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THE SYNTHESIS OF NEW COORDINATION COMPOUNDS OF THE Mo_2^{+4} ION

by

Edward Hochberg

A dissertation submitted to the Graduate Faculty in Chemistry in partial fulfillment of the requirements for the degree of Doctor of Philosophy,

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1976

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Abstract

THE SYNTHESIS OF NEW COORDINATION COMPOUNDS OF THE Mo_2^{+4} ION

by

Edward Hochberg

Adviser: Professor Edwin H. Abbott

This thesis is divided into two parts. In the first part compounds of Mo_2^{+4} were prepared with arylcarboxylate ligands, several for the first time. The following synthetic procedure was used:

$$2\ Mo(CO)_6 + 4\ ArCOOH \xrightarrow[\text{diglyme}]{N_2,\ \text{heat}} Mo_2(ArCOO)_4 + 12\ CO + 2\ H_2$$

These compounds, depending on the nature of Ar, show varying degrees of air sensitivity. It was found that ligands which upon coordination tend to block the axial sites of the binuclear ion produce more stable compounds. As a typical example, the naphthoate complexes which have the formula $Mo_2(C_{10}H_7COO)_4$ were prepared. The 1-naphthoate complex in which the axial sites are blocked lasts for over a year while the 2-naphthoate complex in which the blocking is not as good starts decomposing after two days. Semiquantitative solution studies show that this

is not due to crystal packing effects in the solids.

In the second part of this thesis the compound $Mo_2(CH_3SO_3)_4$ was synthesized as follows:

$$Mo_2(CH_3COO)_4 + 4\ CH_3SO_3H \xrightarrow[\text{diglyme}]{N_2,\ \text{heat}} Mo_2(CH_3SO_3)_4 + 4\ CH_3COOH$$

In this compound the binuclear ion is bridged by four methanesulfonate ligands. A study of the infrared and far infrared spectra shows that there also exists axial coordination from oxygen atoms on neighboring methanesulfonates.

The methanesulfonate compound is easy to prepare, relatively air stable, and undergoes a variety of substitution reactions. With γ-butyrolactone and DMF two molecules of the new ligands are coordinated.

$$Mo_2(CH_3SO_3)_4 + 2\ L \xrightarrow{N_2} Mo_2(CH_3SO_3)_4 \cdot 2L$$

L= $C_4H_6O_2$ or $(CH_3)_2NCHO$

Conductance, infrared and far infrared measurements show that the structure which best accounts for the properties of these compounds is one in which the new ligands are coordinated to the axial positions in effect substituting for axial coordination of neighboring methanesulfonate.

With halide ions the methanesulfonate compound undergoes partial substitution.

$$Mo_2(CH_3SO_3)_4 + 4\ R_4NX \xrightarrow{N_2} 2\ R_4NCH_3SO_3 + (R_4N)_2Mo_2X_4(CH_3SO_3)_2$$

X= Cl, Br, I.

These halide compounds are very similar, all being red-purple in color and diamagnetic. The change in halide does cause differences in the electronic spectra. The position of the $\delta \rightarrow \delta^*$ band changes slightly and the assignment of a band in the ultraviolet by Norman and Kolari to ligand $\rightarrow$ metal charge transfer was confirmed. In the far infrared spectra one intense band was identified as a metal-halide stretching band. Crude calculations show the force constants of these bands to be very close. These compounds were air stable enough to have Raman spectra taken. The bromide and iodide compounds have one large band each, which corresponds to the metal-metal stretching mode. The chloride compound has two bands which shows extensive coupling of the Mo-Mo and Mo-Cl a_1 stretching modes, a phenomenon observed by other authors. For these partially substituted compounds there are two possible isomeric forms. There is the cis form with C_{2v} symmetry and the trans form with C_{2h} symmetry. Although the mutual exclusivity of the far infrared and Raman spectra of these compounds would seem to favor the trans form, comparison of these results with the work done by San Filippo et al. on mixed ligand complexes favor the assignment of the cis structure.

Finally, a thiocyanate complex was prepared in which

full substitution of methanesulfonate took place.

$$Mo_2(CH_3SO_3)_4 + 8\ NH_4NCS \xrightarrow[(NH_4)_4Mo_2(NCS)_8 \cdot 4DME]{N_2,\ DME} 4\ NH_4CH_3SO_3 +$$

DME= $C_4H_{10}O_2$

The product is a green, crystalline, diamagnetic solid. Its infrared spectra shows the thiocyanate ligand to be nitrogen bonding thus making this to be an isothiocyanate compound. There are two ν C-N bands in the infrared spectra at 2095 and 1920 cm^{-1}, which is expected for a binuclear ion with D_{4h} symmetry. This compound is analogous to known isothiocyanate compounds of Re_2^{+6}.

TABLE OF CONTENTS

TABLE OF CONTENTS (cont.)

LIST OF TABLES

LIST OF TABLES (cont)

LIST OF FIGURES

LIST OF FIGURES (cont.)

LIST OF FIGURES (cont.)

INTRODUCTION

The Synthesis of New Coordination Compounds of the Mo_2^{+4} Ion

Since the 1960's there has been considerable interest in the preparation and study of compounds containing multiply bonded transition metal ions. Examples of such ions are Mo_2^{+4}, Cr_2^{+4}, Re_2^{+6}, Ru_2^{+5}, Tc_2^{+5} and Rh_2^{+4}. These and other ions were discussed in a review by Cotton.[1] The coordination chemistry of these ions is expected to be different from that of mononuclear ions. Binuclearity imposes a different geometry which may favor coordination of some ligands more than others. Besides that, several metal atomic orbitals are involved in the formation of metal-metal bonding and antibonding orbitals. The orbitals left over for ligand bonding may not be the same in number, shape or orientation as those found in mononuclear ions. Finally, in binuclear ions the metal atoms are frequently found in unusually low oxidation states.

Mo_2^{+4}, Cr_2^{+4} and Re_2^{+6} are of particular interest because for these ions a very strong quadruple metal-metal bond has been postulated. Therefore, a project was conceived to explore the basic coordination chemistry of one

of these ions. Mo_2^{+4} was chosen after literature survey had shown that with proper precautions compounds containing this ion could be synthesized with relative ease, and that these compounds well illustrated the properties expected for binuclear compounds.

The Mo_2^{+4} Bond

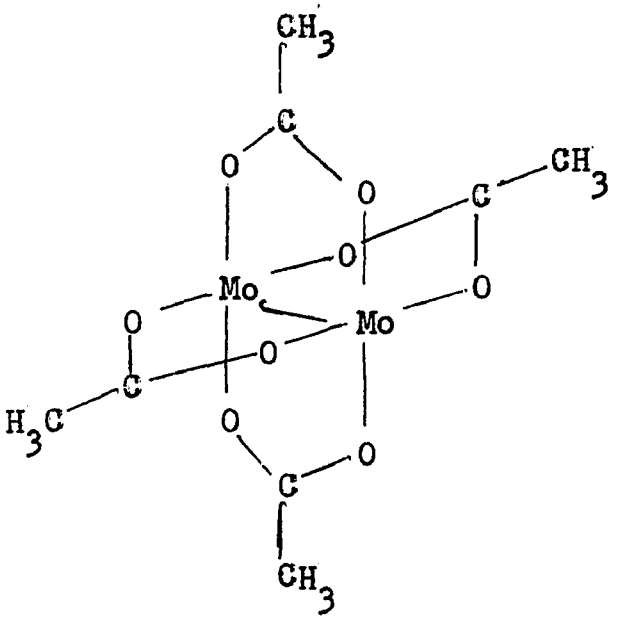
The binuclear molybdenum ion Mo_2^{+4} was first discovered in compounds of the general formula $Mo_2(RCOO)_4$ synthesized by Wilkinson's group as follows:

$$2\ Mo(CO)_6 + 4\ RCOOH \xrightarrow{N_2,\ diglyme} Mo_2(RCOO)_4 + 2\ H_2 + 12\ CO \qquad (1)$$

Several carboxylic acids were used including benzoic, acetic, perfluorobutyric, and cyclohexanecarboxylic acids. The carboxylate compounds were yellow or orange solids, some powdery and some crystalline, with varying degrees of air sensitivity. A benzenesulfonate and a diethylphosphinate compound were also made.[2,3,4] The identity of the gaseous products, CO and H_2, was proven by mass spectroscopy in a later work by Holste and Schafer.[5] An X ray diffraction study of one crystalline product, $Mo_2(CH_3COO)_4$, gave the structure seen in Figure 1 of two molybdenum atoms bridged by four carboxylate ligands. The metal-metal bond distance reported, 2.11 Å, was considered quite short

Figure 1

Structure of $Mo_2(CH_3COO)_4$ as determined by Lawton and Mason.


CH3
C
O
O
C
CH3
O
Mo
O
Mo
O
O
O
C
H3C
O
O
C
CH3

when compared to that in the copper complex, $Cu_2(CH_3COO)_4$, of 2.64 Å.[6] This implied metal-metal bonding.

A few years later Cotton's group synthesized several compounds of the general formula $(Cation)_4Mo_2Cl_8 \cdot 2H_2O$. A typical reaction was as follows:

$$8\ KCl + Mo_2(CH_3COO)_4 \xrightarrow[\text{conc. HCl}]{N_2} K_4Mo_2Cl_8 \cdot 2H_2O + 4\ KCH_3COO \qquad (2)$$

The X ray diffraction study of this compound, a red-purple crystalline solid, showed the presence of the $Mo_2Cl_8^{-4}$ anion. Its structure is shown in Figure 2. The metal-metal distance of 2.14 Å in the absence of bridging ligands proved the existence of metal-metal bonding. Note that the opposing chlorine atoms on the two molybdenum atoms are in the eclipsed rather than the staggered conformation. This implied some kind of multiple bond which would prevent rotation to the staggered conformation. Several complexes with different cations were structured by X ray diffraction[7,8,9] and the syntheses described in detail.[10]

In all of the binuclear complexes discussed thus far the oxidation state of each molybdenum atom is +2. Neutral molybdenum has an electron configuration of $5s^14d^5$. Therefore, dipositive molybdenum has a configuration of $4d^4$. Since all these compounds are diamagnetic, all the

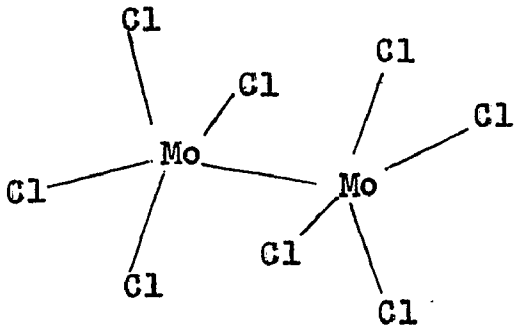
Figure 2

Structure of $Mo_2Cl_8^{-4}$ Anion.

$\measuredangle$ ClMoMo = 105°

$\measuredangle$ ClMoCl = 86°

As determined by Brencic and Cotton.


Cl
Cl
Cl
Mo
Cl
Cl
Mo
Cl
Cl
Cl
Cl

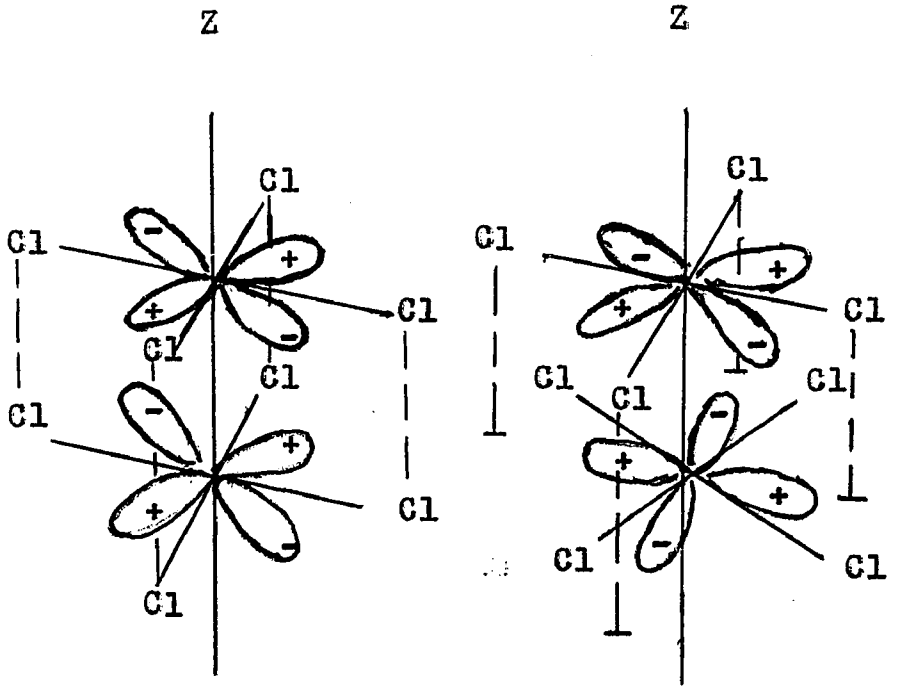
electrons are paired up. Cotton proposed that the two molybdenum atoms were bound by a quadruple bond similar to that which he had proposed for Re_2^{+6} compounds.[11] This quadruple bond consists of a sigma, two pi and one delta bond. From the 5s, 5p and 4d orbitals on each molybdenum atom, eighteen new orbitals are generated. There are four metal-metal bonding and four corresponding antibonding orbitals, four orbitals on each molybdenum atom in a plane perpendicular to the metal-metal axis and two orbitals pointing out from the axial sites on each molybdenum atom. These latter orbitals could be available for ligand bonding in this position, or in the absence of axial ligands would be nonbonding orbitals. The eight electrons from the molybdenum atom d orbitals are paired up in the metal-metal bonding orbitals making the compounds diamagnetic. The presence of the delta bond explains the preference for the eclipsed conformation as illustrated in Figure 3. The quadruple bond itself explains the extreme shortness of the metal-metal distance.

