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Reduction of Molybdenum and Tungsten Halides in Sodium Tetra-
haloaluminate Melts

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Reduction of molybdenum and tungsten halides in sodium
tetrahaloaluminate melts

by

William Clifford Dorman

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TABLE OF CONTENTS

	Page
ABSTRACT	v
INTRODUCTION	1
REVIEW OF PREVIOUS WORK	2
EXPERIMENTAL	15
RESULTS AND DISCUSSION	25
SUMMARY	33
SUGGESTIONS FOR FUTURE WORK	34
ACKNOWLEDGEMENTS	37
BIBLIOGRAPHY	38

ABSTRACT

Aluminum reduction of molybdenum and tungsten higher chlorides and bromides in the appropriate sodium tetrahaloaluminate melt has been shown to be a convenient and safe procedure for the preparation of the corresponding molybdenum and tungsten(II) chlorides and bromides in good yields. The anhydrous dihalides $(M_6X_8)X_4$, their hydrates $(M_6X_8)X_4 \cdot 2H_2O$, and their acid hydrates $(H_3O)_2[(M_6X_8)X_6] \cdot 6H_2O$ are all known to contain the hexanuclear metal cluster configuration with eight bridging internal halides.

The dichloride and dibromide of molybdenum were prepared by reduction of $MoCl_5$ with Al in NaCl- $AlCl_3$, and with Al in NaBr- $AlBr_3$, respectively. The reactions were carried out in a sealed Pyrex ampoule at 450° for two days on a wrist action shaker. After reaction, the products were ground and extracted with water and then with ethanol to remove all of the metal halide cluster species. The volumes of these supernatant solutions were reduced and the acid hydrates, $(H_3O)_2[(Mo_6X_8)X_6] \cdot 6H_2O$, could be crystallized from solution by the addition of a large excess of the appropriate concentrated hydrohalic acid. These acid hydrates were decomposed in vacuo at ca. 200° to give the corresponding dihydrate, $(Mo_6X_8)X_4 \cdot 2H_2O$.

The preparations of the tungsten(II) chloride and bromide were parallel to the techniques and procedures used in the preparations of the analogous molybdenum compounds. Tungsten (II) chloride was prepared by reduction of WCl_6 with Al in NaCl-AlCl₃. The dibromide was prepared by reduction of WBr_5 in NaBr-AlBr₃, also with Al metal. The reactions were carried out in sealed Vycor reaction tubes at 550°, for one and two days respectively, in a rocking furnace. After reaction the products were treated in the same manner as for the molybdenum species to give the corresponding acid hydrates, $(H_3O)_2 [(W_6X_8)X_6] \cdot 6H_2O$. The acid hydrates were decomposed in vacuo at ca. 350° to produce the corresponding anhydrous compounds, $(W_6X_8)X_4$.

Analytical data taken on the dihydrates and the anhydrous compounds confirmed halogen to metal ratios of 2.

INTRODUCTION

Compounds containing hexanuclear clusters of niobium, tantalum, molybdenum and tungsten atoms have been known for many years. Even though these lower oxidation state compounds have been the subject of several recent studies, there remain many problems and anomalies. For example, the attempted synthesis of the dihalides of molybdenum and tungsten, containing hexanuclear cluster of metal atoms, in fused salt media have raised questions about their stability and mode of formation. Although the molybdenum and tungsten cluster compounds appear to be more stable than those of niobium and tantalum, their synthesis up to now has been more difficult to achieve.

Since the successful preparation of the new mixed-metal cluster compounds $[(C_2H_5)_4N]_3[(Ta_5MoCl_{12})Cl_6]$ and $[(C_2H_5)_4N]_2[(Ta_4Mo_2Cl_{12})Cl_6]$ in acidic sodium tetrachloroaluminate melts, by Dr. J. L. Meyer in this laboratory, it was felt that an entire series of mixed-metal hexanuclear clusters might exist. However, early attempts to prepare such species containing more than two molybdenum atoms in the hexanuclear cluster were unsuccessful. Furthermore it appeared that the yields of molybdenum cluster species $(Mo_6X)_8^{4+}$ in the fused salt media were very low. Thus the purpose of this investigation was to find the optimum conditions for the syntheses of the dihalides of molybdenum and tungsten in an acidic molten salt media.

REVIEW OF PREVIOUS WORK

Syntheses.- Investigation of the molybdenum dihalides was begun in 1859 by Blomstrand (1). Repeated volatilizations of molybdenum(III) chlorides and bromides, in a stream of carbon dioxide, produced the corresponding dihalides. Muthmann and Nagel (2) determined the molecular weight of molybdenum(II) chloride in absolute alcohol and found it to correspond to the trimeric formula (Mo_3Cl_6). By evaporation of a strongly acidic hydrochloric acid solution of the dichloride, Rosenheim and Kohn (3) crystallized the acid salt ($\text{Mo}_3\text{Cl}_6 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$). They noted that only three-sevenths of the chlorine in the compound was ionizable.

In the early 1920's, Lindner (4) began a study of the hexanuclear molybdenum clusters with the synthesis of molybdenum(II) chloride by aluminum reduction of molybdenum(V) chloride. Hellriegel (5) and Senderoff and Brenner (6) found molybdenum metal to be a successful reducing agent in the preparation of the dihalides. Lewis et al. (7) thermally decomposed molybdenum(III) iodide in an oxygen free atmosphere to produce the diiodide. Similarly, the trichlorides and bromides can be disproportionated to produce the corresponding dichloride and bromide, as found by Couch and Brenner (8), and Robinson (9). Lindner and Hellwig (10), and Durand et al. (11) prepared molybdenum(II) bromide directly from the ele-

ments at 600°-700°. By reacting molybdenum metal with aqueous hydrogen bromide at 700° under 3000 atmospheres of supporting pressure, Guggenberger and Sleight (12) obtained orange crystals of the dihydrate, $(\text{Mo}_6\text{Br}_8)\text{Br}_4 \cdot 2\text{H}_2\text{O}$. Lindner et al. (13) found that molybdenum(II) chloride could be synthesized by passing phosgene over molybdenum metal in a dry atmosphere at 600°.

Matsuzaki et al. (14) followed the disproportionation and hydrogen reduction of several molybdenum halides by a thermogravimetric method. In this study the compounds MoCl_4 , $\text{MoCl}_{3.3}$, $\text{MoCl}_{3.0}$, and $\text{MoCl}_{2.9}$ were found to disproportionate to MoCl_2 at about 390°. The compounds $\text{MoCl}_{3.3}$ and $\text{MoCl}_{2.9}$ have not been reported elsewhere and their existence needs to be verified.

Three isomers of molybdenum(II) chloride, which do not seem to contain the hexanuclear $(\text{Mo}_6\text{Cl}_8)^{4+}$ moieties, were prepared by Holste and Schäfer (15). After tempering two of these isomers for 14 days at 350° a yield of about 2% of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$ was extracted from each of them. The third isomer provided about 80% of the cluster species after the same treatment.

There are numerous anionic and neutral complexes of the molybdenum dihalides. In the early literature, these complexes were reported as complexes of the trimeric form (Mo_3Cl_6) . Lindner (4,16) prepared the acid hydrates (3), $\text{H}(\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O})$ and $\text{H}(\text{Mo}_3\text{Cl}_4\text{Br}_3 \cdot \text{H}_2\text{O})$ by extracting molybdenum

dichloride in the appropriate aqueous hydrogen halide. Lindner, Kohler and Hellwig (4,10) prepared the pyridinium salts of the hydrates by adding the cation to acidified solutions of the dihalides. Such salts as $(\text{PyH})(\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O})$ and the analogous bromide were precipitated.

