.129(1)	2.11(1)	<u>0.504(15)</u>
	2.774(2)	<u>0.547(4)</u>		$\Sigma s = 2.69(7)$
		$\Sigma n = 3.41(3)$		
Mo7	2.851(2)	0.409(3)	2.01(1)	0.674(20)
	2.698(2)	0.728(5)	2.07(1)	0.565(16)
	2.827(2)	0.448(4)	2.10(1)	0.518(14)
	2.838(2)	0.429(3)	2.05(1)	<u>0.599(17)</u>
	2.720(2)	0.670(5)		$\Sigma s = 2.36(7)$
	2.743(2)	0.615(5)		
	2.775(2)	<u>0.545(4)</u>		
		$\Sigma n = 3.84(3)$		
Mo8	2.765(2)	0.566(5)	2.10(1)	0.518(14)
	2.780(2)	0.534(4)	2.09(1)	0.533(15)
	3.156(2) ^a	0.129(1)	2.08(1)	0.549(16)
	2.998(3) ^a	0.235(3)	2.00(1)	0.694(20)
	2.676(2)	0.791(6)	1.99(1)	<u>0.716(22)</u>
	2.748(2)	0.603(4)		$\Sigma s = 3.01(9)$
	3.128(2) ^a	<u>0.144(1)</u>		
		$\Sigma n = 3.00(2)$		

^aIntercluster Mo-Mo bond distance

Table 3.9. (continued)

Atom	d(Mo-Mo)	n	d(M-O)	s
Mo9	3.019(2)	0.217(2)	2.125(9)	0.483(13)
	2.753(2)	0.592(5)	2.015(9)	0.664(18)
	2.756(2)	0.585(4)	2.01(1)	0.674(20)
	2.942(2)	0.290(2)	1.97(1)	0.760(23)
	2.743(2)	0.615(5)	2.02(1)	<u>0.654(19)</u>
	2.775(2)	<u>0.545(4)</u>		$\Sigma s = 3.23(9)$
		$\Sigma n = 2.84(2)$		
Mo10	2.786(2)	0.522(3)	2.077(9)	0.554(15)
	2.669(2)	0.813(7)	2.05(1)	0.599(17)
	2.785(2)	0.524(3)	2.08(1)	0.549(16)
	2.676(2)	0.791(6)	2.065(9)	0.573(15)
	2.747(2)	<u>0.605(4)</u>	2.06(1)	<u>0.582(17)</u>
		$\Sigma n = 3.26(3)$		$\Sigma s = 2.86(8)$
Mo11	2.730(2)	0.645(4)	2.03(1)	0.635(18)
	2.774(2)	0.547(4)	2.14(1)	0.463(13)
	2.748(2)	0.603(4)	2.21(1)	0.381(10)
	3.128(2) ^a	0.144(1)	1.92(1)	0.887(27)
	2.747(2)	<u>0.605(4)</u>	1.91(1)	<u>0.915(28)</u>
		$\Sigma n = 2.54(1)$		$\Sigma s = 3.30(12)$

Metal-Metal MCE(Σn) = $2\Sigma(\Sigma n) = 72.8(5)e^-$ (w/o intercluster bonds)

Metal-Metal MCE(Σn) = $2\Sigma(\Sigma n) = 74.4(5)e^-$ (with intercluster bonds)

Total valence of Mo₁₄ unit = $2\Sigma(\Sigma s) = 60(2)$ v.u.

$$\text{MCE} = (6 \times 22) - 60(2) = 72(2)e^-$$

Formalized oxidation states^b: $(6 \times 22) - (34 \times 2) + (1 \times 0.19) + (2 \times 3.81) = 71.8e^-$

^bSix electrons from each Mo and using the following oxidation states: O⁻², K⁺, and Ba⁺²

summation of the individual valences of the molybdenum atoms, derived from Mo-O bonds is $2\sum(\Sigma s)=60(2)e^-$. The number of electrons available for metal-metal bonding can also be calculated by subtraction of $60(2)$ from 132 (6×22), the maximum number of valence electrons available for twenty-two molybdenum atoms. The resulting MCE, based on the bond valences, is $72(2)e^-$. This value is in excellent agreement with the $71.8e^-$ expected, based on the formula and formal oxidation states for barium, potassium, and oxygen.

Using Equation 3 to determine the valence of the barium and potassium cations, where $d_1(\text{Ba-O})=2.297$ and its exponent is -7.0 or $d_1(\text{K-O})=2.276$ and its exponent is -9.1 , gives a value of $2.71(6)$ for Ba1 and $1.66(5)$ for K1, or $1.29(4)$

$$s(\text{M-O}) = [d(\text{M-O})/d_1(\text{M-O})]^{-N} \quad (3)$$

for K1 if individual bond valences under 0.1 are excluded. The bond valence sums around Ba2 totalled $2.47(6)$ and K2 was $1.54(5)$ or $1.12(4)$ if the individual bond valences under 0.1 are excluded. Both values are above the expected $+2$ value for barium, however, similar results were obtained for the $n=1$ cluster, $\text{BaMo}_6\text{O}_{10}^{24}$ (2.6), the $n=2$ cluster, $\text{Ba}_2\text{Mo}_{10}\text{O}_{16}^7$ ($2.78(9)$), and the $n=4$ cluster, $\text{Ba}_3\text{Mo}_{18}\text{O}_{28}$ valence sums at $2.56(8)$ and $2.34(5)$. The high valence derived for the potassium cations is not unexpected since bond valence sums for the two unique potassiums in $\text{K}_3\text{Mo}_{14}\text{O}_{22}$ also gave high values of 1.32 and 1.45 . Secondly, because the low concentrations of potassium in the cation sites of the pentameric member result in cation-oxygen bond distances that are essentially based on the barium oxygen bond distances, reliable sums were not expected. Perhaps, the values derived for potassium are reasonable only because the $d_1(\text{K-O})$ and $d_1(\text{Ba-O})$ are nearly equivalent.

Magnetic susceptibility

The magnetic susceptibility of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ was measured on selected crystals. The data were corrected for diamagnetic core contributions, based on the formula determined by the single crystal refinement, using values for individual ions reported by Selwood.⁴⁶ The molar susceptibility for this oligomer is displayed in Figure 3.5. The susceptibility levels off at $\sim 4000 \times 10^{-6}$ emu/mol from 56-356 K. This results in a residual susceptibility, due to temperature independent paramagnetism, χ_{TIP} , of about 180×10^{-6} emu/Mo. The tail from 6-46 K can be fit by the Curie-Weiss relationship and corresponds to a moment of $0.17 \mu_B$. The measured moment is too low for the expected one unpaired electron for every five formula units ($0.77 \mu_B$) based upon formal electron counting. The observed paramagnetic tail most likely arises from an impurity, an electron trapped on a cluster, or a defect within a cluster. This material was taken from the same reaction product that yielded the microprobe results.

Electron spin resonance

Electron spin resonance spectra were obtained on the exact material that was used for magnetic susceptibility measurements. The ESR spectrum, taken at 105 K, corresponds to the material whose magnetic data are shown in Figure 3.5 and can be seen in Figure 3.6. This figure shows two peaks which overlap slightly. Their differing peak shapes would seem to indicate that they arise from different electronic events. The signal at lower field also has noticeable nuclear hyperfine splitting due to ^{95}Mo and ^{97}Mo ($I=5/2$). This material was also examined at 7 K, and no significant change in the peak width or signal to noise ratio was observed. However, the hyperfine splitting of the Mo was resolved better. Even at 7 K neither signal could be power saturated, but some broadening did occur. This result indicates that a very fast relaxation rate dominates the behavior. The ESR results would appear to support the presence of impurities, defects, or atoms on which the electrons are trapped.

Figure 3.5. Molar susceptibility versus temperature of $\text{K}_{0.19}\text{Ba}_{3.81}\text{Mo}_{22}\text{O}_{34}$

Figure 3.6. ESR spectrum at 105 K for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$.

CONCLUSIONS

The synthesis of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$, the $n=5$ oligomer, can be achieved in the form of crystals. Bulk synthesis of this phase has not been realized. Based upon the single crystal x-ray structure refinement, the clusters in this phase are isostructural to the $n=5$ clusters found in Simon's $In_{11}Mo_{40}O_{62}$.²³ The dominant features of $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ include four short and four long apical-apical Mo bond distances, relatively long intercluster metal-metal distances, and interconnections which have a stair-step arrangement from one Mo_{22} unit to the next. Bond valence sums around the molybdenums ($72(2)e^-$) are in good agreement with the value derived from formal oxidation states ($71.8e^-$). Bond order sums, excluding intercluster metal-metal interactions ($72.8(5)e^-$) are nearly within two standard deviations of the formally derived electron count. The net composition of the crystals appears to be consistent within a given reaction product, although there is no evidence indicating that this phase is a line compound. The difficulties encountered during the single crystal structure refinement may indicate intergrowth of oligomers having various chain lengths, with a majority of the domains being Mo_{22} segments. The nearly consistent a and b lattice parameters throughout the oligomeric series make intergrowth a very real possibility. $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ appears to be a diamagnetic material with a small paramagnetic tail at low temperatures and a significant residual χ_{TIP} above 50 K. This result is not consistent with formal electron counting methods, and implies that the underlying difficulty related to the net observed composition versus the real arrangement of cations and their electron transfer to the metal clusters within given domains, is not completely understood. ESR indicates that the paramagnetic tail may be arising from a number of impurities, defects, or noncluster molybdenums on which electrons are trapped.

SECTION 4

**SYNTHESIS AND CHARACTERIZATION OF $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$:
A MATERIAL CONTAINING CLOSEST-PACKING OF
INFINITE CHAINS OF OCTAHEDRAL MOLYBDENUM CLUSTERS**

INTRODUCTION

The synthesis of analogous members in the series $M_2Mo_4O_7$ was undertaken in order to gain a better understanding of the relationship between the number of electrons available for metal-metal bonding and the distortions observed in the metal framework. In particular, the Ti-Fe- Mo_4O_7 system was reexamined because work performed by Lii¹⁵ had shown that such a phase did exist. However, it was only prepared at 1450°C, which resulted in a microcrystalline powder. Six members of this series previously have been prepared and their structures determined by single crystal x-ray refinements: $Sc_{0.75}Zn_{1.25}Mo_4O_7$, $Ti_{0.5}Zn_{1.5}Mo_4O_7$, $Sc_{0.5}Fe_{1.5}Mo_4O_7$, $Fe_{1.89}Mo_{4.11}O_7$, $Al_{0.41}Fe_{1.51}Mo_{4.08}O_7$, and $Al_{0.5}Zn_{1.4}Mo_{4.1}O_7$.^{14,15} Furthermore, preliminary investigation of the $Fe_{1.89}Mo_{4.11}O_7$ member via electron microscopy did reveal a complicated, yet, ordered superstructure. It was anticipated that synthetic efforts directed towards a quaternary member of the Mo_4O_7 phase, one which contained iron, might also have an ordered superstructure. The synthesis of $Ti_{0.31}Fe_{1.69}Mo_4O_7$ is a new combination of two cations which had been used separately in four other members, and most likely the phase initially observed by Lii. The synthesis and characterization of $Ti_{0.31}Fe_{1.69}Mo_4O_7$ via powder and single crystal x-ray diffraction, magnetic susceptibility, x-ray photoelectron spectroscopy, and bond order/bond valence arguments will be discussed.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated ($\sim 2 \times 10^{-5}$ torr) molybdenum tubes. The molybdenum tubes were sealed in fused silica protective jackets for reactions below 1300°C. For reactions above 1300°C the molybdenum tubes were suspended directly in a high temperature, tungsten filament vacuum furnace.

The starting reagents included TiO_2 , Fe_2O_3 , MoO_3 , and Mo. The titanic oxide (Fisher Certified, 99.83%) and ferric oxide (J.T. Baker, "Baker Analyzed", 99.2%) were used directly from the bottles. Molybdenum trioxide was fired at 520°C overnight in an open crucible and then cooled over desiccant. Molybdenum powder (Aldrich, 99.99%) was dried under dynamic vacuum at 120°C overnight. The molybdenum containing reagents were stored in a desiccator. Molybdenum tubing (Thermoelectron Corp., 99.97%) was cleaned by heating at 950°C for five hours under a flowing hydrogen atmosphere. After cooling to room temperature under hydrogen, the tubing also was stored over desiccant. All reactants were thoroughly ground together to produce a homogeneous mixture and subsequently stored in a desiccator.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with Cu $K\alpha_1$ radiation ($\lambda = 1.540562\text{\AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard.

Magnetic susceptibility

The magnetic properties were examined on an as-synthesized pellet fragment with a Quantum Design SQUID magnetosusceptometer. The pellet fragment was tied into a polyethylene straw with dental floss. Neither the floss nor the straw made any significant contribution to the magnetic signal over the temperature range used.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Powdered samples and/or crystals were loaded onto a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Transmission electron microscopy

A Philips CM30 transmission electron microscope was used to determine the presence or absence of any superstructure ordering. An approximate one to one mixture of microcrystalline sample and G-1 Epoxy from Gatan was placed between lens paper, pressed between aluminum plates, and cured at 120°C for ten minutes. A three millimeter disk was punched out, thinned to $\sim 20\text{ }\mu\text{m}$ by dimpling, put on a 200 mesh copper grid for support, and subsequently ion milled

until a hole was observed. The sample and supporting grid assembly were subsequently loaded into the TEM sample holder for investigation.

Microprobe analysis

Elemental analyses were completed by Dr. Alfred Kracher (Department of Geological and Atmospheric Sciences) on an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers (WDS) and operated at 15 kV and 25 nA. Samples were mounted in Epo-Tek 301-2 epoxy resin, dried, and polished to produce a flat surface. Prior to examination, the samples were sputtered with carbon to insure conductivity. Peak profiles and backgrounds were measured for the standards, which included FeTiO_3 , Fe_2SiO_4 , and MoO_2 . Data were analyzed using Probe³⁵ software.

X-ray photoelectron spectroscopy

XPS spectra were collected by James Anderegg at room temperature with a Physical Electronics Industries 5500 multitechnique surface analysis system. This system was equipped with a hemispherical analyzer, a toroidal monochromator, and multichannel detector which sampled a two mm^2 area. The samples were placed on an indium substrate and excited with monochromatic Al $K\alpha$ radiation (1486.6 eV) at 300 watts. The binding energies were calibrated by using the C 1s band at 284.6 eV arising from adventitious carbon.

Synthesis

The title phase, $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$, was initially discovered in a reaction to prepare $\text{Ti}_{0.5}\text{Fe}_{1.5}\text{Mo}_4\text{O}_7$. Stoichiometric quantities of TiO_2 , Fe_2O_3 , MoO_3 , and Mo were thoroughly ground together, pressed into a pellet, and loaded into a molybdenum tube that was subsequently electron beam welded under reduced

pressure. The sample was fired in a vacuum furnace at 1530°C for 48 hours. The contents were then cooled to 1200°C over three hours, to 800°C over 90 minutes, and finally furnace cooled (to 100°C in approximately one hour). The outer surface of the pellet was covered with small, black crystals, from which a single crystal for data collection was selected. Crystals that were large enough to have a distinct shape had the typical dipyramidal morphology reported by Lii.¹⁴ SEM EDS indicated that molybdenum, iron, and titanium were present in the crystals.

Pure $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ could be prepared in the following manner. The same reagents listed above were used in a stoichiometric ratio determined by the single crystal refinement and verified by microprobe analyses. The thoroughly ground and pelletized reagents were loaded into a molybdenum tube, evacuated, fired at 420°C for two hours under dynamic vacuum, and then subsequently electron beam welded under reduced pressure. The sealed tube was then loaded into a fused silica ampoule, as a protective jacket, before firing at 1300°C for 48 hours, followed by 1250°C for six more days. The reaction vessel then was cooled about 50°C/hour to 500°C, at which time it was furnace cooled (overnight to get to room temperature). The crystal size was very small from this reaction, but powder diffraction indicated a rather high degree of crystallinity. A Guinier powder pattern indicated that only $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ was present. Magnetic susceptibility data were also collected on material from this reaction.

X-ray Powder Diffraction

The observed versus calculated d-spacings and relative intensities are given in Table 4.1. A least squares fit of the observed reflections gave the following unit cell parameters: $a=6.010(5)\text{\AA}$, $b=5.765(3)\text{\AA}$, and $c=16.954(11)\text{\AA}$. The calculated d-spacings were derived from the lattice parameters determined by single crystal indexing. All d-spacings are based on Cu $K\alpha_1$ radiation.

Table 4.1. X-ray powder diffraction data for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

d-spacing ($\text{\AA}$)		Intensity ^a	hkl
observed	calculated ^b		
8.535	8.454	s	002
5.679	5.651	s	101
2.956	2.945	m	105
2.887	2.873	w	020
2.832	2.825	w	202
2.731	2.720	w	022
2.569	2.561	m	121
2.456	2.445	w	204
2.385	2.376	m-b	024
2.363	2.354	m	123
2.119	2.113	w	008
2.080	2.074	m-b	220
2.060	2.056	w	125
2.018	2.014	w-b	222 & 026

^aIntensity: s=strong, m=medium, w=weak, and b=broad

^bRefined orthorhombic cell parameters determined from single crystal indexing: $a=5.996(4)\text{\AA}$, $b=5.745(4)\text{\AA}$, and $c=16.907(7)\text{\AA}$

X-ray Single Crystal Data Collection

A small, black, irregularly shaped crystal was taken from the edge of the bulk pellet. The crystal, having the dimensions $0.06 \times 0.05 \times 0.03 \text{ mm}^3$, was mounted on a glass fiber by using Devcon epoxy cement with a five minute setting time. A Rigaku AFC6R rotating anode diffractometer was used with graphite monochromated Mo $K\alpha$ radiation ($\lambda=0.71069\text{\AA}$) at 7 kW. Lattice parameters and an orientation matrix for data collection were derived from 8 randomly located and centered reflections with a two theta range of $13\text{--}18^\circ$. The lattice was determined to be body-centered orthorhombic with cell dimensions: $a=5.996(4)\text{\AA}$, $b=16.90(1)\text{\AA}$, $c=5.746(3)\text{\AA}$, and $\text{volume}=582.3(7)\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. The final idealized cell with the following lattice parameters: $a=5.996(4)\text{\AA}$, $b=5.745(4)\text{\AA}$, $c=16.907(7)\text{\AA}$, and $\text{volume}=582.4(6)\text{\AA}^3$ was calculated after transforming the data. Data were collected at room temperature from 0 to 50° in two theta using an ω - 2θ scan mode. Only data with $h+k+l=2n$ in the octants $(h,\pm k,l)$ were collected, due to the body-centering symmetry. The number of reflections measured was 628, of which 468 were observed and 231 were unique with $I>3.5\sigma(I)$. The linear absorption coefficient for Mo $K\alpha$ was 124.57 cm^{-1} . An empirical absorption correction³⁶ was applied based upon azimuthal scans of 3 reflections with an average transmission range of $0.9074\text{--}1.000$. The intensity data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The space group $Imma$ (#74) was chosen based upon the systematic absences of $hk0$: $k \neq 2n$ and hkl : $h+k+l \neq 2n$; there was only one violation, the (110)

reflection, which was located near the very intense (220). This observation would most likely arise from $\lambda/2$ radiation and can be validly discarded. The structure was solved by direct methods using SHELXS³⁷ ($R=0.046$) and refined on $|F|$ by full matrix least squares techniques³⁸ with the TEXSAN³⁹ package.

Based upon the lattice parameters and Laue information obtained, this phase was presumed to be isostructural to materials prepared by Brough and Lii.^{14,15} Initial atomic positions were taken from $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$.¹⁵ Appropriate positional and thermal parameters were varied. The octahedral metal site, M2 ($M=\text{Fe}$ or Ti), was refined as a combination of titanium and iron, this refinement converged with occupancies at 31(3)% Ti and 69(3)% Fe.

Microprobe analyses on five different grains indicated a composition of $\text{Ti}_{0.271(9)}\square_{0.034}\text{Fe}_{1.695(4)}\text{Mo}_4\text{O}_7$, quite similar to the single crystal refinement. Two further pieces of evidence that suggested molybdenum did not reside, in part, on the octahedral metal sites, are the nearly 2:1 mole ratio of Mo to Ti and Fe cations, and the weight percent of all elements, which totaled 100.58%. Because microprobe analyses indicated that there might be a small percentage of vacancies, structural refinements were carried out by allowing the total occupancy of the octahedral metal site to vary. These refinements indicated vacancies were not present.

A secondary extinction correction was applied and refined to $4.5(2)\times 10^{-6}$. The temperature factors for both molybdenum and iron were refined anisotropically. The anisotropic temperature factor of the lighter titanium was fixed to the same values determined for the iron residing on the same site. Three out of four oxygen atom thermal parameters were refined anisotropically. However, the values obtained for the thermal parameters of all the oxygens are not well behaved. This situation also occurred for some of the thermal parameters of oxygens in previously prepared members.¹⁵ There is no convincing evidence to discern the correct interpretation of these anisotropic

thermal parameters. The final refinement converged at $R=0.0291$ and $R_w=0.0346$. A final electron difference map indicated the largest peak of $1.3 \text{ e}/\text{\AA}^3$, located about $1.6 \text{\AA}$ from Mo2. The smallest peak of $-1.3 \text{ e}/\text{\AA}^3$, was located $1.4 \text{\AA}$ from O4, the oxygen atom whose thermal parameters would not refine anisotropically.

Details of the data collection and refinement for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ are given in Table 4.2. Final positional parameters and isotropic temperature factors are given in Table 4.3. Anisotropic temperature factors are listed in Table 4.4. Selected bond distances and bond angles are found in Tables 4.5 and 4.6, respectively.

Table 4.2. X-ray crystallographic data for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

formula	$\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$
formula weight	604.99
crystal system	orthorhombic
space group	Imma (#74)
a, Å	5.996(4)
b, Å	5.745(4)
c, Å	16.907(7)
volume, Å ³	582.4(7)
Z	4
calculated density, g/cm ³	6.882
F000	1000
crystal size, mm ³	0.06 x 0.05 x 0.03
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	124.570
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.71069
temperature, °C	24
two theta range, degrees	0-50
scan mode	ω -2 θ
No. reflections collected	628
No. observations ($I > 3.5\sigma(I)$), (unique)	468 (231)
No. variables	42
goodness of fit ^a	1.252
max. shift in final cycle	0.000
largest peaks in final diff. map, e/Å ³	+1.3, -1.3
transmission coefficient	0.907-1.000
R^b , R_w^c	0.0291, 0.0346

$$^a \text{Quality of fit} = [\sum \omega (F_o - F_c)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o - F_c| / \sum F_o$$

$$^c R_w = [\sum \omega (F_o - F_c)^2 / \sum \omega F_o^2]^{1/2}; \omega = 1/\sigma^2(F_o)$$

Table 4.3. Atomic coordinates for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

Atom	Wyckoff #	X	Y	Z	B_{eq}^a
Mo1	8h	0.5	0.4912(4)	0.88898(7)	0.88(6)
Mo2	8i	0.2685(2)	0.25	0.00324(8)	0.54(5)
Fe1	4e	0.5	0.25	0.6928(2)	1.1(1)
Fe2/Ti2 ^b	4d	0.75	0.75	0.75	0.8(2)
O1	4a	0.0	0.0	0.0	1.0(6)
O2	8i	0.251(2)	0.25	0.8827(5)	1.2(5)
O3	8i	0.740(2)	0.75	0.8750(6)	1.3(5)
O4	8h	0.5	0.517(2)	0.7635(6)	0.8(2)

^aThe equivalent isotropic temperature factor, B_{eq} , is defined as $8\pi^2/3 \langle \sum_i \sum_j (U_{ij} a_i^* a_j^* a_i a_j) \rangle$, where the summations of i and j range from 1 to 3

^bThe 4d site is fully occupied, 31(3)% Ti and 69(3)% Fe

Table 4.4. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mo1	5.6(7)	22.4(8)	5.6(6)	0.0	0.0	0.4(6)
Mo2	8.1(7)	7.1(7)	5.3(6)	0.0	-0.1(8)	0.0
Fe1	15.(2)	17.(2)	9.(2)	0.0	0.0	0.0
M2 ^b	10.(2)	12.(2)	10.(2)	0.0	4.(2)	0.0
O1	3.(7)	18.(8)	15.(7)	0.0	0.0	-1.2(8)
O2	27.(8)	3.(6)	14.(6)	0.0	3.(7)	0.0
O3	20.(7)	19.(7)	9.(5)	0.0	4.(6)	0.0
O4 ^c	11.(2)					

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$

^bFe2 and Ti2 reside on the same position, M2. Fe2 was refined anisotropically and Ti2 was set to equivalent values.

^cO4 would only refine isotropically

Table 4.5. Selected bond distances ($\text{\AA}$) for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ ^a

Mo1-Mo1'	2.772(5)	Mo1'-Mo1	2.973(5)
Mo1-Mo2	2.753(2) (x2)	Mo1-Mo2'	2.731(2) (x2)
Mo2-Mo2"	2.875(2) (x2)	Mo2-Mo2'	2.776(3)
Fe2-Fe2'	2.998(2) (x2)	Mo1-O2	2.040(9) (x2)
Mo1-O3	2.082(8) (x2)	Mo1-O4	2.13(1)
Mo2-O1	2.158(1) (x2)	Mo2-O2	2.040(9)
Mo2-O3	2.06(1)	Fe1-O2	1.97(1) (x2)
Fe1-O4	1.94(1) (x2)	Fe2-O3	2.11(1) (x2)
Fe2-O4	2.023(8) (x4)	Mo1-Fe2	3.159(2) (x2)

^aAtoms with primed numbers are related to those with unprimed numbers by mirror symmetry

Table 4.6. Selected bond angles^a (degrees) for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ ^b

Mo1-Mo1'-Mo1'	180.0	Mo1-Mo1'-Mo2	59.77(4) (x2)
Mo2-Mo1-Mo2'	93.56(6) (x2)	Mo2-Mo1-Mo2'	61.10(7)
Mo1-Mo1'-Mo2	57.02(4)	Mo2-Mo1-Mo2'	63.23(5) (x2)
Mo1-Mo1'-O4	86.0(3)	Mo2-Mo1-O2	93.6(3)
Mo2-Mo1-O3	95.2(3)	Mo2-Mo1-Mo2'	60.55(7)
O2-Mo1-O4	89.7(3) (x2)	O3-Mo1-O4	80.6(4) (x2)
O2-Mo1-O2	94.1(5)	O2-Mo1-O3	170.0(4) (x2)
O2-Mo1-O3	88.5(3) (x2)	O3-Mo1-O3	87.4(5)
Mo1-Mo2-Mo1'	60.45(9)	Mo1-Mo2-Mo1'	86.44(6) (x2)
Mo1-Mo2-Mo2'	58.01(5) (x2)	Mo1-Mo2-Mo2'	59.73(3) (x2)
Mo1-Mo2-Mo1'	65.97(9)	Mo1-Mo2-Mo2'	58.76(5) (x2)
Mo1-Mo2-Mo2'	59.45(4) (x2)	Mo2-Mo2'-Mo2"	90.0 (x4)
Mo2-Mo2'-Mo2'	180.0	Mo2-Mo2'-Mo2'	175.6(1)
Mo2-Mo2'-O2	87.82(5) (x2)	Mo2-Mo2'-O3	92.19(5) (x2)
Mo1-Mo2-O1	91.94(5) (x2)	Mo2-Mo2'-O2	93.0(3)
Mo2-Mo2'-O3	91.4(3)	Mo2"-Mo2'-O2	87.0(3)
Mo2-Mo2'-O3	88.6(3)	O1-Mo2-O2	86.3(3) (x2)
O1-Mo2-O3	90.4(3) (x2)	O1-Mo2-O4	83.44(7)
O2-Mo2-O3	175.6(5)	Fe2'-Fe2-Fe2'	180.0
O4-Fe1-O4	104.1(7)	O2-Fe1-O4	113.4(2) (x4)
O2-Fe1-O2	99.3(6)	O4-Fe2-O4	82.9(5) (x2)
O2-Fe2-O4	97.1(5) (x2)	O3-Fe2-O4	82.3(4) (x4)
O3-Fe2-O4	97.7(4) (x4)	O3-Fe2-O3	180.0
Mo2-O1-Mo2'	96.49(7) (x2)	Mo2-O1-Mo2'	83.51(7) (x2)
Mo1-O2-Mo1'	85.6(5)	Mo1-O2-Mo2	84.9(4) (x2)
Mo1-O3-Mo1'	91.1(5)	Mo1-O3-Mo2	82.5(3) (x2)
Mo1-O3-Fe2	97.7(4) (x2)	Mo2-O3-Fe2	179.8(7)
Mo1-O4-Fe2	99.1(4) (x2)	Fe2-O4-Fe2'	95.6(5)

^aAngles containing Fe2 are equivalent to angles for Ti2^bAtoms with primed numbers are related to those with unprimed numbers by mirror symmetry

RESULTS AND DISCUSSION

Description of Structure

The $M_2Mo_4O_7$ phases can be described as closest packing of molybdenum-oxide cluster chains, $[Mo_4O_7]_{\infty}^{x-}$, in such a manner that tetrahedral and octahedral sites are created. The cations reside in these two coordination environments. Compounds that have been previously characterized have octahedral sites filled by a combination of cations, including Fe, Zn, Sc, Ti, Al, and/or Mo. Tetrahedral sites in these known materials have been filled by only two cations, Fe or Zn.^{14,15}

The $Ti_{0.31}Fe_{1.69}Mo_4O_7$ structure, as viewed in Figure 4.1, can also be described in terms of layers. The first layer contains infinite metal oxide chains consisting of trans edge-sharing molybdenum octahedra, bridged on the edges by oxygen atoms. The chains then are interconnected via oxygens that bridge the basal plane edges of the octahedra. These oxygens thus are centered between four molybdenum atoms and are essentially coordinated in square planar geometry. The next layer contains metal-centered oxygen octahedra that share trans edges and run orthogonal to the infinite metal-metal bonded Mo chains. This octahedral site, M2, was refined with occupation by both iron and titanium. The layers are then repeated by using the body-centering operation. Also, iron atoms fill sites tetrahedrally coordinated by oxygen between each of the orthogonal layers described above. These four oxygens consist of two edge-bridging atoms in the chains and two terminal atoms in the chains.