Cotton's largely qualitative ideas were put on a more quantitative footing by Norman and Kolari.[12] Using an all electron, first principles SCF-X scattered wave calculation on the $Mo_2Cl_8^{-4}$ anion, they arrived at the energy level diagram seen in Figure 4. The nonbonding orbitals which Cotton had predicted would lie between the metal-

Figure 3

a) Stabilization of eclipsed conformation of $Mo_2Cl_8^{-4}$ by formation of delta bond by overlap of Mo d_{xy} orbitals.

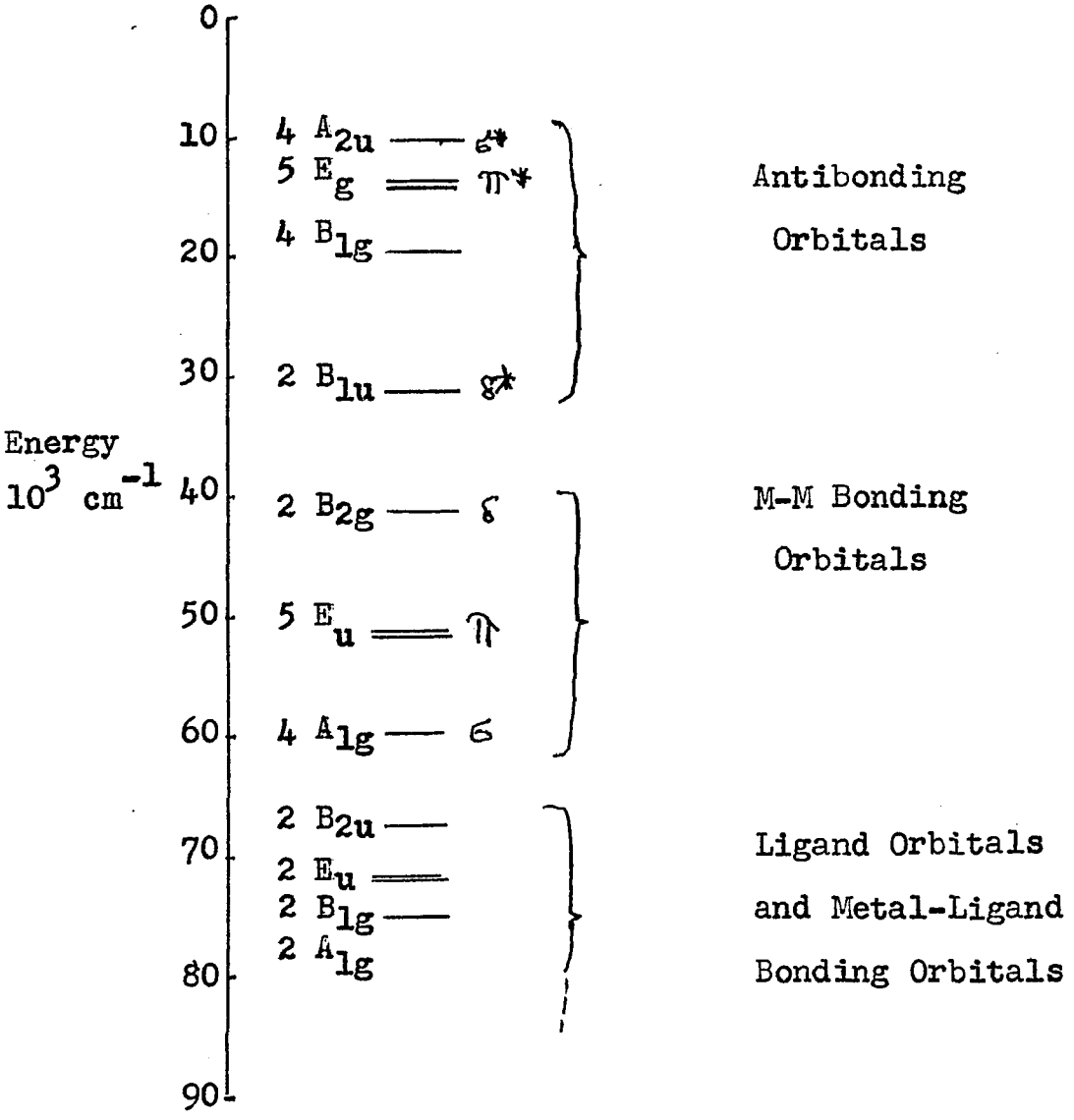
b) Staggered conformation expected with no delta bond formation.



a b

Figure 4

A portion of the energy level diagram for $Mo_2Cl_8^{-4}$ according to an SCF-SW-Xα calculation by Norman and Kolari. Levels shown are those with at least 20 % metal character.


0
10
20
30
40
50
60
70
80
90
Energy
10^3 cm^{-1}
4 A_{2u} — σ^*
5 E_g = π^*
4 B_{1g} —
2 B_{1u} — δ^*
2 B_{2g} — δ
5 E_u = π
4 A_{1g} — σ
2 B_{2u} —
2 E_u =
2 B_{1g} —
2 A_{1g}
Antibonding Orbitals
M-M Bonding Orbitals
Ligand Orbitals and Metal-Ligand Bonding Orbitals

metal bonding and antibonding orbitals are apparently higher in energy than the latter. Norman and Kolari received a rough confirmation of their theory when they compared their calculations to the results of the experimental electronic spectra of $K_4Mo_2Cl_8 \cdot 2H_2O$.

Other proofs of the metal-metal bonding exist. One of these is the diamagnetic anisotropy caused by circulation of electrons in the multiple metal-metal bond which causes the deshielding of the ligand nuclei in the NMR spectra of binuclear complexes of Re_2^{+6} and Mo_2^{+4} in solution. Significant downward shifts in the proton and ^{31}P NMR spectra were seen for trialkylphosphorus ligands coordinated to Mo_2^{+4}.[13] The use of NMR as an analytical tool for structural purposes is limited by the low solubility of most Mo_2^{+4} complexes in suitable solvents.

A second proof comes from the vibrational spectra of Mo_2^{+4} complexes. In $K_4Mo_2Cl_8$, for example, the anion has D_{4h} symmetry. A symmetric a_1 metal-metal stretching mode would be expected to be inactive in the infrared and very intense in the Raman spectra. Such a mode is indeed seen.[14,15,16] The values seen for this band are between 400 and 350 cm^{-1}. By comparison the compound $((h^5C_5H_5)Mo(CO)_3)_2$ which has an Mo-Mo single bond has a band at 193 cm^{-1}.[15]

A consequence of the binuclear nature of the Mo_2^{+4}

compounds can be seen in the mass spectra of these compounds. Several carboxylate compounds of Mo_2^{+4} will sublime upon heating in vacuo. Mass spectra taken of these compounds show molecular ion peaks corresponding to those calculated for $Mo_2(RCOO)_4$. Fragmentation gives ions in which two molybdenum atoms are still present. This has been pointed to as being the result of the strength of the Mo_2^{+4} bond.[17,18,19]

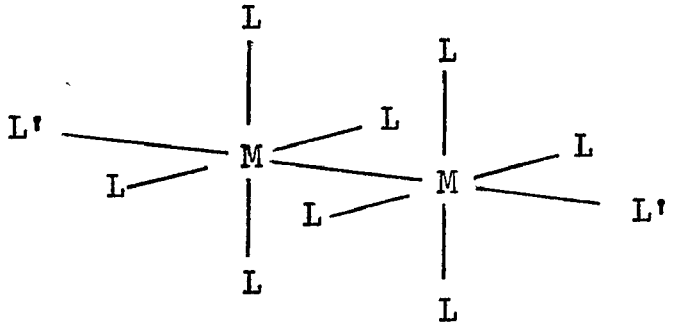
Syntheses of Mo_2^{+4} Compounds

The orbital system worked out for Mo_2^{+4} complexes leaves ten possible ligand coordination sites. As seen in Figure 5 there are eight equatorial and two axial sites available. Equatorial coordination is always present but axial ligands may or may not be present. This may be due to very high energy calculated by Norman and Kolari for electrons in the axial orbitals or to the steric hindrance of these sites by large equatorial ligands.

Binuclear Mo_2^{+4} complexes have molybdenum in a relatively low oxidation state. Many of these complexes are air sensitive as solids and have extremely air sensitive solutions. Syntheses are usually performed under inert atmosphere conditions, in the absence of strong oxidizing agents and frequently for very sensitive compounds at low temperature. Certain compounds such as those containing the octafluorodimolybdate (II) anion could probably never

Figure 5

General structure for $M_2L_8L'_2$, a binuclear compound. L ligands are called equatorial ligands. L' ligands are called axial ligands.


L
L
L'
L
M
L
M
L
L
L'
L
L

be synthesized. Fluoride ligand is generally found in complexes where the metal has high coordination and oxidation numbers.[20] On the other hand, the shortness of the metal-metal distance might prohibit the coordination of eight bulky ligands in the equatorial sites. These limitations must be kept in mind when considering the synthesis of Mo_2^{+4} complexes.

Bridging Ligands

Most binuclear complexes have been made directly or indirectly from the molybdenum carboxylates, usually $Mo_2(CH_3COO)_4$. Certain carboxylate ligands of strong acids could not be made directly from $Mo(CO)_6$ and RCOOH (See equation 1) but were made by substitution of the acetate ligand. An example is provided by Holste's work with the chloroacetic acids:

$$2\ Mo(CO)_6 + 4\ ClCH_2COOH \xrightarrow{\text{toluene}} Mo_2(ClCH_2COO)_4 + 12\ CO + 2\ H_2 \quad (3)$$

The monochloroacetic acid will still react directly with $Mo(CO)_6$ but note the use of toluene as a solvent rather than the higher boiling diglyme. This reaction will not yield the desired product in diglyme. The di- and trichloroacetic acids cannot yield the desired products in either diglyme or toluene. All three acids, however, will substitute with the acetate complex in benzene.

$$Mo_2(CH_3COO)_4 + 4\ ClCH_2COOH \xrightarrow{\text{benzene}} Mo_2(ClCH_2COO)_4 + 4\ CH_3COOH \qquad (4)$$

With increasing chloro substitution the thermal stability of the compounds decreased.[17] A similar situation was found in the synthesis of the trifluoroacetate complex.[18]

Ricard et al. synthesized the ethyl xanthate complex this way:

$$Mo_2(CH_3COO)_4 + 4\ KS_2COC_2H_5 \xrightarrow{\text{alcohol, R.T.}} Mo_2(S_2COC_2H_5)_4 + 4\ KCH_3COO \qquad (5)$$

When the product was recrystallized from tetrahydrofuran two THF molecules became axially coordinated to yield $Mo_2(S_2COC_2H_5)_4 \cdot (C_4H_8O_2)_2$.[21]

Steele and Stephenson synthesized other xanthate complexes which formed adducts with pyridine, 4-picoline and triethylarsine. They also made a thiobenzoate complex:

$$Mo_2(CH_3COO)_4 + 4\ NH_4C_6H_5COS \xrightarrow{\text{methanol}} Mo_2(C_6H_5COS)_4 + 4\ NH_4CH_3COO \qquad (6)$$

An attempt to form a dithiocarbamate complex with $Na_2S_2CNR_2$ yielded a compound not believed to be a binuclear Mo_2^{+4} complex.[22]

One group of compounds with bridging ligands which

can be made directly from $Mo(CO)_6$ are the amidine complexes:

$$2\ Mo(CO)_6 + 4\ C_6H_5NC_6H_5CC_6H_5NH \xrightarrow{120^\circ,\ 27.5\ hrs} Mo_2(C_6H_5NC_6H_5CC_6H_5N)_4 + 12\ CO + 2\ H_2 \quad (7)$$

The amidine ligands bridge the binuclear ion through their nitrogen atoms the way a carboxylate bridges through its oxygen atoms.[23]

Organometallic Chemistry

Some organometallic compounds of Mo_2^{+4} have also been made. A very sensitive compound was the methide complex which was made at ice bath temperatures as follows:

$$Mo_2(CH_3COO)_4 + 8\ LiCH_3 \xrightarrow[6\text{-}12\ hr]{\text{dioxane, THF or } Et_2O} Li_4Mo_2(CH_3)_8 \cdot 4Et_2O \quad (8)$$

With THF as the ether used a crystalline compound was obtained. The crystal structure showed the THF molecule to be coordinating Li.[24]

Some organometallic complexes are not made from $Mo_2(CH_3COO)_4$ but are synthesized by complex redox reactions. One such complex is the allyl complex. This very air sensitive and water sensitive compound was made by Oberkirch by the following route:[25]

$$C_3H_5MgCl + MoCl_5 \xrightarrow{\text{ether, R.T.}} Mo_2(C_3H_5)_4 \quad (9)$$

The product can be recrystallized from pentane. The crystal structure was determined by Cotton and Pipal. The Mo-Mo distance is 2.18 Å. The coordination of the ligands is unusual. Two allyl ligands are bridging ligands while the other two allyl ligands each chelate a single Mo atom.[26]

Another unusual compound was synthesized by Heyn and Still. Below are given the reactions which are believed to take place:

$$5\ Li_3Mo(C_6H_5)_6 + MoCl_3 \cdot 3THF \longrightarrow 6\ Li_2Mo(C_6H_5)_5 + 3\ LiCl \quad (10)$$

$$Li_2Mo(C_6H_5)_5 \longrightarrow 1/2\ C_6H_5\text{-}C_6H_5 + Li_2Mo(C_6H_5)_4 \quad (11)$$

$$Li_2Mo(C_6H_5)_4 \longrightarrow Li_2Mo(C_6H_5)_2H_2 + 2\ C_6H_4 \quad (12)$$

The final product is found to contain THF. Also addition of acetic acid yields $Mo_2(CH_3COO)_4$. If this product is indeed binuclear then its formula would be $Li_4Mo_2(C_6H_5)_4H_4 \cdot 4THF$.[27]

Halide Chemistry

One very big class of compounds are the substituted chloride and bromide compounds of Mo_2^{+4}. Recently some iodide compounds were made too. These compounds have the general formulas $Mo_2X_4L_4$ and $Mo_2X_4(LL)_2$ where LL is a bidentate ligand chelating a single Mo atom. Most of

the work done in this area has been done by the research groups of Brencic and San Filippo.