Sheldon (17-20) prepared an entire series of anionic compounds that are derivatives of the acid hydrates. These compounds of the molybdenum clusters were crystallized from the appropriate hydrohalic acid and the general formula $\text{M}'_2(\text{Mo}_6\text{X}_8)\text{Y}_6$ where $\text{M}' = \text{M}(\text{I})^+$, H_3O^+ , PyH^+ , $(\text{C}_6\text{H}_5)_3\text{PH}^+$, NH_4^+ , or R_4N^+ ; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; $\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{OH}$. Sheldon arrived at the hexanuclear formulation on the basis of molecular weight data. Conductivity studies showed members of this series of compounds to be 2:1 electrolytes in nitrobenzene. Other members of the above series of compounds have been prepared, in a similar manner, and verified by the following workers: Mackay (21), Cotton et al. (22), Clark et al. (23), and Hartley and Ware (24). The bromide derivatives were prepared in iodine monobromide by Opalovskii and Samoilov (25).

Rosenheim and Kohn (3) prepared a new series of anhydrous compounds, $(\text{M}_6\text{X}_8)\text{Y}_4$, by the thermal decomposition of the above mentioned acid hydrate salts. Sheldon (18,20), Mackay (21), and Mattes (26) prepared this series where $\text{M} = \text{Mo}$; $\text{X} = \text{Cl}, \text{Br}, \text{I}$; and $\text{Y} = \text{Cl}, \text{Br}, \text{I}, \text{OH}$. Hogue and McCarley (27) have published a study of this series for $\text{M} = \text{W}$.

Other studies have shown the labile nature of the external halogens and the ease by which they can be removed. Such salts as the nitrates, sulfates and perchlorates can easily be prepared. Other neutral complexes are also known in which the external halides may be substituted by neutral ligands. Although this area of study is pertinent to the elucidation of the chemistry of the lower oxidation states of molybdenum, it is beyond the scope of this work.

Using tracer techniques with radioactive chloride and bromide solutions, Sheldon (19) demonstrated that the outer halogens of $(\text{Mo}_6\text{Cl}_8)\text{X}_6^{2-}$ exchange rapidly but no exchange of the internal halogens was observed. Further study (17) showed that while the cluster is completely disrupted by fluoride, thiocyanate and concentrated hydroxide solutions, there is some exchange, maintaining the integrity of the cluster, of internal halogen with hydroxide in dilute solutions (20,28,29), as demonstrated by the compound $(\text{Et}_4\text{N})_2(\text{Mo}_6\text{Cl}_7(\text{OH}))\text{Cl}_6$ (30). Schäfer et al. (31) has verified the study by Sheldon (20) who, starting with molybdenum(II) chloride, prepared the dibromides and diiodides of molybdenum in melts of the appropriate lithium halide. The study by Schäfer was much more thorough in that he prepared the entire series of compounds: $(\text{Mo}_6\text{X}_4^{\text{i}}\text{X}'^{\text{i}}_4)\text{X}_4^{\text{o}}$, where X^{i} , X'^{i} , X^{o} = Cl, Br, or I. The investigation of the thermal $\text{X}^{\text{i}}/\text{X}^{\text{o}}$ exchange demonstrates that the heavier halogen goes from the X^{o} position into the

X^i position. An exception was found in the case of the reaction of $(Mo_6X_8^i)X_4^O$ with melts of HgY_2 at 400° where $X = Cl, Br, I$; and $Y = Cl, Br, I$ (32). The compounds $Hg(Mo_6X_8)Y_6$ and $Hg(Mo_6Y_8)Y_6$ are found. X-ray evidence (33) shows an inversion of the usually observed direction of substitution in $(Mo_6X_8^i)X_4^O$. That is, in these compounds a heavier halogen initially in the X^i position is always substituted by a lighter halogen originating from the X^O positions or the HgY_2 melt.

In his extensive study, Sheldon noted (17) that $(Mo_6Cl_8)Cl_4$ decomposes above 300° in air and 800° in vacuo. The cluster is unaffected by boiling lithium iodide trihydrate at 200° , disproportionates slowly in fused lithium chloride at 610° , and in potassium chloride at 770° disproportionates very rapidly (20). The disproportionation products were identified as molybdenum metal and potassium hexachloromolybdate(III).

Before beginning a review of the chemistry and preparations of the hexanuclear cluster compounds of tungsten, it is interesting to point out here that there are only two violations of the sanctity of the (M_6X_{12}) configuration for the clusters of niobium and tantalum and the (M_6X_8) configuration for the clusters of molybdenum and tungsten. Siepmann et al. (34), in an attempt to oxidize the tungsten(II) chloride cluster, reacted $(W_6Cl_8)Cl_4$ with liquid chlorine at 100° to produce the (M_6X_{12}) moiety in $(W_6Cl_{12})Cl_6$. The other excep-

tion is $(\text{Nb}_6\text{I}_8)\text{I}_3$ identified by Bauer et al. (35) and Simon et al. (36), who later confirmed its formulation as $(\text{Nb}_6\text{I}_8)\text{I}_{6/2}$ through single crystal X-ray (37) analysis. Independently, Bateman et al. (38) also arrived at the same formulation on crystals prepared by Kust et al. (39). Nb_6I_{11} can be prepared by the disproportionation of $\gamma\text{-(Nb}_3\text{I}_8)$ (37,38) or by the niobium reduction of the same compound (37). Nb_6I_{11} will absorb hydrogen above 300° at atmospheric pressure to form a hydride of limiting composition $\text{H}(\text{Nb}_6\text{I}_{11})$ (37,40).

A variety of methods have been used to synthesize the lower oxidation states of tungsten halides. Higher halides have been reduced with metals, hydrogen and other known reducing agents. Intermediate oxidation states halides have been disproportionated to give the appropriate dihalide, and tungsten metal has been oxidized in controlled halogen atmospheres.

Hill (41) prepared tungsten(II) chloride by the sodium amalgam reduction of tungsten(VI) chloride. It was demonstrated by Lindner and Kohler (42) that aluminum would produce higher yields of the dichloride than would lead, zinc or magnesium when reducing the hexachloride. Murray (43) used aluminum in reducing tungsten(V) bromide to tungsten(II) bromide in a temperature gradient furnace. Hydrogen reduced tungsten(V) bromide, at 450° , will also yield the dibromide as indicated by Emeleus and Gutman (44). McCarley and Brown disproportionated the tetrahalides of tungsten to obtain the corresponding tungsten(II) chlorides and bromides (45).

The reactions of the lower halides have been studied in a variety of aqueous and non-aqueous media. Anionic complexes have been prepared from acidic solutions and neutral complexes from solutions in donor solvents. Oxidation, thermal decomposition and chemical disruption of the halides have also been studied.

Unlike Lindner (4,16), who formulated the chloroacid of molybdenum as a trimer, Hill (41) formulated the chloroacid of tungsten as $(W_6Cl_8)Cl_4 \cdot 2HCl \cdot 9H_2O$. In the same manner as Lindner, Hill extracted the dichloride of tungsten into hydrochloric acid to prepare the chloroacid.