The infinite chains of trans edge-shared molybdenum octahedra have many interesting characteristics. The apical-apical bonding between molybdenum atoms (Mo1) are arranged in an alternating short-long fashion with (Mo1-Mo1') at 2.772(5)Å and (Mo1'-Mo1) at 2.973(5)Å. The length of this bioctahedral subunit

Figure 4.1. An ORTEP drawing (70% thermal ellipsoids) of $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ as viewed parallel to the molybdenum-oxide infinite chains, the b direction

constitutes the repeat distance in the b direction. In addition, the short apical-apical bond alternates from the top of the chain to the bottom of the chain, as followed parallel to the b axis. This alternating bond arrangement between apical molybdenum atoms can be described as a tilting of the octahedra. In this respect, the dihedral angle in the basal plane molybdenums is 175.6° for (Mo2-Mo2'-Mo2). For the bonds corresponding to the shared edges of the octahedra a bond distance of $2.776(3)\text{\AA}$ (Mo2-Mo2') is observed. The basal to apical molybdenum bond distances are shorter than those found in NaMo_4O_6 and the basal Mo-Mo bond distances parallel to the chain are also longer. These results are detailed in Table 4.7. The closest intercluster Mo-Mo bond distance is $3.220(3)\text{\AA}$ for basal plane molybdenum atoms in two adjacent chains.

Both cation sites are slightly distorted from their ideal tetrahedral or octahedral coordination. Fe1 has O-Fe1-O bond angles ranging from $99.3(6)^\circ$ to $113.4(2)^\circ$ for the tetrahedral cavity. M2, the combination of Ti and Fe, has apical oxygens located 180° apart, but the interior angles around M2 vary from $82.9(5)^\circ$ to $97.7(4)^\circ$.

$\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ can be more descriptively formulated as $[\text{}^0(\text{Ti}_{0.62}\text{Fe}_{1.38})\text{}^t\text{Fe}_2][(\text{Mo}_6\text{Mo}_{4/2}\text{O}_{12/2}\text{O}_4^i)\text{O}_4^a]$, which takes into account the doubling in the b axis due to the tilting interactions between molybdenum octahedra. ^tM and ^oM denote tetrahedral and octahedral ternary metal sites, respectively. Oxygens labelled as O^i correspond to O2 and O3, which bridge edges of the molybdenum octahedra within any one infinite chain. O2 is also shared with a ^tM and O3 is shared with a ^oM . Oxygens defined as O^{i-i} constitute the group of O1's that bridge the basal edges and interconnect the neighboring infinite chains of molybdenum octahedra. These oxygens are not coordinated by any other metals and are therefore found in a nearly square planar geometry. Apical molybdenums are capped by O4 which are shared with the ternary or quaternary cation, and are labelled O^a .

Table 4.7. Metal-metal bond distances for seven $M_2Mo_4O_7$ compounds^a

Compound	Mo1-Mo2 ^b	Mo2-Mo2 ^c	Mo1-Mo1 ^d	$\angle^e$	MCE ^f
$Sc_{0.75}Zn_{1.25}Mo_4O_7$	2.748/2.782	2.817/2.886	2.629/3.136	174.0	14.5
$Fe_{1.89}Mo_{4.11}O_7$	2.752/2.760	2.778/2.890	2.771/3.006	176.0	14.4
$Ti_{0.5}Zn_{1.5}Mo_4O_7$	2.742/2.756	2.784/2.893	2.791/2.991	176.1	14.4
$Sc_{0.5}Fe_{1.5}Mo_4O_7$	2.755/2.759	2.792/2.887	2.740/3.028	175.4	14.3
$Ti_{0.31}Fe_{1.69}Mo_4O_7$	2.731/2.753	2.776/2.875	2.772/2.973	175.6	14.2
$Al_{0.41}Fe_{1.51}Mo_{4.08}O_7$	2.750/2.756	2.778/2.879	2.728/3.027	175.8	14.1
$Al_{0.5}Zn_{1.4}Mo_{4.1}O_7$	2.742/2.762	2.772/2.882	2.82/2.95	176.9	na

^aThe associated distances in $NaMo_4O_6$ are: (Mo1-Mo2) at 2.780Å, (Mo2-Mo2) at 2.753Å & 2.862Å, and (Mo1-Mo1) at 2.862Å

^bMo(apical) to Mo(basal) bond distances

^cMo(basal) to Mo(basal) bond distances, $\perp/\parallel$ to the chain direction, respectively

^dMo(apical) to Mo(apical) bond distances

^eDihedral angle between basal planes of adjacent octahedra

^fNumber of electrons available for metal-metal bonding per Mo_4O_7 , based on $\sum s(Mo-O)$

Preliminary investigation of $Ti_{0.31}Fe_{1.69}Mo_4O_7$ indicated no superstructure was present in the [100] and [110] zone axes. However, lower order zone axes, such as the [320] show a tripling in the c axis. This diffraction has not been checked by centered dark field to determine if it is real or due to double diffraction.

Discussion of Properties

One goal of synthesizing the Mo_4O_7 compounds with various cations was to determine how the number of electrons available for metal-metal bonding affected the structural framework. In particular, one must know the oxidation states of the cations. In this case, titanium could be Ti(II), Ti(III), or Ti(IV), and iron could be Fe(II) or Fe(III). More insight into the correct oxidation states for these cations was gained by using bond length-bond strength relationships, measuring the magnetic properties, and obtaining XPS measurements on $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$.

Bond length-bond strength relationships

The numerical values that were calculated from the bond length-bond order relationships, as discussed previously in Section 1, are found in Table 4.8 for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$. The summation for the metal-centered electrons (MCE) included apical-apical interactions. The number of electrons available for metal-metal bonding using Pauling's bond order equation⁴³ and summing over all the metal-metal bonds in the formula unit, $(2\sum(\Sigma n))$, is $14.1(1)e^-$. Alternatively, the number of electrons available for metal-metal bonding can be derived from an empirical bond valence sum for all Mo-O bonds around the molybdenum atoms.⁴⁵ This results in $14.2(2)e^-$ per formula unit. The agreement between these two calculated values may be fortuitous. Previous bond strength analyses of nearly all ternary and quaternary reduced molybdenum oxides, in which the oxidation state of the cation is well established, has shown that the results derived from the Mo-O bond valence sums are more reliable than those derived from Pauling's bond order sums.^{7,15,19b,43} This discrepancy is strikingly evident in most of the $\text{M}_2\text{Mo}_4\text{O}_7$ phases.⁴³ And the problem is compounded in this system when the oxidation states of the cations are unknown. The more reliable bond valence sums are tabulated in Table 4.7. Note that there is no direct correlation between the number of MCE and any set of bond distances, as has been observed in the

Table 4.8. Bond length-bond strength relationships for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

Atom	d(Mo-Mo)	n	d(M-O)	s
Mo1	2.772(5)	0.551(10)	2.13(1)	0.476(13)
	2.973(5)	0.258(5)	2.040(9) (x2)	0.617(17)
	2.753(2) (x2)	0.592(4)	2.082(8) (x2)	<u>0.546(13)</u>
	2.731(2) (x2)	<u>0.643(5)</u>	$\Sigma s = 2.80(7)$	
	$\Sigma n = 3.28(3)$			
Mo2	2.753(2) (x2)	0.592(4)	2.040(9)	0.617(17)
	2.731(2) (x2)	0.643(5)	2.06(1)	0.582(18)
	2.875(2) (x2)	0.373(3)	2.158(1) (x2)	<u>0.4400(13)</u>
	2.776(3)	<u>0.543(6)</u>	$\Sigma s = 2.08(4)$	
	$\Sigma n = 3.76(3)$			
Fe1 (calculated as Fe(II))			1.94(1) (x2)	0.593(17)
			1.97(1) (x2)	<u>0.545(15)</u>
			$\Sigma s = 2.27(6)$	
Fe2 (calculated as Fe(III))			2.023(8) (x4)	0.482(10)
			2.11(1) (x2)	<u>0.379(10)</u>
			$\Sigma s = 2.69(6)$	
Ti2 (calculated as Ti(III))			2.023(8) (x4)	0.528(11)
			2.11(1) (x2)	<u>0.424(10)</u>
			$\Sigma s = 2.96(6)$	
$\text{MCE } (\Sigma n) = 2\Sigma(\Sigma n) = 14.1(1)e^-$				
$\text{Total valence of the Mo}_4 \text{ unit} = 2\Sigma(\Sigma s) = 9.8(2)e^-$				
$\text{MCE} = (6 \times 4) - 9.8(2) = 14.2(2)e^-$				

oligomeric series, $M_{n-x}Mo_{4n+2}O_{6n+4}$.^{7,19b}

For the estimation of the oxidation state of the iron and titanium atoms the empirical bond valence equation (Equation 1) developed by Brown and Wu⁴⁵ was used with $R(1)$ and $(N) = 1.764\text{\AA}$ (5.5), $1.780\text{\AA}$ (5.7), $1.789\text{\AA}$ (5.2), and $1.806\text{\AA}$ (5.2) for Fe^{+2} , Fe^{+3} , Ti^{+3} , and Ti^{+4} , respectively.

$$s(\text{cation-O}) = [R(\text{cation-O})/R(1)]^{-N} \quad (1)$$

Based upon Equation 1, the final bond valence sums around each of the cations are as follows: $Fe1(\text{as } +2) = 2.27(6)$, $Fe1(\text{as } +3) = 2.35$, $Fe2(\text{as } +2) = 2.63$, $Fe2(\text{as } +3) = 2.69(7)$, $Ti2(\text{as } +3) = 2.96(7)$, and $Ti2(\text{as } +4) = 3.11$ valence units. Based upon these calculations, $Fe1$, the tetrahedrally coordinated cation, appears to be essentially $Fe(II)$. Extensive bond valence analyses of oxides known to contain $Fe(II)$ in tetrahedral sites has shown values ranging from 1.95-2.25.¹⁵ Because titanium and iron reside on the same octahedral cation site, the actual M-O bond distances are not observed, but rather a weighted average based on the two cations. This condition inherently gives rise to bond valence sums that must be interpreted cautiously. Bond valence sums on oxides with titanium in octahedral sites, which are fully occupied, have shown that $Ti(IV)$ ranges from 3.58-4.03 and $Ti(III)$ varies from 2.95-3.17.¹⁵ The calculated value of 2.96 for $Ti2$ in $Ti_{0.31}Fe_{1.69}Mo_4O_7$ may be fortuitous, considering its low occupancy, however the separation observed between the known $Ti(III)$ and $Ti(IV)$ compounds is significantly large. Similar bond valence sums for iron in fully occupied octahedral sites of known oxides were also calculated by Lii.¹⁵ These values ranged from 1.91-2.67 for $Fe(II)$ and from 2.82-3.22 for $Fe(III)$. The bond valence sum of 2.63 for $Fe2$ (as $Fe(II)$) and 2.69 (as $Fe(III)$) in $Ti_{0.31}Fe_{1.69}Mo_4O_7$ indicate that no reasonable assignment of an integral oxidation state can be made in this case.

Finally, a general comment should be made about the bond valence approach using this empirical method developed by Brown and Wu. Note that the cationic oxidation states determined using the parameters for any one element in a variety of oxidation states did not result in significantly different values. This observation would imply that this empirical approach should be generalized to any oxidation state, as well as any coordination number. This approach was verified for molybdenum oxides by Bart and Ragaini.⁵⁰

X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy was used to shed more light on the situation of the cationic oxidation states. TiO_2 and Ti_2O_3 were used as titanium references. They each had a pair of peaks arising from the $2p^{3/2}$ and the $2p^{1/2}$: 459.2 and 465.0 eV for TiO_2 and 457.0 and 462.7 eV for Ti_2O_3 . The $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ used for XPS had been synthesized as a pressed pellet and stored in a vial without any special precautions. The sample was ground and loaded for XPS measurements in a drybox with an argon environment within three weeks of the initial synthesis. The $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ had corresponding Ti peaks at 458.3 and 464.0 eV, values between Ti(III) and Ti(IV). The $2p^{3/2}$ value reported for FeO was 709.2 eV.⁵¹ The $2p^{3/2}$ and $2p^{1/2}$ peaks for Fe_2O_3 were located at 710.7 eV and 724.3 eV, respectively.⁵² The XPS for iron in $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ was fit with six peaks, three pairs of $2p^{3/2}$ and $2p^{1/2}$, as viewed in Figure 4.2. The peaks, $2p^{3/2}$ and $2p^{1/2}$, respectively, were located at 709.0 and 722.2 eV, 711.1 and 724.3 eV, and 715.6 and 728.8 eV. These peaks can be understood as Fe(II), Fe(III), and a pair of satellite peaks, respectively. The satellite peaks may be the result of the so-called "shake-up" interaction, in this situation, a transition from O 2p to Fe 3d. Such "shake-up" interactions generally arise when surfaces exhibit an affinity for excess oxygen or nonstoichiometry.⁵³ The molybdenum XPS peaks were in the range expected for

Figure 4.2. Fe 2p core x-ray photoelectron spectrum fit with three pairs of peaks.

a reduced molybdenum oxide with Mo 3d^{5/2} and Mo 3d^{3/2} at 228.7 and 231.9 eV, respectively. The XPS measurements did indicate that the oxidation state of the titanium may be +3 or +4 and did reaffirm that the iron is present in two oxidation states, +2 and +3.

Magnetic susceptibility

Magnetic susceptibility measurements also gave information useful for determining the cationic oxidation states. $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ is ferrimagnetic with a T_C of about 110 K. The Curie temperature was derived from the change in the sign of the slope in plot of molar susceptibility versus temperature. The material reverts to normal paramagnetic behavior above approximately 200 K. The molar and inverse molar susceptibilities, which were corrected for core diamagnetism, are shown in Figure 4.3. A linear least squares fit of the data above 200 K, taken from a plot of $1/\chi$ versus temperature, to the Curie-Weiss relationship resulted in an effective moment that required far too much Fe(III). This conclusion was drawn from the previous magnetic results of Lii¹⁵ and the general viewpoint that the octahedral Fe²⁺ cation would be better suited by crystal field stabilization if it was Fe(II). A nonlinear least squares fit of the data above 200 K to Equation 3

$$\chi = C/(T-\theta) + \chi_o, \quad \chi_o = \chi_{\text{TIP}} + \chi_{\text{diamagnetic}} \quad (3)$$

resulted in an effective moment too small for even total occupancy of Fe(II) and Ti(IV). Also, theta derived from this equation was too small for a ferrimagnetic material and χ_o was too large. The most reasonable assessment of the effective moment was obtained by using data above 200 K and using the nonlinear least squares fit with χ_o fixed at zero. The resulting fit is shown in Figure 4.4 and corresponds to an effective moment of $6.53 \mu_B$. This moment can be interpreted as an infinite number of combinations of Ti(III), Ti(IV), Fe(II), and Fe(III). Figure 4.5 displays the variability of the cation composition at the fixed effective moment

Figure 4.3. Molar and inverse molar susceptibility versus temperature of $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

Figure 4.4. Nonlinear least squares fit of high temperature data of $\text{Tl}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

Figure 4.5. The oxidation state flexibility of titanium & iron in $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ at a fixed effective moment

of $6.53 \mu_B$. The Ti(III) composition is allowed to vary from 0 to 0.31 moles/formula unit and the remaining titanium is d^0 Ti(IV). However, the small concentration of d^1 Ti(III) can be substituted with an even smaller quantity of d^6 Fe(II) or d^5 Fe(III). Thus, the Fe(II) molar composition need only vary from 1.66 to 1.63 and therefore it only necessitates 0.03 to 0.06 moles of Fe(III). The limiting composition ranges are then $Ti_{0.31}^{+3}Fe_{1.66}^{+2}Fe_{0.03}^{+3}Mo_4O_7$ and $Ti_{0.31}^{+4}Fe_{1.63}^{+2}Fe_{0.06}^{+3}Mo_4O_7$, a net difference of only $0.34e^-$ per Mo_4O_7 . This result is in general agreement with the bond valence considerations and XPS which indicate that Fe(III) and Ti(IV) are present. The underlying assumption is made, that the molybdenum-oxide framework contains no unpaired electrons and is basically diamagnetic.

Cation size effect

Evidence supporting the cation assignments can not be easily interpreted from the lattice dimensions of the $Fe_{1.89}Mo_{4.11}O_7$ to those of $Ti_{0.31}Fe_{1.69}Mo_4O_7$. All the $M_2Mo_4O_7$ members are listed in Table 4.9. If the octahedral metal site for this quaternary compound, $Ti_{0.31}Fe_{1.69}Mo_4O_7$, does contain more Fe(III) than the ternary compound, $Fe_{1.89}Mo_{4.11}O_7$, then the a axis length should increase. This increase could be due to greater electrostatic repulsion of the Fe(III). However, this axial increase may be offset by the smaller size of Fe(III) versus Fe(II). Secondly, because Ti(III) or Ti(IV) and Fe(III) are both smaller than Fe(II), the c axis length should decrease, and this is observed. Thus, no generally conclusive relationship can be derived.

Oxidation state summary

All of the evidence related to the titanium oxidation state suggests that Ti(II) is not present. The relatively low molar abundance of titanium creates difficulties in ascertaining its true oxidation state via XPS. The presence of two different cation sites and two possible oxidation states for each cation, based upon XPS,

Table 4.9. Unit cell parameters for all known $M_2Mo_4O_7$

Compound	a(Å)	b(Å)	c(Å)	Volume(Å ³)
Sc _{0.5} Fe _{1.5} Mo ₄ O ₇ ^a	6.0245(8)	5.7686(4)	17.119(2)	595.0(1)
Ti _{0.31} Fe _{1.69} Mo ₄ O ₇	5.996(4)	5.745(4)	16.907(7)	582.4(6)
Al _{0.41} Fe _{1.51} Mo _{4.08} O ₇ ^a	5.991(1)	5.7545(8)	16.878(3)	581.3(2)
Fe _{1.89} Mo _{4.11} O ₇ ^a	5.9793(5)	5.7704(4)	17.036(1)	587.80(8)
Sc _{0.75} Zn _{1.25} Mo ₄ O ₇ ^b	6.085(1)	5.764(1)	17.002(4)	596.3(2)
Ti _{0.5} Zn _{1.5} Mo ₄ O ₇ ^b	6.030(1)	5.782(1)	16.759(4)	584.4(2)
Al _{0.5} Zn _{1.4} Mo _{4.1} O ₇ ^a	5.9652(6)	5.7623(6)	16.764(2)	576.2(1)

^aReference 14 and unpublished results, Brough, L.F. and McCarley, R.E.

^bReference 15

essentially creates an unresolvable set of conditions. The interpretation of the magnetic properties results in an infinite number of solutions over a small composition range. This average composition would allow 14.5e⁻ per Mo₄O₇ unit, in relatively good agreement with the molybdenum bond valence and bond order sums. Cation size effects can be argued either way. Bond valence sums for the irons are not reliable enough to gain further insight, although Fe1 appears to be fundamentally Fe(II). The selection of the iron oxidation state must be derived from the requirements of the metal-metal framework. The similarity of the Mo-O and Fe-O bond strengths in Fe₃O₄, MoO₂, and Fe₂O₃ may accommodate even more electronic flexibility between the cations and the molybdenum framework. Ti_{0.31}Fe_{1.69}Mo₄O₇ would tend to be a more homogeneous metal oxide based upon the above bond strengths observed for the binary oxides.

3 of 4

Other important synthetic relationships to $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

Efforts to prepare single phase material of $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ also included the reactions found in Table 4.10. All starting materials and stoichiometries were identical, as previously reported under Synthesis. From this set of reactions, it can be observed that the $\text{M}_2\text{Mo}_4\text{O}_7$ phases are probably metastable with respect to the spinel, M_3O_4 , phases. Formation of the ternary $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$ is preferred at $\sim 1400^\circ\text{C}$, however the quaternary $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ can be formed at lower temperatures for longer reaction times, or at slightly elevated temperatures, 1475°C and 1530°C . As the reaction time increased at higher reaction temperatures, the final products appeared to be spinels with the general composition $\text{Ti}_x\text{Mo}_y\text{Fe}_{3-x-y}\text{O}_4$. Note the third and fourth reactions given in Table 4.10. Under essentially identical conditions, the reaction appears to be at different stages, this might imply that the reaction is auto-catalytic. All of these

Table 4.10. Other reactions to prepare $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$

Reaction Conditions ^a	Products ^b
1300°C/2d & 1250°C/6d	$\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$
1475°C/52hrs	$\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7 + \text{Mo}$
1530°C/48hrs	$\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7 + \text{Mo}$
1530°C/48hrs ^c	$\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7 + \text{Mo} + \text{M}_3\text{O}_4$
1530°C/84hrs ^c	$\text{M}_3\text{O}_4 + \text{Mo} + \text{MoO}_2$
1400°C/84hrs ^d	$\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7 + \text{Mo}$

^aAll reactions performed in Mo tubes

^bAll products characterized by Guinier powder diffraction

^c $\text{Ti}_x\text{Mo}_y\text{Fe}_{3-x-y}\text{O}_4$, isostructural to Fe_3O_4

^dReference 15: Lii's preparation of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$

products have been observed in bulk materials by Guinier powder diffraction, qualitatively by SEM EDS, and also by morphology ($M_2Mo_4O_7$ as dipyramids and M_3O_4 as truncated octahedra). Molybdenum appeared to be extruded as beads of metal through surface defects in the $M_2Mo_4O_7$ with the formation of M_3O_4 . The total reaction scenario would be interesting to follow by high temperature diffraction, the limiting factors are most likely the long reaction time, high temperature required, and the necessity of eliminating traces of oxygen which would drive this reaction to produce MoO_3 or MoO_2 .

CONCLUSIONS

The $M_2Mo_4O_7$ phases are a simple, yet intricate, arrangement of infinite chains constructed of trans edge-shared molybdenum octahedra in such a manner that octahedral and tetrahedral cavities are formed for the ternary or quaternary cation. The actual number of electrons available for metal-metal bonding is difficult to determine accurately, but it is large enough that the chains distort with apical-apical interactions alternating in a short-long-short fashion. The molar composition has been confirmed by microprobe analysis and the preparation of single phase material has been achieved. This observed stoichiometry of three titaniums and seven irons, on average, over ten octahedral cation sites might result in an ordered superstructure that could be understood by further TEM work. $Ti_{0.31}Fe_{1.69}Mo_4O_7$ is a ferrimagnetic material with a Curie temperature of approximately 110 K.

The ability to substitute a variety of di- and tri-valent cations into the tetrahedral and octahedral cavities of the Mo_4O_7 system reaffirms that this structure is stabilized with electron counts between 14 and $15e^-$ per Mo_4O_7 unit. Unfortunately, iron and titanium can both exhibit more than one oxidation state. Structurally the molybdenum-oxide framework is quite similar to the previously reported members.^{14,15} Therefore one would not expect the number of MCE to be very different from the known members. Determination of the number of electrons available for metal-metal bonding based upon the cationic bond valence sums was not feasible. Bond valence sums around the molybdenums in $Ti_{0.31}Fe_{1.69}Mo_4O_7$ predict 14.2(2) MCE, bond order sums over the metal-metal bonds result in $14.1(1)e^-$, and calculations based upon cationic oxidation states derived from magnetic susceptibility measurements result in $14.5e^-$.

The results obtained for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ do not improve or clarify the intricate relationship between the metal cluster electron count and the observed changes in structural distortions of the molybdenum octahedra.

Attempts to prepare $\text{Fe}_{1.67}\text{Mo}_{1.33}\text{O}_4^{15}$ as single crystals large enough to test for an ordered superstructure have been unsuccessful. Single phase material of this ternary spinel may exhibit an ordered superstructure that could be deduced by TEM.

SECTION 5

**SYNTHESIS AND CHARACTERIZATION OF $K_xM_{2-x}Mo_{10}O_{16}$ (M=Ca,Sr,Gd):
OLIGOMERS WITH TWO TRANS EDGE-SHARING MoO_4 OCTAHEDRA**

INTRODUCTION

The synthetic efforts to prepare new materials containing trans edge-shared molybdenum octahedra of finite length have been quite successful for the $M_2Mo_{10}O_{16}$ members. These materials contain two trans edge-fused octahedra, based upon the general formulation, $M_{n-x}Mo_{4n+2}O_{6n+4}$, where n equals the number of edge-shared Mo octahedra. These discrete segments interconnect with neighboring segments in a stair-step fashion through a strong intercluster metal-metal bond, and multiple Mo-O bonds, parallel to the "chain" direction. A second notable feature of the $n=2$ oligomers is the strong apical Mo-Mo bonding.

The first dimeric oligomer, $La_2Mo_{10}O_{16}$, was structurally characterized by Rietveld analysis.²⁵ Subsequently, single crystal refinements have been performed when the ternary cation was Pb²⁶, Sn²⁷, Gd²⁸, Ba⁷, or La, Ca, Sr, Ce, Pr, Nd, Sm, or Eu.²⁹ The benefit of having a large number of members structurally characterized is that generalizations about the bonding and electronic considerations can be made. The limiting factor of all these compounds is that the formal number of electrons donated by the cations to the metal-metal framework is either four or six. In synthetic efforts to prepare quaternary oligomers with $n=3$ and $n=4$, four new quaternary members of the $n=2$ series were formed. They include $K_{0.06}M_{1.94}Mo_{10}O_{16}$ ($M=Ca, Sr$), $SrBaMo_{10}O_{16}$, and $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$. The first two members result in a slightly more oxidized molybdenum cluster unit, the third member is isoelectronic with the ternary Pb, Sn, Ba, Sr, Ca, and Eu phases, and the last member formally contains an electron count intermediate to all the reported members. This section will only briefly discuss the synthesis and structural characterization of these quaternary members, given the multitude of reported compounds in this area. Emphasis will be placed on the electronic/bonding considerations of this series.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated, fused silica tubes ($\sim 1 \times 10^{-4}$ torr) or molybdenum tubes ($\sim 2 \times 10^{-5}$ torr). All reactants were thoroughly ground to produce a homogeneous mixture before being used as loose powders or pressed pellets. Mixed starting materials were subsequently stored in a desiccator.