The chloride complexes used as the starting materials are those synthesized by Brencic and Cotton.[7-10] These had been synthesized originally from $Mo_2(CH_3COO)_4$ as shown in equation 2. Typical substitution reactions done by San Filippo et al. are as follows:

$$(NH_4)_5Mo_2Cl_9 \cdot H_2O + 4\ P(C_2H_5)_3 \xrightarrow{\text{methanol}} Mo_2Cl_4(P(C_2H_5)_3)_4 \quad [13] \qquad (13)$$

$$(NH_4)_5Mo_2Cl_9 \cdot H_2O + 4\ (C_2H_5)_2S \xrightarrow{\text{methanol}} Mo_2Cl_4(S(C_2H_5)_2)_4 \quad [28] \qquad (14)$$

$$(NH_4)_5Mo_2Cl_9 \cdot H_2O + 2\ DTH \longrightarrow Mo_2Cl_4(DTH)_2 \quad [28] \qquad (15)$$

DTH= $CH_3SCH_2CH_2SCH_3$ 2,5-dithiahexane

(It should be noted that in $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ the extra chloride ion is not part of the $Mo_2Cl_8^{-4}$ entity and occupies a distinct position in the crystal structure.)

Other ligands used were $P(C_3H_7)_3$, $P(C_4H_9)_3$, $P(C_6H_5)(CH_3)_2$, $P(OCH_3)_3$,[13] dimethyl sulfide, 4,7-dithiodecane DTD, 5,8-dithiododecane DTDD, pyridine, 2,2'-bipyridine, and tetramethylenediphosphine TMEDP.[28]

They were also able to prepare some complexes from other complexes. This was the case with the aceto- and benzonitrile and DMF complexes.[28]

$$Mo_2Cl_4((CH_3)_2S)_4 + 4\ CH_3CN \xrightarrow{12\ hr} Mo_2Cl_4(CH_3CN)_4 \quad (16)$$

$$Mo_2Cl_4((CH_3)_2S)_4 + 4\ C_6H_5CN \xrightarrow{1/2\ hr} Mo_2Cl_4(C_6H_5CN)_4 \quad (17)$$

$$Mo_2Cl_4(DTDD)_2 + 4\ DMF \xrightarrow{1\ hr} Mo_2Cl_4(DMF)_4 \quad (18)$$

DTDD= $CH_3(CH_2)_3SCH_2CH_2S(CH_2)_3CH_3$
DMF= $(CH_3)_2NCHO$

Brencic's group prepared a pyridine complex similar to San Filippo's and substituted it with 2,2'-bipyridine, 1,10-phenanthroline and dry ammonia, all at 100°C.[29,30]

$$Mo_2Cl_4(py)_4 + \text{dry } NH_3 \longrightarrow Mo_2Cl_4(NH_3)_4 \quad (19)$$

There have been several bromide complexes prepared also. Oldham and Ketteringham claim to have prepared the octabromodimolybdate (II) anion.[15]

$$Mo_2(CH_3COO)_4 + 8\ CsBr \xrightarrow{48\%\ HBr\ at\ 0°C,\ 4\ hr} Cs_4Mo_2Br_8 + 4\ CsCH_3COO \quad (20)$$

Their claim is based on a reported bromide analysis of 47.3% as compared to a theoretical value of 46.9%. However, using practically the same synthetic method, Brencic reported a different product.

$$Mo_2(CH_3COO)_4 + 7\ CsBr \xrightarrow{48\%\ HBr\ at\ -20°C,\ 2\ hr} Cs_3Mo_2Br_7 \cdot 2H_2O \quad (21)$$

The calculated bromide value here is 47.7% for which 47.1% was actually obtained. The similarity of these values makes the first claim doubtful as the second one is substantiated by a molybdenum analysis also.[30] The molybdenum theoretical value is substantially higher for Brencic's formulation than for Oldham's.

Using the same reagents but heating to 60°C, San Filippo obtained $Cs_3Mo_2Br_8$ which he used for his starting material in bromide complex syntheses.[28]

Brencic was able to make $Mo_2Br_4(py)_4$ by two routes:

$$Mo_2Cl_4(py)_4 + 4\ LiBr \longrightarrow Mo_2Br_4(py)_4 + 4\ LiCl \qquad (22)$$

The equilibrium is to the right because LiCl forms a precipitate more easily than LiBr.

$$Cs_3Mo_2Br_7 \cdot 2H_2O + 4\ py \xrightarrow{\text{room temperature}} Mo_2Br_4(py)_4 + 3\ CsBr \qquad (23)$$

This bromopyridine complex is amenable to substitution as is the chloropyridine complex and Brencic found the following order of stability:[30]

$$Mo_2X_4(2,2'\text{-bipy})_2 > Mo_2X_4(NH_3)_4 > Mo_2X_4(py)_4$$

San Filippo used $Cs_3Mo_2Br_8$ to make compounds of the general formula $Mo_2Br_4L_4$.[28]

$$Cs_3Mo_2Br_8 + 4\ py \longrightarrow Mo_2Br_4(py)_4 \qquad (24)$$

$$Mo_2Br_4(py)_4 + 4\ CH_3SCH_3 \longrightarrow Mo_2Br_4(CH_3SCH_3)_4 \qquad (25)$$

San Filippo's reaction schemes for the chloride and bromide complexes are in Figures 6a and b.

Very recently some iodide complexes were synthesized by Brencic's group. This is summarized in the following reactions:[31]

$$(picH)_2Mo_2Br_6(H_2O)_2 + HI + picHI \xrightarrow{12\ hr} (picH)_2Mo_2I_6(H_2O)_2 \quad (26)$$

$$(picH)_2Mo_2I_6(H_2O)_2 + py \xrightarrow{1\ hr,\ 85°C} Mo_2I_4(py)_4 \quad (27)$$

$$Mo_2I_4(py)_4 + 2,2'\text{-bipy} \xrightarrow{120°C} Mo_2I_4(2,2'\text{-bipy})_2 \quad (28)$$

picH= $CH_3C_5H_5NH^+$ 4-methylpyridinium

A 4-methylpyridine and an ammonia complex were also made from the pyridine complex. The details of the synthesis of $(picH)_2Mo_2Br_6(H_2O)_2$ were not given in the article. They were supposed to be in another paper which was in press.

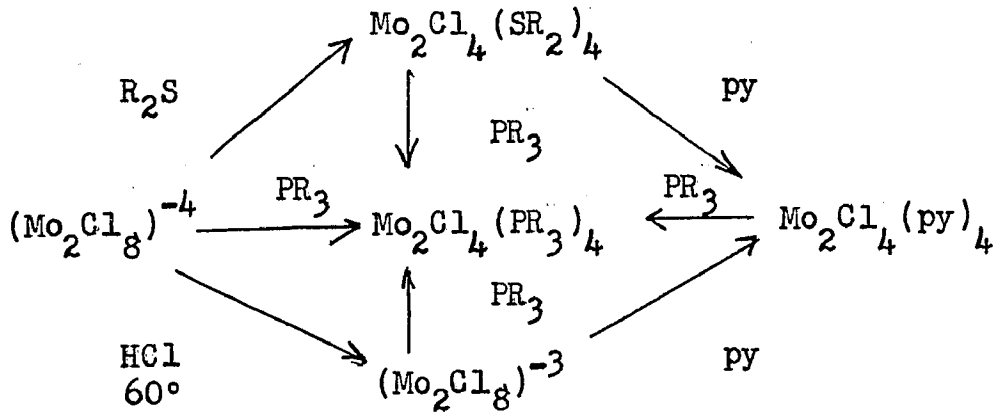
Aqueous Chemistry

The aqueous chemistry of Mo_2^{+4} has been explored by Bowen and Taube.[32] Mo_2^{+4} is known to complex with water but as yet no solid compounds with water directly coordinated to Mo in the equatorial position have yet

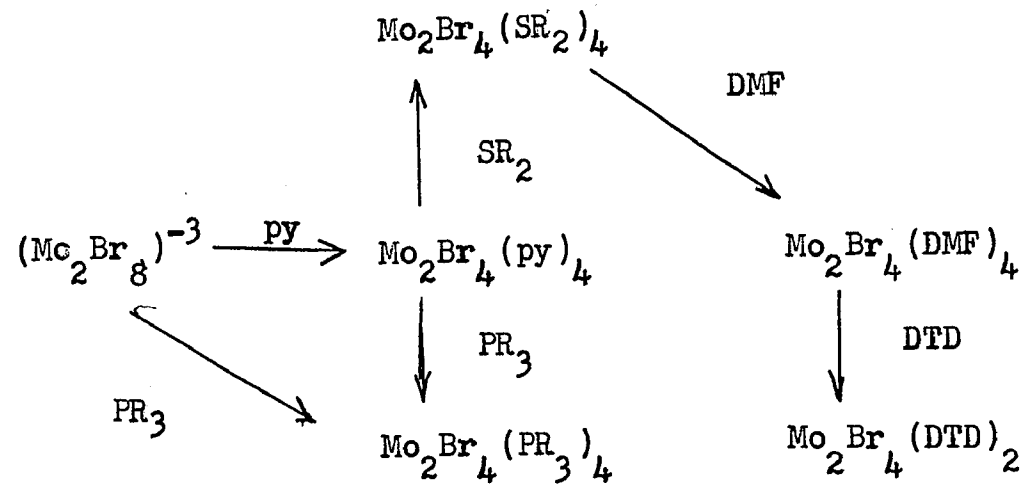
Figure 6

a) San Filippo's reaction scheme for Mo_2^{+4} chloride compounds.

b) San Filippo's reaction scheme for Mo_2^{+4} bromide compounds.


$Mo_2Cl_4(SR_2)_4$
R_2S
py
PR_3
PR_3
PR_3
$(Mo_2Cl_8)^{-4}$
$Mo_2Cl_4(PR_3)_4$
$Mo_2Cl_4(py)_4$
PR_3
HCl
60°
$(Mo_2Cl_8)^{-3}$
py

a


$Mo_2Br_4(SR_2)_4$
DMF
SR_2
$(Mo_2Br_8)^{-3}$
py
$Mo_2Br_4(py)_4$
$Mo_2Br_4(DMF)_4$
PR_3
DTD
PR_3
$Mo_2Br_4(PR_3)_4$
$Mo_2Br_4(DTD)_2$

b

been isolated with the possible exception of the yet unpublished compounds of Brencic, $(picH)_2Mo_2X_6(H_2O)_2$. Some reactions performed by Bowen and Taube in water were those given below.

$$K_4Mo_2Cl_8 + K_2SO_4 \xrightarrow{CF_3SO_3H,\ R.T.} K_4Mo_2(SO_4)_4 \quad (29)$$

$$K_4Mo_2Cl_8 + CH_2NH_2CH_2NH_2 \xrightarrow{heat} Mo_2(en)_4Cl_4 \quad (30)$$

The product of reaction 30 can be recrystallized from water and HCl or water and $CH_3C_6H_4SO_3H$ yielding in the latter case $Mo_2(en)_4(CH_3C_6H_4SO_3)_4$.

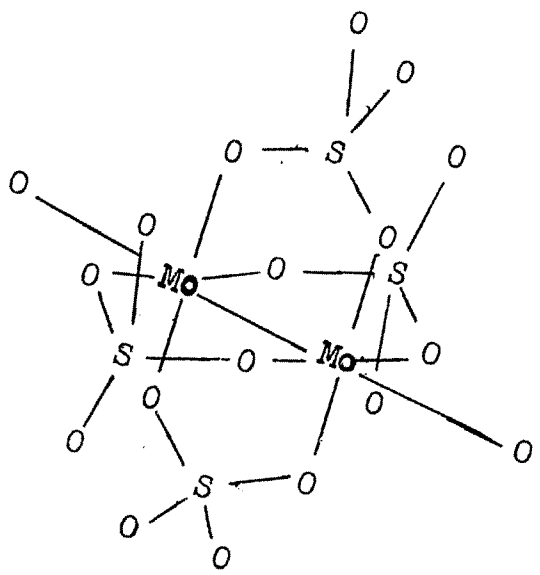
An interesting feature of the sulfate complex $K_4Mo_2(SO_4)_4 \cdot 2H_2O$ was seen in the X ray crystal structure. Each binuclear unit as expected has four bidentate bridging sulfate ligands. In addition a third oxygen on some sulfate ligands coordinates axially.[33] See Figure 7.