As in the analogous case of molybdenum by Rosenheim and Kohn (3), Lindner and Kohler (42) observed the loss of hydrogen chloride upon heating the hydrated tungsten chloroacid. As was mentioned in the review of work pertaining to the preparation of molybdenum(II) halides, the thermal decomposition of the acid hydrates led to an entire series of pure and mixed anhydrous clusters, $(M_6X_8)Y_4$, where $M = Mo$; $X = Cl, Br, I$; $Y = Cl, Br, I, OH$, for Sheldon (18,20), Mackay (21) and Mattes (26), and $M = W$ for Hogue and McCarley (27).

Although oxidation of niobium and tantalum clusters is well documented, little success has been found in oxidizing derivatives of molybdenum and tungsten clusters. McCarley and Brown (46) utilized liquid bromine as solvent and reactant to oxidize tungsten(II) bromide to tungsten(III) bromide.

Siepmann and Schäfer (47-49) studied the system in more detail and found the compounds W_6Br_{14} , W_6Br_{16} , W_6Br_{18} were all derivatives of the $(W_6Br_8)^{6+}$ cluster. Thermal decomposition of any of the oxidized forms produced $(W_6Br_8)Br_4$. Siepmann *et al.*, as mentioned before, (34) in an attempt to oxidize the tungsten(II) chloride cluster to $(W_6Cl_8)^{6+}$ in liquid chlorine, instead converted the $(W_6Cl_8)^{4+}$ cluster to the $(W_6Cl_{12})^{6+}$ cluster, $(W_6Cl_{12})Cl_6$.

Lindner and Kohler (42) reported that tungsten(II) chloride was hydrolyzed in basic solutions, but was stable in sulfuric acid from which they isolated $(W_3Cl_4)SO_4$, which now should be formulated as $(W_6Cl_8)(SO_4)_2$.

Physical Characterizations.- Large amounts of physical data have been recorded for the dihalides of molybdenum and tungsten and their derivatives. Conductivity measurements and molecular weight data have been taken; magnetic susceptibilities and electronic spectra have been interpreted in terms of the configurations of the molecules. Some single crystal X-ray studies have been completed along with some corroborative powder diffraction studies which elucidate the hexanuclear clusters of the metal atoms. Along with the structural data, Raman and infrared spectra have been extended, through normal coordinate analysis, to include similar clusters. Insight into the chemical and physical properties of the hexanuclear metal atom clusters has been gained through theoretical

interpretations of the molecular orbitals and the bonding involved.

Nothing surprising is found in the magnetic studies of the dihalides and their derivatives. The pure and mixed anhydrous dihalides of molybdenum and tungsten, $(M_6X_8)Y_4$, where $M = Mo, W$; $X = Cl, Br, I$; $Y = Cl, Br, I$, were found to be diamagnetic by Tjabbes (50), Klemm and Steinberg (51), Sheldon (18,20), Schäfer and Schnering (52), and Schäfer and Siepmann (49). Sheldon (18,30), and Edwards (53) found that derivatives such as the acid hydrates, their non-proton cation analogs and the dihalide tetraamines were also diamagnetic. It is interesting to note that McCarley and Brown (54), and Schäfer and Siepmann (49) found the oxidized forms, (W_6Br_{14}) , (W_6Br_{16}) , and (W_6Br_{18}) were paramagnetic.

The electronic spectra of the molybdenum(II) and tungsten(II) chlorides and bromides have been investigated by several workers. The molybdenum cluster hexahalo anions, anhydrous dihalides, and neutral adducts have been studied by Sheldon (17,19,20), Edwards (53), Carmichael and Edwards (55), and Fergusson et al. (56). Murray (43) and Schäfer and Siepmann (48,49) studied tungsten(II) bromide. In general, one or more charge transfer bands were observed in the 300-360 nm range, but no indication was found for the ligand field spectra one might expect from a d^4 ion.

The hexanuclear metal clusters have been confirmed by

single crystal X-ray determinations. Brosset (57,58) analyzed single crystals of $(\text{Mo}_3\text{Cl}_4)(\text{OH})_2 \cdot 8\text{H}_2\text{O}$ and $(\text{Mo}_3\text{Cl}_4)\text{Cl}_2 \cdot 4\text{H}_2\text{O}$ and found both to contain the $(\text{Mo}_6\text{Cl}_8)\text{X}_4$ groups, where X = chlorine or the oxygen of hydroxide or water. The inner (M_6X_8) cluster consists of a very nearly regular octahedron of molybdenum atoms with an average Mo-Mo distance of 2.63 Å. A chlorine atom is symmetrically located above each of the eight triangular faces of the metal octahedron forming three molybdenum-chlorine bonds at 2.56 Å. The remaining constituents, X, are located directly out from each molybdenum along the C_4 axes at a distance of 2.43 Å for X = Cl. Brosset (59), from the X-ray radial distribution curves of $\text{H}(\text{Mo}_3\text{Cl}_7 \cdot \text{H}_2\text{O}) \cdot 3\text{H}_2\text{O}$ in concentrated ethanol solution, confirmed the formulation of the ions as $(\text{Mo}_6\text{Cl}_8)\text{Cl}_6^{2-}$. Vaughan (60), utilizing the radial distribution method, studied a powdered sample of $(\text{NH}_4)_2^{+}(\text{Mo}_6\text{Cl}_8)\text{Cl}_6 \cdot \text{H}_2\text{O}$ and also verified the presence of the $(\text{Mo}_6\text{Cl}_8)\text{Cl}_6^{2-}$ group having the above mentioned bond lengths. Single crystal studies led Schäfer et al. (61) to formulate molybdenum dichloride as $(\text{Mo}_6\text{Cl}_8)\text{Cl}_{4/2}\text{Cl}_2$, with the internal $(\text{M}_6\text{X}_8)^{4+}$ cluster. The Mo-Mo bond lengths are 2.61 Å and the Mo-Cl distances are 2.47 Å. The four external chlorines, which bridge to four adjacent clusters, have a Mo-Cl distance of 2.50 Å. The non-bridging external halogens, Cl, had a Mo-Cl distance of 2.38 Å.

Siepmann and Schnering (62) performed a single crystal

X-ray study of the oxidized tungsten bromide clusters. They found that crystals of (W_6Br_{16}) contained the polynuclear $(W_6Br_8)^{6+}$ cluster and polybromide anions, Br_4^{2-} . From their study they arrived at the formulation $(W_6Br_8)Br_4(Br_4)_{2/2}$ indicating that the cluster is surrounded by four terminal bromides and two bridging polybromide anions. Bond lengths reported were: $d(W-W) = 2.64$, $d(W-Br^i) = 2.58$, $d(W-Br^o) = 2.58 \text{ \AA}$.

Schäfer et al. (52,61), McCarley and Brown (45), Murray (43) and Clark et al. (23) have shown that anhydrous compounds having the general composition $(M_6X_8)X_{4/2}X_2$ are all isostructural. Sheldon (20) used powder patterns to show that $(Mo_6Br_8)(OH)_4 \cdot 14H_2O$ was isomorphous with the analogous chloride reported in Brosset's (57) single crystal studies. Mackay (21) found that the $Cs_2(Mo_6Cl_8)X_6$, where $X = Cl, Br, I$, salts were all isomorphous. The haloacids, $H_2(M_6Cl_8)X_6 \cdot 8H_2O$, where $M = Mo, W$; $X = Cl, Br$, are also isostructural as found by Clark et al. (23). Their study also showed the bidentate ligand derivatives $(M_6Cl_8)Cl_2(O\text{-phen})$ for both molybdenum and tungsten to be isomorphous.