The starting materials included K_2MoO_4 , $SrMoO_4$, $CaMoO_4$, $BaMoO_4$, $Gd_2(MoO_4)_3$, SrO , MoO_3 , MoO_2 , and Mo . The synthesis, drying, and/or cleaning of the K_2MoO_4 , $SrMoO_4$, $BaMoO_4$, MoO_3 , MoO_2 , Mo and Mo tubing have been previously reported in Sections 1 and 2. The SrO was prepared by firing $SrCO_3$ in an open crucible at $550^\circ C$ for about one week. The product was then cooled over desiccant. Calcium molybdate was synthesized by mixing an aqueous solution of calcium chloride (Baker Analyzed Reagent) with an aqueous solution containing a stoichiometric quantity of sodium molybdate (Fisher Certified, A.C.S.) The white precipitate was filtered, washed with water, and then dried overnight at $120^\circ C$ under dynamic vacuum. Gadolinium molybdate was prepared by reacting a 1:3 mole ratio of intimately mixed Gd_2O_3 (Ames Lab Rare Earth Center) and MoO_3 at $800^\circ C$ for two days in an evacuated fused silica tube. All starting reagents and Mo tubing were subsequently stored in a desiccator until needed.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with Cu $K\alpha_1$ radiation ($\lambda = 1.540562\text{\AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Powdered samples and/or crystals were loaded on a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Microprobe analysis

Elemental analyses were completed by Dr. Alfred Kracher (Department of Geological and Atmospheric Sciences) on an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers (WDS) and operated at 15 kV and 25 nA. Samples were mounted in Epo-Tek 301-2 epoxy resin, dried, and polished to produce a flat surface. Prior to examination, the samples were sputtered with carbon to insure conductivity. Peak profiles and backgrounds were measured for the standards, which included KAlSi_3O_8 , CaCO_3 , and MoO_2 . Data were analyzed using Probe³⁵ software.

Synthesis

$K_{0.06}Ca_{1.94}Mo_{10}O_{16}$ crystals were grown from a reaction intended to prepare $K_2Ca_2Mo_{18}O_{28}$. The starting materials, K_2MoO_4 , $CaMoO_4$, MoO_3 , and Mo, were thoroughly ground and pressed into a pellet prior to loading into a Mo tube. The tube and its contents were fired at 430°C for two hours under dynamic vacuum, to drive off any volatile materials, before the tube was sealed via electron beam welding. The sealed Mo tube was loaded directly into a tantalum basket, which was then suspended in a high temperature vacuum furnace. The reaction was held at 1500°C for 96 hours before cooling at a rate of 2°C/min to 900°C, at which time the furnace was powered down. This quench resulted in an average cooling rate of about 15°C/min. Black, chunk-like crystals were found on the surface of a silvery (Mo) pellet. SEM EDS on several crystals indicated the presence of K, Ca, and Mo. A Guinier powder pattern of the reaction mixture indicated the presence of K_2MoO_4 , Mo, and the $Mo_{10}O_{16}$ phase. No attempt was made to synthesize single phase material. The observed versus calculated d-spacings and relative intensities are given in Table 5.1 for the $K-CaMo_{10}O_{16}$ member. The calculated d-spacings were derived from the lattice parameters determined by single crystal indexing. All d-spacings are based on Cu $K\alpha_1$ radiation.

$K_{0.06}Sr_{1.94}Mo_{10}O_{16}$ crystals were discovered in a reaction to synthesize $K_2SrMo_{14}O_{22}$. The starting reagents included K_2MoO_4 , $SrMoO_4$, MoO_3 , and Mo. The same procedure as stated above was used, except that the Mo tube and contents were dried overnight at 430°C. The sealed Mo tube was fired at 1500°C for 79 hours, at which time the building power failed. The sample was probably quenched to 800°C in a matter of minutes and reached room temperature within an hour. The black crystals were found between the bottom Mo cap and the pellet. No single phase preparation of this material was attempted.

Table 5.1. X-ray powder diffraction data for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
6.542	6.511	s	011
5.511	5.491	w	$\bar{1}11$
3.103	3.106	w/m-b	$\bar{1}13$
2.956	2.952	vw	013
2.878	2.874	w	031
2.842	2.840	vw	$\bar{2}11$
2.674	2.671	w/m-b	$\bar{1}23$
2.497	2.496	w/m-b	221
2.457	2.456	w	$\bar{1}13$
2.391	2.390	w-b	$\bar{3}12$
2.368	2.365	w-b	212
2.264	2.265	w-vb	040
2.191	2.190	w-b	$\bar{3}21$
2.053	2.052	w-b	$\bar{3}23$
1.976	1.974	vw	213
1.942	1.941	vw	$\bar{2}41$
1.925	1.922	s-b	$\bar{1}34$
1.917	1.916	w	$\bar{3}32$
1.904	1.902	w-b	232
1.846	1.847	w-b	223
1.820	1.820	w-b	$\bar{1}25$
1.780	1.779	w-b	051
1.676	1.676	w-b	$\bar{1}44$
1.662	1.663	w-b	242
1.467	1.466	vw-b	$\bar{1}54$
1.456	1.457	vw-b	252
1.442	1.442	vw-b	406
1.425	1.425	vw-b	106

^aIntensity: s=strong, m=medium, w=weak, b=broad, and v=very

^bRefined monoclinic cell parameters: $a=7.543(1)\text{\AA}$, $b=9.059(2)\text{\AA}$, $c=9.972(1)\text{\AA}$, and $\beta=110.073(9)^\circ$

$\text{BaSrMo}_{10}\text{O}_{16}$ crystals were formed in a reaction for the preparation of $\text{Sr}_2\text{Ba}_2\text{Mo}_{18}\text{O}_{28}$. The starting materials, SrO , BaMoO_4 , MoO_2 , and Mo were thoroughly ground and loaded into a fused silica tube as a powder. About two milligrams of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ was added as a potential flux. The contents were subsequently evacuated and double-sealed in fused silica tubes. The reaction was fired at 1230°C for seven days. It was then cooled at $\sim 50^\circ\text{C}/\text{hour}$ to 800°C , at which time it was quenched to room temperature. Small, black, chunk-like crystals were found on the surface of the black powder. Single phase preparations were not attempted.

$\text{K}_{0.33}\text{Gd}_{1.67}\text{Mo}_{10}\text{O}_{16}$ crystals were grown from a reaction mixture intended for the preparation of $\text{K}_2\text{GdMo}_{14}\text{O}_{22}$. K_2MoO_4 , $\text{Gd}_2(\text{MoO}_4)_3$, MoO_3 , and Mo were thoroughly ground, pressed into a pellet, loaded into a Mo tube, fired at 430°C under dynamic vacuum for 2.5 hours, and left under dynamic vacuum overnight before sealing the Mo tube by electron beam welding. This reaction was fired under identical conditions as reported for the $\text{K-CaMo}_{10}\text{O}_{16}$ member. The furnace was cooled at a rate of $3^\circ\text{C}/\text{min}$ to 800°C , before quenching to 100°C over the period of an hour. The pellet had a few black, chunk-like crystals (title phase) and numerous thin needles (probably $\text{K}_x\text{Gd}_{4-x}\text{Mo}_{18}\text{O}_{32}$) growing on the surface. SEM EDS indicated a significant quantity of potassium along with Gd and Mo in both of the crystal types. No attempts were made to prepare single phase material.

X-ray Single Crystal Data Collection and Structure Refinement

Routine methods were used to collect data and solve the structures of four $\text{Mo}_{10}\text{O}_{16}$ phases. Details of the data collection and refinement for $\text{KMMo}_{10}\text{O}_{16}$ members are found in Tables 5.2, 5.7, and 5.11. Final positional parameters and

isotropic temperature parameters are given in Tables 5.3, 5.8, and 5.12. Anisotropic thermal factors are listed in Tables 5.4, 5.9, and 5.13. Selected metal-metal interatomic distances and metal-oxygen bond distances are found in Tables 5.5, 5.10, and 5.14. Selected bond angles are listed for the K-Ca and K-Gd members in Tables 5.6 and 5.15. A few more details of the data collection and structure refinement are included in a supplementary Table 5.16. This format will be used instead of a descriptive paragraph for each member.

The only structural details of $\text{SrBaMo}_{10}\text{O}_{16}$ will be given here, since the structural refinement was poor. A crystal was indexed on the Hilger-Watts diffractometer with the following lattice parameters: $a=7.471(2)\text{\AA}$, $b=9.122(1)\text{\AA}$, $c=9.888(2)\text{\AA}$, and $\beta=109.11(2)^\circ$. Four octants of data were collected from 0 to 55° in two theta. There were 1136 unique reflections observed after the data was averaged and corrected for absorption based upon one azimuthal scan.³⁶ SHELXS³⁷ direct methods indicated a solution with $R=0.032$ in the space group $P2_1/c$. After applying all the available techniques, the final $R=10.7\%$ and the net composition was refined to $\text{Sr}_{1.02(6)}\text{Ba}_{0.98}\text{Mo}_{10}\text{O}_{16}$.

Table 5.2. X-ray crystallographic data for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$

formula	$K_{0.06}Ca_{1.94}Mo_{10}O_{16}$
formula weight	1295.49
crystal system	monoclinic
space group	$P2_1/c$ (#14)
a, Å	7.543(1)
b, Å	9.059(2)
c, Å	9.972(1)
β , degrees	110.073(9)
volume, Å ³	640.0(2)
Z	2
calculated density, g/cm ³	6.717
F000	1174
crystal size, mm ³	0.1 x 0.06 x 0.04
μ (Mo K α), cm ⁻¹	100.550
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.709580
temperature, °C	24
two theta range, degrees	0-55
scan mode	ω -2 θ
No. reflections collected	3175
No. observations ($I > 3\sigma(I)$), (unique)	2145 (1028)
No. variables	108
goodness of fit ^a	1.232
max. shift in final cycle	0.016
largest peaks in final diff. map, e/Å ³	+2.70, -1.53
transmission coefficient	0.860-1.000
R^b , R_w^c	0.0281, 0.0339

$$^a \text{Quality of fit} = [\sum \omega (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^c R_w = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}; \omega = 1/\sigma^2(|F_o|)$$

Table 5.3. Atomic coordinates for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$

Atom ^a	X	Y	Z	B _{eq} ^b
Ca ^c	0.7649(3)	0.5051(2)	0.5268(2)	0.99(6)
K ^c	0.7649	0.5051	0.5268	1.0
Mo1	0.4993(1)	0.12360(8)	0.41346(7)	0.25(2)
Mo2	0.8887(1)	0.11582(8)	0.51623(7)	0.26(2)
Mo3	0.3224(1)	0.12647(8)	0.61307(7)	0.24(2)
Mo4	0.1169(1)	0.11552(8)	0.31763(8)	0.26(2)
Mo5	0.6877(1)	0.13387(8)	0.69988(7)	0.25(2)
O1	0.4871(8)	0.0018(6)	0.2369(6)	0.4(2)
O2	0.8993(8)	0.9911(7)	0.3415(6)	0.33(9)
O3	0.8940(9)	0.2663(6)	0.6703(7)	0.4(1)
O4	0.0999(8)	0.2467(6)	0.4789(6)	0.2(1)
O5	0.294(1)	0.2528(6)	0.2821(7)	0.5(2)
O6	0.699(1)	0.2549(6)	0.3828(6)	0.3(1)
O7	0.8848(8)	0.4975(7)	0.3337(6)	0.5(2)
O8	0.493(1)	0.2781(7)	0.5645(7)	0.5(2)

^aAll atoms reside on the Wyckoff position 4e

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3 \langle \sum_i \sum_j (U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j) \rangle$, where the summations of i and j range from 1 to 3

^cCa has an occupancy of 97(2)% and K, at the same position, has an occupancy of 3(2)%, based upon microprobe analyses of six data points on five different crystals

Table 5.4. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{K}_{0.06}\text{Ca}_{1.94}\text{Mo}_{10}\text{O}_{16}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ca/K	12.(1)	12.5(9)	11.2(9)	-0.3(8)	1.5(7)	-0.4(8)
Mo1	3.1(3)	3.1(3)	2.9(3)	0.1(3)	0.7(3)	0.6(3)
Mo2	3.1(3)	3.9(3)	2.5(3)	-0.8(3)	0.4(3)	0.3(3)
Mo3	2.8(3)	3.4(4)	3.0(3)	-0.2(3)	1.0(3)	-0.6(3)
Mo4	2.8(3)	3.7(3)	3.1(3)	-0.2(3)	0.6(3)	0.3(3)
Mo5	3.3(3)	3.3(3)	2.4(3)	-0.3(3)	0.3(3)	-0.6(3)
O1	3.(3)	4.(3)	7.(3)	-2.(3)	2.(2)	1.(2)
O2	4.(1)					
O3	6.(1)					
O4	3.(1)					
O5	7.(3)	6.(3)	7.(3)	1.(2)	6.(3)	2.(2)
O6	4.(1)					
O7	4.(3)	7.(3)	8.(3)	-1.(2)	1.(2)	1.(2)
O8	6.(3)	7.(3)	5.(3)	-6.(2)	3.(3)	-4.(2)

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a*b*U_{12}hk+2a*c*U_{13}hl+2b*c*U_{23}kl))$

^bK thermal parameters fixed to those of Ca, and oxygen atom thermal parameters for O2, O3, O4, and O6 only refined isotropically

Table 5.5. Selected interatomic bond distances (Å) for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$ ^a

Mo1-Mo1'	2.825(1)	Mo1-Mo2	2.760(1)
Mo1-Mo3'	2.751(1)	Mo1-Mo3	2.693(1)
Mo1-Mo4	2.710(1)	Mo1-Mo5	2.720(1)
Mo1-Mo5'	2.759(1)	Mo2-Mo2'	2.775(2) inter ^b
Mo2-Mo3'	3.079(1) inter	Mo2-Mo3	2.758(1)
Mo2-Mo4	3.038(1) inter	Mo2-Mo4'	2.681(1)
Mo2-Mo5'	2.754(1)	Mo3-Mo4'	2.821(1)
Mo3-Mo5	2.590(1) apical ^c	Mo4-Mo5	2.736(1)
Ca...Ca'	3.765(2)	Ca...Ca'	3.847(2) inter
Mo1-O1	2.052(6)	Mo1-O5	2.023(6)
Mo1-O6	2.025(6)	Mo1-O8'	2.068(6)
Mo2-O3'	2.044(6)	Mo2-O4'	2.120(6)
Mo2-O6	2.023(6)	Mo2-O7	2.104(6)
Mo2-O7'	2.112(6)	Mo3-O1	2.044(6)
Mo3-O4	2.062(6)	Mo3-O5	2.080(6)
Mo3-O7	2.135(6)	Mo3-O8	2.051(6)
Mo4-O2	1.916(6)	Mo4-O3'	2.106(6)
Mo4-O4'	2.038(6)	Mo4-O5	1.946(6)
Mo4-O7'	2.103(6)	Mo5-O1	2.054(6)
Mo5-O2	2.068(6)	Mo5-O3	2.065(6)
Mo5-O6	2.060(6)	Mo5-O8	2.080(6)
Ca-O1	2.664(6)	Ca-O2	2.396(6)
Ca-O2'	2.421(6)	Ca-O3	2.592(6)
Ca-O4	2.477(6)	Ca-O5	3.037(6)
Ca-O6	2.638(6)	Ca-O7	2.878(6)
Ca-O8	2.694(7)	Ca-O8'	3.017(6)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center. All calcium atom positions also partially occupied by K.

^bIntercluster Mo-Mo bond distances

^cApical-apical Mo-Mo bond distances

Table 5.6. Selected bond angles (degrees) for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$ ^a

Mo1'-Mo1-Mo2	88.43(4)	Mo1'-Mo1-Mo3	57.75(3)
Mo1'-Mo1-Mo3'	59.73(3)	Mo1'-Mo1-Mo4	88.53(4)
Mo1'-Mo1-Mo5	59.65(3)	Mo1'-Mo1-Mo5'	58.29(3)
Mo2-Mo1-Mo3	60.75(3)	Mo2-Mo1-Mo4	176.80(4)
Mo2-Mo1-Mo5'	60.33(3)	Mo3-Mo1'-Mo4	62.20(3)
Mo3-Mo1-Mo5	56.53(3)	Mo3-Mo1-Mo5'	89.86(3)
Mo3-Mo1'-Mo5'	91.91(3)	Mo3-Mo1'-Mo5	56.71(3)
Mo4-Mo1-Mo5	60.01(3)	Mo1-Mo2-Mo3'	175.38(3)
Mo1-Mo2-Mo3	58.44(3)	Mo1-Mo2-Mo4'	90.52(3)
Mo1-Mo2-Mo5'	59.13(3)	Mo3-Mo2-Mo4'	62.46(3)
Mo3-Mo2-Mo5'	89.82(3)	Mo4-Mo2'-Mo5	60.43(3)
Mo1-Mo3-Mo1'	62.52(3)	Mo1'-Mo3-Mo2	89.99(3)
Mo1'-Mo3-Mo4'	58.20(3)	Mo1-Mo3-Mo5	61.15(3)
Mo1-Mo3-Mo2	60.81(3)	Mo1-Mo3-Mo4'	88.96(3)
Mo1-Mo3-Mo5'	62.93(3)	Mo2-Mo3-Mo4'	61.80(3)
Mo2'-Mo3-Mo5	178.80(3)	Mo1-Mo4-Mo2'	92.51(3)
Mo1-Mo4-Mo3'	59.60(3)	Mo1-Mo4-Mo5'	60.89(3)
Mo2-Mo4'-Mo3	60.11(3)	Mo2'-Mo4-Mo5	61.10(3)
Mo3'-Mo4-Mo5	88.90(3)	Mo1-Mo5-Mo1'	62.07(3)
Mo1-Mo5-Mo2	60.54(3)	Mo1'-Mo5-Mo4	90.20(3)
Mo1'-Mo5-Mo2'	89.89(3)	Mo1-Mo5-Mo4	59.11(3)
Mo2-Mo5'-Mo4'	58.47(3)		

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center

Table 5.7. X-ray crystallographic data for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$

formula	$K_{0.06}Sr_{1.94}Mo_{10}O_{16}$
formula weight	1387.72
crystal system	monoclinic
space group	$P2_1/c$ (#14)
a, Å	7.550(2)
b, Å	9.156(2)
c, Å	9.959(2)
β , degrees	109.30(1)
volume, Å ³	649.8(2)
Z	2
calculated density, g/cm ³	6.859
F000	1210
crystal size, mm ³	0.02 x 0.04 x 0.06
μ (Mo K α), cm ⁻¹	134.570
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.709580
temperature, °C	24
two theta range, degrees	0-55
scan mode	ω -2 θ
No. reflections collected	1709
No. observations ($I > 3\sigma(I)$), (unique)	803 (770)
No. variables	78
goodness of fit ^a	1.623
max. shift in final cycle	0.002
largest peaks in final diff. map, e/Å ³	+8.4, -2.8
transmission coefficient	0.832-1.000
R^b , R_w^c	0.0580, 0.0656

$$^a \text{Quality of fit} = [\sum \omega (F_o - F_c)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o - F_c| / \sum F_o$$

$$^c R_w = [\sum \omega (F_o - F_c)^2 / \sum \omega F_o^2]^{1/2}; \omega = 1/\sigma^2(F_o)$$

Table 5.8. Atomic coordinates for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$

Atom ^a	X	Y	Z	B _{eq} ^b
Sr ^c	0.7522(4)	0.5050(4)	0.5391(3)	0.8(1)
K ^c	0.7522	0.5050	0.5391	0.8
Mo1	0.5006(4)	0.1225(3)	0.4139(3)	0.22(8)
Mo2	0.8875(3)	0.1155(3)	0.5171(3)	0.22(8)
Mo3	0.3204(3)	0.1256(3)	0.6127(3)	0.25(8)
Mo4	0.1189(3)	0.1163(3)	0.3183(3)	0.21(8)
Mo5	0.6863(3)	0.1316(3)	0.7015(3)	0.12(4)
O1	0.494(3)	0.002(3)	0.235(2)	0.3(3)
O2	0.890(3)	0.497(3)	0.338(2)	0.4
O3	0.892(3)	0.258(2)	0.671(2)	0.4
O4	0.100(3)	0.245(2)	0.483(2)	0.4
O5	0.298(3)	0.254(2)	0.284(2)	0.4
O6	0.701(3)	0.248(2)	0.383(2)	0.4
O7	0.885(2)	0.495(3)	0.335(2)	0.3(3)
O8	0.496(3)	0.276(2)	0.565(2)	0.5(3)

^aAll atoms reside on the Wyckoff position 4e

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3 \{ \sum_i \sum_j (U_{ij} a_i^* a_j^* a_i \cdot a_j) \}$, where the summations of i and j range from 1 to 3

^cSr has an occupancy of 97(2)% and K, at the same position, has an occupancy of 3(2)%

Table 5.9. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{K}_{0.06}\text{Sr}_{1.94}\text{Mo}_{10}\text{O}_{16}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sr/K	12.(2)	8.(2)	10.(2)	1.(2)	0.(1)	2.(2)
Mo1	2.(1)	4.(1)	3.(1)	0.(1)	11.(8)	0.(1)
Mo2	2.(1)	3.(1)	3.(1)	-2.(1)	0.8(9)	1.(1)
Mo3	3.(1)	3.(1)	3.(1)	-1.(1)	-0.2(9)	1.(1)
Mo4	3.(1)	1.(1)	3.(1)	0.(1)	1.(1)	1.(1)
Mo5	1.6(5)					
O1	3.(4)					
O2	5.1					
O3	5.1					
O4	5.1					
O5	5.1					
O6	5.1					
O7	4.(4)					
O8	6.(4)					

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$

^bK thermal parameters fixed to those of Ca, Mo5 temperature factor refined isotropically, and oxygen atom thermal parameters for O1, O7, and O8 only refined isotropically

Table 5.10. Selected bond distances (Å) for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$ ^a

Mo1-Mo1'	2.827(5)	Mo1-Mo2	2.758(4)
Mo1-Mo3'	2.748(4)	Mo1-Mo3	2.701(4)
Mo1-Mo4	2.721(4)	Mo1-Mo5	2.743(4)
Mo1-Mo5'	2.766(4)	Mo2-Mo2'	2.804(6) inter ^b
Mo2-Mo3'	3.089(3) inter	Mo2-Mo3	2.769(4)
Mo2-Mo4	3.043(3) inter	Mo2-Mo4'	2.691(4)
Mo2-Mo5'	2.746(4)	Mo3-Mo4'	2.823(4)
Mo3-Mo5	2.608(4) apical ^c	Mo4-Mo5	2.747(4)
Mo1-O1	2.08(2)	Mo1-O5	2.04(2)
Mo1-O6	2.00(2)	Mo1-O8'	2.07(2)
Mo2-O3'	2.01(2)	Mo2-O4'	2.11(2)
Mo2-O6	2.00(2)	Mo2-O7	2.11(2)
Mo2-O7'	2.11(2)	Mo3-O1	2.05(2)
Mo3-O4	2.05(2)	Mo3-O5	2.09(2)
Mo3-O7	2.11(2)	Mo3-O8	2.07(2)
Mo4-O2	1.88(2)	Mo4-O3'	2.18(2)
Mo4-O4'	2.06(2)	Mo4-O5	1.96(2)
Mo4-O7'	2.14(2)	Mo5-O1	2.07(2)
Mo5-O2	2.05(2)	Mo5-O3	2.04(2)
Mo5-O6	2.09(2)	Mo5-O8	2.09(2)
Sr-O1	2.75(2)	Sr-O2	2.55(2)
Sr-O2'	2.57(2)	Sr-O3	2.66(2)
Sr-O4	2.59(2)	Sr-O5	2.92(2)
Sr-O6	2.77(2)	Sr-O7	2.79(2)
Sr-O8	2.71(2)	Sr-O8'	2.92(2)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center. All strontium atom positions also partially occupied by K.

^bIntercluster Mo-Mo bond distances

^cApical-apical Mo-Mo bond distances

Table 5.11. X-ray crystallographic data for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$

formula	$K_{0.33}Gd_{1.67}Mo_{10}O_{16}$
formula weight	1490.90
crystal system	monoclinic
space group	$P2_1/c$ (#14)
a, Å	7.554(2)
b, Å	9.020(2)
c, Å	9.932(2)
β , degrees	109.88(2)
volume, Å ³	636.4(2)
Z	2
calculated density, g/cm ³	7.366
F000	1322
crystal size, mm ³	0.03 x 0.03 x 0.04
μ (Mo K α), cm ⁻¹	148.660
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.709580
temperature, °C	24
two theta range, degrees	0-55
scan mode	ω -2 θ
No. reflections collected	3122
No. observations ($I > 3\sigma(I)$), (unique)	1453 (699)
No. variables	103
goodness of fit ^a	0.963
max. shift in final cycle	0.001
largest peaks in final diff. map, e/Å ³	+2.05, -1.51
R^b , R_w^c	0.0288, 0.0340

$$^a \text{Quality of fit} = [\sum \omega (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$$

$$^b R = \sum |F_o| - |F_c| / \sum |F_o|$$

$$^c R_w = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}; \omega = 1/\sigma^2(|F_o|)$$

Table 5.12. Atomic coordinates for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$

Atom ^a	X	Y	Z	B _{eq} ^b
Gd ^c	0.7682(1)	0.5034(2)	0.5293(1)	0.86(3)
K ^c	0.7682	0.5034	0.5293	0.9
Mo1	0.5007(2)	0.1236(2)	0.4139(2)	0.30(5)
Mo2	0.8929(2)	0.1152(2)	0.5149(2)	0.34(5)
Mo3	0.3253(2)	0.1269(2)	0.6159(2)	0.37(5)
Mo4	0.1155(2)	0.1170(2)	0.3204(2)	0.34(5)
Mo5	0.6911(2)	0.1320(2)	0.7009(2)	0.29(5)
O1	0.485(2)	0.004(2)	0.233(1)	0.7(2)
O2	0.901(1)	0.490(2)	0.347(1)	0.4(2)
O3	0.892(2)	0.266(2)	0.668(1)	0.6(4)
O4	0.104(2)	0.253(1)	0.483(1)	0.6(2)
O5	0.299(2)	0.259(2)	0.287(1)	0.7(2)
O6	0.701(2)	0.260(1)	0.386(1)	0.3(1)
O7	0.882(2)	0.999(2)	0.329(1)	0.6(4)
O8	0.496(2)	0.280(2)	0.564(1)	0.7(4)

^aAll atoms reside on the Wyckoff position 4e

^bThe equivalent isotropic temperature factor, B_{eq}, is defined as $8\pi^2/3 \{ \sum_i \sum_j (U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j) \}$, where the summations of i and j range from 1 to 3

^cGd has an occupancy of 83.3(6)% and K, at the same position, has an occupancy of 16.7(6)%

Table 5.13. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{K}_{0.33}\text{Gd}_{1.67}\text{Mo}_{10}\text{O}_{16}$ ^b

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Gd/K	11.2(5)	9.4(5)	10.0(4)	0.4(6)	0.8(4)	-0.8(7)
Mo1	3.1(6)	4.3(7)	4.0(7)	-0.3(7)	0.9(5)	-0.6(7)
Mo2	4.2(7)	4.0(7)	4.1(7)	0.0(7)	0.7(5)	-0.3(7)
Mo3	3.4(7)	6.3(8)	4.6(7)	-0.9(7)	1.8(6)	-1.4(6)
Mo4	4.9(7)	3.0(8)	4.6(7)	1.3(7)	1.1(6)	1.5(7)
Mo5	2.3(7)	3.4(7)	5.2(7)	-0.4(6)	1.1(5)	-0.9(7)
O1	9.(2)					
O2	5.(2)					
O3	9.(6)	7.(7)	5.(6)	-8.(5)	2.(5)	-2.(5)
O4	8.(3)					
O5	9.(3)					
O6	1.(2)					
O7	6.(5)	5.(5)	10.(5)	1.(6)	1.(5)	3.(7)
O8	7.(6)	14.(7)	2.(6)	3.(6)	-1.(5)	-1.(5)

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^2U_{11}h^2+b^2U_{22}k^2+c^2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$

^bK thermal parameters fixed to those of Gd, and oxygen atom temperature factors of O1, O2, O4, O5, and O6 only refined isotropically

Table 5.14. Selected interatomic bond distances (Å) for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$ ^a

Mo1-Mo1'	2.812(3)	Mo1-Mo2	2.788(2)
Mo1-Mo3'	2.755(2)	Mo1-Mo3	2.681(2)
Mo1-Mo4	2.738(2)	Mo1-Mo5	2.723(2)
Mo1-Mo5'	2.755(2)	Mo2-Mo2'	2.711(4) inter ^b
Mo2-Mo3'	3.076(2) inter	Mo2-Mo3	2.778(2)
Mo2-Mo4	2.961(2) inter	Mo2-Mo4'	2.671(2)
Mo2-Mo5'	2.771(2)	Mo3-Mo4'	2.824(2)
Mo3-Mo5	2.601(2) apical ^c	Mo4-Mo5	2.726(3)
Gd...Gd'	3.741(2)	Gd...Gd'	3.895(2) inter
Mo1-O1	2.06(1)	Mo1-O5	2.02(1)
Mo1-O6	2.04(1)	Mo1-O8'	2.06(1)
Mo2-O3'	2.04(1)	Mo2-O4'	2.13(1)
Mo2-O6	2.04(1)	Mo2-O7	2.10(1)
Mo2-O7'	2.14(1)	Mo3-O1	2.06(1)
Mo3-O4	2.08(1)	Mo3-O5	2.06(1)
Mo3-O7	2.15(1)	Mo3-O8	2.07(1)
Mo4-O2	1.99(1)	Mo4-O3'	2.13(1)
Mo4-O4'	2.05(1)	Mo4-O5	1.99(1)
Mo4-O7'	2.09(1)	Mo5-O1	2.07(1)
Mo5-O2	2.07(1)	Mo5-O3	2.05(1)
Mo5-O6	2.06(1)	Mo5-O8	2.10(1)
Gd-O1	2.66(1)	Gd-O2	2.35(1)
Gd-O2'	2.38(1)	Gd-O3	2.55(1)
Gd-O4	2.42(1)	Gd-O5	2.97(1)
Gd-O6	2.58(1)	Gd-O7	2.81(1)
Gd-O8	2.72(1)	Gd-O8'	2.99(1)

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center. All gadolinium atom positions partially occupied by potassium.

