SINGLE CRYSTAL ELECTRONIC SPECTRA FOR THE COMPOUNDS
POTASSIUM OCTACHLORODIMOLYBDATE (II)-DIHYDRATE,
POTASSIUM TETRA- μ -SULFATODIMOLYBDATE (II)-DIHYDRATE AND
POTASSIUM TETRA- μ -SULFATODIMOLYBDATE (II, III)-3.5 HYDRATE

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Single crystal electronic spectra for the compounds
potassium octachlorodimolybdate (II)-dihydrate,
potassium tetra- μ -sulfatodimolybdate (II)-dihydrate and
potassium tetra- μ -sulfatodimolybdate (II,III)-3.5 hydrate

by

Phillip Edward Fanwick

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Single crystal electronic spectra for the compounds
 potassium octachlorodimolybdate (II)-dihydrate,
 potassium tetra- μ -sulfatodimolybdate (II)-dihydrate and
 potassium tetra- μ -sulfatodimolybdate (II,III)-3.5 hydrate*

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The polarized electronic absorption spectra for single crystals of potassium octachlorodimolybdate (II)-dihydrate, potassium tetra- μ -sulfatodimolybdate (II)-dihydrate and potassium tetra- μ -sulfatodimolybdate (II,III)-3.5 hydrate have been obtained at room and liquid helium temperatures. Because of a disorder in the structure of $K_4Mo_2Cl_8 \cdot 2H_2O$ the dipole-allowed transition $^1A_{2u} \leftarrow ^1A_{1g}$ ($\delta^* \leftarrow \delta$) at $19,300\text{ cm}^{-1}$ could be measured at 3.7 K for 7% of the molecules. An irregularly spaced vibrational progression was observed in this band. Pellet spectra of $K_4Mo_2Cl_8 \cdot 2H_2O$ displayed a similar irregularity while pellets of the anhydrous compound did not. Bands were also observed at $22,000\text{ cm}^{-1}$ and $28,800\text{ cm}^{-1}$ but no definitive assignments could be made for them. $K_4Mo_2(SO_4)_4 \cdot 2H_2O$

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displayed a spectrum quite similar to the $\text{Mo}_2\text{Cl}_8^{4-}$ salt with respect to the energy of the transitions. However, the $\delta^* \leftarrow \delta$ transition at $19,400\text{ cm}^{-1}$ displayed no vibrational structure and was much less intense than in $\text{K}_4\text{Mo}_2\text{Cl}_8$. Also, a vibronic component in the opposite polarization was observed. The loss in intensity was explained by a backbonding model in which the δ^* -orbital interacted strongly with a sulfate e antibonding orbital. The transition ${}^2\text{B}_{1u} \leftarrow {}^2\text{B}_{2g}$ ($\delta^* \leftarrow \delta$) was observed in the near-I.R. for $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$. At 5 K it displayed six vibrational progressions. Three were clearly z-polarized and assigned as Mo-Mo and Mo-O stretching modes on the O-O transition. The other series were assigned as vibronic progressions based on exciting e_g modes. Lastly, a proposed assignment, ${}^1\text{A}_{2u} \leftarrow {}^1\text{A}_{1g}$ ($\delta^* \leftarrow \delta$), for the spectra of the alkyl-carboxylate dimers, based on a backbonding model, was offered. Polarized crystal spectra for the compounds $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ and $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$ were obtained to illustrate the model. In the spectrum of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ highly distorted Frank-Condon ratios were observed, and it was proposed that this was due to an a_{1g} Hertzberg-Teller interaction.

I. INTRODUCTION

The purpose of this thesis and research is to elucidate the bonding and energy levels in two dimeric molybdenum complex systems displaying multiple metal-metal bonding. The first system is potassium octachlorodimolybdate (II). This represents a simple molybdenum dimer in that the chloride-ion ligands are incapable of accepting electron density from the metal. The metal-metal bond in this dimer is formally a quadruple bond. The second system is composed of the complexes potassium tetra- μ -sulfatodimolybdate (II) and potassium tetra- μ -sulfatodimolybdate (II,III). The complexity of the sulfate ligands adds new possibilities to the bonding and spectra. This system also allows the study of the effect on the metal-metal bond of removal of an electron.

The history of the quadruple bonded metal dimers began with the rhenium(III) system. In 1958 Kotel'nikov and Tronev studied the reduction of potassium perrhenate with hydrogen in the presence of hydrogen chloride (1). The result of this reduction was a new, dark blue rhenium complex. Their analysis of the complex gave a formula of $KReCl_4$ while the determination of the rhenium oxidation state indicated a value of +2. As these data were inconsistent, the formula was assigned as $KHReCl_4$. X-ray diffraction data were also collected for this compound (2). While the complete

structure was not solved, the metal-metal distance was determined to be 2.22 Å which was surprisingly short. In spite of this, the Russian workers did not change their formulation of this species as a monomer.

The next discovery in this area was made by Taha and Wilkenson in 1963 (3). "Rhenium trichloride" (Re_3Cl_9) was reacted with various carboxylic acid/anhydride mixtures. The compounds synthesized had the formula $\text{Re}_2(\text{RCOO})_4\text{Cl}_2$. Similar dimers were known for other metals including chromium, manganese and copper. The structures of these complexes consisted of two metals bridged by four tetragonally arranged carboxylate groups. The metals occupied a site essentially in the center of a square plane of oxygens. The symmetry of such complexes was D_{4h} . If other ligands were present they occupied terminal positions, that is, positions colinear with the metal-metal axis. It was postulated that the rhenium complex had a similar structure. The terminal chlorides were quite labile and could easily be replaced with thiocyanate or removed by aqueous silver perchlorate to give the diaquo complex. In all such reactions the $[\text{Re}_2(\text{RCOO})_4]^{2-}$ skeleton remained in tact. The fact that these compounds were diamagnetic indicated that the electrons not involved in the ligand bonding were paired. This implied that substantial metal-metal bonding was occurring. Again, this situation was known to be the case in carboxylate complexes

of other metals with similar formulae.

The correct formulation of the halide complex was determined by Dr. F. A. Cotton. The complex $\text{K}_2\text{Re}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ was prepared by the reduction of KReO_4 by H_3PO_2 in the presence of chloride ion (4). The hydrogen reduction of the Russian workers was also duplicated and provided the same complex as the H_3PO_2 reduction. The bromide complex could also be prepared by simply replacing the chloride ion during the reduction with bromide. A metal dimer with eight ligands was quite unique. Only one other complex, $(\text{NH}_4)_3\text{Tc}_2\text{Cl}_8$, with this formulation had been reported and its structure was unknown at that time (5). It was also shown that the octachlorodirhenates could be converted to the carboxylate complexes by treating with the appropriate organic acid and vice versa.

To determine the geometry of this novel complex the crystal structure of $\text{K}_2\text{Re}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ was solved (6). The structure consisted of two square ReCl_4 units bound in an eclipsed configuration. There were no bridging halides. The rhenium-rhenium distance was found to be a very short 2.241 Å. The rhenium atoms did not lie in the plane of the chlorine ligands and consequently there was a Re-Re-Cl angle of about 103° . This produced a distance of about 3.32 Å between eclipsed chlorines. This greater Cl-Cl distance is due to the electrostatic repulsion of the ligands. The ions

possessed D_{4h} symmetry. The water molecules were not bound to the terminal positions.

An extensive chemistry of the $\text{Re}_2\text{Cl}_8^{2-}$ ion has been developed. For example, phosphines (7), thio- and isocyanates (8) and other common ligands could be reacted to replace the chloride ligands. Again, the basic Re-Re structure was left intact and indicated that this unit is quite stable. The interconvertability with the carboxylate complexes has already been mentioned. This provided evidence that the dirhenium unit in these complexes was the same as in the halides. Halogen can also be added across the rhenium-rhenium bond of the complex in solution of methylene chloride. Treatment with halogen produced the non-ahalodirhenate (III) ion.

The bonding in this rhenium dimer was quite a departure from previously studied systems. Any theory of bonding had to account for the properties of this ion. First, the very short Re-Re distance had to be explained. The distance of 2.241 Å is actually shorter than the sum of the atomic radii (1.28 Å) (9). Secondly, the eclipsed configuration had to be accounted for. The stability of this ion had to be explained as well as its ability to add halogen. From simple symmetry arguments a satisfactory picture of the bonding was developed.

From simple symmetry Cotton proposed a quadruple metal-

metal bond (10). On each rhenium atom the $d_{x^2-y^2}$, p_x , p_y and s orbitals were used to form the metal-ligand sigma bonding system. The remaining orbitals interacted as follows: the d_{z^2} and p_z orbitals on each metal formed a metal-metal sigma bond, the d_{xz} and d_{yz} orbitals provided pi-bonds and the d_{xy} orbital formed a delta-bond. As there are eight electrons available for formation of the metal-metal bond, a bond order of four resulted.

This bonding scheme accounted for all of the observed properties. The high bond order gives rise to the very short rhenium-rhenium distance. The delta-bond was considered responsible for the eclipsed configuration. The combined pi-bonds are cylindrically symmetric and hence there is no reduction in overlap between the eclipsed and staggered configurations for them. In fact, in known triply metal-metal bonded complexes of molybdenum and tungsten the preferred configuration is staggered and there is even some evidence for rotation around the triple bond (11, 12). Therefore, the energy required to stabilize the eclipsed configuration must come from the delta-bond. If the two d_{xy} orbitals, which will form the delta-bond, were above each other at a 45° angle to each other, there would be no net overlap. This is exactly the situation in the staggered configuration. The implication is that the energy of the delta-bond is greater than the electrostatic repulsion of

eclipsed configuration. Undoubtedly, the steric repulsion is somewhat lessened by the fact that the chlorine-chlorine distance across the metals is substantially greater than the metal-metal distance. All these considerations made exact calculation of the rotational barrier impossible.

To substantiate this bonding scheme and obtain values for the orbital energies an extended Hückel molecular orbital calculation was performed (13). The calculated orbital ordering is shown in Figure 1. The two orbitals shown in dashed lines represent nonbonding orbitals arising from the p_x and d_{z^2} combinations not used in forming the metal-metal sigma-bonds. In general, the calculations substantiated the quadruple bond concept. Several numbers obtained were of interest. The calculation suggested that the total pi-bonding contribution to the rhenium-rhenium bond was 4.47 times that of the delta-bond and 2.6 times that of the sigma-bond. The total bond stabilization was 366 Kcal/mole as compared to two ReCl_4^- units. The delta-bond contribution was 51 Kcal/mole. As pointed out previously, an exact calculation of the rotational barrier was impossible. However, if it is assumed that this barrier is of the same order of magnitude as in C_2Cl_6 , ≥ 7 Kcal/mole, then it is seen that the delta bond more than compensates for the electrostatic repulsion.

Spectral features of the octochlorodirhenate ion are

Figure 1. The bonding in $\text{Re}_2\text{Cl}_8^{2-}$ as calculated by molecular orbital and X_α methods

Table 1. Spectrum of $\text{Re}_2\text{Cl}_8^{2-}$

$\bar{\nu}(\text{cm}^{-1})^a$	$\bar{\nu}$ calculated (cm^{-1}) ^a	oscillator strength ^a
14,500	18,700	0.023
32,800	19,700	0.31
39,200	34,800	0.65

^aReference 13.

given in Table 1. The compound is blue in color

If the nonbonded orbitals were ignored, the lowest transition should have been from the $\delta^* \leftarrow \delta$ (${}^1A_{2u} \leftarrow {}^1A_{1g}$). This transition would be fully allowed. The calculated oscillator strength for such a transition was predicted to be close to unity (10). Because of the low oscillator strength for the transition at 14,500 cm^{-1} , Cotton was reluctant to assign it as the $\delta^* \leftarrow \delta$ transition (10, 13). Therefore, it was assigned as ${}^1B_{1u} \leftarrow {}^1A_{1g}$ ($\sigma_n(1) \leftarrow \delta$). This transition is electric dipole forbidden but can gain intensity through a vibronic mechanism. However, a vibronic transition would be much weaker and such an assignment would account for the low oscillator strength. Another argument against the $\delta^* \leftarrow \delta$ assignment was that the band at 18,700 cm^{-1}

was missing in the carboxylate complexes with terminal ligands. In these complexes it was expected that the metal-metal bonding would remain nearly unchanged. However, the essentially nonbonding sigma-levels would interact with the terminal ligands and would then be mainly antibonding in character. As such, they should shift to higher energy. Therefore, the absence of this band in complexes with terminal ligands was considered to support the $\sigma_{n(1)} + \delta$ assignment.

The remaining unassigned bands of high intensity were obviously fully allowed. The band at $32,800\text{ cm}^{-1}$ was therefore assigned to the ${}^1A_{2u} + {}^1A_{1g} (\delta^* + \delta)$ transition. The assignment of the band at $39,200\text{ cm}^{-1}$ is not clear in Cotton's papers. This is because the inversion symmetry of the pi-orbitals was reversed. The π orbital was assigned as e_g instead of e_u and vice versa for the π^* . This error was recognized in a later paper (14). However, all the initial assignments were based on the incorrect π orbital symmetry.

A later assignment for the spectrum of $\text{Re}_2\text{Cl}_8^{2-}$ was provided by Cowman and Gray (15). They measured the single crystal polarized spectra for the compound $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Cl}_8$ at room temperature and at 5 K. This compound crystallized in the monoclinic space group P_{21}/c with unit cell parameters $a = 10.91$, $b = 15.34$, $c = 16.43\text{ \AA}$ and

$\beta = 122.66^\circ$. Spectra were measured parallel and perpendicular to the b -axis on the (1,0,0) face. The b -direction displayed the higher absorbance. At 5 K the spectrum displayed vibrational structure. The vibrational structure appeared as pairs with the lower energy peak of each pair being the more intense. The separation between pairs was about 245 cm^{-1} while the separation between the two pair components was 115 cm^{-1} . As these bands appeared as a series, they were considered to be Frank-Condon components of a totally symmetric vibrational progression. The Raman spectrum of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2 \text{Re}_2\text{Cl}_8$ had a very strong band at 273 cm^{-1} and a very weak shoulder at 115 cm^{-1} (16). Force constant calculations provided an assignment of rhenium-rhenium stretch for the 273 cm^{-1} band and Re-Re-Cl bend for the 115 cm^{-1} band. The separation of the pairs corresponded to the frequency of the metal-metal stretch in the excited electronic state. The frequency shift from 273 cm^{-1} in the ground state to 245 cm^{-1} in the excited state was to be expected if one assumed that an electron was being removed from a metal-metal bonding orbital with a resultant weakening of this bond. At 5 K the origin for the system was at $14,183 \text{ cm}^{-1}$ and corresponded to the 0-0 transition of the a_{1g} metal stretch. At 77 K the pairs converged and the spacing of the peaks was 254 cm^{-1} . It is important to note that the integrated intensity of this

electronic transition was invariant to temperature. This is usually indicative of a fully allowed transition. Because of this temperature independence and the appearance of a 0-0 transition in the vibrational fine structure, the transition was assigned as the fully allowed ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$).

For further evidence of this assignment, the spectrum of the compound $\text{Re}_2\text{Cl}_6[\text{P}(\text{C}_2\text{H}_5)_3]_2$ was studied. The geometry of this material was proposed to be the same as $\text{Re}_2\text{Cl}_8^{2-}$ only with two diagonally opposed chlorines replaced by the phosphine (7). The idealized symmetry is then C_{2h} with the C_2 rotation axis being perpendicular to the plane containing the phosphorous and the metal-metal bond. In order to compare the spectrum of this compound with that of $\text{Re}_2\text{Cl}_8^{2-}$, the axis of rotation was assigned as the y -axis. The crystals formed were monoclinic, space group $P_{21/n}$, with lattice constants $a = 7.644$, $b = 10.985$, $c = 14.206$ Å, $\beta = 96.5^\circ$. The crystal face was identified as the (0,1,1) face with extinction directions reported to be parallel and perpendicular to the a -axis. In this symmetry the transition $\delta^* \leftarrow \delta$ is ${}^1B_u \leftarrow {}^1A_g$ which would be allowed in both the molecular x - and z -polarization. The transition to the nonbonding orbital would be ${}^1A_u \leftarrow {}^1A_g$ which would only be allowed in the y -polarization. It was claimed that data better agreed with the $\delta^* \leftarrow \delta$ assignment.

In a later paper by Mortola et al. (17), the $\text{Re}_2\text{Cl}_8^{2-}$ ion was studied in more detail. An X_α scattered-wave technique was used to calculate ground state orbital energies. The results are shown in Figure 1. In the metal-metal region, the calculation agrees well with the previous work of Cotton and Harris (13). There are several differences, however. The nonbonding p_z , d_{z^2} levels were totally absent from the metal-metal region. The energy gap between the highest filled orbital and lowest empty orbital was much smaller in the X_α calculation. Third, many ligand nonbonding orbitals (labeled L_n on Figure 1) were of comparable energy to metal-metal bonding orbitals. Lastly, the ordering of the π^* and σ^* orbitals was reversed from the previous calculation with the σ^* being higher.