Recently the far infrared spectra of a number of cluster compounds have been investigated. The hexahaloanions, $(Mo_6X_8)Y_6^{2-}$ have been studied by Mackay (21), Cotton et al. (22), Clark et al. (23), and Hartley and Ware (24). Mackay (21), Clark et al. (23), and Mattes (26) also investigated the

spectra of the anhydrous compounds $(M_6X_8)Y_4$. The bidentate ligand adducts of the clusters, $(M_6Cl_8)Cl_2B_2Cl_2$, gave similar spectra to the above hexahaloanions and the anhydrous derivatives as reported by Clark et al. (23) and Walton and Edwards (63). Hogue and McCarley (27) reported a study of compounds containing tungsten halide clusters. Their report contains a comprehensive study of the spectra of these compounds.

Although there are some differences in the assignments, the spectra are similar and the authors base their assignments on octahedral symmetry with two M-X modes, one M-M mode, one M-Y and one X-M-Y mode allowed in the infrared. It is generally agreed that these modes are not purely independent.

Sheldon (17), in discussing the bonding in the hexahaloanions of molybdenum, described the halogen configuration about each Mo as a tetragonal pyramid. This bonding configuration used the $d(x^2-y^2)sp^3$ hybrid orbitals for Mo-X (internal halogens) and Mo-Y (external halogens) bonding. The $d(xz,yz)$ orbitals were then used for metal-metal bonding. The remaining molybdenum electrons were considered to occupy the remaining metal d orbitals. Gillespie (64) described the structure in terms of a distorted square antiprism of bonding electrons around the metals. He arrived at a description of the bonding in $(Mo_6Cl_8)^{4+}$ and $(Nb_6Cl_{12})^{2+}$ which utilized all of the metal electrons in the bonding. His description, however, did require severely bent, localized Mo-X bonds.

Crossman et al. (65) first proposed a molecular orbital treatment for the bonding in the $(\text{Mo}_6\text{Cl}_8)^{4+}$ and $(\text{Ta}_6\text{Cl}_{12})^{2+}$ clusters. In each case the bonding orbitals, formed from hybrid metal orbitals, are just filled with the electrons that are available. Cotton and Haas (66) used a similar approach, but reserved some of the available orbitals for specific bonding. Metal orbitals used to bond with the internal halogens were $d(x^2-y^2)$, s , $p(x,y)$. The metal $p(z)$ orbital was used for bonding to atoms located externally to the metal cluster on the C_4 axis. LCAO-MO wave functions of the proper symmetry were constructed for the remaining metal d orbitals. The resulting molecular orbital energy level diagram accounted for the diamagnetism, the metal-metal bond order and the relative chemical reactivity of internal and external halogens in the clusters. Kettle (67) employed a forty electron model including metal-halogen interactions to show the similarity in the bonding of the $(\text{Mo}_6\text{Cl}_8)^{4+}$ and the $(\text{Ta}_6\text{Cl}_{12})^{2+}$ clusters. In the former, 24 electrons were used in 12 metal-metal bonding orbitals along the octahedral edges and 16 electrons were used in 8 bonding orbitals in metal-halogen bonds directed normal to the octahedral faces. In the latter, 16 electrons were used in the metal-metal bonding and 24 electrons in the metal-halogen bonding.

EXPERIMENTAL

Equipment.- All syntheses, of starting materials and products, were carried out in evacuated Pyrex or Vycor glass systems. All air sensitive reactants and products were stored and handled in a dry box under an atmosphere of argon or prepurified nitrogen with a working dew point of ca. -85°. The nitrogen was circulated through Linde 4A molecular sieves to maintain this level of purity and dryness.

Materials.- Molybdenum metal, purity reported to be 99.9%, was obtained from the Rembar Corporation as 4 x 8 inch sheets with a thickness of 15 mil.

Tungsten metal, as 200 mesh powder, 99.9% pure, was obtained from General Electric Co.

Aluminum round of 99.999% nominal purity was obtained from laboratory stock. To maintain the purity, turnings from the aluminum rod were cut with a tungsten carbide bit to prevent iron contamination.

All other chemicals, used in syntheses and separations, were of reagent grade purity and used as obtained.

Analyses.- Analysis for chlorine and bromine was carried out by a potentiometric titration with standard silver nitrate solution in an acidic media. The cluster species, both molybdenum and tungsten, were destroyed in strongly

basic hydrogen peroxide solution. These solutions were carefully acidified with nitric acid to a pH of ca. 5-6. The solutions were then titrated potentiometrically using a standard calomel electrode versus a silver/silver chloride electrode.

Analysis for tungsten metal was the standard gravimetric method weighing the tungsten as the oxide, WO_3 . Weighed samples were placed in tared crucibles and wetted with a few milliliters of acetone. The crucibles were suspended above a hot plate on a porcelain desiccator tray. As soon as the acetone evaporated, a few milliliters of concentrated nitric acid was added to the solid. The process was continued until the solids in the crucible were white or light yellow. All the moisture was removed while the samples were yet above the hot plate. The crucibles were then heated in a muffle furnace at 500° until the solid was completely converted to WO_3 .

The initial analysis for molybdenum was done gravimetrically as the lead(II) molybdate according to the method described by Vogel (68).

A second and generally easier method also was used for the determination of molybdenum. A carefully weighed sample was decomposed in base and peroxide. The solution was made very slightly acidic with sulfuric acid and boiled for an hour to insure complete absence of peroxide. The solution,

roughly 50 ml in volume, was diluted to about 100 ml with 1-2 N sulfuric acid, passed down a Jones Reductor column, reduced to Mo(III), and passed into an excess of iron(III). The molybdenum was oxidized to Mo(VI) and the resulting Fe(II) was titrated with a standard solution of ceric sulfate. The titration was carried out potentiometrically with a standard calomel reference electrode versus a platinum electrode.

Syntheses.- High purity aluminum chloride was obtained by resubliming reagent grade aluminum chloride, under dynamic vacuum at ca. 125°, in the presence of a small amount of high purity aluminum metal. High purity aluminum chloride was also obtained by passing electronic grade (99.99%) hydrogen chloride, obtained from Air Products and Chemicals, Inc., over turnings of the high purity aluminum metal at 300°.

Kuhn (69), using direct chlorination of the metal, has outlined the method for preparation of tantalum pentachloride. As modified by Meyer (70), large amounts (ca. 250 g) of chlorides of tantalum and molybdenum can be prepared in one reaction. The preparation of tungsten(VI) chloride and tungsten(V) bromide was carried out in the same manner, (69) using a Vycor reaction vessel at higher temperatures. It should be mentioned that the tungsten metal, prior to reaction with the appropriate halogen, was reduced in a quartz boat in a Vycor reaction tube at 1000° under a stream of hydrogen gas. The reaction temperatures for the synthesis of these halides

were as follows: MoCl_5 , 450° , WCl_6 , 550° ; WBr_5 , 550° .