Axial Ligands

Some mention has already been made of cases of axial coordination.[21,22,33] This phenomenon occurs much more frequently in the binuclear complexes of other metals such as Re_2^{+6}.[1] With binuclear Mo_2^{+4} it is seen when the equatorial ligands are bridging ligands. Wilkinson et al. reported that the carboxylate compounds formed air sensitive adducts with pyridine.[4] The most thorough study was done by Cotton and Norman, who compared $Mo_2(CF_3COO)_4$ to

Figure 7

Structure of $Mo_2(SO_4)_4^{-4}$ anion showing axial bonding by oxygen from sulfates coordinated to other binuclear ions in an equatorial fashion.
As determined by Cotton, Frenz, Pedersen and Webb.


O
O
O
S
O
O
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O
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Mo
O
S
O
S
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Mo
O
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S
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O
O

$Mo_2(CF_3COO)_4 \cdot 2py$. Some results are summarized below.

	$Mo_2(CF_3COO)_4$	$Mo_2(CF_3COO)_4 \cdot 2py$
Mo-Mo distance	2.090 Å	2.129 Å
Raman Mo-Mo stretching frequency	397 cm^{-1}	367 cm^{-1}
Mo-N distance		2.548 Å

Adduct formation apparently weakens the Mo-Mo bond. The Mo-N distance is quite long showing the weakness of that bond.[34]

The Labile Ligand Synthetic Route

The team of Abbott, Backstrom and Schoenewolf attempted to find a route to a wider variety of Mo_2^{+4} complexes. Their idea was to replace the acetate ligands of $Mo_2(CH_3COO)_4$ with a very labile ligand such as trifluoromethanesulfonate TFMS. The new complex $Mo_2(CF_3SO_3)_4$ would be very amenable to substitution even by very weak ligands. The first step was the synthesis of the TFMS complex.[35]

$$Mo_2(CH_3COO)_4 + 4\ CF_3SO_3H \xrightarrow{100°C} Mo_2(CF_3SO_3)_4 + 4\ CH_3COOH \qquad (31)$$

The product obtained is very air sensitive and is best purified by sublimation. The TFMS complex formed a red solution in HTFMS. When dry ethyl acetate was added a

red-orange solution formed. Upon adding heptane and cooling, red-orange crystals of an ethyl acetate complex, $Mo_2(C_2H_5O_2CCH_3)_4(CF_3SO_3)_4$, was formed. Infrared analysis showed that the ester was coordinated to the binuclear ion like a carboxylate ligand, through its two oxygen atoms.

The above mentioned reactions showed promise for this method. Unfortunately, there are difficulties. The TFMS synthesis is very difficult and messy and there is difficulty in obtaining pure products.

Statement of Thesis

This thesis is divided into two parts. In part 1 several new arylcarboxylate compounds were synthesized according to Wilkinson's scheme. (See equation 1). As previously mentioned, these complexes had varying degrees of air sensitivity. A structural factor was found which was able to account for the stability of some complexes over others. These results were published in a paper entitled "Mass Spectra and Structural Factors in the Air Stability of Carboxylate Complexes of Mo_2^{+4}". As the title says, some mass spectral work was done in relation to these complexes. Since I neither performed nor interpreted the mass spectra, that work will not be part of this thesis.[19]

Part 2 relates to the above mentioned labile ligand approach. This project was essentially exploratory synthetic inorganic chemistry. The complex $Mo_2(CH_3SO_3)_4$ was synthesized as an alternative to $Mo_2(CF_3SO_3)_4$, with which there were associated difficulties. The methanesulfonate complex was reacted with DMF and γ-butyrolactone and the resulting compounds, through their spectra, gave information about the parent methanesulfonate complex. Reactions were also attempted with halides and thiocyanate. Since this was exploratory work, the products obtained were not always those anticipated. However, these products are interesting in their own right because they demonstrate different degrees of partial and full substitution of the parent complex. The effects of the different degrees of substitution are seen especially in the spectral results, which were the chief means of structural determination.

PART ONE

The Synthesis of Several New Arylcarboxylate Complexes of Mo_2^{+4} and the Determination of a Structural Factor Affecting the Air Stability of These Complexes

The molybdenum carboxylates $Mo_2(RCOO)_4$ were the first synthesized compounds of Mo_2^{+4}. When the benzoate complex was first reported in a communication, it was believed to be some kind of sandwich compound.[2] When a similar acetate complex was reported, it was realized that the sandwich structure was impossible. Using many different carboxylic acids Wilkinson's group synthesized other Mo_2^{+4} complexes.[4] Lawton and Mason established the correct structure with the X ray diffraction study of the acetate complex.[6] (See Figure 1).

In these complexes molybdenum has the relatively low oxidation state of +2, so it was not surprising that these complexes were reported to be air sensitive. Because many of these complexes were insoluble in noncoordinating organic solvents, statements concerning air sensitivity referred to the solid compounds. Since these compounds when first synthesized had bright, distinctive colors, any subsequent discoloration was taken as a sign of reaction with oxygen. Wilkinson et al. reported the benzoate and acetate to be fairly stable, with the benzoate more stable

than the acetate. Complexes with dicarboxylate ligands, which could bind to either two binuclear groups or twice to one group, were very air sensitive. The stabilities of other complexes were compared to acetate and benzoate. Higher alkyl carboxylates were less stable than the acetate complex and perfluorobutyrate was more stable.[4] Brignole and Cotton reported that the p-methyl and p-methoxybenzoate complexes were more air sensitive than the benzoate.[36] These results imply that ligands with electron withdrawing groups are more stable than those with electron donating groups. However, it is also known that complexes with electron withdrawing groups frequently cannot be synthesized by the reaction in equation 1. The formate, p-nitrobenzoate, chloroacetate and trifluoroacetate cases are examples of this.[37] Only years later were the trifluoroacetate[18] and the chloroacetate[17] complexes made by substitution from the acetate complex at low temperatures. This in itself does not prove that these complexes are more air sensitive. From personal experience, it is known that the formate is a very sensitive compound. It reacts readily with oxygen. Holste observed that with increasing chloro substitution the thermal stability of the chloroacetate complexes decreased.[17] The idea of correlating the degree of air sensitivity of the carboxylate complexes was one of the aims of the attempted syntheses.

Experiments and Results

Precautions, Chemicals and Instrumentation

The synthesis of binuclear Mo_2^{+4} compounds and their subsequent handling require care. The air sensitivity of these compounds necessitates the use of inert atmosphere techniques. In addition if nonaqueous products are desired care must be taken to exclude water from the system. This required the use of airless ware systems and prepurification of reagents and solvents.

The syntheses of the carboxylate compounds were carried out in a three necked flask flushed with and under a constant stream of nitrogen. The nitrogen used here first passed through a flask containing aqueous chromium (II) solution. The chromium (II) solution is generated by the reaction of zinc amalgam with chromium (III) chloride in acid solution. Any oxygen in the gas will be reduced by the solution.[38] The nitrogen then passed through a dry ice acetone cold trap, a sulfuric acid solution, and finally a tube of drierite to remove any water present.

The diglyme used as a solvent in these syntheses was dried either over $CaCl_2$ or NaOH and distilled at reduced pressure from CaH_2 under nitrogen.[39]

Some of these complexes were used in mass spectral studies which also helped to identify them by molecular

weight. Mass spectra were obtained with a Varian cycloidal instrument. Samples were sublimed into the ionization chamber at 150-200°C. Ionization was achieved by bombardment with 60 eV electrons. Spectra were calibrated by addition of perfluoroalkanes.

Syntheses and Analyses

The compounds were synthesized by refluxing $Mo(CO)_6$ with the appropriate acid in diglyme. The syntheses were originally done on a large scale making several grams at a time. They were repeated by undergraduate Pauline Walks on a smaller scale. The data from these syntheses were published in our paper and appear in Table 1. Except where noted the reflux times were 3-4 hrs and 25 ml of diglyme was used as the solvent. Table 2 gives the analytical results of the syntheses. The analyses were performed by the Schwartzkopf Microanalytical Analysis Company.

Air Sensitivity Studies

Because of the very low solubility of most of the complexes in nonreacting solvents, the compounds were studied as solids. Samples of each compound were ground to fine powders, placed on watch glasses, exposed to laboratory air and the time taken for complete discoloration was recorded. The results are in Table 3.

Table 1

Synthetic Data for the Tetra-μ-carboxylato-dimolybdenum (II) Complexes

Compound	Amount g	
	Ligand	$Mo(CO)_6$
(o-methylbenzoate)$_4Mo_2$	1.85	1.4
(1-naphthoate)$_4Mo_2$ [a]	1.0	0.85
(2-naphthoate)$_4Mo_2$	0.97	0.80
(p-chlorobenzoate)$_4Mo_2$	1.02	0.81
(o-chlorobenzoate)$_4Mo_2$	2.2	2.0
(anthracene-9-carboxylate)$_4Mo_2$	0.49	0.36
(thiophene-2-carboxylate)$_4Mo_2$	1.05	0.80
(furan-2-carboxylate)$_4Mo_2$	0.26	0.20
(p-fluorobenzoate)$_4Mo_2$	2.7	1.6

a) After refluxing, half the solvent was distilled off. The product crystallized upon standing overnight in a refrigerator.

b) Refluxed 3 hr in 10 ml of diglyme; crystallizes overnight at 0°. This compound is quite soluble in ethanol and ether.

c) The solution was refluxed for 6 hr. Half the solvent was distilled off. Orange crystals separated overnight in a refrigerator. The product is rather soluble in ethanol.

Table 2

Analytical Data for the Tetra-μ-carboxylato-dimolybdenum (II) Complexes

Compound	%calcd.		%obsd.	
	C	H	C	H
(o-methylbenzoate)$_4$Mo$_2$	52.4	3.8	52.63	4.06
(1-naphthoate)$_4$Mo$_2$	60.3	3.2	60.41	3.26
(2-naphthoate)$_4$Mo$_2$	60.3	3.2	60.83	3.75
(p-chlorobenzoate)$_4$Mo$_2$	41.3	1.92	42.48	2.55
(o-chlorobenzoate)$_4$Mo$_2$	41.3	1.92	41.38	1.80
(anthracene-9-carboxylate)$_4$Mo$_2$	66.8	3.3	66.80	3.03
(thiophene-2-carboxylate)$_4$Mo$_2$	34.28	1.71	34.43	2.08
(furan-2-carboxylate)$_4$Mo$_2$	37.7	1.9	37.52	1.99
(p-fluorobenzoate)$_4$Mo$_2$[d]				

d) Elemental analyses varied; however, an intense molecular ion was observed in the mass spectrum.

Table 3

Relative Air Stability of Some Tetra-μ-carboxylato dimolybdenum (II) Complexes

Compound	Time Required for Loss of Color
(o-methylbenzoate)$_4Mo_2$	5 days
(p-methylbenzoate)$_4Mo_2$	10 hr
(1-naphthoate)$_4Mo_2$	1 year
(2-naphthoate)$_4Mo_2$	2 days
(p-chlorobenzoate)$_4Mo_2$	12 hr
(o-chlorobenzoate)$_4Mo_2$	2 days
(anthracene-9-carboxylate)$_4Mo_2$	1 year
(benzoate)$_4Mo_2$	2 months
(thiophene-2-carboxylate)$_4Mo_2$	1 year
(furan-2-carboxylate)$_4Mo_2$	2 months

Despite the obvious crudity of this method, differences in air sensitivity were sufficiently great for an important steric factor to be seen.

Results and Discussion

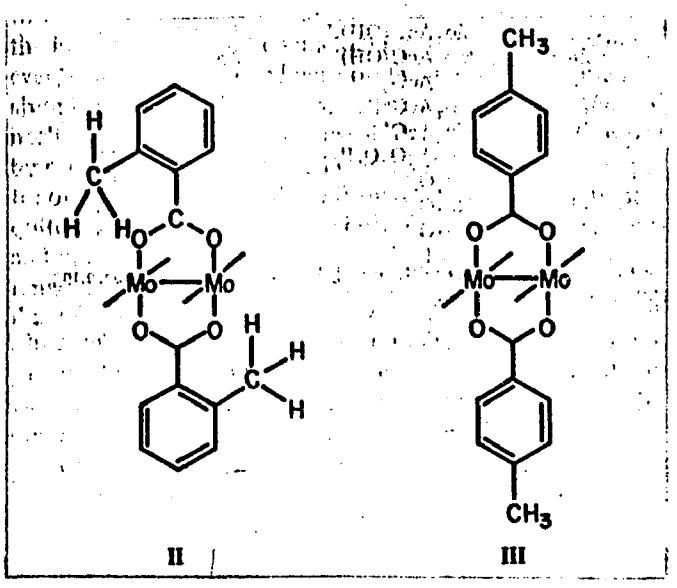
Although electronic and resonance factors no doubt play a role in determining the air sensitivity of these complexes, it is hard to find a consistent pattern. The p-methylbenzoate is more air sensitive than the benzoate but so is the p-chlorobenzoate. The steric factor is consistent, however. Consider the case of the p- and o-methylbenzoates. Models show that in the ortho case there are ortho methyl groups on both sides of the binuclear unit and that these groups tend to block the axial sites. (See Figure 8). It is known that donor groups like pyridine can bind to the axial sites and perhaps this is the site of oxygen attack. The same effect is seen for the p- and o- chlorobenzoates and especially for the 1- and 2- naphthoates illustrated in Figure 9. The anthracene-9-carboxylate illustrated also in Figure 9 was synthesized because in this molecule the binuclear unit would be virtually encapsulated. This molecule would be expected to be air stable and that was proven to be the case. It was unaffected by a year of exposure.

Many objections justly may be raised to conclusions drawn from this type of observation. For example, it may

Figure 8

II) Proposed structure for o-methylbenzoate complex of Mo_2^{+4}, showing hindrance of axial sites.

III) Proposed structure for p-methylbenzoate complex of Mo_2^{+4}, showing less hindrance of axial sites.