The bands from the complete spectrum of $[(n\text{-C}_4\text{H}_9)_4\text{N}]_2\text{Re}_2\text{Cl}_8$ are tabulated in Table 2. The first band had already been assigned. The fact that the band at $30,870\text{ cm}^{-1}$ was xy -polarized meant that it must have involved a nondegenerate orbital and a doubly degenerate orbital with opposite inversion symmetries. There was no such one-electron transition possible from the ground state within the metal-metal bonding system. Therefore, this transition must involve ligand orbitals. It was assigned as $^1E_u \leftarrow ^1A_{1g}$ ($\delta^* \leftarrow$ ligand e_g). This then was the lowest energy charge transfer band. The magnetic circular dichroism (MCD) of this band also

Table 2. Polarized spectra of $[(n-C_4H_9)_4N]_2 Re_2Cl_8^+$ ^a

Observed Energy (cm^{-1})	Calculated Energy (cm^{-1})	Polarization	Assignment
14,140	4,488	z	$^1A_{2u} + ^1A_{1g}(\sigma^* + \delta)$
17,675 (w) ^{b,c}		xy,z	$^1E_g + ^1A_{1g}(\pi^* + \delta)$
20,940 (w) ^b		xy	$^1A_{1u} + ^1A_{1g}(d_{x^2-y^2} + \delta)$
23,645 (w) ^b		xy	$^1B_{1u} + ^1A_{1g}(\sigma^* + \pi)$
27,000- 28,100 (w) ^b			$^1A_{2u} + ^1A_{1g}(\delta^* + e_g(\pi)(Cl))$
30,870 ^a	21,722	xy	$^1E_u + ^1A_{1g}(\sigma^* - \text{ligand})$
31,750 (w)		xy	
34,480 (w)		xy	
35,700 (w)		z ^d	
39,215	24,702	z	$^1A_{2u} + ^1A_{1g}(\pi^* + \pi)$
39,840 (w)		xy	
42,000 (w)		xy	

^aReference 17.^bReference 18.^c(w) = weak peak.^dWrongly listed as xy in Reference 17.

supported this assignment. An A term was observed which was indicative of a band with a nondegenerate initial state and a degenerate final state. Such a term appears as an MCD signal which crosses zero at the wavelength of the absorbance maximum. The transition at $39,215\text{ cm}^{-1}$ was polarized in the same direction as the $\delta^* \leftarrow \delta$. The great intensity and high energy suggested that this was the transition ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($\pi^* \leftarrow \pi$). The assignments for the other bands listed in Table 2 were not given.

There is one fundamental problem with Gray's (in 15, 18) spectra. The exact crystal structures of the compounds whose spectra were observed were unknown. Therefore, crystal polarizations (i.e., parallel or perpendicular to the b -axis) could not be related to their appropriate molecular polarizations. That is, it could not be stated unequivocally that the bands observed had molecular z or xy polarizations. To understand why this is the case an understanding of how light behaves in a crystal is required.

In any anisotropic crystal face there are only two directions along which the electric field vector of a light wave can be directed. These two directions are always mutually perpendicular and in the face. Therefore, when a light wave with arbitrary polarization traveling perpendicular to this crystal face enters, it will be split into beams with polarizations along these two unique directions. The

indices of refraction of the anisotropic crystal in these two directions will be different and will be functions of the frequency of the entering light. Since $\lambda = v/\nu = c/n\nu$ where n is the index of refraction, c the speed of light, v the velocity of the light and ν its frequency which is related to the energy and hence constant in all media, the two rays will have different wavelengths while in the crystal. The result is that upon exiting the crystal the waves may have a new phase relationship. When recombined they may not produce light with the same intensity or plane of polarization as the entering ray. The phase relationship of the exited rays will be a function of the crystal thickness and the difference in the two indices of refraction, called the birefringence.

This behavior gives rise to several interesting optic effects which can be observed on a polarizing microscope. The polarizing microscope consists of a rotating stage between two polarizers. The upper polarizer, called the analyzer, can be removed from the optic path. The analyzer is normally set perpendicular to the polarizer beneath the stage. When the stage is empty, and the analyzer is inserted, no light can pass through the crossed polarizers. If any anisotropic crystal faced is placed on the stage and viewed under monochromatic light, several things will be observed. As the crystal is rotated at some point and

every 90° thereafter, the face will appear opaque. This is called extinction and the directions in the plane of the crystal face where this occurs are called extinction directions. The extinction directions correspond to the directions of polarization for the two unique rays. The explanation for extinction is that since the entering ray is now totally polarized along an allowed direction there is no component of the electric vector to comprise the second ray. Hence, the ray in the crystal is still polarized in the same direction as the entering ray and will be totally eliminated by the analyzer. If the crystal is rotated so that the extinction direction is not aligned with the polarization of the entering light, the crystal will again be transparent. However, the crystal may appear to be a color that does not correspond to either of the dichroic colors when viewed with white light. This is caused by the change in phasing of the two unique rays which are recombined in the analyzer. By using a Michel-Levy chart (19) the observed color of a colorless crystal can be converted to a path difference (retardation) in millimicrons. The retardation is equal to the birefringence times the thickness of the crystal. Since the indices of refraction can be measured accurately if their values are reasonably low and the retardation can be determined accurately by using a compensator, the crystal thickness can be determined.

This interference effect relates directly to spectroscopic measurements on crystals. Because the spectrophotometric measurements involve the intensity of the transmitted light, any process which effects this property will result in unreliable results. Therefore, polarized crystal spectra can only be measured while the light is polarized along an extinction direction. If the polarization is not along an extinction direction a complex interference pattern will be observed which will distort the absorbance spectrum. If polarized spectra are to be used to determine the molecular polarizations of electronic transitions, it is important to be able to relate the molecular polarizations to the crystal directions.

The relationship of the extinction directions to the crystal axes is also of importance. For an orthorhombic crystal, if the observed face is parallel to at least one of the crystallographic axes, that axis will be an extinction direction for all wavelengths. For example, if the face being observed is the (1,0,1) face of an orthorhombic crystal then the extinction directions are parallel and perpendicular to the b -axis. A similar situation results for crystals of higher symmetry except that some faces will be isotropic. For faces not parallel to any crystal axis, the extinction directions are not established by any simple relationship. In fact, the extinction directions for such

a face will be a function of wavelength. This implies that accurate measurements of the absorption may be quite difficult.

The situation for a monoclinic crystal is quite similar. However, only the unique b -axis is a defined extinction direction for all wavelengths. For faces not parallel to the b -axis, the extinction directions are not clearly indicated and again will be functions of wavelength. Any face of a triclinic crystal is essentially a general face and therefore, the extinction directions are not clearly specified and again are a function of wavelength. It is possible to determine the extent to which extinction directions are a function of wavelength if the crystal is observed on the polarizing microscope using white light for illumination. If the extinction directions are strongly altered with wavelength, the crystal face will not extinguish but will pass through a series of colors around the extinction directions. However, many general faces will show relatively clear extinction when viewed under white light. This is because the change in extinction direction with wavelength is quite small, but not because of any required extinction. Of course, if monochromatic light is used for illumination extinction will be observed every 90° for any crystal face.

In order to make crystal spectra useful, a method must be developed to relate the molecular polarizations, which

cannot be measured directly, to the crystal extinction directions. To the first approximation, this is accomplished by using the oriented gas model. In this model the crystal is considered to be an ideal gas in which all the molecules have the same alignment. No allowance is made for intermolecular interactions. Therefore, it is at best an approximation. The perturbations caused by crystal interactions can be quite large and result in experimental data that do not agree well with the calculated polarization ratios. However, the ratios obtained are usually accurate enough to allow the crystal polarization to be related to the proper molecular polarization.

To facilitate the calculation it is important to construct a set of orthogonal unit vectors to which both the crystal and molecular axes can then be related. For orthorhombic crystals or those of higher symmetry this is easy since the crystal a , b and c axes can be used. For lower symmetry crystals a set of vectors $\hat{i}$, $\hat{j}$ and $\hat{k}$ must be determined. To do this the crystal axes are formulated in terms of the orthogonal set. For a monoclinic crystal the following relations can be derived:

$$\begin{array}{ll} \hat{a} = \hat{i} & \hat{a} = (\sin\beta)\hat{i} + (\cos\beta)\hat{k} \\ \hat{b} = \hat{j} & \text{or } \hat{b} = \hat{j} \\ \hat{c} = (\cos\beta)\hat{i} + (\sin\beta)\hat{j} & \hat{c} = \hat{k} \end{array}$$

Usually, the formulation that is most convenient is used. For a triclinic crystal the procedure is essentially the same. One crystal axis is made colinear with an orthogonal axis. The second axis is placed in the plane of the first crystal axis used and any other axis. The third axis is formulated by taking the cross product of the first two orthogonal axes. In practice, this is accomplished by taking the dot product of the unformulated crystal axis with itself and each of the other crystal axes. The dot product with itself must yield unity while the other dot products must provide the cosines of the crystallographic angles between the axes. For example if $\hat{i}$ is placed along $\hat{a}$ and $\hat{j}$ in the $\underline{ab}$ plane, the following equations result:

$$\hat{a} = \hat{i}$$

$$\hat{b} = (\cos\gamma)\hat{i} + (\sin\gamma)\hat{j}$$

$$\hat{c} = c_1\hat{i} + c_2\hat{j} + c_3\hat{k}$$

$$\hat{c} \cdot \hat{a} = \cos\beta = c_1$$

$$\hat{c} \cdot \hat{b} = \cos\alpha = \cos\beta \cos\gamma + \sin\gamma c_2$$

$$c_2 = \frac{\cos\alpha - \cos\beta \cos\gamma}{\sin\gamma}$$

$$\hat{c} \cdot \hat{c} = 1 = (\cos\beta)^2 + (c_2^2) + c_3^2$$

$$c_3 = \sqrt{1 - \cos^2\beta - \left(\frac{\cos\alpha - \cos\beta \cos\gamma}{\sin\gamma}\right)^2} .$$

In matrix notation, these transformations can be written as

$$\begin{pmatrix} \hat{a} \\ \hat{b} \\ \hat{c} \end{pmatrix} = \begin{pmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{pmatrix} \begin{pmatrix} \hat{i} \\ \hat{j} \\ \hat{k} \end{pmatrix} .$$

This matrix can be used to transform from crystal axes to the orthogonal axes. A general crystal position (A,B,C) can be written as the vector $A\hat{a} + B\hat{b} + C\hat{c}$. This is, however,

$$\begin{aligned} & A(T_{11}\hat{i} + T_{12}\hat{j} + T_{13}\hat{k}) + B(T_{21}\hat{i} + T_{22}\hat{j} + T_{23}\hat{k}) \\ & + C(T_{31}\hat{i} + T_{32}\hat{j} + T_{33}\hat{k}) . \end{aligned}$$

The terms of this expression can be rearranged to obtain

$$\begin{aligned} & (AT_{11} + BT_{21} + CT_{31})\hat{i} + (AT_{12} + BT_{22} + CT_{32})\hat{j} \\ & + (AT_{13} + BT_{23} + CT_{33})\hat{k} . \end{aligned}$$

If the desired transformed vector is $I\hat{i} + J\hat{j} + K\hat{k}$ it is

seen that

$$(I,J,K) = (A,B,C) \begin{pmatrix} T_{11} & T_{12} & T_{13} \\ T_{21} & T_{22} & T_{23} \\ T_{31} & T_{32} & T_{33} \end{pmatrix} .$$

The transformed vectors can then be added or subtracted to obtain new vectors, crossed to obtain perpendicular vectors or dotted to obtain angles between them.

The transformed vectors can be used to calculate polarization ratios. If a molecular axis is not aligned along one of the crystal axis, then a band polarized in the direction of this axis will be seen in more than one crystal polarization. The ratio of the particular molecular polarization in the two crystal polarizations is the polarization ratio. To calculate the polarization ratio it is only necessary to know the component in the molecular direction of the electric amplitude of the light polarized along the extinction direction. The intensity of any wave is proportional to its amplitude squared. If θ is the angle between the crystal and molecular polarizations, then the component of the electric field amplitude ϵ_0 is $\epsilon_0 \cos\theta$ along the molecular axis. Therefore, the intensity is proportional to $\cos^2\theta$. This method can be applied directly to the case where the x , y , and z molecular axes are all unique and the

three polarization ratios can be calculated. When the molecular symmetry contains a C_3 or higher rotation axis, two of the axes, usually $\underline{x}$ and $\underline{y}$, are equivalent. This case has been worked out by Piper (20). His formulae are:

$$A_{\parallel} = \cos^2\theta A_{\underline{z}}^{\wedge} + \sin^2\theta A_{\underline{xy}}^{\wedge\wedge}$$

$$A_{\perp} = \sin^2\theta \cos^2\phi A_{\underline{z}}^{\wedge} + (1 - \sin^2\theta \cos^2\phi) A_{\underline{xy}}^{\wedge\wedge}$$

where $A_{\parallel}$ and $A_{\perp}$ represent the absorbances parallel and perpendicular to a determined extinction direction and $A_{\underline{z}}^{\wedge}$ and $A_{\underline{xy}}^{\wedge\wedge}$ are the absorbances with light polarized along the molecular $\underline{z}$ and $\underline{x}, \underline{y}$ directions. The angle θ is the polar angle between $\underline{z}$ and the "parallel" crystal axis while ϕ is the azimuthal angle measured from $\underline{x}$. The polarization ratios are determined by alternately using values of one and zero for $A_{\underline{z}}^{\wedge}$ and $A_{\underline{xy}}^{\wedge\wedge}$. This problem could also be treated like the general case but the $\underline{x}$ and $\underline{y}$ intensity contributions would have to be summed to calculate the ratios.

In Cowman and Gray's work (15) on $\text{Re}_2\text{Cl}_8^{2-}$, since the crystal structure was unknown, the polarization ratios could not be calculated. Therefore, the molecular polarizations were unknown. The crystal structure for $[(n\text{-C}_4\text{H}_9)_2\text{N}]_2\text{Re}_2\text{Cl}_8$ was reported recently by Cotton et al. (21). This structure proved to be rather complex. The cell parameters were $a = 10.933$, $b = 15.412$, $c = 16.435$ Å

and $\beta = 122.27^\circ$. These agreed reasonably well with those reported by Cowman and Gray (15). The space group was $P_{21/c}$. The $\text{Re}_2\text{Cl}_8^{2-}$ ion formed almost a perfect cube with a chlorine atom at each corner. The Re-Re bond can theoretically be placed in three equivalent orientations with no change in any of the bond lengths. In this compound two orientations were observed (see Figure 2), a major fraction with the metal-metal bond oriented primarily along the b -axis and a minor fraction which was perpendicular to b and located nearly along the ac diagonal. The occupancy percentages were found by varying the atomic occupation during structure refinement. It was found that 73.89% were aligned in the major fraction and 26.11% in the minor. The final structure had R values of $R_1 = .042$ and $R_2 = .056$. Cotton then derived a modified form of Piper's equations for calculation of polarization ratios in this case. He assumed $A = \sum_i f_i A_i$ where f_i is the occupancy of the i^{th} orientation of the disorderd structure. In this case

$$A_{\parallel} = \sum f_i (A_z \cos^2 \theta_i + A_{xy} \sin^2 \theta_i)$$

$$A_{\perp} = \sum f_i (A_z \cos^2 \gamma_i + A_{xy} \sin^2 \gamma_i) \quad .$$

The equation for $A_{\perp}$ was different from the original formulation. In this equation γ was the angle between the molecular z axis and the $A_{\perp}$ crystal direction. It can be shown that

Figure 2. A disorder in M_2X_8 species

$\cos\gamma = \sin\theta \cos\phi$. The result of this calculation gave a polarization ratio for a $\underline{z}$ -polarized transition of 2.158. The observed ratio was 2.203. Hence, the assignment of Cowman and Gray (15) were now truly experimentally confirmed.

Recently Gray and coworkers have used a very thick crystal of $[(n-C_4H_9)_4N]_2 Re_2Cl_4$ in an attempt to assign the weaker transitions in the crystal spectrum (in 18). Four new regions of weak absorption between the $\delta^* \leftarrow \delta$ and $\delta^* \leftarrow \pi(Cl)$ bands were observed. These are listed in Table 3. The first weak band maximized at $17,675\text{ cm}^{-1}$ and consisted of three progressions with a spacing of 225 cm^{-1} which corresponds to the Re-Re stretch in the excited electronic state. The lowest energy progression was $\underline{z}$ -polarized, the intermediate one $\underline{xy}$ and the higher energy $\underline{z}$. It was assigned to the transition ${}^1E_g \leftarrow {}^1A_{1g}(\pi^* \leftarrow \delta)$. A second absorption at $20,940\text{ cm}^{-1}$ exhibited only $\underline{xy}$ -polarized progression with a vibrational spacing of 400 cm^{-1} . It was assigned as ${}^1A_{1u} \leftarrow {}^1A_{1g}(d_{x^2-y^2} \leftarrow \delta)$. The third band at $23,645\text{ cm}^{-1}$ was very weak and displayed only one $\underline{xy}$ -polarized progression. It was assigned as ${}^1B_{1u} \leftarrow {}^1A_{1g}(\delta^* \leftarrow \pi)$. The fourth system consisted of two sharp peaks at $27,000$ and $28,100\text{ cm}^{-1}$ which are $\underline{z}$ -polarized. This was assigned to two A_{2u} spin-orbit components derived from the ligand to metal charge transfer states, a 3E_u and

b 3E_u . The assignments in this paper are subject to some question. First, there is some question about polarization ratios because of the disordered crystal structure. But secondly, the energy separations are not reasonably consistent. If the $\delta^* \leftarrow \delta$ band is at $14,140\text{ cm}^{-1}$, the $\pi^* \leftarrow \delta$ at $17,675\text{ cm}^{-1}$ and the $\delta^* \leftarrow \pi$ at $23,645\text{ cm}^{-1}$, it implies that the π^* level is $3,535\text{ cm}^{-1}$ above the δ^* and the π orbital is $9,505\text{ cm}^{-1}$ below the δ level. This implies that the $\pi^* \leftarrow \pi$ should be about $27,180\text{ cm}^{-1}$. The actual transition was at $39,215\text{ cm}^{-1}$. This is a difference of over $12,000\text{ cm}^{-1}$. A calculation of this type will not produce perfect agreement because it fails to include differences in electron correlation. However, $12,000\text{ cm}^{-1}$ is probably larger than any such error.