^bIntercluster Mo-Mo bond distances

^cApical-apical Mo-Mo bond distances

Table 5.15. Selected bond angles (degrees) for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$ ^a

Mo1'-Mo1-Mo2	89.01(8)	Mo1'-Mo1-Mo3	57.57(7)
Mo1'-Mo1-Mo3'	60.15(7)	Mo1'-Mo1-Mo4	88.05(8)
Mo1'-Mo1-Mo5	59.68(6)	Mo1'-Mo1-Mo5'	58.56(7)
Mo2-Mo1-Mo3	61.02(6)	Mo2-Mo1-Mo4	176.96(9)
Mo2-Mo1-Mo5'	60.36(6)	Mo3-Mo1'-Mo4	61.87(6)
Mo3-Mo1-Mo5	56.70(6)	Mo3-Mo1-Mo5'	89.73(7)
Mo3-Mo1'-Mo5'	91.99(7)	Mo3-Mo1'-Mo5	57.16(6)
Mo4-Mo1-Mo5	59.51(6)	Mo1-Mo2-Mo3'	176.00(9)
Mo1-Mo2-Mo3	57.57(6)	Mo1-Mo2-Mo4'	89.87(7)
Mo1-Mo2-Mo5'	58.65(6)	Mo3-Mo2-Mo4'	94.06(7)
Mo3-Mo2-Mo5'	88.91(7)	Mo4-Mo2'-Mo5	60.09(6)
Mo1-Mo3-Mo1'	62.28(7)	Mo1'-Mo3-Mo2	90.39(7)
Mo1'-Mo3-Mo4'	58.78(6)	Mo1-Mo3-Mo5	61.03(6)
Mo1-Mo3-Mo2	61.40(6)	Mo1-Mo3-Mo4'	88.94(7)
Mo1-Mo3-Mo5'	62.85(6)	Mo2-Mo3-Mo4'	60.07(5)
Mo2'-Mo3-Mo5	179.0(1)	Mo1-Mo4-Mo2'	93.05(7)
Mo1-Mo4-Mo3'	59.36(6)	Mo1-Mo4-Mo5'	60.55(6)
Mo2-Mo4'-Mo3	60.67(6)	Mo2'-Mo4-Mo5	61.77(6)
Mo3'-Mo4-Mo5	88.89(7)	Mo1-Mo5-Mo1'	61.77(7)
Mo1-Mo5-Mo2	61.00(6)	Mo1'-Mo5-Mo4	90.13(7)
Mo1'-Mo5-Mo2'	90.54(7)	Mo1-Mo5-Mo4	59.94(6)
Mo2-Mo5'-Mo4'	58.14(6)		

^aAtoms with primed numbers are related to those with unprimed numbers by the inversion center

Table 5.16. Supplementary crystallographic information for $K_xM_{2-x}Mo_{10}O_{16}$

Information	K-Ca	K-Sr	K-Gd
No. of reflections indexed	18	13	19
Two theta range	14-19°	13-19°	13-24°
Initial lattice parameters	7.542(3)Å	7.545(2)Å	7.554(3)Å
(a,b,c,β)	9.057(4)Å	9.152(2)Å	9.020(2)Å
	9.974(4)Å	9.954(3)Å	9.932(2)Å
	109.99(3)°	109.25(2)°	109.88(2)°
No. of standards	3	3	3
Octants collected	h,±k,±l	h,k,±l	±h,k,±l
Absorption corrected	yes	yes	no
Violations of $P2_1/c$	none	none	none
SHELXS ³⁷ solution	0.020	0.021	-----
Secondary extinction	4.2×10^{-7}	-----	5.5×10^{-8}
Largest diff. peak	near Mr	near Mo1	near Mo4
Cation occupancy	microprobe	Sr:97(2)%	Gd:83.3(6)%

RESULTS AND DISCUSSION

Description of the Structure

All the $M_2Mo_{10}O_{16}$ and $K_xM_{2-x}Mo_{10}O_{16}$ phases consist of trans edge-shared Mo_{10} biotetrahedral cluster units, as shown in Figure 5.1 for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$. The shortest metal-metal bonds in this unit are the two apical-apical bonds. A listing of the apical-apical bond distances in the reported $Mo_{10}O_{16}$ members is found in Table 5.17. Figure 5.2 indicates the stair-step manner in which the biotetrahedral units interconnect. The dominant feature for all the known $M_2Mo_{10}O_{16}$ phases, and also the quaternary members, is the short intercluster metal-metal bond. This degree of intercluster bonding is only observed in this oligomeric series, $M_{n-x}Mo_{4n+2}O_{6n+4}$, when $n=1$ or 2. Table 5.17 lists all the intercluster distances associated with the published members. The average intercluster bond distance (Mo2-Mo2') for the compounds containing divalent

Table 5.17. Important metal-metal distances in the $M_2Mo_{10}O_{16}$ series

M (cation)	Apical-apical bond (Å)	Intercluster bonds (Å)
Ba	2.621(2)	2.778(3), 3.053(2), 3.099(2)
Sn	2.608(1)	2.796(1), 3.030(1), 3.077(1)
Pb	2.613(3)	2.784(5), 3.034(4), 3.083(3)
La ²⁵	2.676	2.733, 2.921, 3.065
La ²⁹	2.6129(5)	2.6899(7), 2.9108(5), 3.0941(5)
Gd	2.598(1)	2.674(1), 2.904(1), 3.078(1)
K-Ca	2.590(1)	2.775(2), 3.038(1), 3.079(1)
K-Sr	2.608(4)	2.804(6), 3.043(3), 3.089(3)
K-Gd	2.601(2)	2.711(4), 2.961(2), 3.076(2)

Figure 5.1. An ORTEP representation (70% thermal ellipsoids) of the basic building block found in $\text{K}_{0.06}\text{Ca}_{1.94}\text{Mo}_{10}\text{O}_{16}$, as viewed perpendicular to the *a* axis. Note the strong apical-apical bond.

Figure 5.2. An ORTEP representation (70% thermal ellipsoids) indicating the stair-step manner in which the biotahedral units interconnect in $\text{K}_{0.06}\text{Ca}_{1.94}\text{Mo}_{10}\text{O}_{16}$. Note the strong intercluster bond.

cations is 2.78Å and the average intercluster distance is 2.68Å when the cations are trivalent. These values were calculated using members which have not been published, but are reported in the introduction.²⁹ The mixed K-Ca and K-Sr members have intercluster and apical-apical bonding which is very similar to the pure divalent cation-containing materials. The K-Gd member formally donates 5.34e⁻ to the metal-metal framework. As might have been expected, but not observed until now, the intercluster metal-metal bond for such a K-Gd member is intermediate to those observed in (Mo₁₀O₁₆)⁴⁻ and (Mo₁₀O₁₆)⁶⁻. This result convincingly demonstrates that the electrons filling the HOMO are in orbitals basically involved in intercluster bonding.

The connectivity of these bioctahedral members can be viewed in Figure 5.2 and 5.3. The connectivity can be formulated as $M_2^{x+}[(Mo_{10}O_6^i O_{4/2}^{i-i} O_{8/2}^{i-a}) O_{8/2}^{a-i}]^{x-}$. The oxygen atoms O1, O2, and O8 are edge-bridging only between Mo atoms in the same cluster and are labelled Oⁱ. The oxygen atoms corresponding to Oⁱ⁻ⁱ are edge-sharing between neighboring clusters, these are labelled O7. Oxygens considered O^{i-a} (or O^{a-i}) are edge-bridging between molybdenum atoms of one cluster and terminal to another molybdenum in a neighboring cluster (or vice versa), these include O3, O4, O5, and O6.

The cations in the quaternary KMMo₁₀O₁₆ phases are essentially ten coordinate in oxygen, with all bond distances less than 3.1Å included. Figure 5.4 shows this coordination sphere for both cations within a single pocket for K_{0.06}Ca_{1.94}Mo₁₀O₁₆. Bond valence sums around the cations were calculated based upon the method of Brown and Wu⁴⁵ and have been previously detailed in Section 1. Bond valence sums around the major cations were acceptable, with s(Ca)=1.78(2), s(Sr)=2.0(1), and s(Gd)=2.44(6). The rather low occupancy of potassium on the cation sites will dictate that their calculated bond valence sums will not be reasonable, and this was observed: s(K)=2.80(6) for the K-Ca member, s(K)=2.2(1) for the K-Sr member, and s(K)=3.2(1) for the K-Gd member. These

Figure 5.3. An ORTEP representation (70% thermal ellipsoids) indicating the manner in which the bi-octahedral units interconnect to form a cation pocket in $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$. This view is parallel to the a axis and cation-oxygen bonds have been omitted for clarity.

Figure 5.4. An ORTEP representation (70% thermal ellipsoids) indicating the cation coordination sphere in $\text{K}_{0.06}\text{Ca}_{1.94}\text{Mo}_{10}\text{O}_{16}$.

very large values for the potassium cations in these compounds seems to indicate that potassium would find such a position very unfavorable. Therefore, it is surprising that this series even incorporates any potassium. The potassium content for the K-Ca member was determined by microprobe analyses and the K-Sr and K-Gd members had the cation occupancies determined by their respective single crystal refinements.

Bond order and bond valence sums were also calculated for each of the molybdenums in the three quaternary members discussed. As previously described in Section 1, the goal of such calculations is to determine the number of electrons available for metal-metal bonding. The choice of cations in these quaternary members also allows a formal oxidation state to be calculated. Tables 5.18, 5.19, and 5.20 detail the bond order and bond valence sums. Table 5.21 compares the formal, bond order, and bond valence values. In all three cases, the molybdenum bond order sums are in good agreement with the formally derived electron counts if intercluster bonding is not included. Molybdenum bond valence calculations are in better agreement with the formal electron counts.

Table 5.18. Bond length-bond strength relationships for $K_{0.06}Ca_{1.94}Mo_{10}O_{16}$

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo1	2.825(1)	0.451(2)	2.052(6)	0.595(10)
	2.760(1)	0.576(2)	2.023(6)	0.648(11)
	2.751(1)	0.596(2)	2.025(6)	0.644(11)
	2.693(1)	0.742(2)	2.068(6)	<u>0.568(10)</u>
	2.710(1)	0.696(3)		$\Sigma s = 2.46(4)$
	2.720(1)	0.670(2)		
	2.759(1)	<u>0.578(2)</u>		
		$\Sigma n = 4.31(1)$		
Mo2	2.760(1)	0.576(2)	2.104(6)	0.512(8)
	2.775(2) inter	0.545(5)	2.112(6)	0.501(9)
	3.079(1) inter	0.173(1)	2.044(6)	0.609(10)
	2.758(1)	0.581(3)	2.120(6)	0.489(8)
	3.038(1) inter	0.2018(8)	2.023(6)	<u>0.648(11)</u>
	2.681(1)	0.777(3)		$\Sigma s = 2.76(5)$
	2.754(1)	<u>0.590(3)</u>		
		$\Sigma n = 2.86(2)$		
Mo3	2.751(1)	0.596(2)	2.044(6)	0.609(10)
	2.693(1)	0.742(3)	2.135(6)	0.469(8)
	3.079(1) inter	0.173(1)	2.062(6)	0.578(10)
	2.758(1)	0.581(3)	2.080(6)	0.549(10)
	2.821(1)	0.458(2)	2.051(6)	<u>0.597(10)</u>
	2.590(1)	<u>1.095(4)</u>		$\Sigma s = 2.80(5)$
		$\Sigma n = 3.65(2)$		
Mo4	2.710(1)	0.696(3)	2.103(6)	0.514(9)
	3.038(1) inter	0.202(1)	2.106(6)	0.509(8)
	2.681(1)	0.777(3)	2.038(6)	0.620(11)
	2.821(1)	0.458(2)	1.946(6)	0.818(15)
	2.736(1)	<u>0.631(2)</u>	1.916(6)	<u>0.898(17)</u>
		$\Sigma n = 2.76(1)$		$\Sigma s = 3.36(6)$
Mo5	2.720(1)	0.670(2)	2.054(6)	0.592(11)
	2.759(1)	0.578(2)	2.065(6)	0.573(10)
	2.754(1)	0.590(3)	2.060(6)	0.581(10)
	2.590(1)	1.095(4)	2.068(6)	0.568(10)
	2.736(1)	<u>0.631(2)</u>	2.080(7)	<u>0.549(11)</u>
		$\Sigma n = 3.56(1)$		$\Sigma s = 2.86(5)$

Table 5.19. Bond length-bond strength relationships for $K_{0.06}Sr_{1.94}Mo_{10}O_{16}$

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo1	2.827(5)	0.448(9)	2.08(2)	0.55(3)
	2.758(4)	0.581(9)	2.04(2)	0.62(4)
	2.748(4)	0.603(9)	2.00(2)	0.69(4)
	2.701(4)	0.720(11)	2.07(2)	<u>0.57(3)</u>
	2.721(4)	0.668(10)		$\Sigma s = 2.4(1)$
	2.743(4)	0.615(10)		
	2.766(4)	<u>0.563(8)</u>		
		$\Sigma n = 4.20(7)$		
Mo2	2.758(4)	0.581(9)	2.01(2)	0.67(4)
	2.804(6) inter	0.488(11)	2.11(2)	0.50(3)
	3.089(3) inter	0.166(1)	2.00(2)	0.69(4)
	2.769(4)	0.557(8)	2.11(2)	0.50(3)
	3.043(3) inter	0.198(2)	2.11(2)	<u>0.50(3)</u>
	2.691(4)	0.748(11)		$\Sigma s = 2.9(2)$
	2.746(4)	<u>0.608(10)</u>		
		$\Sigma n = 3.35(5)$		
Mo3	2.748(4)	0.603(9)	2.05(2)	0.60(3)
	2.701(4)	0.720(11)	2.05(2)	0.60(3)
	3.089(3) inter	0.166(1)	2.09(2)	0.53(3)
	2.769(4)	0.557(8)	2.11(2)	0.50(3)
	2.823(4)	0.454(6)	2.07(2)	<u>0.57(3)</u>
	2.608(4)	<u>1.023(15)</u>		$\Sigma s = 2.8(2)$
		$\Sigma n = 3.52(5)$		
Mo4	2.721(4)	0.668(10)	1.88(2)	1.01(6)
	3.043(3) inter	0.198(2)	2.18(2)	0.41(2)
	2.691(4)	0.748(11)	2.06(2)	0.58(3)
	2.823(4)	0.454(6)	1.96(2)	0.78(5)
	2.747(4)	<u>0.605(9)</u>	2.14(2)	<u>0.46(3)</u>
		$\Sigma n = 2.67(4)$		$\Sigma s = 3.2(2)$
Mo5	2.743(4)	0.615(10)	2.07(2)	0.57(3)
	2.766(4)	0.563(8)	2.05(2)	0.60(3)
	2.746(4)	0.608(10)	2.04(2)	0.62(4)
	2.608(4)	1.023(15)	2.09(2)	0.53(3)
	2.747(4)	<u>0.605(9)</u>	2.09(2)	<u>0.53(3)</u>
		$\Sigma n = 3.41(5)$		$\Sigma s = 2.8(2)$

Table 5.20. Bond length-bond strength relationships for $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$

Atom	d(Mo-Mo)	n	d(Mo-O)	s
Mo1	2.812(3)	0.474(6)	2.06(1)	0.581(16)
	2.788(2)	0.519(4)	2.02(1)	0.654(19)
	2.755(2)	0.587(4)	2.04(1)	0.617(18)
	2.681(2)	0.777(6)	2.06(1)	<u>0.581(16)</u>
	2.738(2)	0.626(4)		$\Sigma s = 2.43(7)$
	2.723(2)	0.663(5)		
	2.755(2)	<u>0.587(4)</u>		
	$\Sigma n = 4.23(3)$			
Mo2	2.788(2)	0.519(4)	2.04(1)	0.617(18)
	2.711(4) inter	0.693(10)	2.13(1)	0.476(13)
	3.076(2) inter	0.175(1)	2.04(1)	0.617(18)
	2.778(2)	0.538(4)	2.10(1)	0.518(14)
	2.961(2) inter	0.270(2)	2.14(1)	<u>0.463(13)</u>
	2.671(2)	0.806(6)		$\Sigma s = 2.69(8)$
	2.771(2)	<u>0.553(4)</u>		
	$\Sigma n = 3.55(3)$			
Mo3	2.755(2)	0.587(4)	2.06(1)	0.581(16)
	2.681(2)	0.777(6)	2.08(1)	0.549(16)
	3.076(2) inter	0.175(1)	2.06(1)	0.581(16)
	2.778(2)	0.538(4)	2.15(1)	0.450(12)
	2.824(2)	0.453(4)	2.07(1)	<u>0.565(16)</u>
	2.601(2)	<u>1.050(8)</u>		$\Sigma s = 2.73(8)$
		$\Sigma n = 3.58(3)$		
Mo4	2.738(2)	0.626(4)	1.99(1)	0.715(21)
	2.961(2) inter	0.270(2)	2.13(1)	0.476(13)
	2.671(2)	0.806(6)	2.05(1)	0.599(18)
	2.824(2)	0.453(4)	1.99(1)	0.715(21)
	2.726(3)	<u>0.655(7)</u>	2.09(1)	<u>0.533(15)</u>
		$\Sigma n = 2.81(2)$		$\Sigma s = 3.04(9)$
Mo5	2.723(2)	0.663(5)	2.07(1)	0.565(16)
	2.755(2)	0.587(4)	2.07(1)	0.565(16)
	2.771(2)	0.553(4)	2.05(1)	0.599(18)
	2.601(2)	1.050(8)	2.06(1)	0.581(16)
	2.726(3)	<u>0.655(7)</u>	2.10(1)	<u>0.518(14)</u>
		$\Sigma n = 3.51(3)$		$\Sigma s = 2.83(8)$

Table 5.21. Bond length-bond strength summations for $M_2Mo_{10}O_{16}$

$$K_{0.06}Ca_{1.94}Mo_{10}O_{16}: \text{Metal-Metal MCE}(\Sigma n) = 2\Sigma(\Sigma n) = 34.3(1)e^-$$

$$31.8(1)e^- \text{ no inter}$$

$$\text{Total valence of } Mo_{14} \text{ unit} = 2\Sigma(\Sigma s) = 28.5(5) \text{ v.u.}$$

$$MCE = 6 e^- \times 10 - 28.5(5) = 31.5(5)e^-$$

$$\text{Formalized oxidation states}^a: (6 \times 10) - (2 \times 16) + (1 \times 0.06) + (2 \times 1.94) = 31.94e^-$$

$$K_{0.06}Sr_{1.94}Mo_{10}O_{16}: \text{Metal-Metal MCE}(\Sigma n) = 2\Sigma(\Sigma n) = 34.3(5)e^-$$

$$31.9(4)e^- \text{ no inter}$$

$$\text{Total valence of } Mo_{14} \text{ unit} = 2\Sigma(\Sigma s) = 28(2) \text{ v.u.}$$

$$MCE = 6 e^- \times 10 - 28(2) = 32(2)e^-$$

$$\text{Formalized oxidation states}^a: (6 \times 10) - (2 \times 16) + (1 \times 0.06) + (2 \times 1.94) = 31.94e^-$$

$$K_{0.33}Gd_{1.67}Mo_{10}O_{16}: \text{Metal-Metal MCE}(\Sigma n) = 2\Sigma(\Sigma n) = 35.4(3)e^-$$

$$32.2(2)e^- \text{ no inter}$$

$$\text{Total valence of } Mo_{14} \text{ unit} = 2\Sigma(\Sigma s) = 27.4(8) \text{ v.u.}$$

$$MCE = 6 e^- \times 10 - 27.4(8) = 32.6(8)e^-$$

$$\text{Formalized oxidation states}^a: (6 \times 10) - (2 \times 16) + (1 \times 0.33) + (3 \times 1.67) = 33.34e^-$$

$^a O^{-2}$, K^+ , Sr^{+2} , Ca^{+2} , Gd^{+3} , and six electrons from each Mo

CONCLUSIONS

The $M_2Mo_{10}O_{16}$ series shows a remarkable flexibility to accept a variety of cations and also a significant range of MCE from 32 to $34e^-$. The first synthesized quaternary dimeric oligomers have been reported here. The K-Ca and K-Sr members are essentially analogous to the pure Ca and Sr members, with respect to the prominent metal-metal apical and intercluster bonds, since the incorporation of potassium is so low. The $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$ member exhibits an intermediate electron count. The resultant is an apical-apical Mo bond distance that is similar to the other members and an intercluster bond distance between those reported for the 32 and $34e^-$ members. The direct correlation between intercluster cluster bonding and electron count demonstrates that the electrons in the HOMO are utilized in orbitals for intercluster bonding. The measured resistivity of $Ba_2Mo_{10}O_{16}$ ⁷ indicate semiconducting behavior. The K-Gd member may show metallic behavior since it has an uneven number of electrons and an even stronger intercluster metal-metal bond.

SECTION 6

**SYNTHESIS AND CHARACTERIZATION OF THE $\text{RE}_4\text{Mo}_4\text{O}_{11}$ SERIES:
RE = Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, & Lu**

INTRODUCTION

The series $\text{RE}_4\text{Mo}_4\text{O}_{11}$, where RE=rare earth cation, constitute a structure type containing infinite chains of trans edge-shared molybdenum octahedra similar to those observed in NaMo_4O_6 ,¹ $\text{Sc}_{0.75}\text{Zn}_{1.25}\text{Mo}_4\text{O}_7$,¹⁴ $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$,¹³ $\text{ZnMo}_8\text{O}_{10}$,¹⁷ and $\text{Gd}_4\text{Mo}_{18}\text{O}_{32}$.²⁰ A variety of structure types in these materials results from the manner in which the molybdenum octahedral chains interconnect, and concurrently, the coordination geometry preferred by the ternary metal. Quite unlike previously published work, the infinite octahedral molybdenum chains in the $\text{RE}_4\text{Mo}_4\text{O}_{11}$ series are not interconnected via bridging oxygens. These isolated infinite octahedral chains of Mo are bound through Mo-O-RE-O-Mo connections. This arrangement creates large, nearly rectangular, channels in which, not only the rare earth cations reside, but also oxygen atoms not associated with the molybdenum-oxygen framework. The structure of $\text{Ho}_4\text{Mo}_4\text{O}_{11}$ has been reported¹⁸ and the rare earth members Y, Nd, and Sm-Lu have been prepared and structurally characterized via single x-ray diffraction.¹⁹ The work presented here will cover the single phase preparation of the $\text{RE}_4\text{Mo}_4\text{O}_{11}$ series and their magnetic and conductive properties.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated ($\sim 1 \times 10^{-4}$ torr) vessels made of fused silica. All reactants were thoroughly ground to produce a homogeneous mixture before being used as loose powders or pressed pellets. Mixed starting materials were subsequently stored in a desiccator.

The starting materials included the rare earth oxides (Ames Lab Rare Earth Center), MoO_2 , and Mo. The drying and/or cleaning of the molybdenum containing reagents has been discussed in Section 1. The rare earth oxides were dried in open crucibles at 550°C for 2-5 days, and subsequently, cooled over desiccant.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540562\text{\AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard, due to the proximity of the (231) reflection (100% line) to the (111) of silicon. All materials could be indexed based on the orthorhombic space group Pbam using a least squares fit method. Some samples were also analyzed with a Scintag 2000

powder θ - θ diffractometer using Cu $K\alpha_1$ radiation. For the Scintag measurements, the sample was pressed into a recessed region of a single crystal quartz plate.³³

Magnetic susceptibility

The magnetic properties were examined on pellet and powder samples with a Quantum Design SQUID magnetosusceptometer at magnetic fields of 1 or 3 Tesla and temperatures from 6 to 396 K. Pelletized samples were tied into a polyethylene straw with dental floss and powdered samples were loaded into 3 mm o.d. fused silica tubes. Neither the floss nor the straw made any significant contribution to the magnetic signal over the temperature range used. In the systems where fused silica tubes were used, the empty tube was measured and subtracted as background.

Electrical resistivity

Electrical resistivity measurements were carried out on pressed pellets (8800 psi) that had been sintered in evacuated fused silica ampoules at 1250°C for one day. These measurements were based on the van der Pauw³⁴ four probe method for electrical conductivity. The basic method employs the passage of a constant current through two leads of the sample while, concurrently, measuring the potential drop across the other two leads at a given temperature. The sample was prepared by attaching four platinum wires to the pellet with DuPont Conductor Composition (silver epoxy/n-butyl acetate). The voltage drop across the sample and the temperature were recorded every 2 K with a platinum thermocouple from 78-295 K.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Powdered samples and/or crystals were loaded on a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Transmission electron microscopy

A Philips CM30 transmission electron microscope was used to determine the presence or absence of any superstructure ordering. An approximate one to one mixture of microcrystalline sample and G-1 Epoxy from Gatan was placed between lens paper, pressed between aluminum plates, and cured at 120°C for ten minutes. A three millimeter disk was punched out, thinned to ~20 μm by dimpling, placed on a 200 mesh copper grid for support, and subsequently, ion milled until a hole was observed. The sample and supporting grid assembly then were loaded into the TEM sample holder for investigation.

Synthesis

Crystalline x-ray pure $\text{RE}_4\text{Mo}_4\text{O}_{11}$ (RE=Y,Nd,Sm-Lu) powder can be prepared from intimately mixed powders of RE_2O_3 , MoO_2 , and Mo (4:5:3 mole ratio), except for RE=Tb where the mixed valent oxide, Tb_4O_7 , was used with MoO_2 , and Mo (3:6:6 mole ratio). The thoroughly mixed reagents were loaded into fused silica tubes as powders or pressed pellets, evacuated, and then double-sealed in fused silica tubes. All reactions were fired at 1250°C for 2-13 days and cooled at a rate of 100°C/hr to 800°C, at which time they were quenched to room temperature in air. In particular, the length of firing (and form of the sample) were 11 days (pellet) for Y, 8 days (powder) for Nd, 4 days

(powder) for Sm, 6 days (pellet) for Eu, 2 days (pellet) for Gd, 13 days (pellet) for Tb, 4 days (powder) for Dy, 6 days (pellet) for Ho, 6 days (pellet) for Er, 13 days (pellet) for Tm, 5 days (powder) for Yb, and 12 days (powder) for Lu. In general, the particle size was $\sim 20\text{ }\mu\text{m}$ parallel to the Mo octahedral chains (c axis) and $\sim 4\text{ }\mu\text{m}$ perpendicular to it (a or b axes). A typical powder x-ray diffraction pattern for the $\text{Y}_4\text{Mo}_4\text{O}_{11}$ member is shown in Figure 6.1. Synthesis of the members containing Sc, La, Ce, and Pr was not successful over a range of temperatures and times: 1150-1250°C and 1-21 days.