Preparation of $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$. - A typical reaction for this synthesis is described below. The starting materials, 13.65 g (0.05 moles) MoCl_5 , 1.38 g (0.051 moles) Al, 8.2 g (0.141 moles) NaCl, and 13.33 g (0.10 moles) AlCl_3 were loaded into a flame-outgassed 45 mm x 140 mm Pyrex reaction tube fitted with an 18/9 ball or socket joint. Because of the air sensitivity of the molybdenum and aluminum chlorides, the tube was loaded in the dry box. The tube and contents, under a prepurified nitrogen atmosphere, were attached to the vacuum line, and evacuated to ca. 10^{-5} torr. The reaction vessel was sealed above the reaction tube about 2.5 cm up on the 9 mm connector. The contents were vigorously shaken to insure some degree of homogeneity. The tube was fitted with a thermocouple, chromel/alumel, wrapped in a sheet of aluminum foil, to insure even heating, and then wrapped with a 6 foot heating tape. For insulation, the reaction tube was wrapped thoroughly with 2" asbestos tape. At this time, the tube with contents was ready for reaction. The reaction vessel was placed on a wrist action shaker, thermocouple leads connected to a controller (for temperature monitoring only), and the heating tape plugged into a Variac, variable transformer power supply. The following time/temperature program was used:

<u>Temperature (°C)</u>	<u>Duration (Hrs)</u>
200	6
250	1
300	1
400	1
450	48

At the end of this time, the reaction tube was disconnected from the controller and Variac and removed from the shaker. The tube was unwrapped, allowed to cool, and opened in air. In reactions which provided the highest yields the cooled melt showed only a light yellow-brown color. The products were ground in a mortar and carefully poured into ca. 200 ml of 1 M HCl. A stirring bar was placed in the solution and the contents stirred for about 15 minutes. The solution then was centrifuged and the residue was washed with 1 M HCl until the filtrate no longer showed the color of molybdenum cluster; the filtrate and washings contained the major portion of the molybdenum chloride cluster. The residue was then washed with absolute ethanol and centrifuged until, again, no further color appeared. This ethanol filtrate was kept separate from the aqueous solution.

The residue was further washed with acetone to insure

- 1) that no further molybdenum(II) chloride remained, and
- 2) all other extraction solvents were removed to give a dry residue for weighing.

The respective water and ethanol solutions were reduced

in volume until solids began separating from solution. At this time, concentrated HCl was added to the solutions so as to approximately triple their volumes and cause precipitation of both NaCl and the cluster compound. The solutions were cooled in a cold bath, and filtered through a medium porosity sintered glass frit by aspirator vacuum. The yellow crystalline solids were washed with cold concentrated HCl.

The filtrates were combined, reduced in volume again and reprecipitated with HCl. Again the solids were filtered away and at this time the supernatant solution was discarded.

The solids were left on the frit and thoroughly washed with dry absolute ethanol leaving sodium chloride on the frit and redissolving all of the molybdenum(II) chloride. This ethanol solution was then carefully reduced in volume and the molybdenum chloride cluster precipitated with concentrated HCl (aq).

The crystallized solid was identified, by analysis, as the acid hydrate, $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$. For an exact analysis, the chlorine to molybdenum ratio, ca. 2.0 g of this solid was heated in vacuo at 200° for 8 hours. The remaining residue, as $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, was analyzed for molybdenum and chlorine. Anal. Calc. for $\text{Mo}_6\text{Cl}_{12} \cdot 2\text{H}_2\text{O}$: Mo, 55.51; Cl, 41.02. Found: Mo, 55.5, 55.6; Cl, 41.0, 41.1; Cl/Mo, 1.99, 2.02.

Preparation of $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Br}_8(\text{Br}_6)] \cdot 6\text{H}_2\text{O}$. - The synthesis of the acid hydrate of molybdenum(II) bromide is analogous to the preparation of the corresponding chloride. For this reaction 13.65 g (0.05 moles) MoCl_5 , 1.38 g (0.051 moles) Al, 14.55 g (0.141 moles) NaBr, and 26.68 g (0.10 moles) AlBr_3 were loaded and sealed in a Pyrex reaction tube in the previously described manner. The reaction vessel was prepared for reaction and run at the same temperatures and for the same durations as for the chloride. The products, again taking no precautions for air sensitive components, were opened to the air, ground and poured carefully into ca. 200 ml of cold 1M HBr solution, stirred and centrifuged. Thereafter the respective solutions and residues were treated in the same manner as in the chloride synthesis, only using concentrated HBr instead of HCl.

The crystalline final product was identified as the acid hydrate, $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Br}_8)\text{Br}_6] \cdot 6\text{H}_2\text{O}$. Again, to obtain an exact analysis and bromine to molybdenum ratio, ca. 2.0 g of this solid was heated in vacuo at 200° for 8 hours. The remaining residue, as $(\text{Mo}_6\text{Br}_8)\text{Br}_4 \cdot 2\text{H}_2\text{O}$, was analyzed for molybdenum and bromine. Anal. Calc. for $\text{Mo}_6\text{Br}_{12} \cdot 2\text{H}_2\text{O}$: Mo, 36.63; Br, 61.08. Found: Mo, 36.5, 36.6; Br, 61.0, 61.1; Br/Mo, 2.01, 2.03.

Preparation of $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$. The synthesis of tungsten(II) chloride and bromide follows very closely the corresponding molybdenum halide preparations. In this case 19.85 g (0.05 moles) WCl_6 , 1.81 g (0.066 moles) Al, 9.0 g (0.154 moles) NaCl, and 13.33 g (0.10 moles) AlCl_3 were loaded into a flame outgassed 45 mm x 140 mm Vycor tube as described for MoCl_2 and MoBr_2 . Vycor glass was used in this synthesis because of the increased reaction temperature. After loading under nitrogen, the tube was attached to the vacuum line for evacuation and sealing. The reaction mixture was vigorously shaken and the sealed tube was fit with a thermocouple. This reaction vessel was then mounted inside a rocking furnace whose temperature was regulated by the attached thermocouple. While the furnace slowly rocked from an upright position through an angle of ca. 100° , the following time/temperature program was followed:

<u>Temperature ($^\circ\text{C}$)</u>	<u>Duration (Hrs)</u>
200	2
250	1
300	1
350	1
450	6
550	48

At the end of this period, the reaction tube was removed from the furnace, allowed to cool, and opened in the drybox. This change in procedure was made to allow a thorough examination

of products sublimed from the melt. The bulk of the reaction product was ground in a mortar, removed from the dry box and carefully poured into a cold solution of 1M HCl. From this point, the procedure to separate the salt $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$ was the same as for the corresponding molybdenum(II) chloride acid hydrate.

A small sample of the hydrate was heated to 325° in vacuo to produce the anhydrous $(\text{W}_6\text{Cl}_8)\text{Cl}_4$ for an accurate analysis of tungsten and chlorine, and an accurate chlorine to tungsten ratio. Anal. Calc. for W_6Cl_{12} : W, 72.19; Cl, 27.81. Found: W, 72.0, 72.0; Cl, 27.8, 27.9; Cl/W, 2.02, 2.01.

Preparation of $(\text{H}_3\text{O})_2[(\text{W}_6\text{Br}_8)\text{Br}_6] \cdot 6\text{H}_2\text{O}$. - The preparations of tungsten(II) bromide and its derivatives are exactly analogous to the preparation of tungsten(II) chloride and the separation techniques of molybdenum(II) bromide.

Following the same procedures as in the case of the tungsten(II) chloride, 29.20 g (0.05 moles) WBr_5 , 1.38 g (0.051 moles) Al, 14.55 g (0.141 moles) NaBr and 26.68 g (0.10 moles) AlBr_3 were loaded into a Vycor reaction tube. After reaction, the tube was opened in the dry box and sublimed products, from the melt, were analyzed by X-ray powder patterns.

The procedure to obtain the acid hydrate, $(\text{H}_3\text{O})_2[(\text{W}_6\text{Br}_8)\text{Br}_6] \cdot 6\text{H}_2\text{O}$, is exactly the same as that to obtain the corres-

ponding molybdenum(II) bromide. The acid hydrate was decomposed to $(W_6Br_8)Br_4$ in vacuo at 350° , and subsequently analyzed for tungsten and bromine. Anal. Calc. for W_6Br_{12} : W, 53.49; Br, 46.51. Found: W, 53.61, 53.87; Br, 46.11, 46.87; Br/W, 1.98, 2.02.