Attempts were made to isolate quadruply bonded complexes of other metals. As mentioned, the complex $\text{Tc}_2\text{Cl}_8^{3-}$ had been isolated. However, the expense of technetium and the problems of working with a radioactive element have permitted only limited work with this metal. Interest was also focused on the elements tungsten and molybdenum in the +2 oxidation state. Tungsten shows very little propensity to form quadruple metal-metal bonds. Cotton and Jeremic claimed to have prepared the carboxylate complexes (22). While spectral evidence seemed to support the tungsten carboxylates being isostructural with the known

molybdenum carboxylates (see below), the fact that no crystals were obtained prevented any crystal structure determination; and hence no positive confirmation was obtained. The tungsten complexes were an order of magnitude less stable than the molybdenum complexes which are easily synthesized. Recently Cotton and coworkers reported the X-ray structure of a quadruply bonded tungsten complex (Collins et al., 23). The complex had the formula $\text{Li}_4\text{W}_2(\text{CH}_3)_x\text{Cl}_{8-x}\cdot 2\text{THF}$. There was a disorder in the locations of the methylide and chloride ligands so that the formula could not be totally determined by the X-ray data. The complexes instability prevented accurate analytical determination of the formula but it appeared $x=4$. The tungsten-tungsten distance was 2.261 Å. Molybdenum (II) has been the most facile in forming quadruple bonds.

The history of the molybdenum (II) carboxylates is rather interesting. Abel et al. (24) were interested in preparing sandwich complexes analogous to the dibenzene-chromium (0) and the benzene-tricarbonylchromium (0) complexes. These chromium complexes are prepared by treating chromium hexacarbonyl with benzene. Molybdenum hexacarbonyl was reacted with benzoic acid and a yellow product was obtained. A small amount of this material was soluble in chloroform while the vast majority was insoluble in any solvent. It was postulated that the soluble

material was a monomer consisting of the desired sandwich complex in which the carboxylate oxygens were also bonded to the molybdenum. The insoluble material was postulated to be a related polymer in which the carboxylate groups bonded to neighboring sandwiched molybdenums. These concepts were quickly disproven when a similar reaction using acetic acid was carried out and provided a product similar to the benzoate complex (25). As all the carboxylate complexes were diamagnetic, they were supposed to be tetrahedral molybdenum (II). Later evidence (26) indicated that these were dimeric species. A structure consisting of two bridging carboxylates and one terminal one arranged around two tetrahedral molybdenum (II) atoms was proposed. However, the crystal structure soon proved this to be incorrect.

The first molybdenum carboxylate crystal structure that was solved was for the acetate complex (27). The crystal was triclinic with unit cell parameters $a = 8.35$, $b = 5.46$, $c = 7.50$ Å, $\alpha = 82.9$, $\beta = 105.1$ and $\gamma = 105.1^\circ$. The final value of R_1 , based on 395 reflections, was .071. The molecule consisted of the now familiar square planar arrangement of the four bridging carboxylate oxygens around each of the molybdenums. Unlike the rhenium carboxylates, there were no terminal ligands. For the charge to be balanced, the molybdenums had to be in the +2 oxidation state. The metal-metal distance was a surprisingly short 2.11 Å.

It was proposed that, like the rhenium case, the molybdenums were bonded through a quadruple bond. Because of the low number of reflections used, the structure was redetermined by Cotton et al. in 1974 (28). Their unit cell parameters were $a = 8.418$, $b = 5.500$, $c = 7.529$ Å, $\alpha = 84.13$, $\beta = 105.24$ and $\gamma = 106.00^\circ$. The molybdenum-molybdenum distance was determined to be 2.0934 Å. Several other carboxylates' structures have also been determined including $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ (29) (Mo-Mo distance 2.090 Å), $\text{Mo}_2(\text{O}_2\text{CH})_4$ (30) (Mo-Mo distance 2.091 Å) and $\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4 (\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ (31) (Mo-Mo distance 2.115 Å).

The electron orbital energies for molybdenum carboxylates have been calculated. Again both the molecular orbital and X_α scattered-wave techniques have been used. The molecular orbital calculation was performed using the self-consistent charge and configuration version of the Wolfsberg-Helmholtz molecular orbital method (SCCC-MO) by Dubicki and Martin (32). The results are shown in Figure 3. This is a rather crude calculation. The results were a bit surprising. Two unoccupied orbitals are predicted between the δ and δ^* levels. The first was an orbital which they labeled $\delta\sigma^*_{(x^2-y^2)}$. This was essentially the antibonding sigma orbital of the molybdenum $d_{x^2-y^2}$ and the ligand sigma orbitals. However, there were two such antibonding combinations. The $\delta\sigma^*$ level was the sigma

Figure 3. Bonding in Mo₂(O₂C-R)₄ compounds as calculated by molecular orbital and X_α methods

antibonding orbital with δ -bonding character. The other orbital is then the δ^*o^* . The fact that the δo^* -orbital was so low implied that the molybdenum $d_{x^2-y^2}$ orbitals had substantial δ -bonding overlap. The other unoccupied orbital with energy lower than the δ^* level was the $a_{1g}(d_{z^2}, p_z)$ orbital which was one of the nonbonding orbitals that Cotton (10) proposed to be between the δ and δ^* levels in energy. The second point that must be made about this paper is that the $e_u(\pi_{xz,yz})$ orbital is not included. Whether it is one of the unlabeled doubly degenerate orbitals listed or was left off the drawing either by mistake or because its energy was below the range of the drawing is unknown.

The X_α scattered-wave calculation was done by Norman and Kolari (33). The results were very similar to those for $Re_2Cl_8^{2-}$ (16). The lowest-energy unoccupied orbital in this calculation was the δ^* . The nonbonding orbitals were at very much higher energy. In addition, the amount of delta character in the ligand- $d_{x^2-y^2}$ sigma system was very much reduced in this calculation in contrast to the Dubicki and Martin (32) calculation. The results of the X_α calculation are also shown in Figure 3.

Both Dubicki and Martin (32) and Norman and Kolari (33) studied the electronic spectra of the molybdenum alkyl-carboxylates. In solution the typical spectrum

displayed a weak band at about $23,000\text{ cm}^{-1}$, a very intense band at about $33,000\text{ cm}^{-1}$ and an intense band at about $52,000\text{ cm}^{-1}$. The band at $23,000\text{ cm}^{-1}$ showed a distinct vibrational progression in the 77 K diffuse reflectance spectrum. The vibrational spacing was 350 cm^{-1} in the acetate complex. Because of the weak intensity of the $23,000\text{ cm}^{-1}$ band, Norman and Kolari assigned it to the forbidden $\delta \rightarrow \pi^*$ or $\pi \rightarrow \delta^*$. They claimed this may have resulted because configuration interaction slightly scrambled the orbital energies. The vibrational spectra of these complexes has also been examined both by Bratton et al. (16) and Ketteringham and Oldham (34). These two reports agreed on the observed spectra. The important a_{1g} metal-metal stretch appeared as a very strong band in the Raman at about 400 cm^{-1} . It varied from 410 cm^{-1} for the formate, to 404 cm^{-1} for the acetate to 398 cm^{-1} for the trifluoroacetate to 393 cm^{-1} for the glycine complex. Therefore, the 350 cm^{-1} reported for the vibrational spacing in the acetate electronic spectrum was reasonable for the a_{1g} metal-metal stretch in the excited electronic state. Since the electronic transition required the promotion of an electron from a metal-metal bonding orbital, the bond order in the excited electronic state would be lower producing a correspondingly lower metal-metal stretch.

In order to provide a firm assignment for the first

band in the electronic spectrum of the carboxylate complexes, polarized crystal spectra were required. The first such complex to be examined was $[\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4](\text{SO}_4)_2$. This compound was chosen because of its favorable molecular arrangement. The compound had been reported to crystallize in the tetragonal space group I_4 with unit cell parameters $a = 11.290$ and $c = 9.150 \text{ \AA}$ (31). The z -molecular axis is aligned along the c crystal direction. This meant that the symmetry of the site and the symmetry of the molecule were identical so that there should have been minimal perturbations to the electronic spectra of the crystal. It should be noted that the Mo-Mo distance of $2.115 \text{ \AA}$ is significantly longer than the $2.0934 \text{ \AA}$ of the acetate complex with a corresponding reduction in the metal-metal stretch from 404 cm^{-1} to 393 cm^{-1} . This may be partly because two of the oxygens from the sulfate counter ion are only $2.93 \text{ \AA}$ from the molybdenums. There may, therefore, be weak interactions in the terminal positions. In the case of an isolated terminal adduct, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4 \cdot 2(\text{NC}_5\text{H}_5)$, the Mo-Mo stretch dropped from 397 cm^{-1} to 367 cm^{-1} while the bond length increased from 2.090 to $2.129 \text{ \AA}$ (35). The other interesting feature of the crystal structure was that the formal molecular symmetry was S_4 in the crystal. This reduction occurred because the amino nitrogens are directed alternately along the z -direction.

The solution spectrum of the glycinate complex was quite typical for the alkyl-carboxylate species (31). A moderate band ($\epsilon \sim 100 \text{ cm}^{-1}\text{M}^{-1}$) was located at $22,624 \text{ cm}^{-1}$, an intense band ($\epsilon \sim 8000 \text{ cm}^{-1}\text{M}^{-1}$) at $34,247 \text{ cm}^{-1}$ and a third band ($\epsilon \sim 4000 \text{ cm}^{-1}\text{M}^{-1}$) at $44,053 \text{ cm}^{-1}$. The polarized crystal spectra are shown in Figure 4 (36). The spectra appeared to have greater intensity in the $\underline{z}$ -direction but did show appreciable intensity in the $\underline{xy}$ -polarization. In the $\underline{z}$ -polarization two vibrational series were observed. The first was a weak series beginning at $20,570 \text{ cm}^{-1}$ and consisted of four peaks. The last was observed as a shoulder on the first peak of the second $\underline{z}$ -polarized series which began at $21,510 \text{ cm}^{-1}$. The separation for the first series was $343 \pm 9 \text{ cm}^{-1}$ while for the second was $345 \pm 10 \text{ cm}^{-1}$. These values were consistent with the 350 cm^{-1} reported by Dubicki and Martin (32). The first weak series was proposed to be a transition which is forbidden in D_{4h} symmetry but allowed in S_4 symmetry. The peak at $20,750 \text{ cm}^{-1}$ was presumably the 0-0 transition. Possible transitions which would fulfill this selection rule were ${}^1A_{1u}$, ${}^1B_{1g}$, ${}^1B_{2g}$ + ${}^1A_{1g}$. The other $\underline{z}$ -polarized progression was assigned as a vibronic series. As its first band was at $21,510 \text{ cm}^{-1}$, it implied that the exciting asymmetric vibration had an energy of 940 cm^{-1} ($21,510 - 20,570$). In the $\underline{xy}$ -polarization, the vibrational structure appeared as pairs. The first $\underline{xy}$ -

Figure 4. Polarized absorption spectra for $[\text{Mo}_2(\text{O}_2\text{CCH}_2\text{NH}_3)_4](\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$

progression began at $21,790\text{ cm}^{-1}$ and consisted of seven lines with an average separation of $342 \pm 11\text{ cm}^{-1}$ while the second six peak progressions began at $21,930\text{ cm}^{-1}$ with an average separation of $344 \pm 8\text{ cm}^{-1}$. This electronic transition was also assigned as a vibronic transition excited by two asymmetric vibrations of 1220 and 1360 cm^{-1} . Only one totally symmetric vibration appeared in the four Frank-Condon progressions. This vibrational separation is consistent with the energy of the Mo-Mo stretch in the excited electronic state. This implied that the transitions were localized on the metals and probably involved a transition from a metal-metal bonding to an antibonding orbital. However, as the transition had such low intensity it was not consistent with the $\delta^* \leftarrow \delta$ transition.

The second carboxylate complex crystal spectra studied was the tetra- μ -formatodimolybdenum (II) (37). This complex crystallized in the orthorhombic space group $P_{2_1}2_12_1$ with unit cell parameters $a = 12.288$, $b = 12.930$, and $c = 5.500$ Å (30). In this case the metal-metal bond was not aligned along any crystal axis. The calculated polarization ratios for the observed (0,1,0) face were: For a z -polarized transition $A_c/A_a = 4.3$, for an xy -polarized transition $A_c/A_a = .36$. The observed spectra are shown in Figure 5. The first bond was at $21,870\text{ cm}^{-1}$ in the a -polarization and $21,880\text{ cm}^{-1}$ in c and was quite sharp. This single peak was

Figure 5. Polarized absorption spectra for $\text{Mo}_2(\text{O}_2\text{CH})_4$

followed by a pair of bands and thereafter by groups of three peaks. The separation for all three progressions was $350 \pm 10 \text{ cm}^{-1}$. This implied that a single a_{1g} vibration was the basis for the three Frank-Condon progressions. The second progression consists of the higher energy band in the pair and the middle band in the succeeding three pair groups. The third progression is then the higher energy band of each group of three.

The intensities of all three series appeared to be greater in the $\tilde{a}$ -polarization. From the polarization ratios this would imply $\tilde{xy}$ -polarization. However, the ratios of the intensities of the second progression to the first and third progressions were smaller in $\tilde{a}$ than in $\tilde{c}$ -polarization. This implied that the intermediate transition was probably $\tilde{z}$ -polarized. Because of the overlapping of these bands, it was quite difficult to accurately measure the actual intensities of these bands. This was complicated by the lack of molecular alignment resulting in components in both polarizations. In addition, crystal phonon effects could provide enhancement of intensity in the $\tilde{c}$ -direction. The end result of this was that the spectra of $\text{Mo}_2(\text{O}_2\text{CH})_4$ were believed to be fundamentally the same as for the glycine complex.

A series of carboxylate dimers was studied by Trogler et al. (38). Single crystal polarized spectra were obtained

for the acetate complex. The complexes $\text{Mo}_2(\text{O}_2\text{CCD}_3)_4$, $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ and $\text{Mo}_2(\text{O}_2\text{CH})_4$ were studied as films by subliming the complexes onto quartz disks. The resulting spectra were in good agreement with those reported for the formate complex, however, the assignments in this paper were quite different. First, the $\delta^* \leftarrow \delta$ assignment was not considered for the lowest energy transition because of the low intensity. The oscillator strength for this band in the acetate complex is only 1.1×10^{-4} for an acetonitrile solution. The basis for their assignments was a reduction in symmetry in the carboxylate complexes. In the structure of each of the carboxylates, each square plane of oxygens is distorted along the diagonals. This destroys the equivalence of the x - and y -axes and lowers the symmetry to D_{2h} . By using the location of several hot bands (transitions from excited vibrational states in the ground electronic state) in $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$, the supposedly electric dipole-forbidden origin was located at $21,862 \text{ cm}^{-1}$. The transition was assigned to ${}^1\text{E}_g \leftarrow {}^1\text{A}_{1g}$ ($\pi^* \leftarrow \delta$). This transition is electric dipole-forbidden but magnetic dipole-allowed. Such a transition would be at least 100 times less intense than an electric dipole-allowed one. Since this origin was not observed in the only crystal studied by Trogler et al. (38), its polarization is unknown. The exciting nontotally symmetric vibration was assigned to an a_{2u} mode with a frequency

of 191 cm^{-1} . The important point is that again the lowest energy transition was not $\delta^* \leftarrow \delta$.

The research to be reported here was undertaken to examine the crystal spectra of noncarboxylate molybdenum (II) dimers. Two compound systems were to be studied. The first was the complex $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$. This compound had been prepared by Brencic and Cotton (39). This complex is iso-electronic in the valence shell with $\text{Re}_2\text{Cl}_8^{2-}$ in which the $\delta^* \leftarrow \delta$ transition was observed. The second system to be studied was the tetra- μ -sulfatodimolybdate complexes. Both a molybdenum (II) and an oxidized mixed-oxidation molybdenum (II,III) complex were known. These were first prepared by Bowen and Taube (40) and were fully characterized by Angell et al. (41) and Cotton et al. (42, 43). In these complexes the molybdenum is again surrounded by four oxygen atoms. This system would test whether the oxygen ligands are responsible for the disappearance of the $\delta^* \leftarrow \delta$ transition. Also, the existence of two identical complexes that differ only by one electron would make an interesting study.

II. EXPERIMENTAL

A. Preparation of Crystals

The compounds $K_4Mo_2Cl_8$, $K_4Mo_2(SO_4)_4$ and $K_3Mo_2(SO_4)_4$ were all provided by Dr. Thomas R. Webb of Auburn University.

Crystals of $K_4Mo_2Cl_8 \cdot 2H_2O$ were prepared by dissolving small amounts of the powdered anhydrous compound in constant boiling hydrochloric acid (CBHCl) and allowing this solution to evaporate from between two inch square quartz plates in a dry bag inflated with nitrogen. The constant boiling HCl was prepared by distilling concentrated HCl under nitrogen and collecting only the fraction that distilled above $104^\circ C$. The distilled acid was approximately 6 M. The solutions of $K_4Mo_2Cl_8$ in CBHCl were quite sensitive to oxygen. However, it was noticed that solutions, even under nitrogen, changed from dark purple to yellow over the course of several days. This appeared to be not a decomposition but perhaps an aquation of the complex. In any event, the dark purple crystals of $K_4Mo_2Cl_8 \cdot 2H_2O$ were obtained after about five days of evaporation under nitrogen, sometimes from totally yellow solutions. The crystals appeared to be indefinitely stable in air and required no special handling.

Crystals of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ were prepared by literature methods (42). A U-tube with a glass frit dividing it into two compartments was used as a crystal grower. Into

one compartment was placed a saturated solution of K_2SO_4 dissolved in .1M H_2SO_4 while a solution of $K_4Mo_2(SO_4)_4$ powder in .1M H_2SO_4 was introduced into the other. The H_2SO_4 had been carefully deoxygenated before use and the grower was filled and sealed in a dry bag under nitrogen. Failure to exclude oxygen results in the oxidation of the complex and yields the compound $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$. The crystal grower was placed in a freezer at about $0^\circ C$ for 24 hours. Crystals of the complex were then filtered in air. Again, the crystals were air stable.

The compound $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ was totally insoluble. All attempts to dissolve this complex led to decomposition. The crystals provided by Dr. Webb were satisfactory for spectral work.

Potassium halide pellets were prepared in a standard I.R. pelletpress. Approximately 80 mg of halide-complex mixture was used for each pellet.