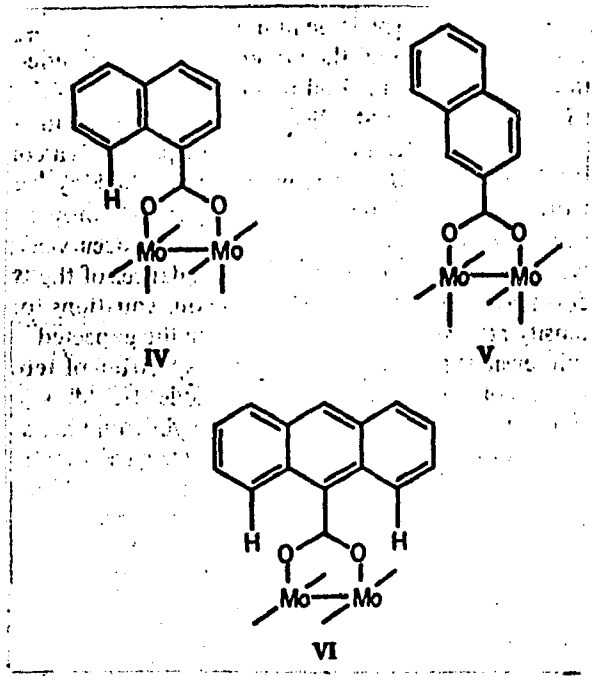
II III

Figure 9

IV) Proposed structure of 1-naphthoate complex of Mo_2^{+4}, showing hindrance of axial sites.

V) Proposed structure of 2-naphthoate complex of Mo_2^{+4}, showing less hindrance of axial sites.

VI) Proposed structure of 9-anthracenecarboxylate complex of Mo_2^{+4}, showing complete hindrance of axial sites.


H
O
O
Mo
Mo
IV
O
O
Mo
Mo
V
H
O
O
H
Mo
Mo
VI

be argued that differences in crystallization energy are responsible for differences in reactivity. Two factors argue against this. First the ortho compound would have to be stabilized over the para by forming a stronger crystal. Such thermodynamic stabilization is improbable because in the cases of ortho vs. para CH_3 and Cl and in the case of the 1- and 2-naphthoates the carboxylate which best hinders the axial site also forms the more soluble complex. This is an indication that these axially hindered complexes actually form weaker crystals. Second, from the kinetic point of view, a difference in crystal structure might be expected to result in a difference in the rate of heterogenous oxidation observed. In other words, the crystal packing of the axially hindered complexes would result in a much higher energy for the activated complex of oxidation. This possibility seems unlikely because the solutions of the axially hindered complexes were all relatively air stable compared to solutions of other molybdenum (II) carboxylates. Once again, the problems of solubility mentioned above precluded a quantitative measurement of these effects; however, solutions of dimolybdenum (II) carboxylates such as benzoate, acetate and p-methylbenzoate are oxidized within seconds after exposure to air while solutions of the axially hindered species such as o-toluate and

o-chlorobenzoate required several minutes to be oxidized.

Conclusion

In Part 1 several arylcarboxylate complexes of Mo_2^{+4} were synthesized. Some like the 1- and 2-naphthoates, the o- and p- chlorobenzoates, and the 9-anthracene-carboxylate for the first time. It was found that those complexes with ligands which tended to block the axial sites of the binuclear unit were more air stable. This effect persisted in solution, proving it was not a result of crystal packing of solids.

PART TWO

The Synthesis of $Mo_2(CH_3SO_3)_4$ and its Reactions With γ-butyrolactone, DMF, Halides and Thiocyanate

This part of the thesis deals with an attempt to make new Mo_2^{+4} by the labile ligand synthetic route. Originally attempts were made to use the trifluoromethanesulfonate compound $Mo_2(CF_3SO_3)_4$ as the labile intermediate. It was reasoned that TFMS would be such a labile ligand that even poorly coordinating ligands would replace it and many new and interesting compounds could be synthesized from its Mo_2^{+4} complex.

However, there were difficulties encountered which made that approach impractical. The TFMS compound is synthesized by the approach in equation 31. HTFMS is added to the acetate complex $Mo_2(CH_3COO)_4$ and heated under nitrogen. Theoretically acetic acid comes off. The acetate complex is yellow and the acid is clear. Upon addition of the acid to the acetate complex a red solution forms. After some of the liquid is pumped off a pink solid forms. If the system is heated to total dryness the solid turns tan. The tan solid is very air sensitive and hard to handle. Since it is soluble in alcohols it may be reacted in situ with alcoholic solutions of reagents one would wish to use in syntheses of new compounds. Attempts to work

with the partially dry pink solid were impractical. The pink solid has a sticky, pasty consistency and is almost impossible to handle in airless ware. It still contains corrosive acid which burns holes in glove bags. Therefore attempts were made to use the dry tan solid instead. Besides being very air sensitive and difficult to handle compounds made from the tan solid gave poor elemental analyses. The infrared spectra of these compounds showed a band at 675 cm^{-1} characteristic of unremoved acetate ligand. The synthesis of $Mo_2(CF_3SO_3)_4$ was repeated many times; using large excesses of HTFMS, heating a long time before putting the system on vacuum, and heating to absolute dryness. The results were still negative. An attempt was made to see if acetic acid could be distilled from a mixture of HTFMS and sodium acetate. At bath temperatures considerably in excess of the 118°C boiling point of acetic acid not a drop would come off. Perhaps there is some reaction between acetic acid and trifluoromethanesulfonic acid which prevents easy distillation of acetic acid. In light of these results it was decided to use the somewhat weaker acid, methanesulfonic acid HMS, as the source of the labile ligand.

It turns out that the complex resulting from the reaction of HMS with the acetate complex, $Mo_2(CH_3SO_3)_4$, is not as labile as first anticipated. Instead it undergoes a variety of reactions illustrating various

degrees of substitution. This part of the thesis deals with the synthesis and characterization of $Mo_2(CH_3SO_3)_4$, several reactions illustrating different degrees of substitution with attempted characterization of the products.

Experimental

Precautions

The difficulties of working with Mo_2^{+4} complexes have already been commented on in Part One. Since this part of the thesis deals with more complicated systems and more instrumental work was done some further comment is necessary. Several syntheses such as those for the bromide and iodide complexes were carried out in a setup similar to that used for the carboxylate compound mentioned in Part One. Other syntheses such as those for the methanesulfonate, chloride, thiocyanate, DMF and butyrolactone complexes were carried out under conditions of either high vacuum or nitrogen. This was achieved by having a manifold which could connect the reacting system to both. Syntheses were carried out in airless ware systems. Most of the techniques used are found in the book by Shriver.[40]

In all cases except in the case of the very stable halide complexes, care had to be taken in the preparation of samples for magnetic, electrical and spectroscopic measurements. Samples were prepared in glove bags. The

sample tubes for magnetic susceptibility, the conductivity cell and sample cells for solution spectra were purged beforehand and flushed with nitrogen. Nitrogen was swept through the nujol and hexachlorobutadiene used for mulls of sensitive compounds. For the electronic mull spectra of the very sensitive thiocyanate compound, argon was swept through the sample compartment of the Cary 14 spectrophotometer.

Chemicals

The nitrogen used for the syntheses of the bromide and iodide complexes was purified by the method used in the syntheses of the carboxylate compounds. The nitrogen used in the manifold setup first passed through an oxygen removal tower and then through a tube of drierite. The oxygen removal tower is a glass column containing BASF catalyst and is externally heated to activate the catalyst. The apparatus is available from the Kontes company and is described in the book by Shriver.[41]

The purification procedures for reagents and solvents come from the book by Perrin et al.[39] Diglyme was purified by the method mentioned in the experimental section of Part One. Dimethoxyethane DME was refluxed over CaH_2 and distilled. These two solvents were stored under nitrogen. Methanesulfonic acid comes 98% pure from the

Aldrich Chem. Co.. It was dried by azeotropic distillation of the water with added benzene. Extra benzene is distilled off and then the acid is distilled under vacuum. N,N-dimethylformamide was dried over molecular sieves and distilled at reduced pressure. Acetonitrile was dried over molecular sieves, stirred with CaH_2 and then fractionally distilled at high reflux. Anhydrous methanol was further dried over molecular sieves and distilled. γ-butyrolactone was dried over $CaSO_4$ and distilled at reduced pressure. Tetramethylammonium chloride was recrystallized from ethanol, dried in an oven and stored in a desiccator. Other reagents were used without further purification.

Sodium methanesulfonate $NaCH_3SO_3$ was synthesized by the neutralization of an NaOH solution with methanesulfonic acid, followed by drying. The dried product was recrystallized from water and dried in an oven for several hours.[42]

Instrumentation

Magnetic susceptibility measurements were carried out on solid samples by the Gouy technique. Conductance measurements were made with a LKB type 3216 conductivity bridge at 25°C. Electronic spectra were performed on a Cary 14 Spectrophotometer. Infrared spectra were performed on a Perkin Elmer 521 Spectrophotometer as nujol

and hexachlorobutadiene mulls for solids on KBr salt plates and in solution cells. Far infrared spectra below 450 cm^{-1} were carried out on a Digilab Model 296 Interferometer Spectrometer as nujol mulls on polyethylene plates. Raman spectra were performed on a SPEX 1401 Double Monochromator spectrophotometer with an exciting line of 5145 Å. Because the molybdenum compounds are highly colored, it was necessary to use the spinning sample technique. The halide compounds were pressed into KBr pellets, mounted by double stick tape on a brass shaft which was in turn spun by a stirring motor. Attempts to take Raman spectra of the more air sensitive compounds proved impossible. These compounds were too air sensitive to be put in a pellet press. Attempts to take their spectra in spinning glass tubes produced unusable spectra because of interference from the glass tube and wobbling of the tube caused by the high rate of spinning. A Raman spectra of the thiocyanate complex was attempted on a nonspinning sample in a capillary tube. Although the exciting line of the Raman falls outside of the visible absorption maximum of this compound, the absence of bands in this spectra associated with Mo-Mo stretch casts doubt upon the reliability of this spectra. The region between 400 and 300 cm^{-1} was flat. This is a very sensitive compound and thermal decomposition may have taken place.

Syntheses

Tetrakis-μ-methanesulfonatodimolybdenum (II)

$Mo_2(CH_3SO_3)_4$

This compound was synthesized by the reaction of tetrakis-μ-acetatodimolybdenum (II) with methanesulfonic acid HMS.

$$Mo_2(CH_3COO)_4 + 4\ CH_3SO_3H \longrightarrow Mo_2(CH_3SO_3)_4 + 4\ CH_3COOH \qquad (32)$$

The acetate complex was synthesized by the method of Holste and Schafer.[5] To 2 g of this was added a degassed solution of 5 ml HMS in 20 ml diglyme. The mixture was stirred and heated to 100°C under N_2. Then the acetic acid formed and excess diglyme were pumped off under vacuum. Upon cooling a pink solid formed. The mixture was filtered and the pink precipitate was washed with anhydrous ether. The product is a light pink, diamagnetic powder. Anal. calcd. for $C_4H_{12}S_4O_{12}Mo_2$; C-8.39%, H-2.09%, Mo-33.56%. Found; C-8.47%, H-2.20%, Mo-33.10%.

Bis γ-butyrolactonetetrakis-μ-methanesulfonatodimolybdenum (II)

$Mo_2(CH_3SO_3)_4(C_4H_6O_2)_2$

To 0.6 g of the methanesulfonate complex was added 30 ml of degassed γ-butyrolactone. The mixture was heated with stirring to a temperature of 70°C. The methanesulfonate complex dissolved giving a red-orange solution.

About half the liquid was pumped off under vacuum. The solution was cooled and a pink precipitate formed. The mixture was filtered and washed with anhydrous ether. The product was a light pink, diamagnetic powder. It was much more air sensitive than the starting material, the methanesulfonate compound. It must be stored under vacuum. Samples stored under N_2 overnight in Schlenk tubes show discoloration. The analysis showed the presence of one lactone group per molybdenum atom. Anal. calcd. for $C_{12}H_{24}S_4O_{16}Mo_2$; C-19.22%, H-3.22%, Mo-25.80%. Found; C-19.59%, H-3.50%, Mo-25.59%.

<u>BisN,Ndimethylformamidetetrakis-μ-methanesulfonato-dimolybdenum (II)</u>

$Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$

To 0.3 g of the methanesulfonate compound was added 10 ml of degassed DMF. With stirring a red solution formed. Then 10 ml of DME was added. After a short time in the freezer a pink precipitate formed. The mixture was then filtered and the pink product was washed with anhydrous ether. The product is a light pink, diamagnetic powder. It was much more air sensitive than the starting material, the methanesulfonate compound. It must be stored under vacuum. Samples stored under N_2 overnight in Schlenk tubes showed discoloration. The analysis showed the presence of one DMF group per molybdenum atom. Anal. calcd. for $C_{10}H_{20}N_2S_4O_{14}Mo_2$; C-16.71%,

H-3.62%, N-3.90%, Mo-26.74%. Found; C-16.49%, H-3.67%, N-3.71%, Mo-26.97%.