RESULTS AND DISCUSSION

The use of sodium tetrahaloaluminate melts for preparing and stabilizing reduced species is well documented. Several workers have made considerable contributions to the study of elements in unusual oxidation states. The most recent is the preparation and characterization of the Hg_3^{2+} species.

Mamantov et al. (71) found that Hg metal is oxidized, or Hg^{2+} and Hg_2^{2+} are reduced in acidic chloroaluminate melts (mole ratio $\text{AlCl}_3:\text{MCl}$ greater than 1, where M is an alkali metal). It is not unreasonable to expect the formation of the mercury (+1/3) chloride, recently reported by Gillespie and Ummat (72), to also be stabilized in these melts.

For several years Corbett and co-workers have been studying species in reduced oxidation states in molten salts. They reported (73,74) the formation of Bi^+ , Bi_5^{3+} , and Bi_4^+ , and discussed their relationship to Bi_9^{5+} and Bi_8^{2+} , in acidic chloroaluminate melts. Corbett and co-workers have also isolated such species as I_3^+ , I_5^+ , and I_2Cl^+ in chloroaluminate melts (75) and discussed the formation of Se_8^{2+} (76), in aluminum chloride melts, and reported the crystal structure of $\text{Se}_8(\text{AlCl}_4)_2$.

With the recent success of McCarley and Meyer (70) in the preparation of mixed-metal hexanuclear cluster species of tantalum and molybdenum in acidic sodium tetrachloroaluminate melts, this environment seemed to be the logical choice for

the reaction solvent in this work. Since there was an unresolved question about the stability of the $(M_6X_8)^{4+}$ cluster species ($M = Mo$ or W) in these melts, a series of experiments was designed and performed to find the optimum conditions for their syntheses. In the past the most common methods used to prepare the dihalides have been the reduction of higher halides, or the disproportionation of intermediate halides in the absence of solvents. The following reactions represent these processes:

Obviously the disproportionation reactions not only involve extra steps in the synthesis procedure (since they also must be prepared from higher halides), but they also can provide yields of no better than 67% in the case of Mo_6Cl_{12} and 33% in the case of W_6Cl_{12} . A disadvantage of the aluminum reduction of the higher halides is the excessive $AlCl_3$ pressures developed during reaction and the contamination of the product by metal.

The study of the following reaction in $AlCl_3$ -rich melts began considering only time and temperature as the most convenient variables.

The first reaction was carried out at 350° for 3 days. The reaction tube was gently shaken for the entire duration of the reaction. The melt became dark brown, with no trace of unreacted Al metal. This time and temperature program was analogous to that used by Meyer (70) and produced a yield that was 50% of the calculated.

A second reaction following the outline of reaction 1 was prepared in the same manner, except the new conditions were 450° for 1 day with gentle shaking. This procedure gave a yield that was 35% of the calculated.

When reaction 1 was maintained at 450° for 2 days, the yield of twice crystallized $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$ was 92% of the calculated. Both this acid hydrate and the subsequent dihydrate, $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, obtained by heating a portion of the acid hydrate in vacuo, were verified by analysis.

It should be pointed out that several reaction tubes did explode because of excessive vapor pressures of AlCl_3 and MoCl_5 . Strictly following the time/temperature program as outlined in the experimental section reduced the number of explosions. The 6 hour pause at 200° allowed the conversion of AlCl_3 and NaCl to molten NaAlCl_4 .

It seemed reasonable, after such excellent success with the molybdenum(II) chloride, that a reaction patterned after (1) using similar conditions should also give excellent yields

of molybdenum dibromide. It was initially felt that the dibromide should be synthesized from an intermediate oxidation state bromide, e.g. MoBr_4 . However because of difficulties in the preparation of MoBr_4 an alternate choice of MoCl_5 was made.

Schäfer (31-33) has pointed out that exchange reactions for the X^i/X^a halogens in these hexanuclear cluster compounds can be promoted. Taking advantage of this exchange, the dibromide was prepared from molybdenum(V) chloride in bromide-rich melts composed of NaAlBr_4 and Al_2Br_6 . It was also felt that aluminum(III), being a better acid toward chloride than bromide, would also facilitate the exchange of bromide for chloride in the final product.

Several reactions of the kind described for the preparation of $(\text{Mo}_6\text{Cl}_8)\text{Cl}_4$ were tried. Two day reactions with temperatures from 350° to 500° , in 50° increments were tried. Although no unreacted aluminum metal was found, the melts were always very dark, contaminated with higher oxidation state halides as evidenced by dark vapors above the melt. Yields were usually 10 to 15%, with 6 to 8 grams of insoluble residue remaining after completed extractions; one component of this residue was identified as molybdenum metal. It was believed that there was some trapped bromine, in the preparation of aluminum tribromide, which could interfere with the desired reduction stoichiometry. Thus, ca. 300 g of reagent

grade AlBr_3 was resublimed in the presence of a small amount of Al metal. Again a reaction was run for 2 days at 450° . This reaction provided the maximum yield for the preparation in this manner, that is 21%.

A reaction to prepare the anionic form of the molybdenum bromide cluster was also tried. A stoichiometric amount of NaBr was added to the reaction mixture in order to completely convert all of the aluminum trihalide to sodium tetrahaloaluminate plus enough to form the sodium salt, $\text{Na}_2(\text{Mo}_6\text{Br}_8)\text{X}_6$; where $\text{X} = \text{Cl}$ and/or Br. However, no observable yield was found. Since this time, later work on the corresponding dihalides of tungsten may have shed some light on the enigma created by the poor yields of molybdenum(II) bromide.

Because of the time element, it was necessary to discontinue the study of the molybdenum halides and go on to the study of the preparation of the corresponding tungsten(II) chloride and bromide. The tungsten species have been an intermediate success story and still need more work. Gentle shaking for 2 days at 450° were the reaction conditions for the first few reactions to prepare tungsten(II) chloride. These conditions gave no better yield than 10%. Under the same conditions, an attempt to synthesize the dihalide in an anionic form, $\text{Na}_2(\text{W}_6\text{Cl}_8)\text{Cl}_6$, gave no yield of the cluster at all.

The question of the instability of the $(\text{W}_6\text{Cl}_8)^{4+}$ species

in these melts was raised and subsequently tested. Anhydrous $(W_6Cl_8)Cl_4$ was sealed in a Pyrex tube with sodium chloride and aluminum chloride, such that this mixture was slightly aluminum chloride rich. The tube was carefully heated to 450° and maintained at this temperature for 48 hours. During this time, the light to dark yellow melt and the undissolved yellow solid showed no evidence of decomposition or disproportionation. Subsequently the temperature was raised to 500° for 24 hours and then cooled. At the end of the 72 hour period, some decomposition was apparent; a small amount of blue solid had crystallized from the melt. It seems reasonable to assume that at 500° the walls of the Pyrex container may have suffered attack by the W(II) species to form oxyhalides and silicides of tungsten.

The decision was then made to try to synthesize the dichloride at 550° in a Vycor reaction tube. At some temperature above 450° excessive pressure developed, and the tube exploded in the first attempt. Subsequent reactions were performed with a six hour pause at 450° to allow reduction to start with conversion of aluminum trihalide to the corresponding sodium tetrahaloaluminate. The first successful reaction at 550° for two days gave a yield of ca. 40% of $(W_6Cl_8)Cl_4$, and about 5 grams of insoluble residue. X-ray powder patterns of products volatilized from the melt during reaction, identified them as WCl_5 and WCl_4 . Visual inspec-

tion also indicated traces of light red WOCl_4 . The melt was very dark, probably due to WCl_5 and WCl_4 content. It should be noted here that the melt in the high yield $\text{Mo}_6\text{Cl}_{12}$ reaction was a light yellow-brown. Melt color was therefore useful as an indication of the success of the reaction.