B. Spectra

All spectra were recorded on a Cary Model 14 spectrophotometer. For spectra in the ultraviolet-visible region ($7000 \text{ \AA}$ and less) a Model 1471200 high intensity light source and a Model 146045 low U.V. phototube were used. For the near-I.R. region ($20,000$ to $7,000 \text{ \AA}$) the standard

tungsten lamp was used as a source with a lead sulfide detector. In near-I.R. operation the optic path on the Cary 14 is reversed so that the radiation passes through the sample and is then monochromated. Polarization was obtained from two glan-type calcite polarizers. The eccentricity of the polarizers was about 40 at $10,000\text{ cm}^{-1}$ and greater than 200 at $30,000\text{ cm}^{-1}$. One polarizer was mounted in the sample compartment and could be rotated by an external crank. Under the U.V.-visible mode the polarizer was behind the crystal. In the I.R. mode it intercepted the beam before the crystal. The polarizer in the reference beam was set to match the sample polarizer to balance absorbance due to calcite and cancel out systematic polarization of the spectrophotometer optics. The reference beam was balanced and attenuated by pinholes and neutral density screens. This allows for the recording of absorbances greater than 2. The use of an attenuated reference beam results in larger slit widths and correspondingly lower resolution. Spectra with slits greater than 1 mm were rejected.

The crystals were mounted on metal plates. Crystals grown on quartz plates were loosened with absolute alcohol. Crystals were transferred to the plates on the tips of sewing needles. As the crystals were moved around they acquired static charge and would cling to the needles. The

crystals were held over the pinholes by a patch of vacuum grease. Two types of plates were used. Crystals for U.V.-visible studies were quite small, often about .5 mm on a side. These were mounted over pinholes made in 3 mil thick platinum sheet. Because of the decreased sensitivity in the near-I.R., much larger crystals were required. Slits of appropriate size were cut into brass sheet and the crystals were mounted over them. The slits were mounted vertically in the Cary 14 to maximize the amount of crystal in the light beam.

Two types of cryostats were used for recording of low temperature spectra. In one type the metal plate on which the crystal was mounted was placed against a copper cold finger in the vacuum space of the cryostat. The top of the cold finger was the bottom of the can containing the coolant and the crystal was cooled by conduction. The coolant can was filled with either liquid nitrogen or helium. Since the crystal was cooled by conduction through the grease holding it in place, the metal plate and the cold finger the temperature of the crystal was somewhat uncertain. Spectra in which liquid helium was the coolant were assigned a temperature of 15 K although they were probably lower. No temperature measurement device was available for these. The second cryostat was an Andonian Cryogenics model which used a separate sample can. Liquid helium was throttled

from the coolant can, past a vapor heater and then cooled the sample. Since the sample was in direct contact with the cooling vapor or liquid, its temperature could be accurately determined. A four lead germanium resistance thermometer was used for temperature measurement. To minimize the resistance of the leads, the resistance was read using a constant current source which was constructed. One milliamperere of current powered the circuit through the power leads, and the voltage was read across the thermometer resistor. The voltage, read in millivolts, was equal to the resistance in ohms. However, at liquid helium temperatures the resistance was over $250\ \Omega$, so a power of over 2.5×10^{-4} watts was heating the resistor. This undoubtedly led to the temperature readings being slightly too high. Therefore, the temperature listed are maximum values but probably are within 1° of the actual value. Temperature was maintained to within $\pm .2^\circ$ while recording spectra.

Baselines were determined by using a blank pinhole and recording blank spectra in the cryostat with the same polarizer settings and reference attenuation. The spectra and baselines were automatically punched on cards by a Cary-Datex digitalization system. The spectra were assembled, baselines subtracted and the finished spectra plotted on the Calcomp plotter by a program that was written. The algorithm for this program was, in part, based on the program IPLLOT by

Dr. L. D. Hunter (44).

To determine the molar absorptivities, the thickness of the crystal had to be determined. Two methods were used. Occasionally, very good crystals with optic faces were obtained. In these crystals interference caused by internal reflection was observed. The interference pattern in the spectra could be used to determine the crystal thickness (45). Secondly, the indices of refraction could be determined and the interference color under crossed polars used to obtain the thickness. Indices of refraction were determined by the Becke line method utilizing a set of standard liquids from the Cargille Co. Accurate measurements of the retardation were made using a rotary compensator. The molar concentrations required for the molar absorptivity calculation could be obtained by determining the volume of the unit cell and the number of molecules in this volume. The molar absorptivity then has the standard form $\epsilon = A/bc$ where ϵ is the molar extinction coefficient, b is the crystal thickness, c the molar concentration and A the absorbance.

For accurate assignment of crystal spectra, the face being observed had to be identified. For $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ this was accomplished by taking rotation photographs using the two facial axes as rotation axes. The axes for the other compounds were identified on an automatic four-circle

diffractometer. The facial axes were identified by aligning the axes vertically. The compound $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ was aligned on the Syntex P_{21} diffractometer while $K_4Mo_2Cl_8$ was aligned on the Ames Laboratory diffractometer (46). In addition, a complete set of diffraction data was taken for $K_4Mo_2Cl_8$ to provide the extent of disorder in the crystals used for spectroscopy as compared to published values.

III. RESULTS AND DISCUSSION

A. $K_4Mo_2Cl_8 \cdot 2H_2O$

The compound $K_4Mo_2Cl_8$ was first prepared by Brencic and Cotton in 1969 (39). The compound was prepared by reacting $Mo_2(CH_3CO_2)_4$ with hydrochloric acid at about 0° . As solutions of $Mo_2Cl_8^{4-}$ decomposed quickly in the presence of oxygen, the acid had to be carefully deoxygenated. The initial product was quite soluble in the acid but was readily precipitated by the addition of KCl. The ion $Mo_2Cl_8^{4-}$ like $Re_2Cl_8^{2-}$ had a d^8 electronic configuration.

The crystal structure of $K_4Mo_2Cl_8 \cdot 2H_2O$ was reported simultaneously with the preparation (39). The compound crystallized in the orthorhombic space group P_{bam} with unit cell dimensions $a = 8.005$, $b = 13.267$ and $c = 8.059$ Å. There were two molecules per unit cell. The structure of the ion was the same as $Re_2Cl_8^{2-}$. It consisted of two square planes stacked in an eclipsed configuration. The molybdenum-molybdenum distance was $2.138(4)$ Å and the molybdenum-chlorine distance was 2.45 Å. As in $Re_2Cl_8^{2-}$ the metal distance was shorter than the eclipsed chlorine-chlorine distance which was an average of 3.41 Å. This distance was only slightly longer than the 3.35 Å between cis-chlorines within a given plane. The chlorines form nearly a cube. As mentioned earlier, this can lead to a disorder in which

the metal-metal bond can flip 90° with nearly no change in the ligand positions (see Figure 2). Such a disorder was observed in this crystal. The majority fraction which represented 93% of the molecules was oriented with the metal-metal bond colinear with the crystal c -axis. For the other 7%, the metal-metal bond was in the ab -plane and made about a 34.1° angle with the b -axis. Lastly, the water molecules were not coordinated to the molybdenums.

When crystals were grown between quartz plates, two types of crystals were obtained. The single crystals of $K_4Mo_2Cl_8 \cdot 2H_2O$ appeared as dark purple-red prisms with a well developed (1,0,0) face. These crystals displayed the typical extinction under crossed polars. They also displayed strong dichroism. The second type of crystal appeared as purple rhomboids. These crystals displayed very little dichroism. When viewed under crossed polars they displayed unusual behavior. The crystals could be divided into four regions by the facial diagonals. At some point, the two opposed quadrants would get very dark and change to various colors. However, they never cleanly extinguished. When the other quadrants assumed an identical alignment, they behaved similarly. These crystals were assumed and later confirmed to be twins.

Both single and twined crystals were studied by X-ray diffraction. The single crystals were studied to determine

if the orientational disorder was the same in the crystals used for spectroscopy as it was in those reported by Brencic and Cotton (39). A complete data set was collected. Unit cell parameters were determined to be $a = 8.019$, $b = 13.302$ and $c = 8.053$ Å which was in good agreement with those previously reported. The structure was not determined because it was apparent that the data set was nearly identical with that of Brencic and Cotton. The twins were mounted with the long diagonal of the face along the fiber. The crystal quickly indexed to a unit cell with identical dimensions as the single crystal. The b -axis was identified as the axis of rotation. However, the rotation photographs, most notably the b -axis rotation, under close examination indicated twinning. The fact that this twin was so reproducible and that it indexed so well was proof of a strong twinning law. This twinning probably involves the similarity in length of the a - and c -axes. No determination was made, though, of the exact plane of twinning.

The vibrational spectra of both the anhydrous and dihydrated $K_4Mo_2Cl_8$ have been studied (16, 34, 47). Both the I.R. and Raman bands are reported in Table 3. The important frequencies were the Raman bands at $\sim 350\text{ cm}^{-1}$ which is the metal-metal stretch and $\sim 280\text{ cm}^{-1}$ which is the totally symmetric metal-chlorine stretch. The 350 cm^{-1} , however, may not be truly representative of the metal-metal stretch.

Table 3. Vibrational frequencies for $K_4Mo_2Cl_8$

$K_4Mo_2Cl_8$		$K_4Mo_2Cl_8 \cdot 2H_2O$	
IR ^a (cm ⁻¹)	Raman ^b (cm ⁻¹)	IR ^a (cm ⁻¹)	Raman ^c (cm ⁻¹)
		3535 ^d m	
		3485 ^d m	
		1640 ^d w	
	345.9 s	434 s	349 s
302 s	315.6 vw	300 sh	320 s
275 s	276.7 m	288 s	280 m
		243 sh	
183 m	191.1 w	188 sh	194 w
160 m		160 m	
128 s		142 vs	
113 m		115 w	
102 vw		108 vw	
91 m		91 vw	
68 ^b vw			
s = strong		m = medium	
w = weak		sh = shoulder	
v = very			

^aReference 16.^bReference 47.^cReference 34.^dWater frequencies.

In the bromide compound $(\text{NH}_4)_4\text{Mo}_2\text{Br}_8$ the metal-metal distance was a comparable 2.135 Å, but the metal-metal stretching frequency was only 335 cm^{-1} (34). Ketteringham and Oldham (34) speculated that the metal-metal stretch was being raised by interaction with the Mo-Cl stretch. Clark and Franks (47) have reported the resonance Raman spectra of $\text{K}_4\text{Mo}_2\text{Cl}_8$ observed by excitation with an Ar^+ laser operating at 5145 Å which nearly corresponded to the wavelength of the first observed transition. Two progressions were observed. The first consisted of six peaks based on the metal-metal stretch. The second five peak progression was based on the combinations of the metal-chlorine ($\nu = 1$) with the metal-metal stretch ($\nu = 0, 1, 2$, etc.). The harmonic constant was determined to be $347.1 \pm .03$ and the anharmonicity constant was 0.52 ± 0.06 .

There have been several previous reports of the electronic spectrum of $\text{K}_4\text{Mo}_2\text{Cl}_8$. No solution spectrum have been reported, however. This is because $\text{Mo}_2\text{Cl}_8^{4-}$ undergoes rapid aquation with a blue shift for the lowest energy transition. Bowen and Taube (40) have investigated this aquation and reported that in noncomplexing acids at least three chloride ligands are replaced by water. However, their study was not thorough enough to determine the exact products or rates. Clark and Franks (47) reported that aquation occurs rapidly even in concentrated hydrochloric acid saturated

with HCl. To obtain a spectrum of the yellow aquated compound solution and some idea of the rate of aquation, the reaction of a 2.9×10^{-3} M solution of $K_4Mo_2Cl_8$ in deoxygenated constant boiling hydrochloric acid (~ 6 M) was studied briefly. At room temperature the reaction appeared to be first order with a half-life of ~ 12.5 minutes. After three hours the spectrum displayed two bands in the visible; one at $13,333\text{ cm}^{-1}$ ($\epsilon = 109$) and one at $23,696\text{ cm}^{-1}$ ($\epsilon = 1,360$). The extinction coefficients were based on the assumption that the chromophore was still dimeric. The band at $23,696\text{ cm}^{-1}$ seemed to gain intensity in proportion to the loss in intensity of the band at $19,300\text{ cm}^{-1}$. This band would then correspond to the lowest energy band in $Mo_2Cl_8^{4-}$. The band at $13,333\text{ cm}^{-1}$ was a band not observed in $Mo_2Cl_8^{4-}$ which could be indicative of terminal coordination or reduced symmetry in the aquated ion. From this data the molar absorptivity of $K_4Mo_2Cl_8$ in hydrochloric acid at $19,300\text{ cm}^{-1}$ was determined to be about $870\text{ M}^{-1}\text{cm}^{-1}$.

The solid state spectrum obtained by diffuse reflectance was reported by Clark and Franks (47). They observed two bands in the compound $K_4Mo_2Cl_8$. One was at about $19,000\text{ cm}^{-1}$ and the other at about $30,000\text{ cm}^{-1}$. For the compounds where the cation was rubidium, cesium, and ammonium, but not potassium, a band at about 6250 cm^{-1} was also observed. At 77 K this band displayed a vibrational progression of

about 285 cm^{-1} . They assigned the band at $\sim 19,000\text{ cm}^{-1}$ as ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$) while the band at $\sim 6250\text{ cm}^{-1}$ was assigned as the corresponding triplet. However, there are some reservations to the triplet assignment. A separation of nearly $13,000\text{ cm}^{-1}$ between a singlet and its triplet would be very large though perhaps not impossible. The cation dependence would also be unusual. The transition at 6250 cm^{-1} was probably due to an impurity. One possible impurity might be the $\text{Mo}_2\text{Cl}_8^{3-}$ ion. This ion has never been isolated. However, the transition energies for the known compounds with bond order 3.5, $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ (see below) and $\text{K}_3\text{Tc}_2\text{Cl}_8$ (48) absorb in this region. Undoubtedly the large counter-ions would help to stabilize this compound. The lower energy of the vibrational progressions would also be consistent with the reduction in bond order.

Cowman and Gray (15) reported the solid state absorption spectrum obtained from a compressed pellet. At 5 K the spectrum revealed richly structured vibrational progressions with an origin at $17,897\text{ cm}^{-1}$ and a spacing of about 351 cm^{-1} . This transition was assigned as ${}^1A_{2u} \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \delta$). Both Cowman and Gray (15) and Clark and Franks (47) commented on the fact that the low temperature vibrational spacing is about 350 cm^{-1} as compared to a ground state spacing of about 349 cm^{-1} . The fact that there was little change between the ground and excited state vibrations

was attributed to a change in the interstate interaction between the metal-metal and metal-chloride totally symmetric stretching modes.

A complete X_α scattered-wave calculation for $\text{Mo}_2\text{Cl}_8^{2-}$ has been reported by Norman and Kolari (49, 50). The results of the calculation are shown in Figure 6. The orbitals shown all have 80% or more metal character. This diagram is quite similar to those shown for $\text{Re}_2\text{Cl}_8^{2-}$ and $\text{Mo}_2(\text{O}_2\text{C-R})_4$ (Figures 1 and 3). In this calculation, the percentage metal and chlorine characters of each orbital were obtained. All the metal-metal orbitals contained some chlorine character. This is not explained well by π -bonding. The π^* and δ^* levels could form π -bonds with various combinations of the 16 nonbonding chlorine 3p-orbitals. However, in all cases there is more chlorine character in the filled metal-metal bonding orbitals than in the empty antibonding orbitals. This would argue against π -bonding. A better explanation is configuration interaction between states with the same symmetry. As the chlorine nonbonding orbitals have energy comparable or slightly less than the metal-metal bonding orbitals they interact strongly with each other and this raises the energy of the metal-metal bonding orbitals. Similar interactions are possible with the metal-metal antibonding orbitals but since the energy difference is greater the interactions are much less. This idea is further

Figure 6. The metal orbital levels in $\text{Mo}_2\text{Cl}_8^{4-}$ calculated by the x_α method

substantiated by the fact that in the compound $K_4Mo_2(CH_3)_8$ the lowest energy transition is blue shifted (51) corresponding to a widening of the gap between bonding and antibonding orbitals. This results because there are no non-bonding orbitals available for interaction and the bonding orbitals are lowered in energy more than the antibonding Mo-Mo orbitals. In Table 4 the calculated transition energies are listed. In general, the calculated transition energies are lower than those observed.

Crystals of $K_4Mo_2Cl_8 \cdot 2H_2O$ displayed very strong dichroism. When the light was polarized along the $\tilde{c}$ -axis the crystals were dark red. When polarized along the $\tilde{b}$ -axis the crystals became light red to pink depending on the crystal thickness. This dichroism was also observed on the spectrophotometer. The $\tilde{c}$ -polarization displayed a very intense band at $\sim 19,000 \text{ cm}^{-1}$. This band was always too intense to be measured for the crystals used. The $\tilde{c}$ -direction corresponds to the metal-metal axis direction for 93% of the molecules. It was possible to record good $\tilde{b}$ -polarized spectra and the lowest energy band in $\tilde{b}$ -polarization is shown in Figure 7 at both room temperature and 3.7 K. It was assumed that this $\tilde{b}$ -polarized spectrum represented a component of the $\tilde{z}$ -polarization of the minority orientation. To obtain an estimate of the intensity of the $\tilde{c}$ -polarized spectrum, polarization ratios were calculated. The molecular

Table 4. Calculated and observed transitions for $\text{Mo}_2\text{Cl}_8^{4-}$ ^a

Transition ^b Symmetry	Type	Observed ^c Transition (cm ⁻¹)	Calculated Transition (cm ⁻¹)
$^1A_{2u}$	$\delta^* \leftarrow \delta$	19,000	13,700
1E_g	$\delta^* \leftarrow \pi$	>~22,000	23,700
$^1A_{2g}$	$\delta\sigma^* \leftarrow \delta$		24,600
1E_u	$\delta\sigma^* \leftarrow \pi$	34,100	34,100
1E_u	$\delta^* \leftarrow L_n^d$		37,500
1E_u	$\delta^* \leftarrow L_n^d$		38,600
$^1A_{2u}$	$\pi^* \leftarrow \pi$		39,400

^aReference 50.^bAll transitions originate from a $^1A_{1g}$ ground state.^cThis work.^d L_n = ligand nonbonding.