Figure 6.1. X-ray powder diffraction pattern of $Y_4Mo_4O_{11}$ from 8-80° two theta using Cu $K\alpha_1$ radiation.

RESULTS AND DISCUSSION

Discussion of Properties

X-ray powder diffraction

The calculated least-squares fit of the x-ray powder diffraction data to derive the lattice parameters for the $\text{RE}_4\text{Mo}_4\text{O}_{11}$ members is given in Table 6.1. A complete listing of the actual reflections measured and used in the least-squares routine can be found in Appendix A. Figures 6.2-6.5 show the nearly linear decrease in all the lattice parameters and unit cell volumes from $\text{Nd}_4\text{Mo}_4\text{O}_{11}$ to $\text{Lu}_4\text{Mo}_4\text{O}_{11}$. These trends correspond quite well with the decrease in ionic radii of the RE(III) cations tabulated by Shannon.⁴² Yttrium and holmium have nearly identical ionic radii and thus the $\text{Y}_4\text{Mo}_4\text{O}_{11}$ member also conforms with the series. The two smallest members of this series, Yb and Lu, have axial lengths

Table 6.1. Lattice parameters for $\text{RE}_4\text{Mo}_4\text{O}_{11}$

Rare Earth	a(Å)	b(Å)	c(Å)	Volume (Å ³)	Number of Reflections
Y	10.654(1)	15.814(2)	5.6497(9)	951.7(6)	93
Nd	10.982(2)	16.245(4)	5.7438(8)	1024.7(6)	36
Sm	10.885(2)	16.114(3)	5.7219(6)	1003.6(5)	35
Eu	10.843(2)	16.046(3)	5.7065(8)	992.9(5)	79
Gd	10.799(1)	15.992(2)	5.6968(8)	983.8(4)	97
Tb	10.738(3)	15.918(4)	5.6795(14)	970.8(8)	43
Dy	10.700(1)	15.868(2)	5.6686(7)	962.5(3)	54
Ho	10.670(1)	15.815(2)	5.6571(8)	954.6(3)	95
Er	10.630(1)	15.768(2)	5.6431(8)	945.9(3)	91
Tm	10.602(3)	15.734(3)	5.6353(8)	940.0(6)	53
Yb	10.606(3)	15.683(5)	5.6207(18)	934.9(9)	66
Lu	10.588(3)	15.652(4)	5.6056(22)	929.0(9)	73

Figure 6.2. Variation of the a axis lattice parameter as a function of rare earth volume for $\text{RE}_4\text{Mo}_4\text{O}_{11}$.

Figure 6.3. Variation of the b axis lattice parameter as a function of rare earth volume for $\text{RE}_4\text{Mo}_4\text{O}_{11}$.

Figure 6.4. Variation of the c axis lattice parameter as a function of rare earth volume for $\text{RE}_4\text{Mo}_4\text{O}_{11}$.

Figure 6.5. Variation of the unit cell volume as a function of rare earth volume for the $\text{RE}_4\text{Mo}_4\text{O}_{11}$ series.

with errors in the *c* direction that have become relatively large. Although these two members could be indexed in the same space group based upon x-ray Guinier work, single crystal studies have indicated a symmetry lower than orthorhombic may be required.¹⁹ The inability to prepare the Ce and Pr members might indicate the upper limit of cation size acceptable to form this phase. Gougeon¹² noted that the preparation of single crystals of $\text{Nd}_4\text{Mo}_4\text{O}_{11}$ has been exceptionally difficult.

The $\text{Gd}_4\text{Mo}_4\text{O}_{11}$ was studied, briefly, by electron microscopy. The results of the electron diffraction appeared to conform to the single x-ray crystal structure determination. No superstructure, or detectable break in the symmetry required by the orthorhombic space group, was expected or observed. Perhaps the Yb and Lu members, which appear to deviate from the trends observed in the lattice parameters of the other members, should be examined by TEM.

Magnetic susceptibility

Magnetic susceptibility measurements verify that the rare earth cations are in the +3 oxidation state and that the molybdenum oxide framework is essentially diamagnetic. The Y and Lu members have small paramagnetic impurity tails at low temperatures, that, when corrected, leave a residual moment that most likely arises from temperature independent paramagnetism (TIP) contributions. The $\text{Eu}_4\text{Mo}_4\text{O}_{11}$ contains a ~15% impurity of Eu(II), which, based on x-ray powder data, corresponds to EuMo_5O_8 .²⁹ Equation 1 was used to fit the magnetic data.

$$\chi_M = C(T-\theta)^{-1} + \chi^\circ \quad (1)$$

Here, $C = N\beta^2\mu^2(3k)^{-1}$ and $\chi^\circ = \chi_D + \chi_{\text{TIP}}$, where χ_D is the diamagnetic core contribution and χ_{TIP} is the contribution from temperature independent paramagnetism. Table 6.2 summarizes these results and Appendix B contains

the plots of magnetic susceptibility versus temperature. The magnetic information derived in Table 6.2 via Equation 1 was programmed by Wayne M. Syvinski.

Electrical resistivity

Four probe resistivity measurements were taken on sintered, pressed pellets of $\text{Gd}_4\text{Mo}_4\text{O}_{11}$ and $\text{Y}_4\text{Mo}_4\text{O}_{11}$. The distinctive increase in resistance with decreasing temperature characterizes these materials as semiconductors. Plots of the resistivity ratio (ρ/ρ_{295}) versus temperature and $\log \rho$ versus $1/\text{temperature}$ (inset) are shown in Figure 6.6 for $\text{Gd}_4\text{Mo}_4\text{O}_{11}$ and Figure 6.7 for $\text{Y}_4\text{Mo}_4\text{O}_{11}$. The $\log \rho$ versus $1/T$ could be fit by a linear least squares method based on Equation 2, where Δ is the band gap and Δ/k is the slope. The data for

$$\log \rho = \Delta/kT \quad (2)$$

$\text{Gd}_4\text{Mo}_4\text{O}_{11}$ was fit from 90-224 K and resulted in a band gap of 25 meV. The

Table 6.2. Magnetic properties of the $\text{RE}_4\text{Mo}_4\text{O}_{11}$

Rare Earth	μ_B/RE	C	θ	χ°	χ_D ($\times 10^{-6}$)	χ_{TIP}	Temperature Range (K)
Y ^a	0.15	---	---	-----	-288	-----	65-376
Nd	3.40	5.8	-30	2752	-320	3070	50-380
Eu ^b	4.37	9.6	-135	108	-320	428	95-390
Gd	7.91	31.3	-10	1321	-320	1641	10-400
Tb	9.61	46.2	-17	1397	-316	1713	10-400
Dy	10.14	52.9	-13	1298	-316	1614	60-330
Tm	7.66	29.4	-10	3011	-312	3323	15-360
Yb	4.07	8.3	-26	2299	-312	2611	60-400
Lu ^a	0.05	---	---	-----	-308	-----	60-400

^aDiamagnetic with a small paramagnetic impurity tail at low temperature

^bContained approximately a 15% impurity of EuMo_5O_8

Figure 6.6. Resistivity ratio of $\text{Gd}_4\text{Mo}_4\text{O}_{11}$ versus temperature. The inset shows the nearly linear relationship between the $\log(\rho/\rho_{295})$ versus $1/T$, indicating its semiconducting behavior.

Figure 6.7. Resistivity ratio of $\text{Y}_4\text{Mo}_4\text{O}_{11}$ versus temperature. The inset shows the nearly linear relationship between the $\log(\rho/\rho_{295})$ versus $1/T$, indicating its semiconducting behavior.

band gap resulting from the data for $\text{Y}_4\text{Mo}_4\text{O}_{11}$ was 27 meV, where the fit was from 100-300 K. The observed behavior, an opening of a small gap, correlates with the Peierls type distortion (pairing) of the apical molybdenum atoms observed in the single crystal structure refinements.^{18,19}

CONCLUSIONS

The $\text{RE}_4\text{Mo}_4\text{O}_{11}$ series forms a class of materials in which the trans edge-shared Mo octahedra are isolated from each other by rare earth cations and oxygen atoms which fill the volume around the chains. The series is well behaved with respect to the unit cell parameters and magnetic and conductive properties. The $\text{RE}_4\text{Mo}_4\text{O}_{11}$ members are small band gap semiconductors with all the rare earth cations found as RE(III). The unit cell parameters decrease from RE=Nd to Lu, as expected by the lanthanide contraction concept. The Yb and Lu members appear to deviate with respect to the unit cell parameter trends; this result may be the consequence of the relatively small cation size. The Sc, La, Ce, and Pr members could not be prepared by the synthetic efforts put forth here. The oxidation or reduction of the molybdenum octahedral chains in these materials is an area of further study that may expand the comprehension of this class. Promising preliminary work was observed for $\text{Ca}_x\text{Gd}_{4-x}\text{Mo}_4\text{O}_{11}$ ($x>0.5$).^{19b}

SECTION 7

**SYNTHESIS AND CHARACTERIZATION OF $\text{Pb}_{0.31}\text{WO}_3$:
A TETRAGONAL TUNGSTEN BRONZE CONTAINING LEAD**

INTRODUCTION

The synthesis of $\text{Pb}_x\text{W}_4\text{O}_6$, the tungsten analog of $\text{Pb}_{0.77}\text{Mo}_4\text{O}_6$, was attempted. Unfortunately, the only products of these synthetic endeavors were tetragonal lead tungsten bronzes, Pb_xWO_3 . The first two structures reported for tetragonal tungsten bronzes came in 1949 by Magnéli.^{54,55} In both cases, the structural details were determined by film work on K_xWO_3 ($0.475 \leq x \leq 0.57$) and Na_xWO_3 ($0.28 \leq x \leq 0.38$). During the 1960's, the bronzes were studied for their electrical properties. A report by Bernoff and Conroy discussed the lead tungsten tetragonal bronzes⁵⁶, but again only film work was reported. A series of barium tetragonal tungsten bronzes was also briefly discussed by Yokokawa and Conroy in 1965.⁵⁷ Magnéli's work on the sodium bronzes mentioned the presence of weak superlattice reflections. In 1976, Takusagawa and Jacobson⁵⁸ reported single crystal structures for $\text{Na}_{0.33}\text{WO}_3$ ($R=0.089$) and $\text{Na}_{0.48}\text{WO}_3$ ($R=0.084$). They discussed the disorder present in these phases and potential superstructure that would be necessary to account for it. Finally, a series of lead tungsten bronzes was studied by Ekström and Tilley.⁵⁹ In this paper, bronzes with the composition Pb_xWO_3 ($0 \leq x \leq 0.17$) were explored. They used HREM to study the intergrowth phases that existed between the bronzes and WO_3 .

Curiously, the structural determination of tetragonal tungsten bronzes by modern diffractometer methods has only been reported for two sodium members. No doubt, the basic tungsten oxide framework, as reported by Magnéli, is correct. Perhaps the true structural interest may lie in the determination of the oxygen coordination environment chosen by the cation, and the role that the cation may perform in any potential superstructure. The synthesis, structure, and characterization of the lead tungsten bronze, $\text{Pb}_{0.31}\text{WO}_3$ will be discussed.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing tungsten in oxidation states less than six requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated ($\sim 1 \times 10^{-4}$ torr) fused silica or nickel tubes.

The starting reagents included Pb, PbO, W, and WO₃. Lead metal (Fisher) was dried under dynamic vacuum at 120°C for six hours, a similar procedure was also followed for tungsten metal (General Electric, 99.9%). The lead(II) oxide (Aldrich, 99.9%) was used directly from the bottle. Tungsten trioxide (Amend Drug & Chemical Co.) was fired overnight in an open crucible at 800°C and subsequently cooled in a desiccator. Nickel tubing (3/8" o.d. & 9/32" i.d., Tube Sales) was dipped in dilute nitric acid, thoroughly rinsed with distilled water and dried at 140°C overnight. All reagents were thoroughly mixed and unfired powders were stored in a desiccator.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with Cu K α_1 radiation ($\lambda = 1.540562 \text{ \AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard.

Magnetic susceptibility

The magnetic properties were examined on microcrystalline powders with a Quantum Design SQUID magnetosusceptometer. The samples were loaded into a 3mm inner diameter quartz tube that had been sealed on the bottom half with 3mm outer diameter quartz rod. A quartz rod also was placed in the top half of the loaded sample tube, which then was mounted in an apparatus that allowed evacuation of the sample tube and purging with helium gas. To eliminate water, the system was heated to 120°C for an hour under dynamic vacuum. After cooling, the system was pumped and purged with helium three more times. The upper quartz rod was pushed into place under a partial pressure of helium (to facilitate temperature equilibration during measurements), sandwiching the sample between "solid" quartz, and sealed off. This procedure was used to eliminate oxygen contamination, which has an antiferromagnetic transition at ~50 K. The experimental data were corrected for the diamagnetic contribution from the quartz. Measurements on empty quartz tube/rod assemblies, with varying gap sizes, indicated that the diamagnetic contribution from the quartz was related to the size of the gap. Since the signal versus gap size could be fit by a line, the correction was simply employed by measuring the length of the gap containing the sample.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Powdered samples and/or crystals were loaded onto a metal disk via Scotch double-stick tape and sputter-coated with gold to improve their conductance.

Transmission electron microscopy

A Phillips CM30 transmission electron microscope was used to determine the presence or absence of any superstructure ordering. An approximate one to one mixture of microcrystalline sample and G-1 Epoxy from Gatan was placed between lens paper, pressed between aluminum plates, and cured at 120°C for ten minutes. A three millimeter disk was punched out, thinned to ~20 μm by dimpling, put on a 200 mesh copper grid for support, and subsequently ion milled until a hole was observed. The sample and supporting grid assembly were subsequently loaded into the TEM sample holder for investigation.

Microprobe analysis

Elemental analyses were completed by Dr. Alfred Kracher (Department of Geological and Atmospheric Sciences) on an ARL SEMQ microprobe. The instrument was equipped with wavelength dispersive spectrometers (WDS) and operated at 15 kV and 25 nA. Single crystal samples were mounted in Epo-Tek 301-2 epoxy resin, dried, and polished to produce a flat surface. Prior to examination, the samples were sputtered with carbon to insure conductivity. Peak profiles and backgrounds were measured for the standards, which included WO_3 and PbS. Data were analyzed using Probe³⁵ software.

Synthesis

The tetragonal lead tungsten bronze was initially prepared from a reaction mixture containing a 3:5:7 mole ratio of Pb, WO_3 , and W (in an attempt to prepare PbW_4O_6). The loose, mixed powders were loaded into a nickel tube that had been pinched off at the bottom. The system was evacuated and the tube pinched off at about 3 cm in length. The loaded nickel tube was placed in a protective fused silica jacket and evacuated before firing. The reactants were

fired at 950°C for five days and furnace cooled. The contents of the nickel tube was composed mainly of blue/black needle crystals (up to 3 mm in length), a few very small tan, transparent needle crystals, and a red/brown powder. A powder pattern of the materials indicated lead tungsten bronzes and tungsten metal. Preliminary film work and TEM selected area diffraction indicated that the blue/black crystals contained a complicated superstructure. Some of these crystals were reloaded into a fused silica tube, evacuated, and subsequently annealed at 900°C for six days, cooled at ~20°C/hour to 400°C, and then furnace cooled. Preliminary film work indicated better crystal quality, and these annealed crystals were subsequently used for single crystal structure determination.

Single phase $\text{Pb}_{0.31}\text{WO}_3$ was obtained by reacting a homogeneous mixture of PbO , WO_3 , and W containing the correct stoichiometric ratio. The sample was fired at 950°C in an evacuated fused silica tube for five days, cooled at ~50°C/hour to 400°C, and then furnace cooled.

X-ray Powder Diffraction

The observed versus calculated d-spacings and relative intensities are given in Table 7.1. The calculated d-spacings were derived from the lattice parameters determined by single crystal indexing. All d-spacings are based on $\text{Cu K}\alpha_1$ radiation and could be matched based upon the sublattice. No superstructure lines were observed.

Table 7.1. X-ray powder diffraction data for $\text{Pb}_{0.31}\text{WO}_3$

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
8.668	8.630	w	110
6.123	6.103	vw	200
4.326	4.315	w	220
3.867	3.860	s	310
3.789	3.778	s	001
3.472	3.461	vw	111
3.392	3.385	s	320
3.223	3.212	m	201
3.113	3.106	s	211
3.060	3.051	vw	400
2.966	2.960	s	410
2.884	2.877	m	330
2.851	2.842	m	221
2.734	2.729	m	420
2.706	2.700	s	311
2.528	2.521	s	321
2.379	2.374	w	401
2.336	2.330	w	411
2.271	2.266	vw	520
2.218	2.212	w	421
2.162	2.158	vw	440
2.099	2.093	w	530
2.056	2.050	vw	501 & 431
2.041	2.034	vw	600
2.026	2.022	vw	511
2.012	2.006	vw	610
1.948	1.944	w	521
1.934	1.930	m	620
1.894	1.889	s	002
1.824	1.819	w	630
1.795	1.791	w	601
1.730	1.726	s	710/550
1.722	1.719	s	621

^aIntensity: s=strong, m=medium, w=weak, v=very, and b=broad

^bRefined tetragonal cell parameters determined from single crystal indexing:
a=b=12.193(4)Å and c=3.774(4)Å

Table 7.1. (continued)

d-spacing (Å)		Intensity ^a	hkl
observed	calculated ^b		
1.706	1.702	m	541
1.701	1.697	w	312
1.654	1.650	w	322
1.643	1.639	w	631
1.596	1.592	s	412
1.583	1.579	w	332
1.573	1.570	s	711/551
1.566	1.563	vw	650
1.557	1.553	w	422
1.548	1.545	w	641
1.536	1.532	w	721
1.529	1.526	w	800
1.517	1.514	w	810 & 740
1.483	1.480	w	820
1.455	1.451	vw	522
1.447	1.444	w	651
1.442	1.438	vw	660
1.431	1.428	w	830
1.422	1.419	w	750
1.416	1.415	vw	801
1.405	1.402	w	532
1.381	1.378	vw	821
1.352	1.350	w	662
1.344	1.342	vw	542
1.339	1.336	w	831
1.331	1.328	w	751
1.313	1.310	w	632
1.276	1.274	s	712 & 552
1.261	1.259	w	003
1.251	1.249	w	921
1.241	1.239	w	940
1.235	1.233	w	770
1.229	1.227	w	213
1.222	1.221	w	1000
1.198	1.197	m-b	313

X-ray Single Crystal Data Collection

A blue/black needle having the dimensions $0.05 \times 0.05 \times 0.2 \text{ mm}^3$ was mounted on a glass fiber with Devcon five minute epoxy resin. A Rigaku AFC6R rotating anode diffractometer was used with graphite monochromated Mo K α radiation ($\lambda=0.71069\text{\AA}$) generated at 7 kW. Lattice parameters and an orientation matrix for data collection were derived from 10 randomly located and centered reflections with a two theta range of $13\text{--}20^\circ$. The tetragonal lattice had cell dimensions of $a=12.188(6)\text{\AA}$, $b=12.191(6)\text{\AA}$, $c=3.777(1)\text{\AA}$, and $\text{volume}=561.2(5)\text{\AA}^3$. Three standard reflections were measured every 150 reflections and showed no apparent variation in intensity during the data collection. A refinement on 20 reflections with strong intensity and two theta values between 33 and 40° gave an idealized cell with the following lattice parameters: $a=b=12.193(4)\text{\AA}$, $c=3.774(4)\text{\AA}$, and $\text{volume}=561.1(9)\text{\AA}^3$. Data were collected at room temperature from 0 to 56° in two theta in the octants ($\pm h, k, l$), using an ω - 2θ scan mode. The number of reflections measured was 818, of which 484 were observed with $I > 3\sigma(I)$ and 281 were unique with $I > 2.65\sigma(I)$. The linear absorption coefficient for Mo K α was 748.52 cm^{-1} . An empirical absorption correction³⁶ was applied based upon two azimuthal scans of reflections with an average transmission range of $0.660\text{--}1.000$. The intensity data were corrected for Lorentz and polarization effects.

Structure Solution and Refinement

The space group P4/mbm (#127) was chosen based upon the systematic absences of $0kl$: $k \neq 2n$ and $hk0$: $h \neq 2n$. There were no violations. The structure was solved by direct methods using SHELXS³⁷ ($R=0.001$) and refined on $|F|$ by full matrix least squares techniques³⁸ with the TEXSAN³⁹ package. Atomic

positions for Pb1, W1, W2, O1, and O2 were located through the direct methods output. Refinement of these positional parameters gave $R=22\%$. From a Fourier difference map, O3, O4, and O5 positions were located and entered. Simultaneously, the Pb1 occupancy was allowed to refine; this set of conditions converged at $R=10\%$. The thermal parameters of the three heavy atoms were allowed to refine isotropically and lowered the refinement to 7.0% . The temperature factors for the oxygens were refined isotropically and, subsequently, the three heavy atom temperature factors were refined anisotropically. This refinement converged at $R=6.0\%$. The largest peak in the electron difference map was located $\sim 0.5\text{\AA}$ away from Pb1; this peak was assigned as Pb2, and entered as a low occupancy lead satellite. Subsequently, the isotropic thermal parameters of Pb2 were fixed equivalent to Pb1 and the occupancy over the two cation sites was varied. The temperature factors for oxygen O1 and O4 could be refine anisotropically, however, their thermal behavior was erratic. The total lead occupancy was manually varied to a final value of $\sim 76\%$, where the lowest R factor was achieved. This occupancy was divided with $62.(2)\%$ of the Pb1 site filled and $14.(2)\%$ of the Pb2 site filled. The anisotropic temperature factor for Pb2 could be refined, however, it proved to be deleterious to the thermal behavior of all the other atoms. Therefore, the isotropic value for Pb2 was used. The final formulation of this bronze was $\text{Pb}_{0.31}\text{WO}_3$. This set of conditions converged at $R=3.06\%$ and $R_w=3.16\%$ when a secondary extinction correction ($2.0(2)\times 10^{-7}$) was included. The largest and smallest peaks in the electron difference map were $+5.2\text{e}/\text{\AA}^3$ located $0.5\text{\AA}$ from O5 and $-2.9\text{e}/\text{\AA}^3$ at $1.5\text{\AA}$ from W1.

Details of the data collection and refinement of $\text{Pb}_{0.31}\text{WO}_3$ are given in Table 7.2. Final positional parameters and isotropic temperature factors are given in Table 7.3. Anisotropic temperature factors are listed in Table 7.4. Selected metal-oxygen interatomic distances and bond angles are found in Table 7.5.

Table 7.2. X-ray crystallographic data for $\text{Pb}_{0.31}\text{WO}_3$

formula	$\text{Pb}_{0.31}\text{WO}_3$
formula weight	295.25
crystal system	tetragonal
space group	P4/mbm (#127)
a, Å	12.193(4)
b, Å	12.193(4)
c, Å	3.774(4)
volume, Å ³	561.1(9)
Z	10
calculated density, g/cm ³	8.701
F000	980
crystal size, mm ³	0.05 x 0.05 x 0.2
$\mu(\text{Mo K}\alpha)$, cm ⁻¹	847.520
diffractometer	Rigaku AFC6R
λ , Å, graphite monochromator	0.71069
temperature, °C	24
two theta range, degrees	0-56
scan mode	ω -2 θ
No. reflections collected	818
No. observations ($I > 3\sigma(I)$), (unique: ($I > 2.65\sigma(I)$))	484 (281)
No. variables	34
goodness of fit ^a	0.895
max. shift in final cycle	0.001
largest peaks in final diff. map, e/Å ³	+5.2, -2.9
transmission coefficient	0.660-1.000
R^b , R_w^c	0.0306, 0.0316

^aQuality of fit = $[\sum \omega (|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{parameters}})]^{1/2}$

^b $R = \sum |F_o| - |F_c| / \sum |F_o|$

^c $R_w = [\sum \omega (|F_o| - |F_c|)^2 / \sum \omega |F_o|^2]^{1/2}$; $\omega = 1/\sigma^2(|F_o|)$

Table 7.3. Atomic coordinates for $\text{Pb}_{0.31}\text{WO}_3$

Atom	Wyckoff #	X	Y	Z	B_{eq}^a
Pb1 ^b	4h	0.8318(2)	1.3313	0.5	2.75(7)
Pb2 ^b	4h	0.807(1)	1.3068	0.5	2.8
W1	2d	0.5	0.0	0.0	0.55(3)
W2	8i	0.79520(7)	0.07538(6)	0.0	0.34(3)
O1	8i	0.498(1)	0.154(1)	0.0	3.(1)
O2	4g	0.714(1)	1.2143	0.0	1.0(4)
O3	8i	0.854(1)	0.931(1)	0.0	1.4(3)
O4	8j	0.710(2)	0.579(2)	0.5	3.(1)
O5	2c	0.0	0.5	0.5	4.(1)

^aThe equivalent isotropic temperature factor, B_{eq} , is defined as $8\pi^2/3 \langle \sum_i \sum_j (U_{ij} a_i^* a_j^* \bar{a}_i \cdot \bar{a}_j) \rangle$, where the summations of i and j range from 1 to 3

^bPb1 and Pb2 have occupancies of 62(2)% and 14(2)%, respectively

Table 7.4. Anisotropic temperature factors^a ($\text{\AA}^2 \times 10^3$) for $\text{Pb}_{0.31}\text{WO}_3$

Atom ^b	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pb1	39.(1)	39.	26.(2)	-6.(1)	0.0	0.0
Pb2 ^c	35.0					
W1	5.2(3)	5.2	10.(1)	-3.2(7)	0.0	0.0
W2	3.2(4)	4.1(4)	5.6(5)	-0.3(3)	0.0	0.0
O1	6.(7)	12.(8)	100.(20)	-2.(7)	0.0	0.0
O2	13.(5)					
O3	17.(4)					
O4	80.(20)	40.(10)	10.(10)	10.(20)	0.0	0.0
O5	50.(10)					

^aThe coefficients U_{ij} of the anisotropic temperature factor expression are defined as $\exp(-2\pi^2(a^*2U_{11}h^2+b^*2U_{22}k^2+c^*2U_{33}l^2+2a^*b^*U_{12}hk+2a^*c^*U_{13}hl+2b^*c^*U_{23}kl))$

^bThermal parameters of oxygens O2, O3, and O5 would refine only isotropically

^cPb2 thermal parameter was refined isotropically, and fixed to the Pb1 value: 2.8

Table 7.5. Select interatomic distances (Å) and angles (degrees) for $\text{Pb}_{0.31}\text{WO}_3$ ^a

Pb1...Pb2 ^b	0.42(2)	Pb1-O1	2.78(1) (x4)
Pb1-O2	2.76(2) (x2)	Pb1-O3	3.19(1) (x4)
Pb1-O4	3.12(2) (x2)	Pb1-O5	2.910(3)
Pb2-O1	3.04(2) (x4)	Pb2-O2	2.47(2) (x2)
Pb2-O3	3.12(1) (x4)	Pb2-O4	2.79(3) (x2)
W1-O1	1.87(2) (x4)	W1-O5	1.887(2) (x2)
W2-O1	1.97(2)	W2-O2	1.960(6)
W2-O3	1.90(2)	W2-O3'	1.87(2)
W2-O4	1.889(2) (x2)	O5-W1-O5'	180.0
O1-W1-O1'	89.(1) (x2)	O1-W1-O1'	91.(1) (x2)
O1-W1-O1'	180.0 (x2)	O1-W1-O5	90.0 (x2)
O1-W2-O2	88.3(8)	O1-W2-O3	83.8(7)
O1-W2-O3	178.7(7)	O1-W2-O4	88.9(7) (x2)
O2-W2-O3	172.2(8)	O2-W2-O3	93.0(8)
O2-W2-O4	87.8(7) (x2)	O3-W2-O3'	95.(1)
O3-W2-O4	92.0(7) (x2)	O3-W2-O4	91.2(7) (x2)
O4-W2-O4	175.(1)	W1-O1-W2	151.(1)
W2-O2-W2'	150.(1)	W2-O3-W2'	175.(1) (x2)
W1-O5-W1'	180.0		

^aAtoms with primed numbers are related to those with unprimed numbers by symmetry constraints of space group 127.