Because of the presence of higher and intermediate oxidation states of tungsten in the reaction vessel, it was felt that the reaction had gone to completion and that the dichloride had begun to disproportionate.

To test this hypothesis, a reaction was set up in the usual manner but was terminated at the end of 24 hours. Although the melt was dark, there were no dark vapors above the melt. It was noted that as the melt cooled, a yellow solid crystallized. The yield of $(\text{W}_6\text{Cl}_8)\text{Cl}_4$ under these conditions was in excess of 54%. These results tend to substantiate the hypothesis. It seems possible, that at 550° , an even shorter reaction period may give a better yield.

If the initial yields of $(\text{Mo}_6\text{Br}_8)\text{Br}_4$ were bad, those for $(\text{W}_6\text{Br}_8)\text{Br}_4$ were worse. Several reaction attempts gave less than 10% yield. Use of carefully purified AlBr_3 did give an improved yield of ca. 21%. Precipitation attempts using gaseous HBr instead of 48% aqueous HBr did not improve the yield. Again raising the reaction temperature from 450° to 550° was tried as a means to improve the yield.

After one particular reaction, 550° for 2 days, and the

usual extraction procedures, it was noted that the remaining residue in the centrifuge tube was a very bright yellow, with a thin layer of blue solid which probably contained the WO^{3+} species. Repeated extractions with a boiling solution of ethanol (50%) and HBr (aq) gave bright yellow solutions. An extraction with 80% ethanol and 20% HBr (aq) refluxing overnight gave a very dark yellow solution. Continued extractions with absolute ethanol gave more yellow solutions. After boiling down these solutions and treating them in the usual manner, a final yield of tungsten(II) bromide was found to be 45%. Because of the very slow dissolution of this bromide, it is expected that prolonged extraction of the products from the molybdenum bromide reduction may give a better yield of the $(Mo_6Br_8)Br_4$.

This acidic ethanol extraction method was tested on the residues which remained from the products of the tungsten chloride reduction and from which most of the $(W_6Cl_8)Cl_4$ had already been extracted. In this case blue solutions resulted and the only species which could be identified from its absorption spectrum was $WOCl_5^{2-}$. The latter anion was readily precipitated from solution as the cesium or tetraethylammonium salts leaving a colorless solution.

SUMMARY

The syntheses and separation techniques for the preparation of the molybdenum and tungsten(II) chlorides and bromides have been studied. All compounds prepared are known to have the $(M_6X_8)^{4+}$ cluster configuration. The chemical and physical properties of these low oxidation state compounds are governed by the high stability of this polynuclear grouping.

The yields of the dihalides of molybdenum and tungsten resulting from reduction of the higher halides in aluminum halide-sodium tetrahaloaluminate melts were highly dependent on duration and temperature of reaction, as well as molten salt composition. This was especially true in the case of the chlorides where NaCl-rich melts destroyed all recoverable yield of the cluster species. It was also noted that the dihalides have only moderate stability at these reaction temperatures. The apparent order of stability in the molten salt, as obtained from yield data, was observed to be $(Mo_6Cl_8)Cl_4 > (W_6Cl_8)Cl_4 > (W_6Br_8)Br_4 > (Mo_6Br_8)Br_4$.

All products were carefully verified by elemental analysis, X-ray powder diffraction patterns, and X-ray Guinier diffraction patterns.

SUGGESTIONS FOR FUTURE WORK

McCarley and Meyer (70) successfully synthesized the two mixed-metal hexanuclear species $(M^+)_2[(Ta_5MoCl_{12})Cl_6]$ and $(M^+)_2[(Ta_4Mo_2Cl_{12})Cl_6]$ according to the following reactions in molten $NaAlCl_4-AlCl_3$:

There are two interesting aspects of the reaction mixtures resulting from the co-reduction of $TaCl_5$ and $MoCl_5$: 1) a high yield of pure tantalum cluster, and 2) low yields of the mixed-metal species were obtained. From our completed research, it seems likely that variation of the temperature or the duration of the reaction might well overcome the low yield of mixed-metal clusters.

This study was initiated because of the failure in the previous work to extend the series of mixed-metal clusters beyond those prepared by McCarley and Meyer. With a better understanding of the conditions needed to optimize the yield of the dihalides of molybdenum, it may now be possible to extend the series as follows:

$M_6X_{12}^{n+}$	$M_6X_8^{n+}$
$Ta_6Cl_{12}^{2+,3+,4+}$	$Mo_3Ta_3Cl_8^{1+}$
$Ta_5MoCl_{12}^{3+,4+}$	$Mo_4Ta_2Cl_8^{2+}$
$Ta_4Mo_2Cl_{12}^{4+}$	$Mo_5Ta_1Cl_8^{3+}$
$Ta_3Mo_3Cl_{12}^{5+}$	$Mo_6Cl_8^{4+}$

Because the bonding orbitals in the (M_6X_8) cluster can accommodate 24 electrons as opposed to 16 electrons in the (M_6X_{12}) clusters, a change in configuration may develop. As molybdenum atoms are substituted into the tantalum cage, the oxidation state of the cluster increases in preference to having an electron occupy an antibonding orbital. However, at that cluster configuration which includes three tantalum and three molybdenum atoms, a change in configuration might be preferable to alleviate excessive positive charge. That is, by changing configuration to the (M_6X_8) form, the cluster charge drops from 5+ to 1+. Initially the bromides were studied, because it was felt that a larger halide might help induce this configurational change. It will be recalled that in the case of niobium and iodine, the $(Nb_6I_8)I_3$ cluster was formed. Continuation of this work may very well prove fruitful. For example, there are also the areas of bimetal hexanuclear clusters of Mo and W, Nb and Mo, Ta and W, and the continuation of the work by Schäfer and Juza (77) with the

Nb and Ta mixed-metal clusters.

With the advent of nuclear power by the fission process, a most interesting series of molybdenum, tungsten, niobium and tantalum species may be encountered. If these reactors are to be cooled by molten salt media, e.g. Li_2BeF_4 , some interesting compounds from the degradation of the reactor walls could be formed. A series of studies of the fluorides of the heavy transition metals would be fruitful, not only in expanding the understanding of these elements and their chemistry, but also may be of benefit to the engineering of fission reactors.