Figure 7. The b-polarized spectrum of the lowest-energy transition of $K_4Mo_2Cl_8 \cdot 2H_2O$

z-axis was coincident with the crystal c-axis for the majority fractions but was 34.1° from b for the minority. The resulting polarization relationship was $c:b = .93/ (.07 \times .68) = 19.7$ where the $.68 = \cos^2 34.1$ and the $.93$ and $.07$ are the occupational percentages. These occupational percentages may vary slightly for crystal to crystal which would result in some error in the molar absorptivity. For the spectrum shown in Figure 7 the crystal was determined to be $12 \pm 3 \mu$ thick. Therefore, the molar absorptivity may be found by multiplying the absorbancies by $215 \pm 50 \text{ cm}^{-1} \text{M}^{-1}$. Using this factor and the calculated polarization ratio the oscillator strength was determined to be about 3.1×10^{-2} . This was quite comparable to the 2.3×10^{-2} reported for $\text{Re}_2\text{Cl}_8^{2-}$ in methanol (4). Again the oscillator strength was lower than what would be expected for a fully allowed transition. The band at $19,000 \text{ cm}^{-1}$, however, was assigned as in $\text{Re}_2\text{Cl}_8^{2-}$ (15) as $^1\text{A}_{2u} + ^1\text{A}_{1g} (\delta^* + \delta)$.

The $19,000 \text{ cm}^{-1}$ band exhibited vibrational structure at 3.7 K which was almost but not totally lost at room temperature. There were three A_{1g} vibrations in $\text{Mo}_2\text{Cl}_8^{4-}$ which were the bases for Frank-Condon progressions. These were the metal-metal stretch, a metal-chloride stretch and a Mo-Mo-Cl bending mode. Since the lowest observed transition, $\delta^* + \delta$, is metal localized, the metal-metal stretch should produce the most intense progression. The separa-

tion of the peaks in an observed progression would then correspond to the frequency of this metal-metal stretch in the excited electronic state.

In the observed 3.7 K b-polarized $\delta^* \leftarrow \delta$ transition for the minority orientation, shown in Figure 7, at first there appeared to be only one vibrational progression. The actual separations as read from the recorder chart are given in Table 5. The first separation is 381 cm^{-1} whereas the average for the next five well resolved bands is $327 \pm 7.5 \text{ cm}^{-1}$. This large separation between the first two observed vibrational levels was reproducible and was observed in all crystals studied. This value of 381 cm^{-1} was greater than either the metal-metal stretch of $\sim 349 \text{ cm}^{-1}$ or the Mo-Cl stretch of $\sim 280 \text{ cm}^{-1}$ and implied that what was being observed is fairly complex. The separation of 347 cm^{-1} between the second and third members was probably also high. The remaining separations were reasonable for the metal-metal stretching frequency in the excited state. It was also noticed that the vibrational components were quite broad. It was postulated that the irregularity in the separations is due to the contribution of more than just the one totally symmetric vibration. These vibrations would have different Frank-Condon factors. As the $\delta^* \leftarrow \delta$ transition would most alter the Mo-Mo bond, the metal-metal stretch would be most distorted and have the most pronounced

Table 5. Vibrational structure in the 19,000 cm^{-1} band for b-polarization of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ and for KCl pellets of $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ and for $\text{K}_4\text{Mo}_2\text{Cl}_8$ at liquid helium temperatures

Single Crystal $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ 3.7 K		KCl Pellet $\text{K}_4\text{Mo}_2\text{Cl}_8 \cdot 2\text{H}_2\text{O}$ 3.7 K		KCl Pellet $\text{K}_4\text{Mo}_2\text{Cl}_8$ 15 K	
$\bar{\nu}$ cm^{-1}	$\Delta\bar{\nu}$ cm^{-1}	$\bar{\nu}$ cm^{-1}	$\Delta\bar{\nu}$ cm^{-1}	$\bar{\nu}$ cm^{-1}	$\Delta\bar{\nu}$ cm^{-1}
18,083 $\pm$ 6		17,912 $\pm$ 20		17,930 $\pm$ 15	
18,464 $\pm$ 6	381	18,280 $\pm$ 20	370	18,260 $\pm$ 15	330
18,804 $\pm$ 6	340	18,660 $\pm$ 20	380	18,620 $\pm$ 15	300
19,128 $\pm$ 6	324	19,000 $\pm$ 20	340	18,960 $\pm$ 15	340
19,445 $\pm$ 10	327	19,340 $\pm$ 20	340	19,280 $\pm$ 20	320
19,775 $\pm$ 15	320	19,660 $\pm$ 30	320	19,620 $\pm$ 20	340
20,101 $\pm$ 20	<u>325</u>	19,990 $\pm$ 30	<u>330</u>	19,920 $\pm$ 20	<u>300</u>
Ave. 336 $\pm$ 23		Ave. 347 $\pm$ 23		Ave. 322 $\pm$ 18	
Overall Average = 335 $\pm$ 23					

and longest series. The involvement of more than one a_{1g} vibration would be consistent with the spectrum of $\text{Re}_2\text{Cl}_8^{2-}$ (15) and the resonance Raman spectrum of $\text{Mo}_2\text{Cl}_8^{4-}$ (47).

In order to observe the extent of this irregularity in the vibrational progressions, spectra of both the anhydrous

and dihydrated $\text{Mo}_2\text{Cl}_8^{4-}$ compounds were obtained from compressed KCl pellets. The pellet spectra in the region of the $\delta^* \leftarrow \delta$ transition are shown in Figure 8 and the observed vibrational progressions tabulated in Table 5. The energy of the bands in the pellets was lowered by over 100 cm^{-1} from that in the single crystal. There were two possible explanations for this. The first was that the pellet spectra correspond to the spectrum of the majority fraction in the crystal. As none of the vibrational structure was located in the c-polarized spectrum, the agreement with the pellet spectrum could not be confirmed by our experiments. However, this would imply that the spectrum of the minority fraction may be distorted by the crystal field because of its different orientation. A second explanation was that the change in environment from the crystal to the pellet resulted in this lowering of energy. With regards to the vibrational progressions, the dihydrate pellet appeared to exhibit the unusually large separations observed in the crystal while the anhydrous compound did not. In fact, the 322 cm^{-1} average separation for the anhydrous compound agrees well with the 324 cm^{-1} average separation for the last four bands in the dihydrate crystal. Lastly, the dihydrate pellet spectrum agrees well with that of Cowman and Gray (15).

Returning to the b-polarized crystal spectrum, the

Figure 8. KCl pellet spectra for $K_4Mo_2Cl_8$ and $K_4Mo_2Cl_8 \cdot 2H_2O$ at ~5 K

first observed vibrational band at $18,083\text{ cm}^{-1}$ seemed to display a low energy tail. As this first band was presumed to be the 0-0 transition, it should be quite sharp. It was possible that this tail represented the spin-forbidden transition ${}^3A_{2u} \leftarrow {}^1A_{1g}$. The spin-orbit coupling of molybdenum is sufficiently low that such a transition should be quite weak. However, the proposed ${}^3A_{2u} \leftarrow {}^1A_{1g}$ transition would be polarized in the xy -polarization. Therefore this absorption in the b -polarization would be associated with the majority orientation and the intensity observed in the $17,200$ - $17,800\text{ cm}^{-1}$ region might be reasonable. However, a separation of only $1,000\text{ cm}^{-1}$ between ${}^3A_{2u}$ and ${}^1A_{2u}$ seems somewhat small and in the absence of vibrational structure, this assignment is only problematical.

The polarized crystal spectra for $K_4Mo_2Cl_8 \cdot 2H_2O$ between $20,000$ and $32,000\text{ cm}^{-1}$ are shown in Figure 9. There was weak absorption between $22,000$ and $24,000\text{ cm}^{-1}$. This absorption was poorly characterized both with regards to its polarization and with regard to its temperature dependence. Norman and Kolari (50) calculated that there should be two vibronic transitions in this region. One would be ${}^1E_g \leftarrow {}^1A_{1g}$ ($\delta^* \leftarrow \pi$) at $23,700\text{ cm}^{-1}$ and the other ${}^1A_{+g} \leftarrow {}^1A_{1g}$ ($\delta\sigma^* \leftarrow \delta$) at $24,600\text{ cm}^{-1}$. These assignments would be consistent with the observed spectra.

The next observed band was at $28,800$. It was strongly

Figure 9. Polarized absorption spectra for $K_4Mo_2Cl_8 \cdot 2H_2O$

c-polarized. This band represents the majority orientation and is, therefore, z-polarized. While this band was not very intense, it did narrow and gain intensity upon cooling. It, therefore, behaved as a dipole-allowed transition.

There are two possible assignments for this band. The first is ${}^1A_{2u} + {}^1A_{1g} (\delta\sigma^* + b_{1g}L_n)$. This transition would be dipole-allowed and c-polarized for the majority orientation. The low intensity would occur because it corresponds to a promotion of an electron from a chlorine 3p-orbital with pure π -symmetry, with respect to an Mo-Cl bond, into an antibonding orbital with pure sigma character. Jorgensen (52) has commented that such charge transfer bands typically have low intensity. However, such an assignment would be in disagreement with the calculations of Norman and Kolari (50) which indicate that such a transition should have an energy of at least $48,000 \text{ cm}^{-1}$. A second possible assignment is as the triplet of the nearest higher energy fully allowed transition. The KCl pellet spectrum indicated this band was at $31,400 \text{ cm}^{-1}$. The c-polarized crystal spectrum could be recorded from low energy to $31,800 \text{ cm}^{-1}$ whereas the b-polarized spectrum could only be obtained out to $28,600 \text{ cm}^{-1}$. This implies that this band at $31,400 \text{ cm}^{-1}$ is xy-polarized. This band is then akin to the $30,870 \text{ cm}^{-1}$ band in $\text{Re}_2\text{Cl}_8^{2-}$ (17). Gray and coworkers (in 17) attributed this band to the transition from a chlorine e_g level to

the δ^* level (${}^1E_u + {}^1A_{1g}$). Norman and Kolarik (50) have calculated that the transition ${}^1E_u + {}^1A_{1g}$ ($\delta\sigma^* + \pi$) should occur at $31,400\text{ cm}^{-1}$, precisely the energy for this band. The charge transfer band akin to the one in $\text{Re}_2\text{Cl}_8^{2-}$ is calculated to be at $37,500\text{ cm}^{-1}$. Either of these possible assignments satisfies the symmetry requirements. The transition at $28,800\text{ cm}^{-1}$ could then possibly be ${}^3E_u + {}^1A_{1g}$. However, this triplet transition would have intensity in both the $\underline{z}$ - and $\underline{xy}$ -polarizations. It is nearly totally $\underline{z}$ -polarized ($\underline{z}$ -polarized for the majority orientation). While there is a little shoulder in the $\underline{b}$ -polarization, it probably represents the minority orientation. In addition, a similar band was observed in $\text{Re}_2\text{Cl}_8^{2-}$ (17). This band was at about $35,700\text{ cm}^{-1}$. While it is shown in the figure in the reference as being $\underline{z}$ -polarized, it is reported in the table as being $\underline{xy}$ -polarized. It is assumed that the table is in error. If the drawing is correct, this band in $\text{Re}_2\text{Cl}_8^{2-}$ could not have been the triplet band, ${}^3E_u + {}^1A_{1g}$, because it was on the high energy side of the $\underline{xy}$ -polarized transitions at $30,870$; $31,750$; and $34,480\text{ cm}^{-1}$. Therefore, the first assignment is favored. This would imply that the chlorine nonbonding orbitals may have higher energies than calculated.

The observed spectrum is summarized in Table 4.

The spectra of other nonbridged molybdenum dimers are

very similar in the location of their bands. The bands in the spectra of $\text{Mo}_2(\text{CH}_3)_8^{4-}$, $\text{Mo}_2(\text{en})_4^{4+}$ and $\text{Mo}_2^{4+}(\text{aq})$ as well as $\text{Mo}_2\text{Cl}_8^{4-}$ are reported in Table 6. It will be noted that the lowest energy band is blue shifted from $\text{Mo}_2\text{Cl}_8^{4-}$ as would be expected because of the chlorine nonbonding interactions with the metal-metal orbitals.

B. $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ and $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$

As mentioned in the introduction, the spectra of the tetra-carboxylate dimolybdenum compounds were somewhat anomalous in that the lowest energy band has not been assigned as the $\delta^* \leftarrow \delta$ transition. To determine if there was something unique about bridged dimers with oxygen ligands, the compounds $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ and $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ were studied. These compounds also provided a unique opportunity to study the effects of oxidation on the electronic spectrum.

The compound $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ was first prepared by Bowen and Taube (40). The compound was prepared by reacting $\text{K}_4\text{Mo}_2\text{Cl}_8$ with H_2SO_4 and then precipitating the product by the addition of solid K_2SO_4 . All reactions must be carried out under nitrogen. If oxygen were not excluded from the system, the oxidized compound $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ was produced. This oxidized species was quite insoluble in almost all solvents.

The crystal structure of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$ was reported by

Table 6. Solution spectra of various unbridged molybdenum dimers

$\text{Mo}_2(\text{en})_4^{4+}$ ^a		$\text{Mo}_2^{4+}(\text{aq})$ ^a		$\text{Mo}_2(\text{CH}_3)_4^{4-}$ ^b		$\text{Mo}_2\text{Cl}_8^{4-}$	
Energy (cm^{-1})	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	Energy (cm^{-1})	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	Energy (cm^{-1})	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)	Energy (cm^{-1})	ϵ ($\text{M}^{-1}\text{cm}^{-1}$)
20,920	483	19,841	377	19,500	<15,600	19,300	870 ^c
27,778	36.4	27,027	40	25,000		~22,000	
42,553	966			30,800		28,800	

^aReference 40.

^bReference 51.

^cCorrected for aquation.

Cotton et al. (43), and the unit cell is shown in Figure 10. The compound crystallized in the monoclinic space group $C_{2/c}$ with unit cell parameters $a = 17.206$, $b = 10.193$, $c = 10.061$ Å and $\beta = 94.92^\circ$. There were four molecules per unit cell. The structure was rather complex. The basic molecular unit was quite similar to the carboxylate complexes consisting of four sulfates bridging the two molybdenums. The Mo-Mo distance was 2.111 Å. The molybdenums did not lie in the plane of the four oxygen ligands but were displaced towards each other by about .32 Å producing Mo-Mo-O angles of about 94.2° . Each of the molybdenums was also coordinated in both terminal positions to oxygens from the sulfates on neighboring ions. The Mo-O distance for this terminal coordination was 2.591 Å, indicative of weak coordination. Again, the waters were not involved in the molybdenum coordination. The crystals displayed well developed (1,0,0) faces. The crystals usually grew as square plates with the b and c -axes as diagonals. The compound was dark red and the absorption was most intense in the c -polarization

The oxidized compound $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ also crystallized in the monoclinic space group $C_{2/c}$ (41). The unit cell parameters were $a = 30.654$, $b = 9.528$, $c = 12.727$ Å, and $\beta = 97.43^\circ$. The unit cell is shown in Figure 11. There were eight molecules per unit cell with two crystallograph-

Figure 10. The unit cell of $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$

Figure 11. The unit cell of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$

ically distinct dimers. Not only were these dimers crystallographically distinct but they also differed in their stoichiometry. An example of the first type was centered at $(1/4, 1/4, 0)$. This type of dimer was coordinated to two, unshared waters in the terminal position. Molecules of this type will be referred to as isolated molecules. The second type was exemplified by the molecule at $(0, 0, 1/2)$. Here the waters used for terminal coordination bridged two dimers and hence these molecules formed chains. This type of molecule will be referred to as the chain type. The odd amount of waters was because each dimer averaged $1\frac{1}{2}$ water molecules and there were also two waters of hydration. The molybdenum-molybdenum distances were $2.167\text{ \AA}$ for the isolated and $2.162\text{ \AA}$ for the chain dimers. This was only about $.05\text{ \AA}$ longer than in $\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$. Again the molybdenums did not lie in the plane of the oxygens, resulting in an Mo-Mo-O angle of about 93.6° . This indicates that the molybdenums are more plainer than in the reduced dimer. The terminal Mo-O distance averaged $2.547\text{ \AA}$, again indicative of only a weak bond. The crystals tended to grow as needles with a pronounced $(1, 0, 0)$ face with the needle axis being the c -axis. The crystals were blue-gray in color and displayed very little dichroism in the visible region.

The Raman and I.R. vibrational spectra are given in

Table 7. Infrared and Raman frequencies for $K_4Mo_2(SO_4)_4$ and $K_3Mo_2(SO_4)_4$ ^a

$K_4Mo_2(SO_4)_4 \cdot 2H_2O$		$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$		Suggested Assignment
Raman (cm^{-1})	I.R. (cm^{-1})	Raman (cm^{-1})	I.R. (cm^{-1})	
	60 vw ^b	76(9) ^c		out-of-plane
85(37) ^c	86 vw		80 m	MoO ₄
95(28)				deformations
107(46)	105 vw	106(15)	105 m	
		122(2)		in-plane
	140 sh		130 m	O-Mo-O
	165 sh		160 m	bends
		175(37)		
	193 sh		200 m	
225(5)				
246(27)		251 sh		Mo-O stretches
		256(100)		
		274(73)		
	292 s		300 sh	
			310 s	

^aReference 53.

^bs = strong, m = medium, w = weak, v = very, sh = shoulder.

^cNumbers in parentheses are percent intensity as compared to the most intense peak.