^bBoth lead sites are partially occupied.

RESULTS AND DISCUSSION

Description of Structure

The basic building block in the tetragonal tungsten bronze structures is the tungsten centered oxygen octahedra. These octahedra share waist vertices to form a network in the *ab* plane and apical vertices are shared with octahedra in adjacent layers in the *c* direction. This arrangement in which octahedra share vertices, as viewed in the ORTEP⁴⁰ Figure 7.1, creates three different types of channels that extend parallel to the *c* axis. The vacant sites in the smallest channels are surrounded by six oxygen atoms in a trigonal prismatic array and are too small to be occupied by a cation. The medium-sized channel has a square arrangement of oxygens, which would allow a cation to have either square planar coordination or reside in the center of a cube of oxygens. In the sodium tetragonal tungsten bronzes, where the sodium content is greater than 0.3, this channel is occupied. For large cations, such as lead, the only channel occupied is the largest one, with a pentagonal opening formed by five vertex-sharing octahedra. Since all octahedral waist oxygen atoms are shared at the same height in the *c* direction, the channels undulate, wider at the level of the apical oxygen of the octahedra and narrower at the waist level. Both Pb1 and Pb2 reside at the same height in the *c* direction as the apical oxygen atoms. Consequently, they are only separated in the *ab* plane by 0.42(2)Å. The Pb1 coordination environment is depicted in Figure 7.2. Pb1 has a more uniform set of lead-oxygen distances (2.76-2.91Å) forming a monocapped trigonal prism, where the trigonal prism consists of six oxygen atoms which also belong to the waist octahedra, and the capping oxygen atom which is also an apical oxygen in the octahedra. Six other oxygens (four waist and two apical) have long lead-oxygen distances, Pb1-O3 at 3.19(1)Å and Pb1-O4 at 3.12(2)Å. As viewed in

Figure 7.1. The ORTEP representation (70% thermal ellipsoids) of the $\text{Pb}_{0.31}\text{WO}_3$ unit cell, as viewed parallel to the c axis.

Figure 7.2. An ORTEP drawing (70% thermal ellipsoids) of the Pb1 coordination environment by oxygen

Figure 7.3, the oxygen coordination environment is quite irregular around Pb2, the satellite position. The coordination sphere includes two short Pb2-O2 bonds at 2.47(2)Å and two medium Pb2-O4 bonds at 2.79(3)Å. All four of these oxygen atoms are located on one side of the tunnel and there are eight more oxygens at long coordination distances (3.04-3.12Å), located on the opposite side of the tunnel.

The structures of the tetragonal sodium tungsten bronzes⁵⁸ contained disorder in the oxygen positions which was interpreted as two different domains in which the metal centered oxygen octahedra tilt in different directions. The structural refinement of the $\text{Pb}_{0.31}\text{WO}_3$ did not seem to exhibit oxygen disorder, although the thermal parameters of the oxygens were not well behaved. Instead, the $\text{Pb}_{0.31}\text{WO}_3$ phase displays two positions in which the lead cation can reside within the pentagonal tunnel. The majority site, Pb1, is equivalent (within 1σ standard deviation) to the position of the sodium cation in the $\text{Na}_{0.48}\text{WO}_3$ and $\text{Na}_{0.33}\text{WO}_3$. Perhaps, the flexibility of the lead cation to adjust to a variety of coordination environments promotes this behavior.

Microprobe analyses on crystals of Pb_xWO_3 confirmed the composition determined by the single crystal refinement. Five measurements on five different grains gave an average molar composition of $\text{Pb}_{0.306(1)}\text{WO}_3$.

The octahedral oxygen coordination environment around W1 is quite regular, in terms of bond distances (~1.88Å) and bond angles ($90 \pm 1^\circ$). However, the W2 coordination environment is noticeably distorted. The tungsten-oxygen bond distances range from 1.87(2)Å to 1.97(2)Å and interior bond angles, O-W-O, vary from 87 to 95° . Both octahedra are shown in Figure 7.4, although the perspective views do not accentuate the distortions.

Figure 7.3. The ORTEP drawing (70% thermal ellipsoids) of the Pb2 coordination environment by oxygen

a)

b)

Figure 7.4. The octahedral coordination of oxygen around (a) W1 and (b) W2, drawn with 70% thermal ellipsoids

Discussion of Properties

Bond length-bond strength relationships

The numerical values resulting from bond length-bond valence calculations, as discussed previously in Section 1, are found in Table 7.6 for $\text{Pb}_{0.31}\text{WO}_3$. The empirical bond valence equation (Equation 1) developed by Brown and Wu⁴⁵ was

$$s(\text{cation-O}) = [R(\text{cation-O})/R(1)]^{-N} \quad (1)$$

used with values of $R(1)$ and (N) , for W and Pb^{2+} respectively, of 1.904Å (6.0) and 2.044Å (5.5). These calculations indicate that both tungstens have a valence of about six, however, W2, which is found in a more distorted coordination environment, is also slightly more reduced than W1. Bond valence sums around the two lead position indicate that they are both divalent, as expected.

Magnetic properties

The magnetic susceptibility of $\text{Pb}_{0.31}\text{WO}_3$ was measured on a polycrystalline sample over the temperature range 6-376 K. The data were corrected for diamagnetic core contributions, based on atomic values reported by Selwood.⁴⁶ Figure 7.5 displays the molar susceptibility of $\text{Pb}_{0.31}\text{WO}_3$ versus temperature. The tail at low temperature most likely arises from a small concentration of paramagnetic impurities. The relative constant and positive susceptibility observed above 100 K is characteristic of a Pauli paramagnetic material.

Because access to a four probe single crystal resistivity unit was not available, a qualitative measurement of the resistivity was made on the bronze. A needle crystal of $\text{Pb}_{0.31}\text{WO}_3$ was placed on a glass slide and a pair of platinum wires were attached to it with silver epoxy resin. A measurement of the resistance at room temperature with a typical multimeter indicated ~400 ohms.

The sample was cooled with liquid nitrogen and the resistance across the crystal decreased, behavior typical of a metal. This value can be contrasted to semiconducting materials which usually gave readings of ~3000-10000 ohms using this method. This interpretation is in agreement with the metallic behavior observed by Bernoff and Conroy.⁵⁶

Table 7.6. Bond length-bond strength relationships for $\text{Pb}_{0.31}\text{WO}_3$

Atom	d(M-O)	s
Pb1 ^a	2.78(1)	0.184(3) (x4)
	2.76(2)	0.192(8) (x2)
	3.19(1)	0.087(2) (x4)
	3.12(2)	0.098(4) (x2)
	2.910(3)	<u>0.1433(8)</u>
		$\Sigma s = 1.80(4)$
Pb2 ^a	3.04(2)	0.113(4) (x4)
	2.47(2)	0.353(15) (x2)
	3.12(1)	0.098(2) (x4)
	2.79(3)	<u>0.181(9)</u> (x2)
		$\Sigma s = 1.91(8)$
W1	1.87(2)	1.11(6) (x4)
	1.887(2)	<u>1.06(1)</u> (x2)
		$\Sigma s = 6.6(3)$
W2	1.97(2)	0.82(5)
	1.960(6)	0.840(15)
	1.90(2)	1.01(6)
	1.87(2)	1.11(6)
	1.889(2)	<u>1.049(4)</u> (x2)
		$\Sigma s = 5.9(2)$

^aCalculations for both lead atoms were performed using the radius for Pb(II)

Figure 7.5. Molar susceptibility versus temperature for $\text{Pb}_{0.31}\text{WO}_3$

CONCLUSIONS

The synthesis of $\text{Pb}_x\text{W}_4\text{O}_6$ at temperatures under 1000°C and in a reducing environment results in the formation of a tetragonal lead tungsten bronze, $\text{Pb}_{0.31}\text{WO}_3$, in which the tungsten is only slightly reduced. The structure type has been known for nearly 45 years, yet only two such structures have been studied by modern diffractometer methods.⁵⁸ $\text{Pb}_{0.31}\text{WO}_3$ fits the known structure type in which corner-sharing octahedra of oxygens, centered by tungsten, create a pentagonal channel in which the lead resides. However, the cation arrangement of two disordered sites may imply a complicated superstructure. Bond valence analyses confirm that the lead is divalent and that the tungsten is slightly reduced. Magnetic susceptibility measurements indicate that $\text{Pb}_{0.31}\text{WO}_3$ is a Pauli paramagnetic material.

SECTION 8

**EXAMINATION OF THE SUPERSTRUCTURE IN $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$, $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$,
 InMo_4O_6 , AND $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ BY ELECTRON MICROSCOPY**

INTRODUCTION

The structural determinations of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$, $\text{Sn}_{0.91}\text{Mo}_4\text{O}_{11}$, InMo_4O_6 , and $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ by single crystal x-ray diffraction have been completed by previous co-workers.^{5,13,15} However, complex, unsolved superstructures were suspected for at least three of the four materials because their structural refinements indicated that some atoms had irregular thermal parameters, mixed metal occupation, and/or partial vacancies. The presence of superstructural ordering was examined on the Fe, Sn, and Mn single crystal members, however, the results were inconclusive or the intensity information was too weak. This problem provoked the structural investigation of these phases by transmission electron microscopy (TEM). The benefit of this technique is that the beam intensity is greater and large crystals are not necessary. These materials were primarily studied by selected area electron diffraction (SAD) and periodically complemented with convergent beam electron diffraction (CBED) and centered dark field. Since the subcell structures were known, most zone axes could be easily indexed from the derived single crystal d-spacings. All materials, except InMo_4O_6 , exhibited superstructure. From this information and previous characterization of these systems, models accounting for the superstructures are proposed.

EXPERIMENTAL

Materials and Methods

The synthesis of oxides containing molybdenum in relatively low oxidation states requires that the oxygen content be controlled stoichiometrically. Therefore, all reactions were carried out in evacuated ($\sim 2 \times 10^{-5}$ torr) molybdenum tubes or evacuated ($\sim 1 \times 10^{-4}$ torr) fused silica ampoules.

The starting reagents included Fe_2O_3 , SnO , MoO_3 , and Mo . The synthesis, drying, and cleaning of these reagents has been discussed in Sections 2 and 4.

Physical Measurements

X-ray powder diffraction

An Enraf Nonius Delft FR552 triple focusing Guinier x-ray powder diffraction camera was used with $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.540562 \text{ \AA}$) generated from an AEG fine focus tube powered by a General Electric XRD-5 generator. National Bureau of Standards silicon powder was used as an external standard.

Transmission electron microscopy

A Philips CM30 transmission electron microscope was used to evaluate the superstructural ordering of the ternary reduced molybdenum oxides. An approximate one to one mixture of microcrystalline $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$, $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, or InMo_4O_6 and G-1 Epoxy from Gatan was placed between lens paper, pressed between aluminum plates, and cured at 120°C for ten minutes. In the case of $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$, a combination of ground sample and long needles was used. A

three millimeter disk was punched out, thinned to $\sim 20\mu\text{m}$ by dimpling, put on a 200 mesh copper grid for support, and subsequently ion milled until a hole was observed. The sample and supporting grid assembly were subsequently loaded into the TEM sample holder for investigation.

Scanning electron microscopy

A Cambridge S-200 scanning electron microscope was employed for qualitative elemental analysis using a Tracor Northern Micro Z-II energy dispersive spectrometer (EDS) with a beryllium window. Crystals and/or microcrystalline powder were loaded onto a metal disk via Scotch double-stick tape and sputter-coated with gold to improve the conductance.

Synthesis

The $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$ phase was prepared using the method described by Lii.¹⁵ Fe_2O_3 , MoO_3 , and Mo were thoroughly mixed in the correct stoichiometric ratio, loaded in a Mo tube, and sealed under reduced pressure via electron beam welding. The Mo tube was loaded into a closed-end alumina tube, evacuated, and then left under a partial pressure of argon over the length of the reaction. The sample was fired at 1300°C for three days and cooled to 500°C at an average rate of $100^\circ\text{C}/\text{hour}$. The reaction was then furnace cooled. A Guinier powder diffractogram of the black, microcrystalline product matched the calculated powder pattern derived from the single crystal parameters.

The $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ was prepared based on the method described by Aufdembrink.⁵ SnO , MoO_3 , and Mo were thoroughly mixed in the correct stoichiometric ratio, loaded into an open Mo tube, which was placed in a fused silica jacket, and sealed under reduced pressure. The sample was fired 12 hours

at 1100°C, 12 days at 1200°C, 12 hours at 1250°C, then cooled to 800°C at 100°C/hour, and finally quenched to room temperature. A Guinier powder pattern of the product indicated the presence of the title phase and trace amounts of Mo metal.

$\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ was used from a reaction completed by Carlson.¹³ The InMo_4O_6 phase was taken from a reaction fired by Lii.¹⁵ A Guinier powder pattern of these materials matched their title phases and SEM EDS indicated that In or Mn and Mo were present.

RESULTS AND DISCUSSION

Diffraction information in electron microscopy is obtained by examining the diffraction patterns in a variety of directions. These specific directions are termed zone axes, and refer to the condition when Bragg's law is satisfied. For example, the [100] zone axis will have diffraction maxima for the hkl planes that are nearly parallel to the electron beam direction: $\{010\}$, $\{001\}$, and any of their vector sums.

Intensity information for electron diffraction is not easily quantified, and can be significantly altered by a variety of conditions.⁶⁰ Thus, the absence of superstructure reflections does not exclude the possibility that it exists. Factors which affect the diffraction intensity include: 1) crystal thickness, if the intensity of superlattice reflections is very weak they may be rediffracted and/or absorbed within the sample, 2) short range order, which results in diffuse or streaked intensity, and 3) extinction distance (the thickness of a sample at which a specific reflection's intensity will be reduced to zero) which becomes shorter for small unit cell volumes, large Bragg angles, large incidental beam wavelengths (low energy), and large structure factors.

The SAD micrographs for the major zone axes were collected at a variety of exposure times (10-70 seconds); with very long exposure times (40-70 seconds) the incident beam was blocked to lower the background intensity. This methodology was utilized so that all vital diffraction information could be collected. In the following discussion, subscripted "sub" and "sup" will represent indices of the subcell and supercell, respectively, and unlabelled indices can be assumed to be related to the subcell.

The diffraction patterns for the [100], [010], [001], [110], [101], and [011] subcell zone axes were collected for $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. The strong reflections could all be indexed based upon the d-spacings derived from the single crystal parameters. Any other reflections observed were presumed to be the result of superstructural ordering. The SAD's of the [100] and [110] zone axes, as shown in Figure 8.1, and simulated in Figure 8.2, can be fully indexed based on the known body-centered ($h+k+l=2n$) orthorhombic symmetry and show no superstructural information. The CBED and SAD of the [001] are shown in Figure 8.3 and the SAD is simulated in Figure 8.4. Between pairs of subcell reflections in the SAD, [i.e., (000) and (200)_{sub}] a very weak pair of reflections is observed and corresponds to {2k0}_{sup} and {4k0}_{sup}. The strongest superlattice reflections appear in the region between (000) and (hk0)_{sub}, and can also be indexed as {2k0}_{sup} and {4k0}_{sup}. This information can be interpreted as a tripling in the a direction, thus these supercell reflections deviate from the body-centering condition. Note the slight streaking in the superlattice reflections, this observation would imply that the ordering in the a direction is not completely well-behaved, i.e., it is short range. The CBED shown in Figure 8.3a emphasizes that the orthorhombic symmetry (2mm) of the [001] appears to be preserved. Close examination of the [101] zone axis, shown in Figure 8.5a (simulation Figure 8.6a), reveals that two maxima exist within the supercell streaking and can be indexed as {h2h}_{sup} and {h4h}_{sup}. These supercell reflections indicate a tripling in the b axis, however, only with short range order. The same {h2h}_{sup} and {h4h}_{sup} can also be faintly observed between strong subcell reflections. The [011] zone axis displays a pair of superlattice reflections beside each subcell reflection, as exhibited in Figure 8.5b (simulation Figure 8.6b). These d-spacings correspond to the {1kl}_{sup} and {5kl}_{sup} and a tripling in the a direction; again significant streaking is visible. Figure 8.7 displays the SAD of the [010] zone axis.

Figure 8.1. a) Selected area diffraction pattern for the [100] and b) the [110] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. All observed reflections, for both patterns, were indexed for the subcell.

a)

b)

Figure 8.2. a) Simulated SAD for the [100] and b) the [110] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$

a)

b)

Figure 8.3. a) Convergent beam electron diffraction pattern and b) selected area diffraction pattern for the [001] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. The CBED is rotated $\sim 45^\circ$ from the SAD view shown.

Figure 8.4. Simulated SAD of the [001] for $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. The intensities are not representative of the collected SAD, i.e., the (110) type reflections are much weaker than the superstructure.

a)

b)

Figure 8.5. a) Selected area diffraction pattern for the [101] and b) the [011] of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$.

a)

b)

Figure 8.6. a) Simulation of the SAD for the [101] and b) the [011] in $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. All reflection intensities in b) are shown as equivalent and streaking in both have been omitted.

a)

b)

Figure 8.7. a) SAD for the [010] and b) its simulation for $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$

In broad perspective, the superlattice diffraction appears as a pair of reflections above and below every subcell reflection. Based upon the interplanar spacings, the supercell diffraction reflects a tripling in the *a* and *c* axes. All the observed reflections also conform to the body-centering condition ($h+k+l=2n$), although some reflections that fit this condition such as the $(200)_{\text{sup}}$ are too weak to be observed.

The SAD information reveals an ordered superstructure where all three lattice dimensions are tripled: $a' \sim 17.9\text{\AA}$, $b' \sim 17.3\text{\AA}$, and $c' \sim 51.1\text{\AA}$. The molybdenum-oxide framework may still be body-centered; however, the violations of this condition in the supercell may imply otherwise, or that the cations are not ordered in a body-centered arrangement. The streaking observed in the SAD was variable from crystal to crystal, therefore, this phase has various degrees of ordering.

The $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$ structure type has been described in Section 4 for $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ and an ORTEP drawing of the unit cell is shown in Figure 8.8. One underlying presumption in the model to be discussed is that the iron and molybdenum atoms which are mixed on the octahedral sites (M2) of the subcell, are the root of the superstructure that is observed. A tripling in the lattice parameters will generate six layers of octahedral sites, each layer must contain two molybdenum and sixteen iron (11% and 89%). For discussion purposes, a body-centered symmetry operation will be used, with the realization that this symmetry constraint is easily violated by interchanging a single Mo and Fe atom. The consequence would be an even larger supercell, although such a situation would be difficult to observe by TEM. Finally, Mössbauer experiments on $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$ indicated that for every Fe with a Mo neighbor (to be represented 1 Fe/Mo) there are three irons with iron neighbors (3 Fe/Fe). Based on these conditions, representations of the supercell octahedral layers are shown in Figures 8.9-8.11. Layers 1 & 4, 2 & 5, and 3 & 6 are related to each other by the

4 of 4

Figure 8.8. The unit cell of $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ is isostructural to $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. The octahedral metal site, M2, is 89% Fe & 11% Mo.

Layer 1

Layer 4

Figure 8.9. Two layers of MO_6 indicating the Mo/Fe ordering in a superstructure of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. Open circles are oxygen atoms, solid circles are molybdenum atoms, and cross-hatched circles are iron atoms. The dashed lines indicate the subcell a and b axes.

Layer 2

Layer 5

Figure 8.10. Two layers of MO_6 indicating the Mo/Fe ordering in a superstructure of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. Open circles are oxygen atoms, solid circles are molybdenum atoms, and cross-hatched circles are iron atoms.

Layer 3

Layer 6

Figure 8.11. Two layers of FeO_6 units in a superstructure of $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$. Open circles are oxygen atoms and cross-hatched circles are iron atoms.

body-centering operation. Note that in all cases the 2mm symmetry is preserved. Layers 1 & 4 conform to the Mössbauer requirements with 4 Fe/Mo to 12 Fe/Fe. Layers 2 & 5 have 8 Fe/Mo to 6 Fe/Fe, these values are twice the ratio shown by Mössbauer, however, if layers 3 & 6 are all iron (0 Fe/Mo to 18 Fe/Fe), then layers 2, 3, 5, and 6 average to 1 Fe/Mo to 3 Fe/Fe. This superstructure results in the following formulation: $(\text{Fe}_{24}\text{Mo}_3)^{\text{o}}\text{Fe}_{27}^{\text{t}}\text{Mo}_{108}\text{O}_{189}$, where t and o represent tetrahedral and octahedral ternary metal sites, respectively. Based on the multitude of crystals examined, $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$ either has an ordered superstructure as described above, or the SAD indicate streaking, implying that short range order exists.

All samples prepared for TEM work, using $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, contained crystals oriented in such a manner that the [010] and [100] could not be reached. The CBED and SAD of the [001] appear in Figures 8.12 and 8.13. No superlattice reflections are observed. The [001] CBED confirms the 4mm symmetry of the subcell. The SAD of the [101] and [110], shown in Figures 8.14 and 8.15, indicate a doubling along $\{111\}_{\text{sub}}$ planes. These quite intense and discrete superlattice reflections have been verified as real, and not due to double diffraction, based on centered dark field. (Double diffraction is the resultant of rescattering of a diffracted beam, thus giving rise to diffraction where structure factor considerations suggest that the beam intensity should be zero.) A second [101] zone axis, shown in Figure 8.16a, found on another crystal, indicated significant streaking, where Figure 8.14b showed discrete points. Therefore, the degree of ordering appears to vary from crystal to crystal within a given reaction product. As previously mentioned, the [100] and [010] zone axes have been difficult to reach. Close inspection of a [100] that could not be centered due to

a)

b)

Figure 8.12. a) CBED of the [001] and b) SAD of the [001] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$

Figure 8.13. SAD simulation of the [001] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$

a)

b)

Figure 8.14. a) SAD of the [101] and b) the [110] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$

a)

b)

Figure 8.15. a) Simulation of the $[101]$ and b) the $[110]$ in $\text{Sn}_{0.8}\text{Mo}_4\text{O}_6$. Intensities of supercell reflections in b) are depicted as nearly equivalent to the subcell reflections.

a)

b)

Figure 8.16. a) SAD of another [110] and b) the [111] for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$

limits on the tilting, indicated very faint reflections at half the distance to the $\{001\}_{\text{sub}}$, implying a doubling in the c axis. All of the $[111]$ zone axes that were found, after examining many crystals, had streaking at $1/4$ and $3/4$ of the distance to the $\{112\}_{\text{sub}}$, as seen in Figures 8.16b and simulated in 8.17. This observation might imply a very complicated ordering, necessitating that every fourth $\{112\}$ plane repeats itself, however, no definitive maxima are observed within the streaking. This streaking might imply that the arrangement of the tin atoms within the tunnels have a range of positional stability and thus only have short range order.

Based upon the single crystal refinement, $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ is constructed of infinite chains of trans edge-shared Mo octahedra, which are interconnected through bridging oxygens. This framework results in the formation of tunnels suitable for the location of tin atoms, as shown in Figure 8.18. Within these tunnels, two partially occupied positions were located and refined in the subcell structure for the tin atoms. Structural questions remained, in particular, a potential doubling of the c axis, which did give a slightly improved single crystal refinement and was observed in oscillation photos.⁵

The model to be proposed, based on SAD of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, is consistent with the results found by single crystal x-ray diffraction. The structure factor for $\{111\}_{\text{sub}}$ contains information from all the atoms in the unit cell, although one might expect the largest component of the structure factor to be derived from the tin, based on the greater electron density and larger scattering factor. Therefore, the initial hypothesis will be that the tin population and/or ordering are the most likely reason for the observed superstructure, and that the molybdenum oxide framework is quite rigid. Furthermore, this model will assume that the tin is essentially located at the origin, i.e., in the major subcell position at 0,0,0.04.

A supercell derived from selected area diffraction patterns is based on the three dimensional ordering of tin atoms. The new superstructural unit cell can be

Figure 8.17. SAD simulation of the $[111]$ for $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, streaking depicted as lines.

Figure 8.18. View parallel to the c axis of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, indicating the tunnels in which the tin cations reside.

derived by assuming alternating {111} planes have different tin populations. One can visualize the $\sqrt{2} \times \sqrt{2} \times 2$ supercell within the subcells via Figures 8.19. Even though $a'=b'\sim 13.6\text{\AA}$, the cell is now orthorhombic due to the occupancy of the tin atoms on alternating subcell {111} planes, creating a situation where the ac plane is face centered but the bc plane is not. If one considers only the tin atoms, the new unit cell is either body or face centered, however, the molybdenum octahedral chains eliminate these possibilities because all the centered orthorhombic space groups have imposed screw axes parallel to the a and/or b unit cell axes. Therefore, the supercell space group should be primitive orthorhombic. Note that this model accounts for the doubling in the c axis.

The nature of the tin occupancies is still not known; there are eight possible cation positions in the supercell, if seven positions are filled then the composition would be $\text{Sn}_{0.875}\text{Mo}_4\text{O}_6$, very close to the single crystal refinement of $\text{Sn}_{0.88}\text{Mo}_4\text{O}_6$. If only seven cation positions are filled, this model might not be the ideal choice, since there still appears to be short range order that cannot be accounted, or the diffraction is very weak from the long range order. The single crystal refinement of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ included two partially occupied tin sites, with the major one accounting for $\sim 85\%$ of the total tin content. Perhaps, the minor tin site might really correspond to a position where neighboring tin atoms are vacant, and thus the "minor" cation resides in a slightly different environment than the major tin atom. The metal-metal distance in grey tin is $2.81\text{\AA}$ and the repeat distance down the tunnel is $2.84\text{\AA}$ in $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$, therefore segments of metal-metal bonded tin atoms in the tunnel are not unreasonable. The discrepancy in repeat distances might then be accommodated by cation vacancies.

a)

b)

Figure 8.19. a) Subcells, $2 \times 2 \times 2$, of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ emphasizing the alternating $\{111\}$ planes. b) The new supercell of $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ showing the orthorhombic symmetry of the tin atoms in the supercell. Only tin atoms are shown, shading implies different populations of tin.

Only preliminary work on the $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ system has been completed at this time. Because this phase is monoclinic, collecting all the unique zone axes with indices of zero or one is difficult. The [100] and [110] zone axes indicate a doubling in the c axis, as shown in Figures 8.20 and 8.21. The superlattice reflections necessitating this result are very sharp and intense. The implication is that a single crystal x-ray refinement should have been able to observe such reflections. However, this phase grows as very fine needles that tend to fray at the ends, therefore, the selection of a suitable crystal for x-ray work becomes difficult. The TEM allows a small spot size to be utilized, and thus, crystal selection becomes less crucial. The [100] contains more information, at four times the subcell c direction a weak streak is observed. The [101] and [010], shown in Figures 8.22 and 8.23, have streaking at 1/4 and 3/4 of the distance to the {101} planes. The [010] also shows a doubling of the c axis. Streaking at 1/4, 1/2, and 3/4 is also observed in the SAD of the [011] and [111], as shown in Figure 8.24 and Figure 8.25.