An attempt was made to use the methanesulfonate compound to synthesize compounds containing the octahalodimolybdate (II) anions. Since water is known to be a strong ligand for Mo_2^{+4}, these attempts were made in nonaqueous systems. The first route tried involved using methanolic solutions of tetraalkylammonium halides. The methanesulfonate complex, abbreviated $Mo_2(MS)_4$, is not soluble in methanol so the reactions were done heterogeneously. The following reaction was tried. For solubility reasons the tetramethylammonium cation was used for the chloride and the tetra-n-butylammonium cation was used for the bromide and iodide.

$$Mo_2(CH_3SO_3)_4 + 4\,R_4NX \xrightarrow{\text{methanol, R.T.}} 2\,R_4NCH_3SO_3 + (R_4N)_2Mo_2X_4(CH_3SO_3)_2 \qquad (33)$$

When X=Cl, Br, and I, an instant reaction is seen as the pink starting material turns red-purple. After stirring a few minutes the products were filtered and washed with methanol. The products were found to be soluble when redissolved in methanol. This solubility decreases in the presence in solution of dissolved tetraalkylammonium halide starting material. Therefore, the products must be ionic in nature with tetraalkylammonium cations. In the presence of the common ion the

solubility decreases. Originally these reactions were run with a molar ratio of $R_4NX:Mo_2(MS)_4$ of greater than 8:1. However, the infrared spectra of the red-purple products showed the presence of methanesulfonate even after repeated washings. It was obvious that partial substitution was taking place. When the chloride compound was analyzed, it was seen that two of the methanesulfonate groups had been replaced by four chloride ions. This is seen in equation 33. The bromide and iodide compounds were very similar in appearance and had similar spectra but the elemental analyses obtained were not good. The syntheses for those two compounds were repeated several times using great excesses of halide, more solvent to dissolve the products, longer stirring times, etc. Attempts to heat the alcoholic solutions of these compounds gave oxidized products. Attempts to recrystallize these compounds from alcohol overnight also gave oxidized products. The oxidized products have a characteristic brown solution. Attempts to prepare a fluoride analogue of these compounds in alcohol gave immediate oxidation with the same brown color.

Eventually benzene was tried as a solvent. Tetra-n-butylammonium bromide and iodide will dissolve in hot benzene. The bromide reaction worked fine in benzene but the iodide didn't. Noticing that the iodide reacted slower than the bromide, toluene was substituted for benzene to

allow a hotter reaction temperature. The iodide reaction finally worked right. The details of each halide synthesis are discussed below.

Tetramethylammonium Tetrachlorobis-μ-methanesulfonato-dimolybdate (II)

$((CH_3)_4N)_2Mo_2Cl_4(CH_3SO_3)_2$

This synthesis is performed under inert atmosphere conditions using Schlenk ware. To 0.44 g of $Mo_2(MS)_4$ was added a solution of 0.84 g $(CH_3)_4NCl$ in 20 ml methanol. The mixture showed an immediate red-purple color. It was stirred for 15 minutes and filtered. The red-purple precipitate was washed with ether and pumped dry. The red-purple compound formed is air stable. It is soluble in methanol and insoluble in nonpolar solvents. Attempts to recrystallize it from methanol were unsuccessful. Kept overnight methanolic solutions showed discoloration to a brown color. The same brown color is seen if the solutions are exposed to air. Analysis showed partial substitution had taken place. Anal. calcd. for $C_{10}H_{30}N_2Mo_2Cl_4S_2O_6$; C-17.85%, H-4.45%, N-4.17%, Mo-28.57%, Cl-21.13%. Found; C-17.86%, H-4.70%, N-4.09%, Mo-28.71%, Cl-21.13%.

Attempts to perform a similar synthesis with $(C_2H_5)_4NF$ produced immediate discoloration to a brown color. In view of the tendency of fluoride to stabilize compounds of high metal coordination and oxidation numbers, this was not surprising.[20]

Tetra-n-butylammonium Tetrabromobis-μ-methanesulfonatodimolybdate (II)

$((C_4H_9)_4N)_2Mo_2Br_4(CH_3SO_3)_2$

To a three necked 500 ml flask was added 0.4 g of $Mo_2(MS)_4$, 0.8 g of $(C_4H_9)_4NBr$, and 300 ml benzene. The mixture was stirred while being flushed with nitrogen for 15 minutes. The mixture was then refluxed for two hours under nitrogen with stirring. It was then cooled. The red-purple product formed is air stable. The mixture can be filtered in air. The precipitate is then transferred to an airless ware flask and the rest of the operations are carried out under inert atmosphere conditions. 10 ml of benzene are added. The mixture is stirred and filtered and washed with cold methanol. This is to wash out any remaining $(C_4H_9)_4NCH_3SO_3$. The product is then washed with ether and pumped dry. Attempts in previous syntheses to further wash the product with water or methanolic solutions of acetonitrile to remove any remaining $Mo_2(MS)_4$ resulted in reaction of the product with these reagents and so was not tried here. The product analysis showed partial substitution had taken place. Anal. calcd. for $C_{34}H_{78}N_2Mo_2Br_4S_2O_6$; C-34.40%, H-6.58%, N-2.36%, Mo-16.19%, Br-26.99%. Found; C-34.63%, H-6.74%, N-2.54%, Mo-16.02%, Br-26.89%. By way of comparison, attempts to run the reaction in

methanol gave the following analysis.
Found; C-34.01%, H-6.66%, N-2.38%, Mo-16.22%, Br-22.48%. Repeat analysis of the same sample gave similar values for Br.

Tetra-n-butylammonium Tetraiodobis-μ-methanesulfonato-dimolybdate (II)

$((C_4H_9)_4N)_2Mo_2I_4(CH_3SO_3)_2$

The procedure is exactly the same as for the bromide synthesis except that 0.9 g of $(C_4H_9)_4NI$ is used instead of $(C_4H_9)_4NBr$ and toluene is used instead of benzene. Anal. calcd. for $C_{34}H_{78}N_2Mo_2I_4S_2O_6$; C-29.69%, H-5.67%, N-2.04%, Mo-13.95%, I-36.97%. Found; C-30.56%, H-5.99%, N-1.94%, Mo-13.89%, I-36.12%.
By way of comparison attempts to run the reaction in benzene gave the following analysis. Found; C-28.34%, H-5.63%, N-2.24%, Mo-13.25%, I-35.09%.

After seeing the reaction of $Mo_2(MS)_4$ with halide ions a reaction was tried with thiocyanate ion. Wishing to avoid aqueous and alcoholic media, advantage was taken of the solubility of NH_4NCS in ethers. The ether used was dimethoxyethane, DME.

$$Mo_2(CH_3SO_3)_4 + 8\ NH_4NCS \xrightarrow{DME,\ R.T.} 4\ NH_4CH_3SO_3 + (NH_4)_4Mo_2(NCS)_8 \cdot 4DME \qquad (34)$$

As equation 34 shows full substitution of the methanesulfonate ligands takes place. An immediate reaction

occurs giving a blue-green solution and a white precipitate, which infrared analysis shows to be ammonium methanesulfonate. This can be filtered out. The full details of the synthesis are given below.

Ammonium Octaisothiocyanatodimolybdate (II) Tetradimethoxyethane

$(NH_4)_4Mo_2(NCS)_8 \cdot 4(C_4H_{10}O_2)$

This is a synthesis which must be done stoichiometrically because it would be extremely difficult to separate the product from any excess NH_4NCS starting material. Both are soluble in DME and insoluble in hexane. One should use a molar ratio of 8:1 for NH_4NCS and $Mo_2(MS)_4$. To 0.519 g of the methanesulfonate compound was added 0.553 g of NH_4NCS. This reaction must be done under inert atmosphere conditions. To this mixture is added 40 ml of degassed DME. An immediate blue-green color is seen. The mixture is stirred for 15 minutes. It is filtered. The white precipitate of $NH_4CH_3SO_3$ is discarded. To the filtrate is added hexane. This causes precipitation of a green crystalline solid. The same effect can be caused by freezing. The product can be recrystallized from DME in a freezer. The solution that hasn't crystallized has turned red. The crystals are filtered and washed with hexane. They are then dried under vacuum. The analysis shows that complete

substitution has taken place. The product consists of green, needlelike, diamagnetic, highly air sensitive crystals. The analysis shows that there are two dimethoxyethane molecules for every Mo atom. Since KNCS is not nearly as soluble as NH_4NCS in DME, it appears that the solvent solvates the NH_4^+ ion. Anal. calcd. for $C_{24}H_{56}N_{12}Mo_2S_8O_8$; C-26.46%, H-5.15%, N-15.45%, Mo-17.64%. Found; C-26.88%, H-5.22%, N-15.87%, Mo-17.56%.

Other syntheses were attempted with $Mo_2(MS)_4$. In several cases there was obvious reaction but pure products could not be obtained. Three such cases were the acetonitrile, hypophosphite and urea syntheses.

$Mo_2(MS)_4$ is very slightly soluble in boiling acetonitrile giving a blue color. It will dissolve in a methanolic solution of acetonitrile giving a brilliant blue color. Acetonitrile is known to form complexes with Mo_2^{+4} such as $Mo_2Cl_4(CH_3CN)_4$.[28] An attempt was made to precipitate a product by adding DME. The blue solution turned violet. An attempt to pump off liquid to a lesser volume resulted in precipitation of $Mo_2(MS)_4$.

$Mo_2(MS)_4$ was reacted with sodium hypophosphite in methanol solution. A reddish compound formed which was extremely air sensitive. The infrared spectrum showed hypophosphite coordination with no sign of methanesulfonate. The elemental analysis was unsatisfactory with

37.25% phosphorus reported, which was much too high even for four bidentate hypophosphite ligands. Also the elemental analysis reported the presence of carbon which should have been absent for four bidentate hypophosphite ligands. This project was abandoned.

Following the success of the DMF and γ-butyrolactone syntheses a urea synthesis was tried. Urea has three possible binding sites, two nitrogen and one oxygen atoms. The mode of coordination has known effects on the infrared spectra.[43] Urea in methanol solution will coordinate $Mo_2(MS)_4$ giving a bright red solution. These solutions were extremely sensitive and decomposed easily. One of the problems in working with urea is its insolubility in nonpolar solvents. If one tries to precipitate the complex from solution by adding a nonpolar solvent, any excess urea present will coprecipitate. It was found that urea would coordinate $Mo_2(MS)_4$ when stirred with it in a DME suspension. An arbitrary ratio of four moles urea to one mole $Mo_2(MS)_4$ was used. A pink solid was obtained which was extremely air sensitive. The infrared spectra showed urea bonding through its carbonyl oxygen. Additional bonding through its nitrogen atoms could not be ruled out, however. No satisfactory elemental analysis could be obtained and the project was abandoned.

Results and Discussion

The Methanesulfonate Complex

$Mo_2(MS)_4$ is a light pink, powdery, diamagnetic substance. It can stand for over an hour without discoloration. It is soluble in water and in DMF giving in both cases bright red solutions. It is insoluble in methanol and nonpolar solvents at room temperature. It will dissolve solve in methanol if complexing agents such as urea or acetonitrile are present.

Because of its relative air stability and insolubility in noncoordinating solvents, its electronic spectrum was taken as a nujol mull. This spectrum is very similar to the ones seen for $Mo_2^{+4}(aq)$ and $Mo_2(en)_4^{+4}$ taken by Bowen and Taube.[32] It is also similar to the one for $K_4Mo_2Cl_8 \cdot 2H_2O$. The spectrum of $Mo_2(MS)_4$ and $K_4Mo_2Cl_8 \cdot 2H_2O$ are tabulated in Table 4 together with the assignments for the latter compound given by Norman and Kolari.[12]

The structure for $Mo_2(MS)_4$ would appear to be like those of the trifluoromethanesulfonate[35] and benzenesulfonate[4] complexes with four methanesulfonate groups bridging the binuclear ion. The infrared and far infrared spectra of $Mo_2(MS)_4$ appear together in Table 5 with the spectra of $NaCH_3SO_3$ and band assignments from the work of Miles et al.[42] Band assignments are made for the $Mo_2(MS)_4$ compound. The methanesulfonate bands are somewhat displaced from the ionic positions due to coordination. The

Table 4

Electronic Spectra of $Mo_2(CH_3SO_3)_4$ Taken on a Nujol Mull[a,b]

values are in nm.

$Mo_2(CH_3SO_3)_4$	$K_4Mo_2Cl_8 \cdot 2H_2O$	Assignment
522	532	$\delta \longrightarrow \delta^*$
405 w	417 w	$\pi \longrightarrow \delta^*$
		$\delta \rightarrow d_{x^2-y^2}$
305	318	$\pi \rightarrow d_{x^2-y^2}$
238	294	$Cl \longrightarrow \delta^*$
225		$\pi \longrightarrow \pi^*$

a) $NaCH_3SO_3$ in nujol mull has a peak at 238 nm.

b) The spectra and assignments for $K_4Mo_2Cl_8 \cdot 2H_2O$ are from reference 12.

Table 5

Infrared and Far Infrared Spectra of $Mo_2(CH_3SO_3)_4$ [a,b]

values in cm^{-1}

$Mo_2(CH_3SO_3)_4$	assign.	$NaCH_3SO_3$	symm.	assign.
3040 m	ν asCH$_3$	3018 m	E	ν asCH$_3$
3025 m				
2950 w	ν sCH$_3$	2943 m	A_1	ν sCH$_3$
1630 w,br				
1426 w	δ dCH$_3$	1432 w	E	δ dCH$_3$
1415 m		1413 m		
1365 w,sh	δ sCH$_3$	1350 w	A_1	δ sCH$_3$
1333 m		1136 m	E	*

* This is assigned to a combination band of C-S and dSO_3.

1265 vs	SO_3	1246 s	E	ν asSO_3
1220 vs	stretches	1190 vs		
1100 sh				
1083 vs				
1056 s		1059 s	A_1	ν sSO_3
1015 vs				
985 m	ρ rCH$_3$?			
964 m		961 vw	E	ρrCH$_3$
773 s		786 s	A_1	ν C-S

Table 5 cont.