Table 7 (Continued)

<u>$K_4Mo_2(SO_4)_4 \cdot 2H_2O$</u>		<u>$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$</u>		Suggested Assignment
Raman (cm^{-1})	I.R. (cm^{-1})	Raman (cm^{-1})	I.R. (cm^{-1})	
322(3)		319(13)		
		331(10)		
	352 w	250 vw		
364 sh				
371(100)		373(55)		Mo-Mo stretch
		386(59)		
	415 m		412 m	Mo-O stretches
			425 sh	
		442(9)		ν_2 bend of
464(9)		464 sh		free SO_4
500(9)	498 m			ν_2 bend of
		513(9)	515 sh	coordinated SO_4
		529(23)	530 m	
		589 sh	589 m	ν_4 bend of SO_4
604(5)	600 s	598(10)		
	610 s		610 s	
622(5)		618(19)		
635(3)		638(24)		
	662 m		665 m	
670(3)			675 m	
721 sh				

Table 7 (Continued)

<u>$K_4Mo_2(SO_4)_4 \cdot 2H_2O$</u>		<u>$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$</u>		Suggested Assignment
Raman (cm^{-1})	I.R. (cm^{-1})	Raman (cm^{-1})	I.R. (cm^{-1})	
744(9)				Overtone Mo-Mo stretch
806(3)				
			855 sh	free
			875 s	S-O
		914(12)	905 sh	stretches
		923(19)	920 vs	
		931(24)	932 sh	
	940(5)			
960(72)	950 vs	956(84)		
	995 s			coordinated S-O
	1015 sh			stretches
1119(9)	1116 vs			
		1130(9)	1130 vs	
			1150 vs	
1158(14)		1167(62)		
1202(9)		1193(41)		
	1215 sh			

Table 7 (Continued)

<u>$K_4Mo_2(SO_4)_4 \cdot 2H_2O$</u>		<u>$K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$</u>		Suggested Assignment
Raman (cm^{-1})	I.R. (cm^{-1})	Raman (cm^{-1})	I.R. (cm^{-1})	
1243(7)	1247 s	1248(2)	1245 sh	
		1272(10)	1262 s	
			1285 s	
		1301(5)		

Table 7. The presence of two metal-metal stretching frequencies in $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ was due to the two types of molecules in the unit cell. The assignments are those proposed by Loewenschuss et al. (53). It should be noted that the metal-metal stretching frequencies for $K_3Mo_2(SO_4)_4$ were 3 and 16 cm^{-1} greater than for the reduced compound. This was surprising in that the reduced compound has a bond order of 4 versus 3.5 for the oxidized form.

The polarized crystal spectra of $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ are shown in Figure 12. The crystal was determined to be about 15 μ thick. The molar absorptivity can be calculated by multiplying the absorbance by 180. As this crystal was monoclinic and the molecular axes were not aligned with the

Figure 12. Polarized spectra for $K_4Mo_2(SO_4)_4 \cdot 2H_2O$

crystal axes, polarization ratios need to be calculated in order to interpret the spectra. Using the crystallographic data the ratios were for a $\tilde{z}$ -polarized transition $c/b = 5.291$, while for an $\tilde{xy}$ -polarized transition $c/b = 1/5.26$. The fact that these ratios were so similar was coincidental. The crystal spectra had several similarities to $K_4Mo_2Cl_8 \cdot 2H_2O$. There was a band at $19,400\text{ cm}^{-1}$ which was $\tilde{z}$ -polarized, a weak absorption centered at $25,000\text{ cm}^{-1}$ which was unpolarized, and a moderate peak at $32,300\text{ cm}^{-1}$. The band at $19,400\text{ cm}^{-1}$ was assigned as $^1A_{2u} + ^1A_{1g} (\delta^* + \delta)$ and its energy was comparable to that of $K_4Mo_2Cl_8$. However, the intensity of this band was much smaller, having a room temperature oscillator strength of $\sim 1.3 \times 10^{-3}$. A possible explanation for the diminished intensity will be discussed later. No vibrational progressions were observed on this band. This was the only quadruple bonded molybdenum dimer studied so far to be devoid of such progressions.

One important factor regarding the $\delta^* + \delta$ transition at $19,400\text{ cm}^{-1}$ in $K_4Mo_2(SO_4) \cdot 2H_2O$ was its temperature dependence. At room temperature the measured c/b intensity ratio was only about $4/1$ versus the calculated $5.29/1$. At 15 K the $\tilde{c}$ -polarized component grew narrower and increased in intensity by about 15%. If the $\tilde{b}$ -polarization were simply a component of the $\tilde{z}$ -polarization, its behavior would have been identical. However, it was observed that while

the b -component peak narrowed it did not increase in height upon cooling. The c/b intensity ratio at 15 K was $\sim 5/1$. This was most readily explained by the existence of a vibronic component for this band which is xy -polarized. Such a component would require an e_g exciting vibration. The vibronic component would lose intensity as the temperature was decreased.

The other bands in the visible spectrum were more difficult to assign. The band centered at $25,000\text{ cm}^{-1}$ was probably due to a vibronic transition. The transitions $\pi^* \leftarrow \delta$ and $\delta^* \leftarrow \pi$ were possible assignments as in $\text{Mo}_2\text{Cl}_8^{4-}$. $\text{Mo}_2\text{Cl}_8^{4-}$ also showed a weak z -polarized band at $28,800\text{ cm}^{-1}$. This band appeared to be either shifted or missing in $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$. The next band observed in the sulfate was at $32,300\text{ cm}^{-1}$ but was very poorly polarized. This could be assigned as ${}^3E_u \leftarrow {}^1A_{1g}$ which has components in both polarizations. As discussed earlier this was a possible assignment for the $28,800\text{ cm}^{-1}$ band in $\text{Mo}_2\text{Cl}_8^{4-}$. If this assignment is correct, then the band in $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ has been blue shifted. On the other hand, the band in $\text{Mo}_2\text{Cl}_8^{4-}$ appeared to be cleanly z -polarized while this band in $\text{Mo}_2(\text{SO}_4)_4^{4-}$ is not.

Before examining the spectra of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ the effect of oxidation on the quadruple bond must be considered. When an electron is removed from the δ -orbital, the bond is

weakened and the energy difference between the δ and δ^* levels should be lessened. This same effect should occur upon reduction. The dimer $\text{Tc}_2\text{Cl}_8^{3-}$ is a known species (5) in which the bond order has been lowered to 3.5 by addition of an electron into the δ^* -orbital. The spectrum of $\text{K}_3\text{Tc}_2\text{Cl}_8$ has recently been investigated (48). The lowest energy transition calculated using the X_α -SCF method was at 6050 cm^{-1} . The observed spectrum in a CsI pellet had a band with a maximum at $\sim 6500 \text{ cm}^{-1}$. This band was assigned as ${}^2B_{2g} + {}^2B_{1u} (\delta^* + \delta)$. Similarly, the lowest energy band in $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ would be expected to be in the near-infrared region.

The near-infrared spectra of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ are shown in Figure 13 and the major progressions as read from the $\underline{c}$ -polarized spectrum are tabulated in Table 8. The crystal whose spectra are shown was 14μ thick. The absorbancies can be converted to molar absorptivity by multiplying by 190. With experimental limits, the bands designated as $\underline{b}$ and $\underline{c}$ -polarized occurred at the same energies. As the two polarizations arise from different factor group states, the Davydov splitting must be quite small. The polarization ratios for the two types of dimers and the combined ratio for bands where the two types cannot be resolved are given in Table 9.

Before discussing possible assignments for this band,

Figure 13. Near-I.R. polarized spectra of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$ at 5 K

Table 8. Major vibrational progressions in $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$

$\bar{\nu}(cm^{-1})$	$\Delta\bar{\nu}(cm^{-1})$	$\bar{\nu}(cm^{-1})$	$\Delta\bar{\nu}(cm^{-1})$	$\bar{\nu}(cm^{-1})$	$\Delta\bar{\nu}(cm^{-1})$
c-Polarized Progressions					
6311		6339		6577	
	348		353		345
6659		6692		6922	
	344		365		337
7003		7057		7259	
	347	Ave. 359 ± 8			342
7350				7601	
	347				346
7697				7947	
	350				340 ^a
8047				8626	
	339				362
8386				8988	
	336				357
8722				9345	
	334				Ave. 347 ± 9
9056					
Ave. 343 ± 6					

^aBand at about 8290 cm^{-1} is unobserved. The 340 cm^{-1} is the spacing divided by 2.

Table 8 (Continued)

$\bar{\nu}(\text{cm}^{-1})$	$\Delta\bar{\nu}(\text{cm}^{-1})$	$\bar{\nu}(\text{cm}^{-1})$	$\Delta\bar{\nu}(\text{cm}^{-1})$	$\bar{\nu}(\text{cm}^{-1})$	$\Delta\bar{\nu}(\text{cm}^{-1})$
c- and b-Polarized ^b					
6415		6745		7430	
	364		361		352
6779		7106		7782	
	355		349		361
7134		7455		8143 ^c	
	345		354		Ave. 357 $\pm$ 6
7479		7809			
	Ave. 355 $\pm$ 10		354		
		8143 ^c			
			345		
		8488 ^c			
			Ave. 349 $\pm$ 10		

^bRead from the c-polarized spectrum.

^cVery broad bands. There are two more bands at 8891 and 9241 cm^{-1} which cannot be assigned to either of these series.

Table 9. Oriented gas polarization ratios for the (1,0,0) face of $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$

Type	Molecular Polarization			
	$\tilde{z}$		$\tilde{xy}$	
	Ratio c/b	% Intensity in (1,0,0) Face	Ratio c/b	% Intensity in (1,0,0) Face
Isolated Molecules	11,600/1	46.3	1/1.86	76.8
Chain Molecules	5.79/1	99.4	1/5.59	50.3
Combined	8.95/1		1/2.69	

the important features must be discussed. At room temperature this band displayed very broad, unresolved vibrational structure. The room temperature oscillator strength was 1.2×10^{-3} . The lowest energy feature at 5 K was the pair of $\tilde{c}$ -polarized bands at 6311 and 6339 cm^{-1} . Even in crystals four times thicker no lower energy structure was observed. These appeared to obey the oriented gas polarization ratios as only a small component of these bands was seen in the $\tilde{b}$ -polarization. The band at 6311 cm^{-1} was the more intense of the two and resulted in a progression of nine bands with

a separation of $343 \pm 6 \text{ cm}^{-1}$. The band at 6339 cm^{-1} produced a three peak progression with a spacing of $359 \pm 8 \text{ cm}^{-1}$. However, since this was only based on two intervals the error may well be greater than this standard deviation. There was one other vibrational progression that appeared to obey the oriented gas polarization ratios. This was a $\underline{c}$ -polarized progression which began at 6577 cm^{-1} with an average spacing of $347 \pm 9 \text{ cm}^{-1}$. The remaining progressions do not agree well with the polarization ratios. The bands appear to be slightly stronger in $\underline{c}$ than $\underline{b}$ -polarization with a ratio of about 1.2/1. The first four peak progression began with a very sharp band at 6415 cm^{-1} and had a spacing of $355 \pm 10 \text{ cm}^{-1}$. A similar six peak progression began at 6745 cm^{-1} with a separation of $349 \pm 10 \text{ cm}^{-1}$. A third such progression began at 7430 cm^{-1} with separation of $357 \pm 6 \text{ cm}^{-1}$. Beyond 8143 cm^{-1} the last two progressions could not be clearly resolved and two very broad bands which probably represented these series were observed at 8891 and 9241 cm^{-1} .

Providing a positive assignment for this band was rather difficult. Normally, a band with such low intensity and with as many vibrational progressions would be assigned as a vibronic transition. However, as McClure points out (54), vibronic bands do not normally obey polarization ratios. For an allowed transition, the direction of the transition

dipole vector is firmly fixed. For a simple crystal with one molecule per unit cell, there are no crystal interactions to change its direction. For molecules with more than one molecule in the unit cell, the Davydov states must be considered. Again the direction of the dipole will be firmly established. The only thing then that will distort the polarization ratios calculated for the Davydov states is that these states need not have equal intensity in a given face. Vibronic transitions, however, obtain their intensity by borrowing it from dipole-allowed electronic transitions of the same symmetry as the vibronic wave function. In a crystal, this intensity can be borrowed from the molecule on which the transition is centered on or from a neighboring molecule. Hence the polarization ratios must take into account such interactions which will change the direction of the transition dipole. This can drastically change the polarization ratios even to the point of reversing the polarization in which a band is observed. This is the case even when more sophisticated Davydov state polarization ratios are used. It must also be remembered that the mixing of the electronic states is governed by the symmetry of the factor group and not the molecular symmetry. For molecules in low symmetry crystals this can allow for many more states to mix than would be possible for an isolated molecule. The fact that three progressions agree very well with the

oriented gas model was cause to question a vibronic assignment. Of course, the vibronic interactions could have been such that the polarization ratios were left unchanged. However, there were several other odd features to this band. First, its room temperature oscillator strength was nearly the same as for the $\delta^* \leftarrow \delta$ transition in $K_4Mo_2(SO_4)_4$. Secondly, its energy was about what the $\delta^* \leftarrow \delta$ transition would be expected to have. Third, those bands that do obey the polarization ratios are molecularly z -polarized which would be correct for the $\delta^* \leftarrow \delta$ transition. Lastly, the spectrum could be assigned reasonably if the transition was assigned as $\delta^* \leftarrow \delta$. The bands at 6311 and 6339 cm^{-1} represented the 0-0 bands. There were apparently two such bands because of the two crystallographically independent dimers in the unit cell. Their separation of 28 cm^{-1} was, within experimental error, in agreement with the 13 cm^{-1} difference reported for two Raman lines for the ground electronic state. The intensity difference was due to the fact that the chain molecules put 86% of their intensity into the c -polarization while the isolated molecules put only 46%. Hence, the 6311 cm^{-1} band would be the 0-0 band for the chain molecules and the separation of 343 ± 6 for the resulting progression would represent the excited state Mo-Mo stretch for these dimers. The 6339 cm^{-1} would represent the isolated dimers 0-0 band with an excited state

separation of $359 \pm 8 \text{ cm}^{-1}$. The other clearly $\underline{z}$ -polarized progression began at 6577 cm^{-1} which was 266 and 238 cm^{-1} above the 0-0 bands. This could be assigned to the totally symmetric Mo-O stretch which was at 274 and 256 cm^{-1} in the Raman spectrum. This would be analogous to $\text{Re}_2\text{Cl}_8^{2-}$ where there two progressions each built on the Re-Re stretch and separated by the Re-Cl stretch. The other progressions observed would then be vibronic bands excited by e_g vibrations and should be $\underline{xy}$ -polarized. The greater intensity in the $\underline{c}$ -direction would be caused by several factors. First, the breakdown in the oriented gas model as discussed earlier might well be enough to produce this change in polarization. Secondly, the site symmetry for both types of dimers was C_1 and the factor group symmetry was C_{2h} . The vibronic components could mix slightly with the allowed component. Lastly, lattice phonons could scramble the polarizations. The first such nonpolarized band was quite sharp and was at 6415 cm^{-1} . This is 104 cm^{-1} and 79 cm^{-1} above the supposed 0-0 bands. This band would then correspond to the e_g out-of-plane deformation mode seen at 106 and 76 cm^{-1} in the Raman spectrum. The second series begins at 6745 cm^{-1} which is 434 and 406 cm^{-1} above the 0-0 bands. This might well correspond to the 442 cm^{-1} ν_2 bend of free SO_4 . This ν_2 mode does have the correct symmetry. The last such system began at 7430 cm^{-1} and was 1119 and 1091 cm^{-1} above the 0-0

bands. This could be attributed to the coordinated S-O stretch at 1130 cm^{-1} in the Raman spectrum. If the assignment of this transition as $\delta^* \leftarrow \delta$ was correct, then the situation would be virtually analogous to $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ in that the transition was surprisingly weak and there was a vibronic component in the opposite polarization.

The question as to why the dipole allowed transition $\delta^* \leftarrow \delta$ was so weak in both sulfate dimers remains to be answered. One possible explanation is that the δ or δ^* levels became involved in metal-to-ligand π -bonding. If one level were to acquire mostly metal-to-ligand character while the other would remain mostly metal-to-metal in character, the overlap between the bonding and antibonding orbitals would be greatly reduced. This would result in a decrease in the intensity of the $\delta^* \leftarrow \delta$ transition. Such a change in character will also lower the metal orbital and raise the empty-level in the ligand assuming they are empty antibonding orbitals and higher in energy than the metal-metal system. The lowering of an orbital should be observed in the electronic spectrum.

Applying this concept to the three compounds studied, $\text{K}_4\text{Mo}_2\text{Cl}_8$, $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ and $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ is fairly simple. The chloride ion has no low energy orbitals with which it can accept metal backbonding. The lowest available empty orbital would be a 4s- or 3d-orbital which would probably be of too

great an energy to allow for much bonding. The sulfate case is only slightly more complex. If only the s- and p-orbitals on sulfur are considered such backbonding is again unlikely. This is because all the orbitals are involved in the sigma system. The empty σ^* -orbitals are again likely to be of too great an energy to interact. However, the situation improves if one allows for sulfur-oxygen π -bonding by including the sulfur 3d-orbitals. In this case, the lowest energy antibonding orbital will be e with respect to T_d symmetry. One of these orbital combinations is shown in Figure 14. The makeup of this orbital was calculated using the usual projection operator methods. If the Mo-Mo bond rested along the $\underline{xy}$ diagonal in the top face of the cube in Figure 14, the δ^* -orbital will have maximum overlap with the π^* -orbital on SO_4^{2-} . However, there is no sulfate π^* -orbital that can interact with the δ -orbital. Hence, the loss of intensity was due to the δ^* -orbital acquiring metal-to-ligand π -bonding character.