No model has been proposed, however some results appear likely. First, the doubling in the c axis is probably the result of apical molybdenum atoms pairing in the infinite trans edge-shared Mo chains. The streaking which might be interpreted as quadrupling in the c direction is weak. Thus, it is the result of short range order; most likely due to the manganese cations. The manganese in the subcell was refined as two partially occupied positions, and it does not appear to be well behaved. The ordering (streaking) along {101} and {011} planes are also likely to be related to the cation order/disorder. The monoclinic subcell and ordering along a variety of planes appears to imply a very complicated three dimensional ordering of manganese, or perhaps a random distribution of manganese over a couple of different coordination sites. Perhaps, more ordered

a)

b)

Figure 8.20. a) SAD of the [100] and b) [110] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$

a)

b)

Figure 8.21. a) Simulation of the [100] and b) the [110] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$. The streaking in the [100] is represented by lines. All the superstructure in the [110] is depicted as discrete points.

a)

b)

Figure 8.22. a) SAD of the [101] and b) [010] for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$

Figure 8.23. a) Simulation of the $[101]$ and b) the $[010]$ for $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$. The streaking in the $[101]$ is depicted with lines. The subcell reflections of the $[010]$ are shown with a constant, stronger intensity than the supercell reflections.

a)

b)

Figure 8.24. a) SAD of the [011] and b) the [111] of $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$. The outer edges of both photos contain first order Laue zone information.

a)

b)

Figure 8.25. SAD simulation of a) the [011] and b) the [111] in $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$. The streaking in both zone axes depicted as lines. The weak supercell reflections in the [111] shown as points are maxima within streaking.

crystals can be found, however, the manganese coordination environment may be such that short range order predominates.

InMo_4O_6 does not exhibit any well-defined superstructure. At half the distance to the {001} in the [100] zone axis there is a faint streak. This streak is only observed at very long exposure times. Short range order, in which indium atoms have a small range of positional stability within the tunnel, might be a valid interpretation. This positional range of the indium cations might be small enough that the indium thermal parameters of the single crystal refinement mask the various real positions.

CONCLUSIONS

The $\text{Fe}_{1.89}\text{Mo}_{4.11}\text{O}_7$ superstructure can be modelled with a body-centered orthorhombic cell by the appropriate positioning of Mo atoms within the layers having MO_6 coordination. The variable streaking and reflections that violate the body-centering symmetry operation imply that the ordering of ternary metals within the octahedral layers might not be well-behaved from crystal to crystal. The collection of data by single crystal x-ray diffraction has not been attempted on this proposed supercell. The extremely large c axis lattice parameter would necessitate the use of Cu radiation, however, such a phase containing a significant quantity of heavy metals might result in large absorption corrections which would hinder the search for, or interpretation of, weak superlattice reflections.

The superstructural ordering observed in $\text{Sn}_{0.9}\text{Mo}_4\text{O}_6$ is based on the alternate {111} planes that differ in tin population. The consequence of this ordering is a supercell, $\sqrt{2}a \times \sqrt{2}b \times 2c$. This supercell has primitive orthorhombic symmetry, based on tin occupation and the molybdenum oxide framework. A simple explanation of the tin population is not evident from the TEM data collected.

The $\text{Mn}_{1.5}\text{Mo}_8\text{O}_{11}$ phase appears to have a very complicated superstructural ordering. However, the material does have a doubled c lattice parameter, most likely the result of apical molybdenum atom pairing. Further TEM investigation might provide more insight into the ordering behavior of this material.

GENERAL SUMMARY

The synthesis of ten members in the series, $M_{n-x}Mo_{4n+2}O_{6n+4}$, has been achieved. These oligomers consist of trans edge-shared molybdenum octahedra of varying length, ranging from two to five octahedra. The variation of the electron count available for metal-metal bonding in these materials dictates the arrangement of the apical-apical interactions and/or the degree of intercluster metal-metal bonding. All but one member ($Ba_{4.2}Mo_{22}O_{34}$) are interconnected to neighboring clusters in a stair-step fashion. The cations reside in pockets created by the interconnection of the clusters. These cation pockets have occupancies that range from 75% to 100% of capacity.

The materials containing bioctahedral Mo_{10} units have exceptionally strong apical-apical bonding ($\sim 2.61\text{\AA}$), regardless of the electron count. Intercluster bond distances, however, become shorter ($\sim 2.78\text{--}2.68\text{\AA}$) as the total number of electrons available for metal-metal bonding increases from 32 to $34e^-$. The cation sites for all the known $n=2$ members are fully occupied. The first member prepared with an intermediate electron count, $33.3e^-$, was $K_{0.33}Gd_{1.67}Mo_{10}O_{16}$. It was found to have an appropriately short intercluster bond distance of $\sim 2.71\text{\AA}$.

The trimeric oligomers, Mo_{14} , exhibit a more complex relationship between metal-metal bonding and electron counts. At $43e^-$, the clusters have a short-long arrangement of apical-apical bond distances ($\sim 2.64, 3.06\text{\AA}$) and no intercluster metal-metal bonding ($\sim 3.2\text{\AA}$). From 43 to $\sim 44e^-$, as seen in $K_{0.76}Pb_{1.53}Mo_{14}O_{22}$ and $K_{2.6}Sr_{0.4}Mo_{14}O_{22}$, the apical interactions remain nearly constant as compared to the $43e^-$ $K_3Mo_{14}O_{22}$ member, however, the intercluster molybdenum interactions become significantly stronger ($\sim 2.84\text{\AA}$). Above $\sim 44e^-$, the intercluster metal-metal bond distances increase to about $3\text{\AA}$ and the apical-apical molybdenum bond distances become nearly equivalent ($\sim 2.83\text{\AA}$). Thus, in the

$K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ ($44.7e^-$), and $Tl_{1.6}Sn_{1.2}Mo_{14}O_{22}$ ($45.6e^-$) members, the electrons appear to be entering antibonding orbitals. The cation sites for all the $n=3$ members reported here are fully occupied, unlike Simon's Tl-Sn compound. The K-Sn member has all its cation sites occupied. However, four unique partially occupied sites are defined, as opposed to the normal two, crystallographically occupied sites.

The first tetrameric oligomer, $Ba_3Mo_{18}O_{28}$, was reported here. Its short-long-short arrangement of apical-apical interactions ($\sim 2.60, 3.11, 2.59\text{\AA}$) is similar to the $n=4$ cluster found in $In_{11}Mo_{40}O_{62}$ ²³, and consistent with the calculations performed by Hoffmann and Wheeler.⁴¹ The shortest intercluster metal-metal distance is quite long, at $\sim 3.18\text{\AA}$. Three of the four possible cation sites are occupied by barium, however, the central cation position is disordered about the origin with two sites 50% occupied. Arndt Simon has graciously communicated that $In_5Mo_{18}O_{28}$ has been structured; however, it has the orthorhombic symmetry seen in oligomers which have the clusters interconnected in a zig-zag fashion.

The $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ member contains five trans edge-fused molybdenum octahedra. This phase has four short and four long apical-apical molybdenum interactions ($\sim 2.61, 2.67, 2.94$, and $3.02\text{\AA}$), while the shortest intercluster Mo-Mo bond distance is $\sim 3.00\text{\AA}$. The central cation position, located at the origin, is vacant and the two other unique positions are fully occupied.

Further efforts are needed to synthesize more new tetrameric and pentameric oligomers, and thus establish relationships between the electron count and metal-metal bonding in these relatively large cluster units.

$K_{1.29}Sn_{1.71}Mo_{14}O_{22}$ appears to be a paramagnetic material; however, the apparent moment does not correspond to the number of available unpaired electrons. The composition of this K-Sn member is variable based upon microprobe analysis, therefore, the formula derived for the single crystal structure

may not be valid for the bulk crystals used in the measurement of magnetic susceptibility. Diamagnetic behavior is observed for $K_{0.76}Pb_{1.53}Mo_{14}O_{22}$; again, this result does not fit the electron count derived from the single crystal refinement. $Ba_3Mo_{18}O_{28}$ was determined to be diamagnetic and semiconducting. These properties do agree with the even electron count and the relatively isolated nature of the cluster units in the tetrameric oligomer. The diamagnetic behavior determined for $K_{0.19}Ba_{3.81}Mo_{22}O_{34}$ also does not correlate to the electron count based on the formula.

The general problem of correlating the observed magnetic behavior with the calculated number of unpaired electrons is symptomatic of the present lack of understanding in such complicated systems. The preparation of bulk, single phase, oligomeric materials is hampered, in part, by the very structural nature of these compounds. Essentially the only differences between the various oligomers are the chain axis length and the mode of interconnection (stair-step or zig-zag). Thus, the already line-rich x-ray powder diffraction patterns are virtually identical. Although the structures are basically sound, their overall evaluation is hindered by two interpenetrating factors: 1) the real composition might vary from crystal to crystal and 2) the systems can easily accommodate intergrowth of members with varying chain length and modes of interconnection within a given crystal. A very precise and dedicated effort will be needed to untangle the many factors controlling the various degrees of freedom in the $M_{n-x}Mo_{4n+2}O_{6n+4}$ system.

Transmission electron microscopy was used to gain further insight into the superstructural ordering of $Fe_{1.89}Mo_{4.11}O_7$, $Sn_{0.9}Mo_4O_6$, $InMo_4O_6$, and $Mn_{1.5}Mo_8O_{11}$. Based upon the electron diffraction observed, models that also fit the known structural and physical properties were proposed. In all cases, these models extend the quantity of information available on these phases, however, they do not result in one definitive superstructural arrangement.

The members of the series, $\text{RE}_4\text{Mo}_4\text{O}_{11}$, (RE=rare earth elements) were synthesized as single phase materials. The lattice parameters of the Sm to Tm members decrease linearly with lanthanide contraction. The Nd, Yb, and Lu members deviate from this relationship and the latter two appear to possess lower symmetry than orthorhombic. Their magnetic properties indicate simple RE(III) cations with Curie-Weiss behavior and their electrical resistivity properties show that they are small band gap semiconductors. This work was completed in conjunction with Dr. Patrick Gougeon.

A new member in the series $^t\text{M}_x\text{M}'_{2-x}\text{Mo}_4\text{O}_7$ has been prepared. It consists of closest packed $[\text{Mo}_4\text{O}_7]_\infty$ units with cations in tetrahedral (t) and octahedral (o) coordination sites. $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ contains iron in the tetrahedral site and 31% Ti and 69% Fe in the octahedral site. Iron and titanium can be found in the +2/+3 and +3/+4 oxidation states, respectively. $\text{Ti}_{0.31}\text{Fe}_{1.69}\text{Mo}_4\text{O}_7$ is a ferrimagnetic material with a $T_c \sim 110$ K and an effective moment of $6.53 \mu_B$. However, based upon the calculated effective magnetic moment, this phase contains no more than four mole percent Fe(III), which can be varied to satisfy the full range of Ti(III) to Ti(IV).

The synthesis of ternary reduced tungsten oxides, containing significant metal-metal bonding, similar to the materials known for molybdenum, has not been successful. Instead, the formation of a tetragonal lead tungsten bronze, $\text{Pb}_{0.31}\text{WO}_3$, was observed. It is a Pauli paramagnetic conductor. The tungsten-oxide framework is analogous to the known tetragonal tungsten bronzes.⁵⁴⁻⁵⁹ In $\text{Pb}_{0.31}\text{WO}_3$, two lead sites were refined. The potential superstructure was not examined, although TEM might provide valuable insight into this situation.

REFERENCES

1. Torardi, C.C.; McCarley, R.E. *J. Am. Chem. Soc.* 1979, 101, 3963.
2. Schäfer, H.; von Schnering, H.G. *Angew. Chem.* 1964, 20, 833.
3. Lii, K.H.; Edwards, P.A.; Brough, L.F.; McCarley, R.E. *J. Solid State Chem.* 1985, 57, 17.
4. Torardi, C.C.; McCarley, R.E. *J. Solid State Chem.* 1981, 37, 393.
5. Aufdembrink, B.A. Ph.D. Dissertation, Iowa State University, 1985.
6. Torardi, C.C.; McCarley, R.E. *J. Less-Common Metals* 1986, 116, 169.
7. Chen, S.C. Ph.D. Dissertation, Iowa State University, 1991.
8. Bauer, K.; Rau, F.; Abriel, W.; Range, K-J. 2. Vortragstagung Fachgruppe Festkörperchemie in der GDCh, Stuttgart, FRG, 1980.
9. Ramanujachary, K.V.; Greenblatt, M.; Jones, E.B.; McCarroll, W.H. *J. Solid State Chem.* 1993, 102(1), 69.
10. Simon, A. *Angew. Chem. Int. Ed. Engl.* 1988, 27, 159.
11. Mattausch, H.; Simon A., unpublished results.
12. Gougeon, P., personal communication with R.E. McCarley.
13. Carlson, C.D.; Brough, L.F.; Edwards, P.A.; McCarley, R.E. *J. Less-Common Metals* 1989, 156, 325.
14. a) McCarley, R.E. *ACS Symp. Ser.* 1983, 211, 273. b) McCarley, R.E. *Philos. Trans. R. Soc. London A* 1982, 308, 141.
15. Lii, K.H. Ph.D. Dissertation, Iowa State University, 1985.
16. McCarley, R.E.; Schimek, G.L.; Chen, S.C.; Nagaki, D. Abstract of Papers, 203rd National Meeting of the American Chemical Society; San Francisco, CA, 1992.

17. Lii, K.H.; McCarley, R.E.; Kim, S.; Jacobson, R.A. *J. Solid State Chem.* 1986, 64, 347.
18. Gall, P.; Gougeon, P.; McCarley, R.E. *Acta Cryst.* 1991, C47, 1585.
19. a) Schimek, G.L.; McCarley, R.E.; Gall, P.; Gougeon, P.; Wang, Z. to be published. b) Schimek, G.L., this work.
20. Gall, P.; Gougeon, P.; McCarley, R.E. *Acta Cryst.* 1991, C47, 2026.
21. Gougeon, P.; McCarley, R.E. *Acta Cryst.* 1991, C47, 241.
22. Leligny, H.; Ledesert, M.; Labbé, PH.; McCarroll, W.H. *J. Solid State Chem.* 1990, 87, 35.
23. Mattausch, Hj.; Simon A.; Peters, E.-M. *Inorg. Chem.* 1986, 25, 3428.
24. Lii, K.H.; Wang C.C.; Wang, S.L. *J. Solid State Chem.* 1988, 77, 407.
25. Hibble, S.J.; Cheetham, A.K.; Bogle, A.R.L.; Wakerley, H.R.; Cox, D.E. *J. Am. Chem. Soc.* 1988, 110, 3295.
26. a) Dronskowski, R.; Simon, A. *Angew. Chem. Int. Ed. Engl.* 1989, 28(5), 758.
b) Dronskowski, R.; Simon, A.; Mertin, W. *Z. Anorg. Allg. Chem.* 1991, 602, 49.
27. Gougeon, P.; Potel, M.; Sergent, M. *Acta Cryst.* 1990, C46, 1188.
28. a) Gougeon, P.; Gall, P.; Sergent, M. *Acta Cryst.* 1991, C47, 421.
b) Gougeon, P.; Gall, P. *Acta Cryst.* 1993, C49, 659.
29. Gougeon, P.; Gall, P., to be published.
30. Dronskowski, R.; Simon, A. *Acta Chemica Scandinavica* 1991, 45, 850.
31. Simon, A.; Mertin, W.; Mattausch, Hj.; Gruëhn, R. *Angew. Chem. Int. Ed. Engl.* 1986, 25(9), 845.
32. McCarley, R.E.; Schimek, G.L. Abstract of Papers, 205th National Meeting of the American Chemical Society; Denver, CO, 1993.
33. Gem Dugout, Deane Smith, 1652 Princeton Dr., State College, PA 16803.

34. van der Pauw, L.J. *Phillips Research Reports* 1958, 13, 1.
35. Donovan, John J. "Probe: WDS Micro-analysis", Version 1.60, University of California, Berkeley, 1992.
36. North, A.C.T.; Phillips, D.C.; Mathews, F.S. *Acta Cryst.* 1968, A24, 351.
37. Sheldrick, G.M. *Crystallographic Computing* 3, Oxford University Press, 1985.
38. Busing, W.R.; Martin, K.O.; Levy, H.A. "ORFLS, A FORTRAN Crystallographic Least Squares Program", Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1962.
39. TEXSAN: Single Crystal Structure Analysis Software, Version 5.0, 1989. Molecular Structure Corporation, The Woodlands, TX. 77381.
40. Johnson, C.K. "ORTEP-II, A FORTRAN Thermal-Ellipsoid Plot Program", Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1976.
41. Wheeler, R.A.; Hoffmann, R. *J. Am. Chem. Soc.* 1988, 110(22), 7315.
42. Shannon, R.D. *Acta Cryst.* 1976, A32, 751.
43. McCarley, R.E. *Polyhedron* 1986, 5, 51.
44. Pauling, L. *The Nature of the Chemical Bond*, 3rd ed.; Cornell University Press: Ithaca, New York, 1960.
45. Brown, I.D.; Wu, K.K. *Acta Cryst.* 1976, B32, 1957.
46. Selwood, P.W. *Magnetochemistry*, 2nd ed.; Interscience Publishers: New York, New York, 1956, page 78.
47. Weiser, H. Milligan, O. *Inorganic Colloid Chemistry: The Hydrous Oxides and Hydroxides*, J. Wiley & Sons, Inc.: London, 1933.
48. Jacobson, R.A.: CHES: Single crystal x-ray data preparation and structure refinement programs.
49. Walker; Stuart *Acta Cryst.* 1983, A39, 158.

50. Bart, J.C.J.; Ragaini, V. *Inorg. Chim. Acta* 1979, 36, 261.
51. McIntyre, N.S.; Zetaruk, D.G. *Anal. Chem.* 1977, 49, 1521.
52. *Handbook of X-Ray Photoelectron Spectroscopy*, Muilenberg, G.E.; Perkin-Elmer Corporation: Eden Prairie, MN, 1979.
53. Allen, G.C.; Curtis, M.T.; Hooper, A.J.; Tucker, P.M. *J. Chem. Soc. Dalton Trans.* 1974, 1525.
54. Magnéli, A. *Arkiv För Kemi* 1949, 1(24), 213.
55. Magnéli, A. *Arkiv För Kemi* 1949, 1(32), 269.
56. Bernoff, R.A.; Conroy, L.E. *J. Am. Chem. Soc.*, 1960, 82, 6261.
57. Conroy, L.E.; Yokokawa, T. *Inorg. Chem.* 1965, 4(7), 994.
58. Takusagawa, F.; Jacobson, R.A. *J. Solid State Chem.* 1976, 18, 163.
59. Ekström, T.; Tilley, R.J.D. *J. Solid State Chem.* 1978, 24, 209.
60. Loretto, M.H. *Electron Beam Analysis of Materials*, 1st ed.; University Press: Cambridge, Great Britain, 1984, page 66.

ACKNOWLEDGEMENTS

I am grateful to Dr. Robert E. McCarley for his guidance and insight. Our discussions were always fruitful and motivating. The McCarley group, past (Clark Carlson, Deb Spink, S.C. Chen, Xiang Zhang, Mike Close, and Jude Hollingshead) and present (Shane Hilsenbeck, Brian Xie, and Zhihong Zhang), have been a source of strength, information, friendship, and challenges, most of them were positive. In particular, I would like to thank Dr. Dick Nagaki for guiding my first footsteps into solid state chemistry. My "thank yous" have been too few and far between for my roommate and labmate of over four years, Shane Hilsenbeck. His patience has been tremendous, and he has lent a generous hand in the preparation of this document when time was running short.

The investigation of novel materials can not be completed alone; the following people have given generously of their time and talent: Jerry Ostenson (magnetism), Dr. Robert Jacobson (diffraction), Dr. Scott Chumbley (TEM), Dr. Alfred Kracher (microprobe), Jim Anderegg (XPS), Fran Laabs (SEM), Zhaorong Wang (conductivity), Dave Scott (ESR), Victor Young (diffraction), and Charlie Burg (welding).

Ames has been a more hospitable place with friends who are also my coworkers, namely: Richard MacKay, Greg Marking, Ru-Yi Qi, Dan Smith, and Sharon Ringrose. And finally, a special thanks to Leslie Perkins, who could always make me blush.

I knew I could make Ames a second home after attending St. Thomas Aquinas Church (STA). STA has exemplified "community" and put their words into practice. I can only hope that their concern for others will be something that I can take with me.

I would not be at this juncture without the initial scientific spark of my high school science teacher, Mr. Eldon Coyle. St. Mary's College may not have had all the facilities, however, they could reach you one-on-one. Many thanks go out to Dr. Robert Drake, Dr. Roger Kugel, Dr. Larry Dieterman, Dr. Paul Froeschl, Djonggi Situmeang, Matt Paquette, Steve Anderle, Bob Koezly, Roger Mueller, Jean Boduch, and Shelly Haas.

My foundation has always been family and farm. The love and support given by all my (extended) family has been immense. In particular, I would like to thank Mom and Dad (Diane and John), who have unconditionally supported me in all my career choices. Over these graduate years the family has grown, and they have made going back to the Easton farm entertaining. Bob, Michelle, Ariel, Kyle, John, and Tanya; Randy, Traci, and Courtney; Louie and Cheryl; and Angela, Melanie, and Jonna have all been in my thoughts as I have studied these past five years.

This work was performed at Ames Laboratory under contract number W-7405-eng-82 with the U.S. Department of Energy. The United States government has assigned the DOE Report number IS-T 1651 to this dissertation.

APPENDIX A

MEASURED AND CALCULATED D-SPACINGS FOR THE $\text{RE}_4\text{Mo}_4\text{O}_{11}$ SERIES:

RE = Y, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, & Lu

The lattice parameters calculated and reported in Section 6 on the $\text{RE}_4\text{Mo}_4\text{O}_{11}$ series were determined by using a least squares fit of the d-spacings to their respective hkl indices. Table A.1 contains the observed and calculated d-spacings, in Ångströms, determined for the early $\text{RE}_4\text{Mo}_4\text{O}_{11}$ members, where RE = Y, Nd, Sm, Eu, Gd, and Tb. Table A.2 contains the observed and calculated d-spacings, also in Ångströms, determined for the late $\text{RE}_4\text{Mo}_4\text{O}_{11}$ members, where RE = Dy, Ho, Er, Tm, Yb, and Lu.

Table A.1. X-ray powder diffraction data for the early RE₄Mo₄O₁₁^a

hkl	Y		Nd		Sm		Eu		Gd		Tb	
110	8.794	8.836	9.084	9.098	9.083	9.020	8.924	8.984	8.998	8.950	8.972	8.902
020	7.859	7.907	8.129	8.123	8.104	8.057	8.001	8.023	8.035	7.996	8.009	7.959
120	6.298	6.349	no		no		6.520	6.449	6.461	6.426	no	
001	5.640	5.650	no		no		no		no		no	
200	5.304	5.327	no		5.445	5.443	5.401	5.422	5.405	5.400	5.394	5.369
130	4.704	4.760	4.858	4.857	4.820	4.817	4.788	4.797	4.792	4.780	4.768	4.757
021	4.583	4.597	no		no		4.685	4.650	no		no	
220	4.403	4.418	4.539	4.549	4.512	4.510	4.481	4.492	4.481	4.475	4.461	4.451
121	4.217	4.221	4.315	4.313	4.294	4.288	4.264	4.274	4.268	4.263	4.256	4.246
040	3.948	3.954	no		no		no		4.002	3.998	no	
201	3.872	3.876	no		no		3.923	3.930	3.910	3.919	3.911	3.902
211	3.759	3.764	3.852	3.856	3.829	3.830	3.811	3.818	3.806	3.806	no	
230	no		no		no		no		"	3.793	3.795	3.775
131	no		no		no		no		3.672	3.662	no	
221	no		3.567	3.566	3.542	3.542	3.526	3.530	3.521	3.519	3.508	3.503
310	3.464	3.465	no		"	3.540	no		no		no	
041	3.235	3.239	no		no		3.280	3.282	3.276	3.273	no	
240	3.167	3.175	no		no		3.226	3.225	3.214	3.213	3.202	3.197
231	3.119	3.123	3.201	3.201	3.180	3.179	3.169	3.167	3.158	3.157	3.145	3.143
141	3.103	3.099	3.171	3.175	3.153	3.153	no		3.134	3.132	3.120	3.119
150	3.025	3.032	no		no		3.101	3.078	3.069	3.067	3.055	3.052
311	2.947	2.954	no		no		2.996	3.000	2.987	2.989	no	
330	no		no		no		2.965	2.993	no		no	
321	2.810	2.812	2.881	2.886	2.861	2.864	2.853	2.853	2.847	2.844	2.832	2.830
002	2.820	2.825	2.871	2.872	"	2.861	"	"	"	2.848	2.842	2.840
241	2.765	2.768	2.837	2.839	2.818	2.818	2.809	2.807	2.798	2.799	2.789	2.786
112	2.684	2.691	no		no		2.718	2.719	2.717	2.714	2.706	2.705
400	2.661	2.664	2.746	2.746	2.720	2.721	2.710	2.711	2.702	2.700	2.685	2.685
060	2.631	2.636	2.707	2.708	2.685	2.686	2.675	2.674	2.665	2.665	2.656	2.653
340	no		no		no		2.682	2.685	no		no	
331	no		2.681	2.682	no		2.653	2.652	2.642	2.643	no	
410	no		no		no		no		no		2.656	2.647
122	2.579	2.581	2.629	2.629	2.618	2.617	2.610	2.609	2.603	2.604	2.595	2.595
160	2.555	2.524	no		no		2.598	2.597	2.588	2.588	2.576	2.576
420	2.520	2.524	no		no		2.566	2.568	2.558	2.558	2.546	2.544
202	2.493	2.496	no		no		2.523	2.525	2.518	2.519	2.509	2.510
212	2.463	2.465	2.514	2.514	2.503	2.507	2.494	2.494	2.491	2.489	2.482	2.480

^ano=not observed; observed and calculated values are in the 1st & 2nd columns under each element, respectively

Table A.1. (continued)

hkl	Y	Nd	Sm	Eu	Gd	Tb
251	no	no	no	no	2.478 2.478	2.469 2.467
401	no	no	no	2.452 2.449	2.444 2.440	no
132	2.421 2.425	no	no	no	" 2.447	no
341	no	2.456 2.458	2.438 2.439	2.431 2.430	2.424 2.421	2.410 2.410
222	no	no	no	no	2.406 2.403	no
430	no	no	no	2.419 2.418	" 2.408	no
260	no	no	2.409 2.410	2.401 2.398	2.392 2.390	2.380 2.378
350	2.360 2.362	no	" 2.408	no	" 2.391	" "
061	2.390 2.389	no	no	no	no	no
411	2.381 2.382	no	no	no	no	2.396 2.399
161	2.327 2.331	no	2.372 2.373	no	2.356 2.356	2.345 2.346
421	no	no	no	2.365 2.364	2.333 2.333	no
042	2.296 2.298	2.343 2.345	2.333 2.333	2.326 2.325	2.320 2.320	2.311 2.312
232	2.255 2.256	2.303 2.303	2.292 2.291	2.284 2.283	2.278 2.278	2.270 2.269
142	2.468 2.247	2.293 2.293	2.279 2.281	2.274 2.273	2.269 2.268	2.259 2.260
431	no	no	no	2.220 2.225	no	no
440	2.207 2.209	no	no	2.246 2.246	no	2.225 2.225
312	2.187 2.189	2.239 2.238	2.223 2.225	2.218 2.218	2.213 2.212	2.203 2.203
351	no	no	no	no	no	no
261	no	no	no	2.202 2.211	2.204 2.204	no
251	no	no	no	no	" 2.205	2.194 2.194
322	2.128 2.129	no	no	no	2.150 2.151	no
360	no	2.176 2.177	2.161 2.159	2.158 2.157	2.142 2.142	no
510	no	no	no	2.150 2.149	no	no
242	2.109 2.110	2.152 2.156	2.145 2.144	2.138 2.137	2.131 2.131	2.123 2.123
152	2.065 2.067	2.113 2.112	2.099 2.099	2.092 2.092	2.087 2.087	no
441	no	no	no	no	no	no
171	no	no	no	no	no	no
450	2.036 2.037	2.097 2.097	2.079 2.079	2.072 2.071	2.063 2.063	2.052 2.053
511	no	no	no	no	no	no
332	no	no	no	2.053 2.066	no	no
530	no	no	no	2.007 2.010	no	no
080	1.975 1.977	no	no	no	2.000 1.999	no
252	1.957 1.959	2.004 2.003	1.991 1.991	1.986 1.984	1.979 1.979	1.972 1.971
180	no	no	no	no	no	no
402	no	no	no	1.966 1.965	1.960 1.960	no
342	1.928 1.930	1.972 1.975	no	1.955 1.955	1.951 1.950	1.937 1.942
412	no	no	no	no	1.945 1.945	" 1.936