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BIBLIOGRAPHY

1. Blomstrand, C. W., J. Prakt. Chem. 77, 88 (1859).
2. Muthmann, W. and Nagel, W., Berichte 31, 2009 (1898).
3. Rosenheim, A. and Kohn, F., Z. Anorg. Allg. Chem. 66, 1 (1910).
4. Lindner, K., Ber. dt. chem. Ges. 55, 1458 (1922).
5. Hellriegel, W., German Patent 703,895. 1941.
6. Senderoff, S. and Brenner, A., J. Electrochem. Soc. 101, (1954).
7. Lewis, J., Machin, D. J., Nyholm, R. S., Pauling, P. and Smith, P. W., Chem. Ind. 1960, 259 (1960).
8. Couch, D. E. and Brenner, A., J. Res. Nat. Bur. Stand. 63A, 185 (1959).
9. Robinson, R. E., U.S. Patent 3,298,778. 1967.
10. Lindner, K., Helwig, H. and Kohler, A., Z. Anorg. Allg. Chem. 142, 180 (1925).
11. Durand, C., Schaal, R. and Souchag, P., Compt. Rend. 248, 979 (1959).
12. Guggenberger, L. J. and Sleight, A. W., Inorg. Chem. 8, 2041 (1969).
13. Lindner, K., Heller, E. H. and Helwig, H., Z. Anorg. Allg. Chem. 130, 209 (1923).
14. Matsuzaki, R., Saeki, Y. and Matsushima, T., Denki Kagaku 35, 448 (1967).
15. Holste, G. and Schäfer, H., J. Less-Common Metals 20, 164 (1970).
16. Lindner, K., Z. Anorg. Allg. Chem. 162, 203 (1927).
17. Sheldon, J. C., Nature 184, 1210 (1959).
18. Sheldon, J. C., J. Chem. Soc., 1007 (1960).
19. Sheldon, J. C., J. Chem. Soc., 3106 (1960).

20. Sheldon, J. C., J. Chem. Soc., 410 (1962).
21. Mackay, R. A. Chemical and physical studies on metal atom cluster compounds. Unpublished Ph.D. thesis. Stony Brook, New York, Library, State University of New York at Stony Brook. 1966.
22. Cotton, F. A., Wing, R. M. and Zimmerman, R. H., Inorg. Chem. 6, 11 (1967).
23. Clark, R. J. H., Kepert, D. L., Nyholm, R. S. and Rodley, G. A., Spectrochim. Acta 22, 1697 (1966).
24. Hartley, D. and Ware, M. J., Chem. Commun. 1967, 912 (1967).
25. Opalovskii, A. A. and Samoilov, P. O., Dokl. Akad. Nauk. USSR 174, 550 (1967).
26. Mattes, R., Z. Anorg. Allg. Chem. 357, 30 (1968).
27. Hogue, R. D. and McCarley, R. E., Inorg. Chem. 9, 1354 (1970).
28. Sheldon, J. C., J. Chem. Soc., 4183 (1963).
29. Sheldon, J. C., J. Chem. Soc., 1287 (1964).
30. Sheldon, J. C., Chem. Ind. 1961, 323 (1961).
31. Schäfer, H., Baumann, H., Plautz, H., J. Less-Common Metals 24, 301 (1971).
32. Lesaar, H. and Schafer, H., Z. Anorg. Allg. Chem. 385, 65 (1971).
33. Schnering, H. G., Z. Anorg. Allg. Chem. 385, 75 (1971).
34. Siepman, R., Schnering, H. G., and Schafer, H., Angew. Chem. Internat. Edit. 6, 637 (1967).
35. Bauer, D., Schnering, H. G. and Schafer, H., J. Less-Common Metals 8, 388 (1965).
36. Simon, A., Schnering, H. G., Wohrle, J. and Schafer, H., Z. Anorg. Allg. Chem. 339, 155 (1965).
37. Simon, A., Schnering, H. G., and Schafer, H., Z. Anorg. Allg. Chem. 355, 295 (1967).

38. Bateman, L. R., Blount, J. F. and Dahl, L. F., J. Am. Chem. Soc. 88, 1082 (1966).
39. Kust, M. A., Corbett, J. D. and Friedman, R. M., Inorg. Chem. 7, 2081 (1968).
40. Simon, A., Z. Anorg. Allg. Chem. 355, 311 (1967).
41. Hill, J. B., J. Am. Chem. Soc. 38, 2383 (1916).
42. Lindner, K. and Kohler, A., Z. Anorg. Chem. 140, 357 (1924).
43. Murray, G. A. A study of tungsten(II) and tungsten(III) bromides. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University. 1965.
44. Emeleus, H. J. and Gutman, V., J. Chem. Soc., 2115 (1950).
45. McCarley, R. E. and Brown, T. M., Inorg. Chem. 3, 1232 (1964).
46. McCarley, R. E. and Brown, T. M., J. Am. Chem. Soc. 84, 3216 (1962).
47. Siepmann, R. and Schäfer, H., Naturwissenschaften 52, 344 (1965).
48. Schäfer, H., and Siepmann, R., J. Less-Common Metals 11, 76 (1966).
49. Schäfer, H. and Siepmann, R., Z. Anorg. Allg. Chem. 357, 273 (1968).
50. Tjabbes, B. T., Acad. Sci. Amst., Proc. 35, 696 (1932).
51. Klemm, W. and Steinberg, H., Z. Anorg. Allg. Chem. 227, 193 (1936).
52. Schäfer, H. and Schnering, H. G., Angew. Chem. 76, 833 (1964).
53. Edwards, D. A., J. Less-Common Metals 7, 159 (1964).
54. Brown, T. M. Preparation and reactions of some lower tungsten halides and halide complexes. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University. 1963.

55. Carmichael, W. M. and Edwards, D. A., J. Inorg. Nucl. Chem. 29, 1535 (1967).
56. Fergusson, J. E., Robinson, B. H., and Wilkins, C. J., J. Chem. Soc., A, 486 (1967).
57. Brosset, C., Ark. Kemi. Miner. Geol. 20A, No. 7 (1945).
58. Brosset, C., Ark. Kemi. Miner. Geol. 22A, No. 11 (1946).
59. Brosset, C., Ark. Kemi. 1, 353 (1950).
60. Vaughan, P. A., Nat. Acad. Sci. Proc., U.S.A. 36, 461 (1950).
61. Schäfer, H., Schnering, H. G., Tillack, J., Kuhn, F., Wohrle, H., and Baumann, H., Z. Anorg. Allg. Chem. 353, 281 (1967).
62. Siepmann, R. and Schnering, H. G., Z. Anorg. Allg. Chem. 357, 289 (1968).
63. Walton, R. A. and Edwards, D. A., Spectrochim. Acta 24A, 833 (1968).
64. Gillespie, R. G., Canadian J. Chem. 39, 2336 (1961).
65. Crossman, L. D., Olsen, D. P., and Duffey, G. H., J. Chem. Phys. 38, 73 (1963).
66. Cotton, R. A. and Haas, T. E., Inorg. Chem. 3, 10 (1964).
67. Kettle, S. F. A., Theoret. Chim. Acta 3, 211 (1965).
68. Vogel, A. I., "A Textbook of Quantitative Inorganic Analysis" 3rd ed. 1961. John Wiley and Sons Inc.
69. Kuhn, P. J. Synthesis of some polynuclear tantalum halides. Unpublished M.S. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1964.
70. Meyer, J. L. A study of some hexanuclear mixed-metal cluster compounds containing tantalum and molybdenum. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1970.
71. Mamantov, G., Torsi, G., Fung, K. W., Begun, G. M., Inorg. Chem. 10, 2285 (1971).

72. Gillespie, R. J. and Ummat, P. K., Chem. Comm. 19, 1168 (1971).
73. Corbett, J. D. and Lynde, R. A., Inorg. Chem. 10, 1746 (1971).
74. Corbett, J. D., Inorg. Chem. 7, 198 (1968).
75. Merryman, D. The synthesis and characterization of three polyhalogen tetrachloraluminates. Unpublished Ph.D. thesis. Ames, Iowa, Library, Iowa State University of Science and Technology. 1972.
76. Corbett, J. D., McMullan, R. K., and Prince, D. J., Inorg. Chem. 10, 1749 (1971).
77. Schäfer, H. and Juza, D., Z. Anorg. Allg. Chem. 379, 122 (1970).