As further substantiation of this concept, the energy of $\delta^* \leftarrow \delta$ transition would have to be lessened if the δ^* -orbital was lowered by interaction with the vacant sulfate π^* -orbital. It has been observed by Cotton and Norman (29) that there is a strong correlation between the Mo-Mo stretch in the Raman spectrum and the energy of the lowest energy band in the electronic spectrum. Values for various compounds

Figure 14. An antibonding e orbital in SO_4^{2-}

are given in Table 10 and are plotted in Figure 15. It can be seen that the Mo-Mo stretch would predict a much higher energy in $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ than the observed $19,400 \text{ cm}^{-1}$. Therefore, there is some credence to this interaction with the sulfate e-orbital resulting in a lowering in the $\delta^* \leftarrow \delta$ energy. As the δ^* -orbital is unoccupied in the ground state, the Raman spectrum does not reflect this change in the electronic energy. A comparison of the energy of the proposed $\delta^* \leftarrow \delta$ transition in $\text{K}_3\text{Mo}_4(\text{SO}_4)_4$ is impossible since there are no other Mo_2^{5+} dimers for comparison.

The visible spectra of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$ is shown in Figure 16. The crystal used for these spectra was much thicker than that used for the near-I.R. work. The observed bands, therefore were relatively weak features which were centered at $18,500 \text{ cm}^{-1}$ and $24,000 \text{ cm}^{-1}$. These bands had very poorly defined polarization and low temperature dependence of the intensity. These were probably vibronic transitions and could be ${}^2\text{E}_g \leftarrow {}^2\text{B}_{2g}$ ($\pi^* \leftarrow \delta$ or $\delta^* \leftarrow \pi$). No definitive assignment can be made for these bands from the present data.

Lastly, it should be mentioned that it was rather surprising that the transition ${}^2\text{E}_u \leftarrow {}^2\text{B}_{2g}$ ($\delta \leftarrow \pi$) was not observed. This transition would be dipole allowed in the xy-polarization. If the proposed reason for the low intensity in the supposed $\delta^* \leftarrow \delta$ transition is correct, it would not

Table 10. Correlation between Mo-Mo stretching frequency, Mo-Mo distance and energy of first electronic state in solution

Compound	Mo-Mo Stretch (cm^{-1})	Mo-Mo Distance $\text{\AA}$	Energy First Electronic State (cm^{-1})
$\text{Mo}_2(\text{HCO}_2)_4$	406 ^a	2.091 ^a	22,830 ^a
$\text{Mo}_2(\text{CH}_3\text{CO}_2)_4$	404 ^b	2.0934 ^c	22,800 ^d
$\text{Mo}_2(\text{C}_6\text{H}_5\text{CO}_2)_4$	404 ^b	2.096 ^e	22,470 ^f
$\text{Mo}_2(\text{F}_3\text{CCO}_2)_4$	398 ^b	2.091 ^g	22,700 ^d
$\text{Mo}_2(\text{NH}_3\text{-CH}_2\text{-CO}_2)_4(\text{SO}_4)_2$	393 ^h	2.115 ^h	22,420 ^h
$\text{K}_4\text{Mo}_2(\text{SO}_4)_4 \cdot 2\text{H}_2\text{O}$	371 ⁱ	2.111 ^j	19,400
$\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$	363 ^k	2.129 ^k	32,700 ^l
$\text{K}_4\text{Mo}_2\text{Cl}_8$	349 ^b	2.139 ^m	19,300

^aReference 30.

^bReference 32.

^cReference 28.

^dReference 38.

^eF. A. Cotton, College Station, Texas. Private Communication. 1976.

^fFrom crystal spectrum.

^gReference 29.

^hReference 31.

ⁱReference 43.

^jReference 29.

^kReference 35.

^lIn this case this is not the lowest energy transition. However, crystal spectra clearly indicate this transition is equivalent to the others listed. The listed energy is from the crystal spectrum.

^mReference 39.

Figure 15. The correlation between the Mo-Mo stretching frequency and the frequency of the lowest-energy electronic transition in solution

Figure 16. U.V.-visible polarized spectra of $\text{K}_3\text{Mo}_2(\text{SO}_4)_4 \cdot 3.5\text{H}_2\text{O}$

reduce the intensity of the $\delta \leftarrow \pi$ transition while this transition could be at higher energy than the cut-off of $30,000 \text{ cm}^{-1}$, such a large separation between the π - and δ -orbitals would be surprising. It would also rule out the $\delta^* \leftarrow \pi$ transition for the vibronic transitions. Perhaps the high energy of this 2E_u electronic state above the ground state may have been related to a high electron correlation energy required to move an electron from a filled to a half-filled orbital when compared to removal from a filled to an empty orbital.

C. Carboxylate Compounds

In this section an assignment will be considered for the lowest energy transition in the carboxylate dimers which is based on the information gained for the octachloro- and tetra- μ -sulfato dimolybdates previously discussed. In some respects this section is speculative in that the assignment made is consistent with the observed data but is not necessarily the only assignment possible. It is believed that the proposed assignment is consistent with the observed phenomena. Again, more data will be required to completely substantiate this model.

The lowest energy transition for the alkyl-carboxylates has proven difficult to assign because it has a lower intensity and somewhat higher energy than those for other

quadruply bonded molybdenum dimers. In general, the ${}^1A_{2u} + {}^1A_{1g} (\delta^* + \delta)$ transition had not been considered previously for the above reasons. Recently, Norman et al. (55) have proposed the assignments in Table 11. Although, it will be noted that the $\delta^* + \delta$ transition was calculated to have the lowest energy; the lowest energy transition was assigned as $\pi^* + \delta$. This was done mainly because of the low intensity and the polarization for this band.

To try to explain the character of this transition the theory of backbonding, used for the sulfato dimers, was applied to the carboxylates. The carboxylate π^* orbital of the alkyl-carboxylate ligands is shown in Figure 17. The irreducible representations for the linear combination of four such orbitals are b_{2g} , e_u , and a_{2g} . The a_{2g} orbital must be nonbonding with respect to overlap with the metal-metal orbitals. The e_u combination can interact with the metal-metal π -orbital. However, especially if the molybdenums were situated exactly in the plane of the oxygens, the net overlap would be quite small. The b_{2g} combination can interact strongly with the δ -orbital. As the carboxylate π -levels are expected to be at higher energy than the metal-metal system, such an interaction would then lower the energy of the δ -orbital. There is no low-lying vacant orbital that can interact similarly with the δ^* -orbital. Therefore, this would be the reverse of the sulfate case. The δ^* -orbital

Table 11. Calculated and experimental electronic spectrum of $\text{Mo}(\text{HCO}_2)_4^a$

Transition	Excited ^b State	Type	Calculated (Kcm^{-1})	Experimental (Kcm^{-1})	Oscillation Strength
$b_{2g} \rightarrow e_g$	1E_g	$\delta \rightarrow \pi^*$	25.6	22.9	0.0008
$b_{2g} \rightarrow b_{1u}$	$^1A_{2u}$	$\delta \rightarrow \delta^*$	14.7	30.8	0.03
$e_g \rightarrow b_{1u}$	1E_u	$0 \rightarrow \delta^*{}^c$	37.1		
$e_g \rightarrow b_{1u}$	1E_u	$0 \rightarrow \delta^*$	40.9		
$b_{2g} \rightarrow e_u$	1E_u	$\delta \rightarrow \text{C-O}\pi^*$	41.9	33.5	0.19
$e_u \rightarrow e_g$	$^1A_{2u}$	$\pi \rightarrow \pi^*$	41.4	44.4	0.02

^aReference 55.

^bFrom an $^1A_{1g}$ ground state.

^c0 represents an oxygen nonbonding orbital.

π -antibonding System in R-CO_2^-

Figure 17. π -antibonding system in R-CO_2^-

will be relatively unaffected by the backbonding while the δ -level will be lowered. Therefore, the $\delta^* \leftarrow \delta$ transition would be expected to shift to higher energy. Since the δ -bond would have substantially metal-ligand character while the δ^* will retain metal-metal character, the transition intensity would be weakened. Lastly, unlike the sulfate case, the orbital involved in backbonding is occupied in the ground state configuration and the results of this backbonding may be observed in other features of the carboxylates.

The spectrum of the lowest-energy transition of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$, as reported by Trogler et al. (38) is tabulated in Table 12. The spectrum was obtained from a film of the compound that had been sublimed onto a quartz disk. There were three strong progressions observed. Trogler et al. (38) attributed these to different asymmetric vibrations producing different vibronic origins for the degenerate state that itself was split by the reduction in symmetry in the crystal. However, it will be noticed that the band at 22,217 was 355 cm^{-1} from the origin. This separation was exactly the frequency of the a_{1g} vibration involved in the Frank-Condon progressions. A similar result is observed for the band at 22,327 with respect to the band at 21,973. Only one totally symmetric vibration, the metal-metal stretch, was involved in all three progressions and therefore, all three progressions should be based on the same set of Frank-Condon factors.

Table 12. The spectrum of $\text{Mo}_2(\text{O}_2\text{CCF}_3)_4$ at 15 K^a

nm	cm ⁻¹	Progressions		
		1	2	0
461.45	21671			
459.28	21773			
457.41	21862 ^{b,c}			
455.58	21950 ^b	1		
455.10	21973 ^b		-	355 ^d
453.23	22064	-		
451.22	22162 ^b			
450.11	22217 ^b		354 ^d	-
449.46	22249 ^b			
447.89	22327	361	-	348 ^d
445.93	22425	-		
443.16	22565 ^e		364	=
440.70	22691	366	-	
438.77	22791	-		362
436.17	22927		358	=
433.86	23049	352	-	
432.10	23143	-		356
429.50	23283		354	=
427.30	23403	349	-	
425.68	23492	-		353

^aReference 38.^bWeak bands observed in thick path length sample.^c0-0 band observed in the spectrum and confirmed as such by the hot band temperature dependence.^dNot in reference.^eThis band is broad with a distinct high energy shoulder and remains as such throughout the progression, indicating two overlapping weak progressions.

Table 12 (Continued)

nm	cm ⁻¹	Progressions		
423.08	23636		358	=
420.86	23761	348	-	
419.46	23840	-		350
416.91	23986		335	=
415.00	24096	352	-	
413.36	24192	-		355
410.83	24341		368	=
408.76	24464	357		
407.35	24549			358
404.87	24699			=
Average = 355 cm ⁻¹ ± 7				

The three progressions have been numbered 0, 1, and 2 as shown in Table 12.

The compound $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ and crystals were prepared by literature methods (29). The polarized spectra at 5.1 K are shown in Figures 18 and 19. The vibrational progressions are numbered with respect to Table 12. These spectra are quite preliminary. The crystals were triclinic with unit cell dimensions $a = 8.293$, $b = 9.209$, $c = 5.568 \text{ \AA}$, $\alpha = 91.18^\circ$, $\beta = 100.561^\circ$ and $\gamma = 89.670^\circ$ (29). The crystals grew as

Figure 18. The maximum polarization spectrum of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ at 5 K

Figure 19. The minimum polarization spectrum of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ at 5 K

needles with a well developed $(1, \bar{1}, 0)$ face. The c -axis was the needle axis, and the extinction direction which was 7° off the c -axis will be referred to as Min. The polarization ratios were for a z -polarized transition $\text{Max/Min} = 1/713$ and for an xy -polarized transition $\text{Max/Min} = 3148/1$. None of the observed bands possessed these polarization ratios. This implied that they were most likely vibronic in origin. The energies of the bands in the observed spectrum were in good agreement with those reported by Trogler et al. (38). The polarization of the spectrum did aid in assigning it. The peaks in Progression 1 were clearly polarized in the maximum polarization. While the intensity of Progression 0 was greater in the maximum polarization, the intensity difference between Max and Min was quite low. Therefore, this progression which appears to include the origin will be assigned to the molecular z -polarization. The polarization of Progression 2 is at this time a bit more uncertain. The spectra of the other carboxylates studied and of the pyridine adduct of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ (see below) displayed two xy - and one z -polarized progressions. For this reason Progression 2 will be assigned as xy -polarized. However, it is not clear that the spectra obtained so far confirm this assignment. The polarization of this progression is not critical to the bonding model being proposed. If the polarizations above are correct then the progression that originates on the O-O

band was $\tilde{z}$ -polarized and has the correct polarization for the $\delta^* \leftarrow \delta$ transition. Lastly, note that the Frank-Condon ratios for Progression 0 were quite different than for Progressions 1 and 2, which in turn were quite similar. Progressions 1 and 2, which were $\tilde{xy}$ -polarized, had the maximum intensity in the third members. On the other hand Progression 0, which is $\tilde{z}$ -polarized, had maximum intensity in the fourth member for the assignment of Trogler et al. (38) or the fifth member for the presently proposed assignments. Also Progression 0 lost intensity more slowly in later members. Since these progressions were all based on one totally symmetric vibration, there should only be one set of Frank-Condon factors. The fact that there are two must be explained.

As noted earlier, all three progressions appear to be vibronic in origin. If Progression 0 does extend to the origin then that progression must be totally symmetric and at least in part dipole-allowed. An a_{1g} vibration can be involved in vibronic coupling. An example of this has been seen in the 3400 Å system for phenanthrene (56). The theory for a totally symmetric band producing both a Frank-Condon progression and Hertzberg-Teller coupling was derived by Craig and Small (57). It is well known that for a dipole-allowed transition, the intensity from the initial vibrational state $\langle 0,0|$ to the final vibrational state $|f,v\rangle$ is

proportional to $\langle 0,0|M|f,v \rangle^2$ where M is the transition moment $\langle \psi_{e_i} | \vec{\mu} | \psi_{e_f} \rangle$. Where the Born-Oppenheimer approximation holds this becomes $M^2 \langle 0,0|f,v \rangle^2$, where $\langle 0,0|f,v \rangle$ is the Frank-Condon factor. If a vibrational motion influences the transition, then to the first approximation the new transition moment can be expanded with a linear dependence on Q , the normal coordinate. The result is that $M = M_0 + m_1 Q_1 + \dots$. The m term will be dependent on the particular normal coordinate involved. Obviously, the $m_1 Q_1$ term will only be important where it is of the same order of magnitude as M_0 . This is not normally the case for a dipole-allowed transition. Therefore, the intensity of the transition is now proportional to

$$\begin{aligned} \langle 0,0|M|f,v \rangle^2 &= [M_0^2 \langle 00|fv_1 \rangle^2 + 2m_1 \cdot M_0 \langle 00|fv_1 \rangle \langle 00|Q_1|fv_1 \rangle \\ &\quad + m_1^2 \langle 0,0|Q_1|f_1v_1 \rangle^2] \\ &\quad \prod_{i=1}^{3N-6} \langle 00|fv_i \rangle^2 \end{aligned}$$

For the normal vibronic transition v_1 will be nontotally symmetric. In this case only $v_1 = 1$ will produce a nonzero value for $\langle 0,0|Q_1|f,v_1 \rangle$. The first two terms will vanish because $\langle 0,0|f_1v_1 \rangle = 0$. Also $m_1 \cdot M_0$ equals zero because of the different symmetries of m_1 and M_0 . For a dipole-forbidden transition m_1 will not equal zero and be totally

symmetric while M_0 will have some other symmetry. The situation is quite different if ν_1 is totally symmetric. Now, none of the integrals are zero. The $M_0 \cdot m_1$ product is no longer zero because M_0 and m_1 must both be totally symmetric. In fact this term may become quite important as the signs of $\langle 0,0 | f \nu_1 \rangle$ (the Frank-Condon factor) and $\langle 0,0 | Q_1 | f \nu_1 \rangle$ can be either positive or negative and could drastically alter the observed intensities for Frank-Condon progression.

Using this concept the spectra of the carboxylates can be explained. As the intensity of this transition is quite low even though it is dipole-allowed the transition moment, M_0 , would be of the order of the vibronic moment m_1 . The fact that the greatest intensity was observed in a vibronic series, Progression 1, which is polarized opposite from the origin added credence to this. Progression 0 would be the totally symmetric series involving both the Frank-Condon and Hertzberg-Teller interactions. Its appearance could be quite different from that of the other progressions because of the $m_1 \cdot M_0$ term as appeared to be the case. If assigned to the correct polarizations, Progressions 1 and 2 would result from e_g perturbing vibrations as was the case for $K_3Mo_2(SO_4)_4 \cdot 3.5H_2O$. These two progressions begin at 21,973 and 22,064 cm^{-1} and are 111 and 202 cm^{-1} above the origin. Force field calculations predicted e_g vibrations with energies of 131 and 215 cm^{-1} (16) and the Raman spectrum of $Mo_2(CF_3CO_2)_4$ showed a

band at 206 cm^{-1} (32). Unfortunately, Rayleigh scattering prevented the Raman spectrum from being recorded below 180 cm^{-1} . An attempt was made to calculate the intensity ratios for both a Frank-Condon and a mixed Frank-Condon, Hertzberg-Teller series. The results are given in Table 13. These factors were calculated using the method of Hutchisson (58). The observed trends were reflected in the calculations qualitatively. Note especially the very low intensity for the 0-0 band in the series where the Hertzberg-Teller term m_1 was half as great as the dipole-allowed moment, M_0 . However, the calculated ratios were all too large. This is probably not surprising since the calculations were rather crude. Harmonic oscillator wave functions were used, and the metal-metal stretch for the carboxylate dimer was treated as a simple Mo_2 diatomic. Hutchisson noted (59) that even for a simple diatomic molecule, H_2 in this case, the harmonic oscillator approximation produced ratios that were too large. Application of anharmonic corrections, or better yet a Morse potential lowered the ratios substantially without shifting the relative position of the maximum. Very likely, more sophisticated calculations would produce better agreement for $\text{Mo}_2(\text{RCO}_2)_4$. All of these factors lead to an assignment of ${}^1\text{A}_{2u} \leftarrow {}^1\text{A}_{1g}$ ($\delta^* \leftarrow \delta$) for this lowest-energy transition.

To summarize, the bonding concept derived proposes that the δ -orbital interacts strongly with the empty π^* -orbital

Table 13. Frank-Condon and mixed Frank-Condon, Hertzberg-Teller ratios

Transition ^a	xy-Polarized		z-Polarized	
	Observed Ratio ^{a,b}	Calculated Ratio ^c	Observed Ratio ^b	Calculated Ratio ^{c,d}
0-0	1.00	1.00	--	.03
1-0	1.60	7.26	1.00	1.00
2-0	1.76	13.42	5.50	26.67
3-0	1.69	11.22	8.75	83.33
4-0	1.57	5.37	12.75	97.17
5-0	1.26	1.67	12.25	59.70
6-0	1.00	.37	8.00	22.67
7-0	.76	.06	6.25	5.83
8-0			5.00	1.00

^aAs determined from the vibronic bands.