$Mo_2(CH_3SO_3)_4$	assign.	$NaCH_3SO_3$	symm.	assign.
		779 w		
560 vs	δsSO_3	561 s	A_1	δsSO_3
527 s	δdSO_3	536 s	E	δdSO_3
395 s	ν Mo-O			
		344 w	E	ρrSO_3
295 s	ν Mo-O			
265 s	ν Mo-O			
157 m	δ OMoO			
136 m	bend			
100 m	bend			

a) Spectra and assignments for $NaCH_3SO_3$ from reference 42. C_{3v} symmetry assumed for $CH_3SO_3^-$ anion.

b) Assignments for Mo-O stretches and bending modes assigned by comparison to spectra of sulfate complex in reference 44.

assignments in the far infrared are made by comparison to the sulfate complex. The vibrational spectra of this compound was studied by Loewenschuss et al.[44]

Examination of the infrared spectrum of the methanesulfonate compound shows that it is somewhat more complicated than what would be expected for the simple model of a binuclear Mo_2^{+4} ion bridged by four methanesulfonate ligands. According to Miles et al.[42] there should be only three methanesulfonate SO_3 stretching modes. Here there are more than that. Secondly, there are three bands in the far infrared assigned to Mo-O stretching modes. According to Bratton et al.[13] who studied the vibrational spectra of the acetate and octachloro compounds of Mo_2^{+4} there should be two Mo-O stretching modes for an Mo_2O_8 skeleton. The region between 400 and 200 cm^{-1} is the region where these bands are found.

These results can be explained if one assumes that the methanesulfonate complex has a structure similar to the sulfate complex. (See Figure 7.) An X ray diffraction study of the sulfate complex revealed that oxygen atoms of the sulfate ligand which are not binding to the equatorial sites can bind to the axial sites of other binuclear ions. Since there are four sulfate ligands and only two axial sites per binuclear ion, only half the sulfate ligands can be participating in axial bonding meaning that there are essentially two types of sulfate ligands present.[33] If

this situation occurs in the methanesulfonate complex that would mean that there are two kinds of methanesulfonate ligands present. One kind would just bind in the equatorial sites. The other kind would have the third oxygen atom binding to the axial site of a neighboring binuclear ion. Therefore, there would be more than three sulfur oxygen stretches expected. Also the basic skeleton of the molecule would not be Mo_2O_8 but $Mo_2O_8O'_2$. According to Bratton et al., who also studied Re_2^{+6} complexes of the formula $Re_2(RCOO)_4X_2$, there are three metal ligand modes expected.[13] For some reaon the condition of many sulfur oxygen stretches but not the condition of the three metal ligand stretches are seen in the sulfate complex spectra.[44] Some band assignments are doubtful. The bands at 985 and 964 cm^{-1} in the methanesulfonate complex are probably ρrCH_3 but sulfur oxygen stretching bands have been found that low in the sulfate complex.[44] The ρrSO_3 band in ionic methanesulfonate may be too weak to be seen here. Perhaps the polymeric nature of this compound is responsible for its air stability and insolubility.

<u>The γ-butyrolactone and DMF Complexes</u>

These two complexes are light pink, powdery, diamagnetic substances also, but are much more air sensitive than $Mo_2(MS)_4$. They will dissolve in methanol giving bright pink solutions. Because of their similar proper-

ties it seemed obvious that they have the same type of structure.

It was previously stated that ethyl acetate can form a complex with Mo_2^{+4} in which the ester bridges the binuclear ion and binds like a carboxylate ligand. It was of interest to see if another ester could do the same and if an ester could why not an amide?

It was desirable to use a liquid ester and eliminate the possiblity of solvent interference. A complex was made with ethyl pyruvate but it was very unstable and converted to the more stable pyruvate complex. The idea of a lactone in which the ester form might be further stabilized by ring formation seemed appealing. So the attempt was made using γ-butyrolactone.

A reaction was attempted between $Mo_2(MS)_4$ and a methanolic solution of benzamide. There seemed to be some reaction but it appeared incomplete. Again the use of a liquid reagent seemed preferable. $Mo_2(MS)_4$ dissolves readily in the amide DMF. It will also dissolve in methanolic solutions of DMF. The solubility of the DMF complex in methanol appears to be very great. This complex cannot be precipitated even at dry ice temperatures. Therefore, it was necessary to use straight DMF.

Because of their air sensitivity the electronic spectra of the γ-butyrolactone and DMF complexes were taken of their methanol solutions rather than as nujol

mulls. It was later seen that these complexes undergo solvolysis in methanol. The position of the visible peak is what is expected, however. For the butyrolactone complex the visible peak is at 522 nm with $\epsilon = 1.9 \times 10^2$. For the DMF complex the visible peak is at 525 nm with $\epsilon = 2.0 \times 10^2$.

The infrared and far infrared spectra of both complexes were taken. Table 6 contains the spectra of the γ-butyrolactone complex, the spectra and literature assignments for γ-butyrolactone and the spectra of $Mo_2(MS)_4$ for comparison. In the work by Mecke et al.[45] most of the assignments were labeled either ring or CH_2. These assignments are kept here but it may be possible to label one of the ring modes as the C-O stretch. There is an intense band at 1166 cm^{-1} in the free ligand which seems to be shifted to 1191 cm^{-1} in the complex. According to Nakanishi's tables the 1166 cm^{-1} band is in the region expected for C-O stretch.[46] Since this band is not found in the DMF complex it is safe to assume that it is a ligand band. Durig et al. showed that the peaks in the far infrared are very weak, a result confirmed by personal observation.[47]

The infrared and far infrared spectra of the DMF complex are given in Table 7 along with the spectra of the uncoordinated ligand and $Mo_2(MS)_4$. The assignments for the infrared are from Jones[48] and for the far infra-

Table 6

Infrared and Far Infrared Spectra of the Complex $Mo_2(CH_3SO_3)_4(C_4H_6O_2)$[a,b]

values are in cm^{-1}

$Mo_2(CH_3SO_3)_4$	$Mo_2(CH_3SO_3)_4 \cdot (C_4H_6O_2)_2$	Assign.	$C_4H_6O_2$	Assign.
	3038 vw, sh			
3040 m	3029 m	$\nu asCH_3$		
3025 m				
			3010 m	CH_2
2950 w	2950 w, sh	νsCH_3		
	2941 w		2940 m	CH_2
	1728 vs	$\nu C=O$	1770 vs	$\nu C=O$
1630 w, br				
	1488 vw	CH_2	1490 vw	CH_2
	1468 vw	CH_2	1466 w	CH_2
1426 w	1421 m	CH_2	1426 w	CH_2
1415 m		+ δdCH_3		
	1390 m			
	1385 sh		1379 m	CH_2
1365 sh				
1333 m	1332 w	comb. band $\nu C-S + \delta dSO_3$		

Table 6 cont.

$Mo_2(CH_3SO_3)_4$	$Mo_2(CH_3SO_3)_4 \cdot (C_4H_6O_2)_2$	Assign.	$C_4H_6O_2$	Assign.
	1320 vw			
			1284 w	CH_2
1265 vs	1260 vs	νSO_3		
	1238 m, sh			
1220 vs				
	1205 m, sh			
	1191 vs	νC-O	1166 vs	ring
1100 sh				
1083 vs	1073 vs	νSO_3		
1056 s	1055 m, sh			
	1031 vs	ring	1037 s	ring
1015 vs	1010 vs	νSO_3		
985 m	980 s	CH_2 +		
964 m		ρrCH_3		
	932 m		929 w	ring
	872 w		890 w	ring
	800 w		800 w	ring
773 s	772 s	νC-S		
	675 w		675 w	ring
	640 w		635 w	ring
561 s	565 vs	δSO_3		
			535 w	ring
527 s	530 s	δSO_3		

Table 6

$Mo_2(CH_3SO_3)_4$	$Mo_2(CH_3SO_3)_4 \cdot (C_4H_6O_2)_2$	Assign.	$C_4H_6O_2$	Assign.
	495 w	ring	494 w	ring
395 s	400 vs	νMo-O		
	380 w			
295 s	292 s	νMo-O		
265 s	260 vs	ν Mo-O		
			219 vw	ring
157 m	160 w	δ OMoO	160 vw	
136 m	112 w	bend		
100 m	94 w	bend		

a) Assignments for the infrared spectra of $C_4H_6O_2$ are from reference 45.

b) Assignments for the far infrared spectra of $C_4H_6O_2$ are from reference 47.

Table 7

Infrared and Far Infrared Spectra of the Complex

$Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$

values are in cm^{-1}

$Mo_2(CH_3SO_3)_4$	$Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$	Assign.	$(CH_3)_2NCHO$	Assign.
3040 m	3030 m	$\nu asCH_3$		
3025 m				
2950 w	2945 m	νCH_3	2940 m	$\nu asCH_3$
			2780 w	νsCH_3
	1659 vs	$\nu C=O$	1672 vs	$\nu C=O$
1630 w, br				
	1500 w		1506 sh	
			1495 m	
	1375 m	δCH	1386 s	δCH
1365 w, sh				
1333 m	1330 w	comb. band $\nu C-S + \delta dSO_3$		
1265 vs	1260 vs	νSO_3		
			1256 m	$\nu asCNC$
1220 vs				
1100 sh	1110 w		1092 w	rCH_3
1083 vs	1072 vs	νSO_3		

Table 7 cont.

$Mo_2(CH_3SO_3)_4$	$Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$	Assign.	$(CH_3)_2NCHO$	Assign.
1056 s	1055 sh		1061 m	
1015 vs	1010 vs	νSO_3		
985 m	980 m	$prCH_3$		
964 m				
			865 w	$\nu sCNC$
773 s	770 s	$\nu C-S$		
	660 m	δOCN	657 m	δOCN
560 vs	561 vs	δSO_3		
527 s	525 s	δSO_3		
395 s	400 vs	$\nu Mo-O$		
	370 s		353 s	out of plane bending
	325 s		321 m	
295 s	292 vs	$\nu Mo-O$		
265 s	260 s	$\nu Mo-O$		
157 m	150 m	$\delta OMoO$		
136 m	133 m	bend		
100 m	110 m	bend		
	90 w	bend		

a) Assignments for infrared spectra of $(CH_3)_2NCHO$ are from reference 48.

b) Assignments for far infrared spectra of $(CH_3)_2NCHO$ are from reference 49.

red from Katon et al.[49] In this case the far infrared bands are quite intense and somewhat shifted from their positions in the uncoordinated case.

What remains to be determined is the structure of these compounds. It is obvious from the infrared spectra that the ligands are bonding at least partly through their carbonyl oxygens. This can be seen in the lower value of ν C=O in both cases from the value in the uncoordinated ligand. However, there are several possibilities. Consider Figure 10. In 10a the four methanesulfonate ligands are bridging the binuclear ion and the carbonyl ligands are binding in the axial position. This kind of bonding is seen for the binuclear compound $Rh_2(Ac)_4 \cdot 2DMF$. This was determined partly by infrared spectroscopy and partly by thermal analysis. Unfortunately the infrared results are not tabulated and the pictures provided are too small to be useful.[50] In 10b three methanesulfonate ligands are bridging the binuclear ion. The two carbonyl ligands have displaced one methanesulfonate ligand and are at a dihedral angle of 0° to each other. This is an ionic compound with one ionic methanesulfonate. In 10c two methanesulfonate ligands are bridging and two are bound in a monodentate fashion. The two carbonyl ligands are at a dihedral angle of either 90° or 180° to each other. In 10d the carbonyl ligands are bidentate. The result is a divalent cation with two ionic

Figure 10

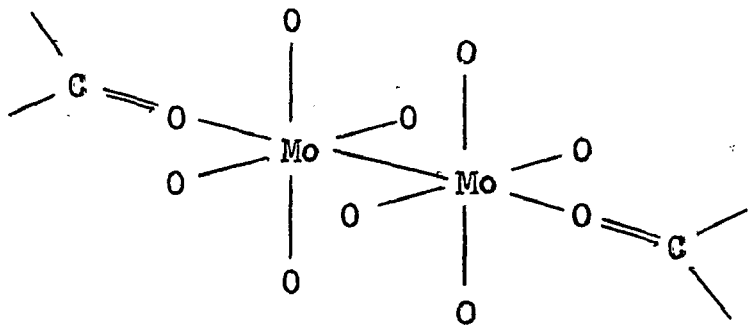
Possible structures for γbutyrolactone and DMF Complexes of $Mo_2(CH_3SO_3)_4$ Drawn Schematically

a) Carbonyl ligands are axially bonded. All methanesulfonate ligands are equatorially bonded.

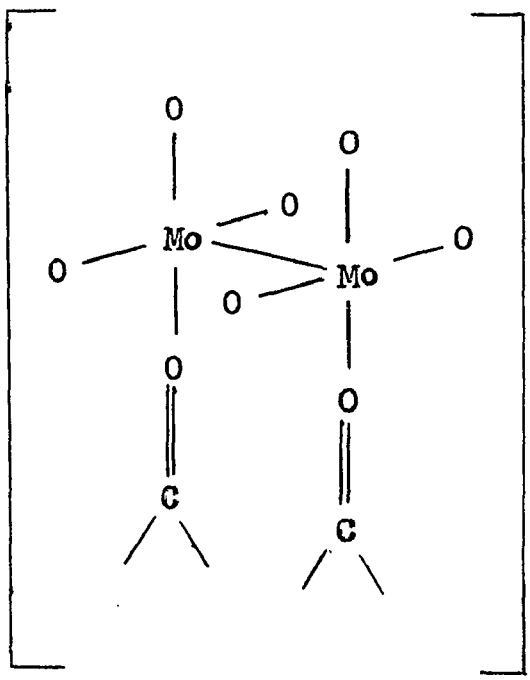
b) Carbonyl ligands are equatorially bonded with dihedral angle of 0°. One methanesulfonate ligand has become a free ion.

c) Carbonyl ligands are equatorially bonded with dihedral angle of 90° or 180°. Two methanesulfonate ligands are now monodentate.

d) Carbonyl ligands are equatorially bonded in a bidentate fashion. Two methanesulfonate ligands are now free ions.