Table A.1. (continued)

hkl	Y	Nd	Sm	Eu	Gd	Tb
370	no	no	no	1.941 1.936	1.930 1.929	no
062	1.926 1.927	no	1.959 1.958	1.953 1.951	no	no
162	1.896 1.896	no	no	1.931 1.921	1.916 1.915	no
540	no	no	no	no	no	no
460	1.872 1.873	1.928 1.928	1.911 1.912	1.904 1.904	1.897 1.897	1.886 1.887
280	no	no	no	no	no	no
081	no	no	no	no	no	no
113	no	no	no	1.865 1.861	1.858 1.858	no
023	no	no	no	no	no	no
262	no	no	no	no	1.831 1.831	no
213	no	no	no	no	no	no
352	1.811 1.812	no	no	1.836 1.837	no	no
461	no	no	no	1.808 1.806	no	no
600	1.776 1.776	no	no	no	no	no
541	no	no	no	no	no	no
610	no	no	no	1.799 1.794	no	no
172	no	no	no	1.763 1.763	1.759 1.758	no
442	1.740 1.740	no	no	no	no	no
620	no	no	no	no	no	no
190	1.732 1.734	no	no	no	1.754 1.753	no
380	1.728 1.727	no	no	1.753 1.754	1.747 1.748	no
470	1.725 1.723	no	no	no	no	no
601	no	no	no	no	1.719 1.716	no
512	no	no	no	no	1.712 1.711	no
362	1.691 1.694	no	no	no	no	no
043	no	no	no	1.718 1.719	no	no
630	1.682 1.683	1.734 1.734	no	1.712 1.712	1.705 1.705	no
233	no	1.715 1.715	1.707 1.757	1.702 1.702	1.698 1.698	1.691 1.692
272	no	no	no	1.697 1.698	1.693 1.692	no
143	no	no	no	1.695 1.697	no	no
560	no	no	no	1.687 1.684	no	no
621	no	1.705 1.706	no	no	1.677 1.678	no
313	no	no	no	no	1.671 1.670	no
381	no	no	no	no	" 1.671	no
452	1.653 1.653	1.694 1.694	no	1.676 1.676	" "	no
471	no	" "	no	no	1.666 1.668	no
290	1.668 1.669	no	no	no	no	no
522	1.663 1.663	no	no	no	no	no
323	no	no	no	1.648 1.647	1.644 1.644	no

Table A.1. (continued)

hkl	Y	Nd	Sm	Eu	Gd	Tb
532	no	no	no	no	no	no
631	no	no	no	no	1.634 1.634	no
243	no	no	no	no	no	no
082	1.620 1.620	no	no	no	no	no
333	no	no	no	no	no	no
182	no	no	no	no	1.619 1.618	no
291	1.600 1.600	no	1.630 1.630	1.624 1.624	" "	1.610 1.611
561	no	no	no	no	1.612 1.610	no
480	1.586 1.587	no	no	1.613 1.612	1.606 1.607	no
462	no	no	no	no	no	no
372	1.580 1.580	1.616 1.619	no	1.603 1.602	1.597 1.597	no
1100	no	no	no	no	no	no
641	1.557 1.557	1.603 1.602	1.589 1.589	1.583 1.583	1.577 1.577	no
650	no	no	no	no	no	no
403	no	no	no	1.557 1.557	1.552 1.553	no
063	no	no	no	no	no	no
413	no	no	no	no	no	no
282	no	no	no	no	no	no
570	1.550 1.550	no	no	no	no	no
343	no	no	no	no	no	no
0101	1.522 1.523	no	no	1.544 1.545	1.539 1.540	no
710	no	no	no	no	no	no
602	1.503 1.503	no	no	1.526 1.527	1.522 1.522	no
571	1.495 1.495	no	1.523 1.525	no	1.513 1.513	no
163	1.519 1.517	no	no	1.530 1.535	no	no
2100	1.517 1.516	no	no	no	no	no
651	no	no	no	1.519 1.518	no	no
1101	no	no	no	no	no	no
552	1.499 1.498	no	no	no	no	no
612	1.496 1.497	1.537 1.537	no	no	no	no
720	" 1.495	no	no	no	no	no
263	no	no	no	1.488 1.491	no	no
660	no	no	no	no	no	no
192	1.477 1.477	no	no	1.498 1.498	1.492 1.493	no
622	1.475 1.477	no	no	no	no	no
472	no	no	no	no	no	no
2101	no	no	no	no	1.481 1.481	no
711	1.463 1.463	no	no	no	no	no
721	no	no	no	1.469 1.469	no	no

Table A.1. (continued)

hkl	Y	Nd	Sm	Eu	Gd	Tb
632	no	no	no	" 1.468	no	no
3100	1.445 1.444	no	no	no	1.460 1.462	no
292	1.437 1.437	no	no	1.458 1.457	1.451 1.452	no
740	no	no	no	no	no	no
642	no	no	no	1.434 1.427	no	no
661	no	no	no	no	1.444 1.443	no
731	no	no	no	no	1.434 1.434	no
491	1.420 1.420	no	no	no	no	no
1110	no	no	no	no	no	no
004	1.412 1.412	1.436 1.436	1.430 1.431	1.427 1.427	1.424 1.424	no
670	no	no	no	no	no	no
0102	no	no	no	1.389 1.387	1.395 1.395	no
523	no	no	no	no	no	no
1102	1.370 1.368	no	no	no	1.384	no
204	1.366 1.365	no	no	no	no	no
2111	no	no	no	no	1.363 1.363	no
800	no	no	no	no	1.350 1.350	no
741	no	no	no	no	no	no
750	no	no	no	no	no	no
134	no	no	no	no	no	no
712	no	no	no	no	no	no
722	no	no	no	no	no	no
463	no	no	no	no	no	no
751	no	no	no	no	1.350 1.350	no
3110	1.333 1.333	no	no	no	no	no
821	no	no	no	1.300 1.301	1.331 1.331	no
543	1.329 1.329	no	no	no	no	no
810	no	no	no	no	no	no
820	no	no	no	no	no	no
4101	no	no	no	no	no	no
680	1.322 1.321	no	no	no	no	no
0120	1.318 1.318	no	no	1.326 1.327	no	no
3111	no	no	no	no	1.312 1.312	no
662	1.307 1.306	no	no	no	1.322 1.321	no
801	no	no	no	no	no	no
582	1.290 1.289	no	no	1.309 1.309	no	no
830	no	no	no	no	no	no
3102	1.287 1.286	no	no	no	1.301 1.301	no
613	no	no	no	1.305 1.306	no	no

Table A.1. (continued)

hkl	Y	Nd	Sm	Eu	Gd	Tb
<u>623</u>	no	no	no	no	1.289 1.289	no
<u>0121</u>	no	no	no	no	no	no
<u>473</u>	no	no	no	no	1.284 1.285	no
<u>1112</u>	no	no	no	no	no	no
<u>770</u>	no	no	no	no	1.278 1.279	no
<u>831</u>	no	no	no	1.280 1.280	1.275 1.276	no
<u>633</u>	1.256 1.255	no	no	no	1.269 1.269	no
<u>732</u>	no	no	no	1.318 1.319	no	no
<u>154</u>	no	no	no	1.293 1.294	no	no
<u>742</u>	1.270 1.269	no	no	1.289 1.289	no	no
<u>293</u>	no	no	no	1.265 1.265	1.262 1.262	no
<u>404</u>	no	no	no	no	1.260 1.260	no
<u>831</u>	1.260 1.259	no	no	no	no	no
<u>414</u>	no	no	no	no	1.256 1.256	no
<u>690</u>	1.249 1.249	no	no	no	no	no
<u>2112</u>	1.246 1.246	no	no	no	no	no
<u>064</u>	" 1.245	no	no	1.259 1.259	1.256 1.256	no
<u>264</u>	no	no	no	1.226 1.226	no	no
<u>752</u>	1.233 1.234	no	no	no	no	no
<u>643</u>	1.229 1.228	no	no	no	no	no
<u>802</u>	1.205 1.205	no	no	no	no	no
<u>164</u>	no	no	no	no	no	no
<u>424</u>	no	no	no	no	no	no
<u>4102</u>	no	no	no	no	no	no
<u>354</u>	no	no	no	no	no	no
<u>1103</u>	1.203 1.203	no	no	no	no	no
<u>781</u>	no	no	no	1.199 1.199	no	no
<u>790</u>	no	no	no	1.169 1.169	no	no
<u>841</u>	no	no	no	no	no	no
<u>812</u>	no	no	no	no	no	no
<u>653</u>	no	no	no	no	no	no
<u>910</u>	no	no	no	no	no	no
<u>832</u>	no	no	no	no	no	no
<u>920</u>	no	no	no	no	no	no
<u>1122</u>	no	no	no	no	no	no
<u>514</u>	no	no	no	no	no	no
<u>454</u>	no	no	no	no	no	no
<u>4121</u>	no	no	no	no	no	no

Table A.2. X-ray powder diffraction data for the late RE₄Mo₄O₁₁^a

hkl	Dy		Ho		Er		Tm		Yb		Lu	
110	8.906	8.872	8.862	8.845	8.794	8.814	8.873	8.792	8.896	8.786	8.805	8.770
020	7.976	7.934	7.933	7.908	7.863	7.884	7.926	7.867	7.894	7.842	7.868	7.826
120	no		6.362	6.353	6.324	6.332	no		no		no	
001	no		5.639	5.657	5.623	5.643	no		no		5.615	5.606
200	5.351	5.350	5.338	5.335	5.304	5.315	5.318	5.301	5.296	5.303	5.286	5.294
130	4.748	4.742	4.732	4.726	4.707	4.712	4.713	4.701	4.693	4.689	4.686	4.680
021	no		no		4.589	4.589	no		no		no	
220	4.441	4.436	4.421	4.423	4.401	4.407	4.407	4.396	4.390	4.393	4.368	4.385
121	4.240	4.236	4.227	4.225	4.210	4.213	4.217	4.205	4.202	4.196	4.190	4.186
040	no		3.957	3.954	3.938	3.942	3.945	3.934	3.929	3.921	3.922	3.913
201	3.896	3.891	3.880	3.881	3.889	3.869	3.866	3.862	3.856	3.857	3.848	3.849
211	3.780	3.779	3.770	3.769	3.755	3.758	3.758	3.750	3.745	3.746	3.732	3.738
230	no		3.749	3.750	3.734	3.737	3.733	3.728	no		no	
131	no		no		3.615	3.617	no		3.601	3.601	3.595	3.593
221	no		3.486	3.484	3.473	3.473	3.473	3.466	3.461	3.461	3.447	3.454
310	no		3.467	3.470	3.453	3.457	3.454	3.448	3.440	3.449	no	
041	3.251	3.250	3.241	3.241	3.231	3.232	3.230	3.225	3.221	3.216	3.212	3.209
240	3.190	3.187	3.177	3.177	no		3.164	3.159	no		no	
231	3.135	3.134	3.123	3.126	3.118	3.116	3.107	3.109	3.098	3.104	no	
141	3.112	3.110	3.101	3.101	3.091	3.092	3.088	3.086	3.079	3.078	3.071	3.071
150	3.041	3.043	3.033	3.033	3.022	3.023	3.022	3.017	3.010	3.008	3.001	3.002
311	no		2.955	2.958	2.948	2.948	2.943	2.941	2.933	2.940	2.927	2.934
330	2.962	2.957	no		2.935	2.938	no		no		no	
321	2.822	2.821	2.813	2.814	2.804	2.805	2.799	2.798	2.785	2.796	no	
002	2.837	2.834	2.829	2.829	2.823	2.822	2.819	2.818	2.813	2.810	2.807	2.803
241	2.779	2.778	2.769	2.770	2.761	2.761	2.757	2.755	2.741	2.750	no	
112	2.699	2.700	2.694	2.694	2.685	2.687	2.685	2.683	2.678	2.677	2.673	2.670
400	2.677	2.675	2.667	2.668	2.658	2.658	2.650	2.651	2.643	2.652	2.634	2.647
060	2.645	2.645	2.637	2.636	2.629	2.628	2.623	2.622	2.618	2.614	2.610	2.609
340	no		no		no		no		no		no	
331	no		2.614	2.615	2.605	2.606	no		2.604	2.597	no	
410	no		2.628	2.630	2.619	2.621	no		no		no	
122	2.590	2.590	2.584	2.584	2.578	2.577	2.575	2.573	2.567	2.567	2.562	2.560
160	2.569	2.567	2.559	2.559	2.551	2.551	2.548	2.546	2.539	2.538	2.531	2.533
420	2.534	2.535	2.527	2.528	2.518	2.518	no		no		2.504	2.507
202	2.504	2.505	2.498	2.499	2.493	2.492	no		2.482	2.483	2.475	2.477
212	2.475	2.474	2.468	2.468	2.462	2.462	2.457	2.457	2.452	2.453	2.446	2.447

^ano=not observed; observed and calculated values are in the 1st & 2nd columns under each element, respectively

Table A.2. (continued)

hkl	Dy	Ho	Er	Tm	Yb	Lu
<u>251</u>	2.460 2.459	2.450 2.452	2.444 2.444	2.441 2.439	no	2.420 2.429
<u>401</u>	no	2.412 2.413	no	2.400 2.398	2.393 2.398	2.384 2.394
<u>132</u>	2.433 2.433	2.427 2.427	2.422 2.421	2.418 2.417	2.412 2.411	2.404 2.405
<u>341</u>	2.404 2.402	2.395 2.395	2.388 2.388	no	no	no
<u>222</u>	2.389 2.388	no	no	2.370 2.372	no	no
<u>430</u>	no	no	no	no	no	no
<u>260</u>	no	no	no	no	no	no
<u>350</u>	2.371 2.371	2.363 2.364	2.356 2.356	2.350 2.350	no	2.329 2.340
<u>061</u>	no	no	no	2.370 2.378	2.364 2.370	2.361 2.366
<u>411</u>	no	2.383 2.385	2.376 2.377	no	no	no
<u>161</u>	2.338 2.339	2.331 2.331	2.325 2.325	2.320 2.320	2.313 2.313	2.305 2.308
<u>421</u>	no	no	no	no	no	no
<u>042</u>	2.307 2.306	2.301 2.300	2.296 2.294	2.293 2.291	2.286 2.284	2.280 2.279
<u>232</u>	2.264 2.264	2.258 2.258	2.252 2.252	2.249 2.248	2.244 2.243	no
<u>142</u>	2.255 2.224	2.245 2.249	2.243 2.243	2.241 2.239	2.234 2.233	2.229 2.228
<u>431</u>	no	no	2.204 2.186	no	no	no
<u>440</u>	no	2.211 2.211	2.224 2.204	no	no	no
<u>312</u>	2.199 2.198	2.192 2.192	2.186 2.186	2.182 2.182	2.175 2.179	2.171 2.174
<u>351</u>	2.188 2.187	2.181 2.181	2.174 2.174	2.169 2.169	2.157 2.165	no
<u>261</u>	no	no	no	no	no	no
<u>251</u>	no	no	no	no	no	no
<u>322</u>	no	2.132 2.132	2.149 2.126	no	no	2.108 2.113
<u>360</u>	no	no	no	no	no	no
<u>510</u>	no	2.118 2.115	no	no	no	no
<u>242</u>	no	2.112 2.112	2.108 2.106	2.103 2.103	2.094 2.098	2.088 2.093
<u>152</u>	2.075 2.074	2.069 2.068	2.064 2.063	2.059 2.059	2.054 2.053	2.050 2.049
<u>441</u>	2.065 2.065	2.059 2.060	2.052 2.053	2.048 2.048	no	no
<u>171</u>	no	no	no	" "	no	no
<u>450</u>	2.046 2.045	2.039 2.039	2.033 2.032	2.026 2.027	2.029 2.025	no
<u>511</u>	no	no	1.972 1.974	no	no	no
<u>332</u>	no	no	no	no	no	2.023 2.023
<u>530</u>	no	no	no	no	no	no
<u>080</u>	no	1.977 1.977	no	1.965 1.967	1.962 1.960	1.957 1.957
<u>252</u>	1.966 1.966	1.961 1.961	1.956 1.955	1.950 1.952	1.944 1.945	1.940 1.943
<u>180</u>	no	1.940 1.944	no	no	1.925 1.928	no
<u>402</u>	no	no	1.936 1.935	no	no	no
<u>342</u>	no	1.931 1.932	1.927 1.926	no	no	no
<u>412</u>	no	1.925 1.926	no	no	no	no

Table A.2. (continued)

hkl	Dy	Ho	Er	Tm	Yb	..	Lu
370	no	no	no	no	no		no
062	no	no	no	no	no		1.906 1.910
162	1.903 1.903	1.898 1.898	1.893 1.892	1.889 1.889	1.883 1.884		1.879 1.879
540	no	no	no	no	1.866 1.866		no
460	1.881 1.881	1.875 1.876	1.869 1.869	1.862 1.864	no		1.861 1.858
280	no	1.853 1.854	no	no	no		no
081	no	no	no	no	no		1.847 1.847
113	no	1.844 1.844	no	no	no		no
023	no	1.833 1.834	no	no	no		no
262	no	1.814 1.814	1.809 1.809	1.805 1.805	1.797 1.800		1.793 1.796
213	no	no	1.762 1.762	no	no		no
352	1.818 1.819	no	no	no	no		no
461	no	1.778 1.780	no	no	no		no
600	1.784 1.783	no	1.773 1.772	1.767 1.767	no		1.766 1.765
541	no	no	no	no	1.772 1.771		no
610	no	no	no	no	no		1.757 1.754
172	no	1.742 1.742	1.737 1.737	1.734 1.734	1.731 1.729		no
442	1.746 1.745	no	no	no	no		no
620	1.740 1.740	1.734 1.735	no	no	no		no
190	no	no	1.730 1.729	1.725 1.725	1.720 1.720		1.715 1.716
380	no	1.728 1.728	1.720 1.723	no	no		no
470	no	1.724 1.724	1.718 1.718	no	no		no
601	no	no	no	no	no		no
512	no	1.695 1.694	1.690 1.688	no	no		no
362	no	no	no	no	no		no
043	no	no	1.709 1.698	no	no		no
630	no	1.685 1.685	no	no	no		no
233	1.689 1.689	no	1.680 1.680	1.677 1.678	1.672 1.674		1.668 1.669
272	no	1.676 1.676	1.672 1.671	no	no		no
143	no	no	no	no	no		no
560	no	no	no	no	no		no
621	no	1.658 1.659	1.653 1.653	no	no		no
313	no	no	no	no	no		no
381	no	no	no	no	no		no
452	no	1.654 1.654	1.649 1.649	no	1.648 1.643		no
471	no	no	1.644 1.644	no	no		no
290	no	1.670 1.669	1.662 1.644	no	no		no
522	no	1.665 1.665	1.660 1.660	no	no		1.649 1.652
323	no	1.630 1.630	1.627 1.626	1.623 1.623	no		1.615 1.616

Table A.2. (continued)

hkl	Dy	Ho	Er	Tm	Yb	Lu
532	no	1.622 1.621	no	no	no	no
631	no	1.614 1.615	no	no	no	no
243	no	no	1.618 1.617	no	no	1.605 1.607
082	no	no	no	no	no	no
333	no	no	1.583 1.584	no	no	no
182	no	no	1.597 1.598	no	1.592 1.590	no
291	1.606 1.606	1.602 1.601	no	no	1.585 1.588	1.583 1.585
561	no	no	no	no	no	no
480	no	1.588 1.588	no	no	no	no
462	no	no	1.559 1.558	no	no	no
372	1.586 1.586	1.581 1.581	1.577 1.577	1.572 1.573	no	no
1100	no	1.564 1.564	no	no	no	no
641	no	1.559 1.559	1.554 1.554	no	1.549 1.549	1.544 1.546
650	no	1.551 1.550	no	no	1.540 1.540	1.538 1.537
403	no	1.539 1.539	1.536 1.535	no	no	no
063	no	no	no	no	no	no
413	no	1.534 1.534	no	no	no	1.519 1.519
282	no	no	1.546 1.546	no	no	no
570	no	no	no	no	no	no
343	no	no	1.530 1.531	no	no	no
0101	no	1.524 1.523	1.519 1.518	no	no	1.506 1.508
710	no	1.518 1.517	no	no	no	no
602	no	1.509 1.506	1.501 1.500	no	1.498 1.496	no
571	no	1.496 1.496	no	no	no	no
163	no	no	1.514 1.514	no	1.508 1.507	no
2100	no	no	no	no	no	no
651	no	no	no	no	no	no
1101	1.512 1.513	1.505 1.508	1.504 1.503	no	1.492 1.496	1.489 1.493
552	no	no	1.495 1.495	no	no	no
612	1.502 1.503	1.499 1.499	no	no	no	no
720	no	no	no	no	no	no
263	no	no	no	no	no	no
660	no	no	1.469 1.469	no	no	no
192	no	1.479 1.479	1.474 1.474	no	no	1.462 1.464
622	1.483 1.483	no	no	no	no	no
472	no	1.473 1.472	no	no	no	no
2101	no	no	no	no	no	no
711	no	1.465 1.466	1.460 1.460	no	no	no
721	no	no	no	no	no	no

Table A.2. (continued)

hkl	Dy	Ho	Er	Tm	Yb	Lu
632	no	no	no	no	no	no
3100	no	1.446 1.445	1.441 1.441	no	no	no
292	no	1.438 1.437	1.434 1.433	no	no	no
740	no	no	1.417 1.417	no	no	no
642	no	no	no	no	no	no
661	no	no	no	no	no	no
731	no	no	no	no	no	no
491	no	1.422 1.420	no	no	no	1.410 1.410
1110	no	no	no	no	no	no
004	1.417 1.417	1.414 1.414	1.412 1.411	1.409 1.409	no	1.404 1.401
670	no	no	1.396 1.393	no	no	no
0102	no	no	no	no	no	no
523	no	no	1.387 1.387	no	no	no
1102	no	1.370 1.369	1.365 1.365	no	1.358 1.358	no
204	no	no	no	no	no	no
2111	no	no	no	no	no	no
800	no	1.337 1.334	no	no	1.325 1.326	1.323 1.324
741	no	no	1.377 1.374	no	no	no
750	no	no	1.372 1.368	no	no	no
134	no	no	1.351 1.368	no	no	no
712	no	no	1.332 1.332	no	no	no
722	no	no	no	no	1.315 1.315	1.313 1.312
463	no	no	1.324 1.326	no	no	no
751	no	no	1.329 1.330	no	no	no
3110	no	no	no	no	no	no
821	no	no	no	no	no	no
543	no	1.333 1.331	no	no	no	no
810	no	1.329 1.329	no	no	no	no
820	no	no	1.310 1.310	no	no	no
4101	no	1.323 1.323	no	no	no	no
680	no	no	no	no	no	no
0120	no	1.318 1.318	no	no	1.308 1.307	1.306 1.304
3111	no	1.298 1.297	no	no	no	no
662	no	1.308 1.307	1.303 1.303	no	1.300 1.299	1.297 1.296
801	no	no	1.293 1.293	no	no	1.290 1.288
582	no	1.291 1.291	1.286 1.286	no	no	no
830	no	no	no	no	no	1.284 1.285
3102	no	1.287 1.287	1.283 1.283	no	no	no
613	no	no	no	no	no	1.278 1.279

Table A.2. (continued)

hkl	Dy	Ho	Er	Tm	Yb	Lu
<u>623</u>	no	1.276 1.277	no	no	no	no
<u>0121</u>	no	no	no	no	no	1.272 1.270
<u>473</u>	no	no	no	no	no	no
<u>1112</u>	no	no	no	no	no	1.261 1.260
<u>770</u>	no	no	no	no	no	1.255 1.253
<u>831</u>	no	1.260 1.261	1.255 1.256	no	no	no
<u>633</u>	no	1.256 1.257	no	no	no	no
<u>732</u>	no	no	no	no	no	no
<u>742</u>	no	1.270 1.271	1.266 1.266	no	no	no
<u>154</u>	no	no	no	no	no	no
<u>293</u>	no	no	no	no	1.241 1.241	no
<u>404</u>	no	no	no	no	no	no
<u>831</u>	no	no	no	no	no	no
<u>414</u>	no	no	no	no	no	no
<u>064</u>	no	no	1.242 1.243	no	1.238 1.238	1.236 1.235
<u>690</u>	no	1.250 1.250	no	no	no	no
<u>2112</u>	no	no	no	no	no	no
<u>264</u>	no	1.213 1.214	no	no	no	no
<u>752</u>	no	no	no	no	no	no
<u>643</u>	no	1.229 1.230	no	no	no	no
<u>802</u>	no	no	1.201 1.202	no	no	no
<u>164</u>	no	no	1.235 1.235	no	no	no
<u>424</u>	no	no	1.230 1.231	no	no	no
<u>4102</u>	no	no	1.225 1.222	no	no	no
<u>354</u>	no	no	1.209 1.210	no	no	no
<u>1103</u>	no	no	no	no	no	no
<u>781</u>	no	1.182 1.181	1.177 1.177	no	no	no
<u>790</u>	no	no	no	no	no	no
<u>841</u>	no	1.234 1.233	no	no	no	no
<u>812</u>	no	1.206 1.203	no	no	no	no
<u>653</u>	no	1.197 1.198	1.193 1.194	no	no	no
<u>910</u>	no	1.186 1.182	no	no	no	no
<u>832</u>	no	1.175 1.176	no	no	no	no
<u>920</u>	no	1.171 1.172	1.167 1.168	no	no	no
<u>1122</u>	no	no	1.183 1.184	no	no	no
<u>514</u>	no	no	1.172 1.173	no	no	no
<u>454</u>	no	no	1.158 1.159	no	no	no
<u>4121</u>	no	no	1.152 1.153	no	no	no

APPENDIX B

**MAGNETIC SUSCEPTIBILITY FIGURES FOR SELECTED
 $\text{RE}_4\text{Mo}_4\text{O}_{11}$ MEMBERS**

Magnetic susceptibility measurements for the $\text{RE}_4\text{Mo}_4\text{O}_{11}$ series where $\text{RE} = \text{Y, Nd, Eu, Gd, Tb, Dy, Tm, Yb, and Lu}$ are given in the following pages. For those members which are not reported, the magnetic measurements did not give results characteristic of single phase material containing RE(III) cations. This behavior is not unusual since the purity, based upon x-ray powder diffraction, is only reliable in detecting impurities of ~5-20% in samples. Molar susceptibilities are denoted by a line through data points drawn as vertical bars. Inverse molar susceptibilities are shown with a line through data points drawn as horizontal bars. The Curie-Weiss fit, if appropriate, is drawn as a line through the inverse molar susceptibility data.

Figure B.1. Molar susceptibility versus temperature of $\text{Y}_4\text{Mo}_4\text{O}_{11}$ with paramagnetic impurity tail.

Figure B.2. Molar and inverse molar susceptibility versus temperature of $\text{Nd}_4\text{Mo}_4\text{O}_{11}$.

Figure B.3. Molar and inverse molar susceptibility versus temperature of $\text{Eu}_4\text{Mo}_4\text{O}_{11}$.

Figure B.4. Molar and inverse molar susceptibility versus temperature of $\text{Gd}_4\text{Mo}_4\text{O}_{11}$.

Figure B.5. Molar and inverse molar susceptibility versus temperature of $\text{Tb}_4\text{Mo}_4\text{O}_{11}$.

Figure B.6. Molar and inverse molar susceptibility versus temperature of $\text{Dy}_4\text{Mo}_4\text{O}_{11}$.

Figure B.7. Molar and inverse molar susceptibility versus temperature of $\text{Tm}_4\text{Mo}_4\text{O}_{11}$.

Figure B.8. Molar and inverse molar susceptibility versus temperature of $\text{Yb}_4\text{Mo}_4\text{O}_{11}$.

Figure B.9. Molar susceptibility versus temperature of $\text{Lu}_4\text{Mo}_4\text{O}_{11}$ with paramagnetic impurity tail.

DATE

FILMED

2 / 14 / 94

END