^bReference 38.

^c $\nu' = 350 \text{ cm}^{-1}$, $\nu'' = 400 \text{ cm}^{-1}$, $\mu = 48 \text{ A.M.U.}$, $(R'' - R')$
 $= .16 \text{ A.}$

^d $m_1 = .5M_o.$

on the alkyl-carboxylate. This results in several features:

- 1) A lowering in energy of the δ -orbital results.
- 2) A great reduction in the intensity of the ${}^1A_{2u} \leftarrow {}^1A_{1g} (\delta^* \leftarrow \delta)$ transition results.
- 3) Because of the low intensity, vibronic mechanisms become very important including a vibronic component induced by the a_{1g} metal-metal stretch.
- 4) Because of the strong vibronic interactions, large deviations from the calculated polarization ratios result.

This bonding model is not in agreement with the X_α -SCF calculation of Norman et al. (55). Their calculation showed only 3% oxygen and 8% carbon character in the δ -orbital but 14% oxygen character in the δ^* -orbital. Also, the three C-O π^* -orbital combinations, listed in order of increasing energy, had the following % Mo character:

$$b_{2g} \quad 8\%, \quad e_g \quad 0\%, \quad a_{2g} \quad 0\% \quad .$$

In the model proposed, the b_{2g} combination would interact with the δ -orbital and would be expected to have the highest, and not the lowest, energy. However, the model proposed here requires the interaction of molecular orbitals to form new orbitals. This type of bonding might be hard to anticipate in an energy calculation.

In order to further test this theory, a compound whose

spectrum was between $\text{Mo}_2\text{Cl}_8^{4-}$ and the carboxylates was required. As the $\delta^* \leftarrow \delta$ band moved back to lower energy the intensity of the $\tilde{z}$ -polarized components should increase and the O-O band should be observed. It was also important to test the model proposed by Trogler et al. (18) and determine if at some point the π^* level does drop below the δ^* level. It had been reported that when $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ was dissolved in pyridine a bright red solution resulted (35). The spectrum of this solution displayed a band at $\sim 19,600 \text{ cm}^{-1}$. From this solution the adduct $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$ could be isolated. The crystals obtained were yellow-orange in color. As this compound appeared to have the desired intermediate spectrum, crystals were prepared by the literature method (35). The crystal spectra are shown in Figures 20 and 21. It will be noted that the band at $\sim 19,600 \text{ cm}^{-1}$ was quite weak and poorly polarized. At best it was the result of a vibronic transition and could have been an impurity peak. In any case it was not the band that was equivalent to the lowest-energy band in the other carboxylates. The band that was equivalent was located at $\sim 22,700 \text{ cm}^{-1}$. If compared with $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ in Table 10 it appears that this band was nearly unshifted by the further coordination. However, the two values in the table are not quite comparable as the reported value for $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ was for the solution while the pyridine adduct value is for a crystal. The solid state value for the

Figure 20. The maximum polarization spectrum of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$

Figure 21. The minimum polarization spectrum of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$

transition in $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ is $\sim 23,700 \text{ cm}^{-1}$. This implies that the band was red shifted $\sim 1,000 \text{ cm}^{-1}$ in the pyridine adduct.

The spectra for the band at $\sim 22,700 \text{ cm}^{-1}$ are shown in Figures 22 and 23. The unit cell for this compound was triclinic with unit cell parameters $a = 10.245$, $b = 8.736$, $c = 8.564 \text{ \AA}$ and $\alpha = 85.538^\circ$, $\beta = 101.923^\circ$ and $\gamma = 113.478^\circ$ (35). The face used for crystal spectroscopy was determined to be the (0,1,0) face. The pyridines were terminally coordinated and essentially lie in the plane of two trans-carboxylates (35). The molecular axes were assigned as follows: Mo-Mo = $\hat{z}$, the vector perpendicular to $\hat{z}$ and approximately lying in the pyridine plane = $\hat{x}$, and $\hat{z} \times \hat{x} = \hat{y}$. The resulting polarization ratios are given in Table 14. The extinction direction MIN was determined to be 18° off the c-needle axis and was approximately along the projection of $\hat{z}$ onto the (0,1,0) face. The maximum intensity then was essentially the $\hat{y}$ -polarization. The origin peak was observed at $21,454 \text{ cm}^{-1}$. In this compound, the oriented gas polarization ratios for the $\hat{z}$ -polarized transitions were much closer in agreement with the observed spectrum than in the other carboxylates. The fact that the origin was observed and in the $\hat{z}$ -polarization, that the Frank-Condon ratios for the $\hat{z}$ -polarized bands were much more regular, and that the oriented gas model was being more closely obeyed seems to agree with

Figure 22. The maximum polarization spectrum of Mo₂(CF₃CO₂)₄·2(C₅H₅N) at 5.1 K in the region of the lowest-energy transition

Figure 23. The minimum polarization spectrum of $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$ at 5.1 K in the region of the lowest-energy transition

Table 14. Polarization ratios for $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2\text{P}_y$

Molecular Polarization	Polarization MAX/MIN	Ratio % Intensity in the (0,1,0) Face
$\tilde{z}$	1/288	95%
$\tilde{x}$	1/1.14	8%
$\tilde{y}$	95.5/1	95%

the proposed backbonding model. The fact that the allowed components in $\tilde{z}$ -polarization were much greater in the pyridine adduct than in $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4$ implied that the allowed transition moment was considerably higher for the adduct but still not as great as the vibronically induced moment in the $\tilde{xy}$ -polarization.

Lastly, the failure for the energy of the supposed $\delta^* \leftarrow \delta$ transition to change much in $\text{Mo}_2(\text{CF}_3\text{CO}_2)_4 \cdot 2(\text{C}_5\text{H}_5\text{N})$ from the simple carboxylate provides some insight into the relationship between the Mo-Mo stretching frequency and the energy of this transition. The pyridines cannot interact with the δ - or δ^* -orbitals for reasons of symmetry. The nonbonding orbital on the pyridine nitrogen can interact with the Mo-Mo σ -system and the pyridine π -system can interact with the π - and π^* -orbitals. This implies that the

increase in the Mo-Mo bond length of .039 Å and the decrease in the Mo-Mo stretch of 30 cm^{-1} (35) upon addition of the pyridines must be caused by a weakening of the σ - and π -bonds. If the δ -bond is weakened, it is because of the greater intramolecular separation. The δ -bond could also appear to be weakened because of less overlap with the carboxylate π^* -orbitals. A reduction in backbonding was evident in the increased intensity of the z -polarized progression in the pyridine adduct. The fact that the pyridine adduct does not lie on the line in Figure 15 indicates that the mechanism which served to weaken the metal-metal system here is different than that causing the changes in the other dimers. One can offer two models that fit this observation. The first is that the changes in bond length in the other carboxylates are due entirely to changes in the δ -bonding system. The pyridine adduct does not fit this scheme because here the σ - and π -bonds are being weakened. However, if the carboxylates are truly backbonding, it seems unlikely that the δ -bond is being strengthened by removing electron density from it. Therefore, there must be an interaction between the strengths of the three bonds to explain the observed data. Unlike multiple bonded carbons, the orbitals used to form the metal-metal system are not geometrically at right angles to each other. Therefore, the bulk of the electron density in the metal-metal system must be in the

narrow region between the metals. Because of the short bond distances, there may be high electron-electron repulsions which may be important in determining the final geometry. This implies that the extra electrons in the quadruple bond may not shorten the bond distance because of the increased electron-electron repulsion. Therefore, a balance must be achieved between a strong bond and the strong repulsion. In $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2(\text{CH}_3)_8^{4-}$ there is no way to remove any of the metal-metal density so the nuclei move apart to provide more room. In these compounds it appears that even one electron oxidation will not better the situation which may explain why the $\text{Mo}_2\text{Cl}_8^{3-}$ ion has not been isolated. The excess electron density could also be relieved by terminal coordination. However, in complexes like $\text{Mo}_2\text{Cl}_8^{4-}$ steric hinderance in the terminal positions possibly prevent this. The molybdenum is more than .63 Å out of the chlorine plane. To effectively bond a terminal ligand would force the axial ligands back closer to a planar situation. The repulsion across the metal-metal bond might well prevent this. In the compound $\text{K}_4\text{Mo}_2(\text{SO}_4)_4$ the electron density has been somewhat lessened, as judged by the shorter Mo-Mo distance, possibly by terminal coordination. Here the forces are such that a one electron oxidation may provide a better situation. Therefore, the compound $\text{K}_3\text{Mo}_2(\text{SO}_4)_4$ exists and appears to be as stable as the reduced species. Certainly the change in bond length of

.05 Å supports this. This change is less than the ~.06 Å between $\text{Mo}_2\text{Cl}_8^{4-}$ and $\text{Mo}_2(\text{HCO}_2)_4$. The carboxylate compounds of molybdenum present the most ideal situation. The π^* -orbitals of the ligands can serve as a reservoir into which excess electron density can be placed or removed. For the carboxylates density is stored there. When electron density is removed from between the metals by terminal complexation, density is withdrawn back to stabilize the bond. Because electron repulsion forces can be minimized by this backbonding, the molybdenum carboxylates have the shortest bond distances.

These ideas can also be applied to the other metals forming quadruply bonded dimers. In technetium (III), which is isoelectronic with Mo (II), the core electrons should now be smaller. Apparently, this leads to the case where lowering the bond order provides the most stability. In rhenium (III) a situation similar to molybdenum (II) exists. Unfortunately, because of the greater Re-Re distance the rheniums cannot acquire as favorable an overlap with the carboxylate π^* -orbitals. Therefore, the rhenium carboxylates lose electron density by terminal coordination. Lastly is the case of tungsten. Tungsten has one less proton than rhenium and hence a larger core. Apparently, to obtain sufficient room for eight metal-metal electrons, the W-W distance must be so great as to weaken the bonding. In fact the W-W distance

was the longest quadruple bond observed (23) and by far the least stable. While the ideas presented above are quite unusual so is the quadruple bond.

Again, much of what has been discussed in this last section is speculative and based on very preliminary results. More data will be required to conclusively prove these theories.

V. BIBLIOGRAPHY

1. A. S. Kotel'nikov and V. G. Tronev, Zhurnal Neorganichskoi Khimii, 4 1008 (1958); J. Russ. Inorg. Chem. 3 (4), 268 (1958).
2. B. G. Kuznetsov and P. A. Koz'min, Zhur. Struct. Khimii, 3 (10), 1003 (1958).
3. F. Taha and G. Wilkenson, J. Chem. Soc., 5406, (1963).
4. F. A. Cotton, N. F. Curtis, B. F. G. Johnson and W. R. Robinson, Inorg. Chem., 4 (3), 327 (1965).
5. J. D. Eakins, D. G. Humphreys, and G. E. Mellish, J. Chem. Soc., 6012 (1963).
6. F. A. Cotton and C. B. Harris, Inorg. Chem., 4 (3), 330 (1965).
7. F. A. Cotton, N. F. Curtis, and W. R. Robinson, Inorg. Chem., 4 (12), 1696 (1965).
8. F. A. Cotton, W. R. Robinson, R. A. Walton, and R. Whyman, Inorg. Chem., 6 (5), 929 (1967).
9. B. E. Douglas and D. H. McDaniel, "Concepts and Models of Inorganic Chemistry", Blaisdell Publishing Co., Waltham, Mass., 1965, p. 321.
10. F. A. Cotton, Inorg. Chem., 4 (3), 334 (1965).
11. M. Chisholm, F. A. Cotton, M. Extine, and B. R. Stults, J. Am. Chem. Soc., 98, 4477 (1976).
12. M. Chisholm, F. A. Cotton, M. Extine, M. Millan, and B. R. Stults, J. Am. Chem. Soc., 98, 4486 (1976).
13. F. A. Cotton and C. B. Harris, Inorg. Chem., 6 (5), 924 (1965).
14. F. A. Cotton, Accounts of Chemical Research, 2, 240 (1965).
15. C. D. Cowman and H. B. Gray, J. Am. Chem. Soc., 95 (24), 8177 (1973).
16. W. K. Bratton, F. A. Cotton, M. Debeau, and R. A. Walton, J. Coord. Chem., 1, 121 (1971).

17. A. P. Mortola, J. W. Moskowitz, N. Rosch, C. D. Cowman, and H. B. Gray, Chem. Phys. Ltrs., 32 (2), 283 (1975).
18. W. C. Trogler, C. D. Cowman, H. B. Gray, and F. A. Cotton, J. Am. Chem. Soc., in press.
19. E. E. Wahlstrom, "Optical Crystallography", J. Wiley and Sons, New York, N.Y., 1969, p. 174.
20. T. S. Piper, J. Chem. Phys., 35 (4), 1240 (1961).
21. F. A. Cotton, B. A. Frenzy, B. R. Stults, and T. R. Webb, J. of Am. Chem. Soc., 98 (10), 2768 (1976).
22. F. A. Cotton and M. Jeremic, Synth. Inorg. and Metal-Inorg. Chem., 1 (4), 265 (1971).
23. D. M. Collins, F. A. Cotton, A. Koch, M. Millar and C. A. Murillo, J. Am. Chem. Soc., 99 (4), 1259 (1977).
24. E. W. Abel, A. Singh, and G. Wilkinson, J. Chem. Soc., 3087 (1959).
25. E. Bannister and G. Wilkinson, Chem. and Ind., 319 (1960).
26. T. A. Stephenson, E. Bannister, and G. Wilkinson, J. Chem. Soc., 2538 (1964).
27. D. Lawton and R. Mason, J. Am. Chem. Soc., 87 (4), 921 (1965).
28. F. A. Cotton, Z. C. Mester, and T. R. Webb, Acta Cryst., B30, 2768 (1974).
29. F. A. Cotton and J. G. Norman, Jr., J. Coord. Chem., 1, 161 (1971).
30. F. A. Cotton, J. G. Norman, Jr., B. R. Stults, and T. R. Webb, J. Coord. Chem., 5, 217 (1976).
31. F. A. Cotton and T. R. Webb, Inorg. Chem., 15 (1), 68 (1976).
32. L. Dubicki and R. L. Martin, Aust. J. Chem., 22 (8), 1571 (1969).
33. J. G. Norman, Jr. and H. J. Kolari, J. Chem. Soc. Chem. Comm., 649 (1975).

34. A. P. Kettingham and C. Oldham, J. Chem. Soc. Dalton Trans., 1067 (1963).
35. F. A. Cotton and J. G. Norman, Jr., J. Am. Chem. Soc., 94 (16), 5697 (1972).
36. F. A. Cotton, D. A. Martin, T. R. Webb, and T. J. Peters, Inorg. Chem., 15, 1199 (1976).
37. F. A. Cotton, D. A. Martin, P. E. Fanwick, T. J. Peters, and T. R. Webb, J. Am. Chem. Soc., 98 (15), 4681 (1976).
38. W. C. Trogler, E. I. Solomon, I. Trajberg, C. J. Balhousen, and H. B. Gray, J. Am. Chem. Soc., 16 (4), 828 (1977).
39. J. V. Brenic and F. A. Cotton, Inorg. Chem., 8 (1), 7 (1969).
40. A. R. Bowen and H. Taube, J. Am. Chem. Soc., 93, 3287 (1971).
41. C. L. Angell, F. A. Cotton, B. A. Frenz, and T. R. Webb, J. Chem. Soc. Chem. Comm., 399 (1973).
42. F. A. Cotton, B. A. Frenz, and T. R. Webb, J. Am. Chem. Soc., 95, 4431 (1973).
43. F. A. Cotton, B. A. Frenz, E. Pedersen, and T. R. Webb, Inorg. Chem., 14 (2), 391 (1975).
44. Hunter, L. D., Polarized absorption spectra for single crystals of dichloro (ethylenediammine) platinum (II). Unpublished Ph.D. thesis, Ames, Iowa, Library, Iowa State University, 1971.
45. R. M. Rush, D. S. Martin, Jr., and R. G. LeGrand, Inorg. Chem., 14 (10), 2543 (1975).
46. Jacobsen, R.A., "An algorithm for automatic indexing and bravis latticeselection", National Technical Information Service, Springfield, Va., Sept. 1974.
47. R. J. H. Clark and M. L. Franks, J. Am. Chem. Soc., 97 (10), 2691 (1975).
48. F. A. Cotton, P. E. Fanwick, L. W. Gage, B. Kalbacher, and D. S. Martin, Inorg. Chem., in press.

49. J. G. Norman, Jr., and H. J. Kolari, J. Chem. Soc. Chem. Comm., 303 (1974).
50. J. G. Norman, Jr., and H. J. Kolari, J. Am. Chem. Soc., 97 (1), 33 (1975).
51. A. P. Sattelberger and J. P. Fackler, J. Am. Chem. Soc., 99 (4), 1258 (1977).
52. C. K. Jorgensen, Proc. Inorg. Chem., 12, 130 (1970).
53. A. Loewenschuss, J. Shamir, and M. Ardon, Inorg. Chem., 15 (1), 238 (1976).
54. D. A. McClure, "Electronic Spectra of Molecules and Ions in Crystals", Academic Press, New York, 1959, Part I.
55. J. G. Norman, Jr., H. J. Kolari, H. B. Gray, and W. C. Trogler, Inorg. Chem., in press.
56. D. P. Craig and R. D. Gordon, Proc. Roy. Soc., 288A, 69 (1965).
57. D. P. Craig and G. J. Small, J. Chem. Phys., 50 (9), 3827 (1969).
58. E. Hutchisson, Phys. Rev., 36, 410 (1930).
59. E. Hutchisson, Phys. Rev., 37, 45 (1931).

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