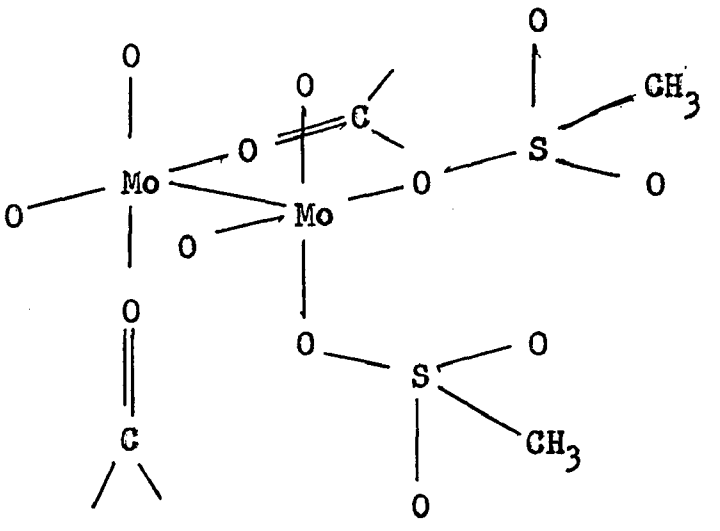


a

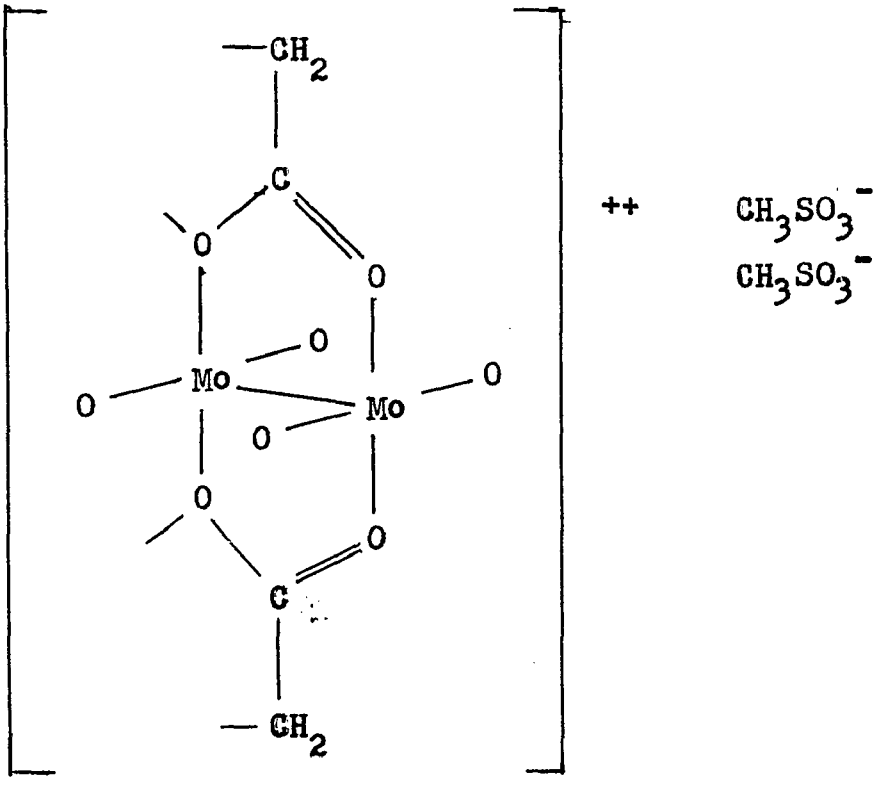


+ $CH_3SO_3^-$

b



c



d

methanesulfonate anions.

If 10d is the correct structure then it should be possible to detect the divalent nature of the cation. A molecule with the structure 10d should have twice the conductivity in solution as an equimolar solution of $NaCH_3SO_3$. At first conductivity measurements were made using methanol as the solvent because it would dissolve both $NaCH_3SO_3$ and the Mo_2^{+4} complexes. Dilute solutions of $NaCH_3SO_3$ were prepared and conductance readings were taken at 25°C. Solutions of the lactone and DMF complexes of similar concentration in methanol were prepared. A conductivity cell was degassed. The solutions were transferred to the conductivity cell in a glove bag. Then the cell was allowed to stand for a few minutes in the thermostat. What was found was that the solutions of the Mo_2^{+4} complexes gave readings close to the values of $NaCH_3SO_3$ solutions of similar concentrations. In other words, they behaved like univalent electrolytes. Furthemore, the conductance values increased with time without apparent discoloration. Solutions were then prepared of the complexes in solutions of the complexing agents themselves. $Mo_2(MS)_4$ was dissolved in DMF to give a solution which was calculated to be 2.70×10^{-3} in the DMF complex. The conductance value was also like that for a univalent electrolyte but the value remained fairly constant with

time. $Mo_2(MS)_4$ was then dissolved in γ-butyrolactone. Mild heating was necessary to effect solution. The solution at 25°C was nonconducting. The solution was tested with HCl. The resulting purple color showed that Mo_2^{+4} was still present. Finally solutions of the complexes were tested out in a relatively nonpolar solvent. The complexes were prepared and dissolved in diglyme. The DMF complex is much more soluble. Both solutions are nonconducting and still contain the binuclear ion Mo_2^{+4} as shown by the HCl test. The results of the conductance measurements are in Table 8.

The conductance measurements definitely rule out the structure shown in Figure 10d. A compound with a divalent cation should have approximately twice the conductance shown in methanol. This structure can also be ruled out by reference to the infrared spectra. Consider Figure 11. The resonance structures for γ-butyrolactone are shown. In his study of ester coordination Lappert concluded that structure b plays an important part if the ester coordinates in a monodentate fashion through its carbonyl oxygen. The stretching frequency associated with the C_1O_2 band should increase upon coordination. The C_1O_1 and the C_2O_2 bands should both decrease.[51] On the other hand, Abbott et. al. saw all three stretching frequencies decrease in the ethyl acetate complex.[35] As previously mentioned there is a large band at 1191 cm^{-1} in the lactone complex

Table 8

Conductance Measurements of Solutions of the Compounds[a]

$Mo_2(CH_3SO_3)_4(C_4H_6O_2)_2$ = Y

$Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$ = Z

Solution	Conc. mole/liter x10^3	mhos x10^4	Time minutes
$NaCH_3SO_3$ in methanol	9.17	13.9	
	7.42	12.5	
	3.00	4.67	
	2.18	3.93	
Y in methanol	2.19	3.74	7
		3.89	10
		4.01	13
		4.17	16
Z in methanol	2.43	4.48	7
		4.88	10
		5.05	13
		5.26	16
Y in γ-butyro lactone	3.19	0	

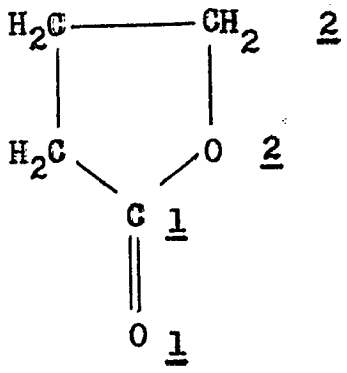
Table 8 cont.

Solution	Conc. mole/liter $x10^3$	mhos $x10^4$	Time minutes
Z in DMF	2.70	5.10	
Y in diglyme	3.98	0	
Z in diglyme	12.3	0	

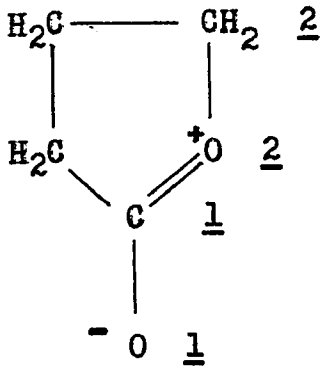
a) All measurements were made in the same conductivity cell using the same conductivity bridge. All measurements were made at 25°C.

Figure 11

Resonance structures for γ butyrolactone. Derived from similar illustrations about ester coordination in reference 51 by Lappert.



a



b

which is not present in the DMF complex, and which is in the region expected for a C_1O_2 stretch. It would seem that this is a shifted ester band and confirms the evidence from the conductance measurements.

It is instructive to actually compare the spectra of the species in question. In Figure 12 a-d are the infrared spectra of the region 3100-2900 cm^{-1}. This is the region of $\nu asCH_3$ and νsCH_3 stretches. Figure 12a shows that there are two peaks seen for $NaCH_3SO_3$. Figure 12b shows the spectra of $Mo_2(MS)_4$ in which the $\nu asCH_3$ appears to be split. This can be due to the splitting of the E mode of $\nu asCH_3$ caused by coordination of the methanesulfonate group. In this case the symmetry of the ligand decreases from C_{3v} to C_s. However, the methyl group may be itself unaffected and the split may be due to two types of methanesulfonate, those axially bonding and those not axially bonding. In Figures 12c and d are shown the spectra of the lactone and DMF complexes respectively. Here only one prominent peak is seen in each spectra for $\nu asCH_3$ indicating only one type of methanesulfonate. Only the structure in Figure 10a has one type of methanesulfonate. This by itself, however, is not sufficient proof.

Next consider Figures 13a-d. The same four compounds are now seen in the region 1300-900 cm^{-1}. This is the region of $\nu asSO_3$ and νsSO_3 bands. There are basically three strong bands in the spectra of the ionic methane-

Figure 12

Observed infrared spectra in the region 3100-2900 cm^{-1} for the compounds:

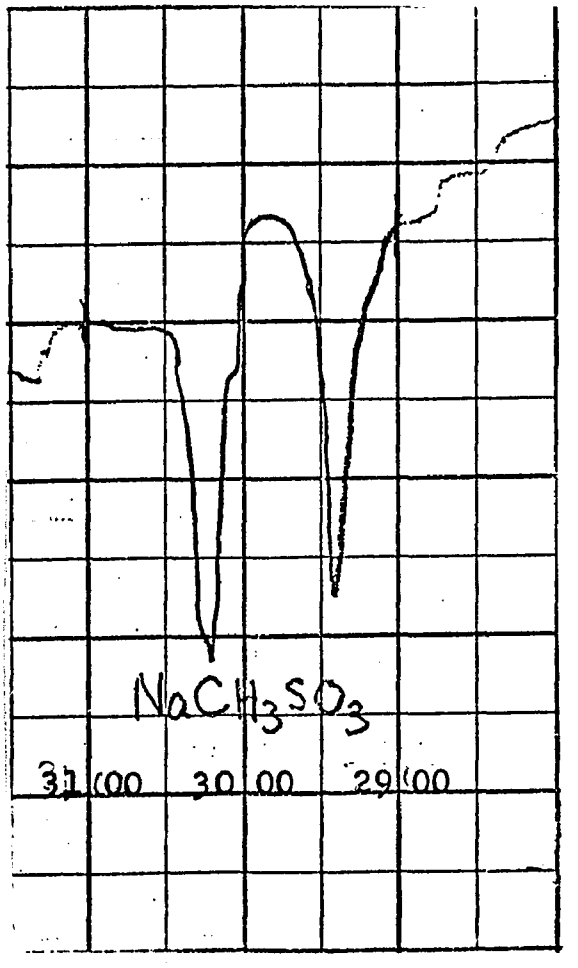
a) $NaCH_3SO_3$

b) $Mo_2(CH_3SO_3)_4$

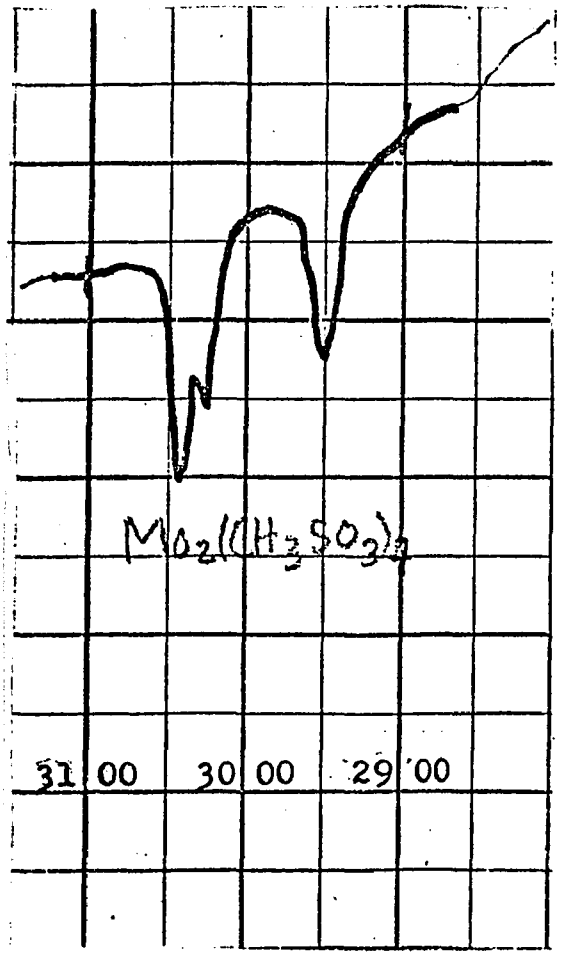
c) $Mo_2(CH_3SO_3)_4(C_4H_6O_2)_2$

d) $Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$

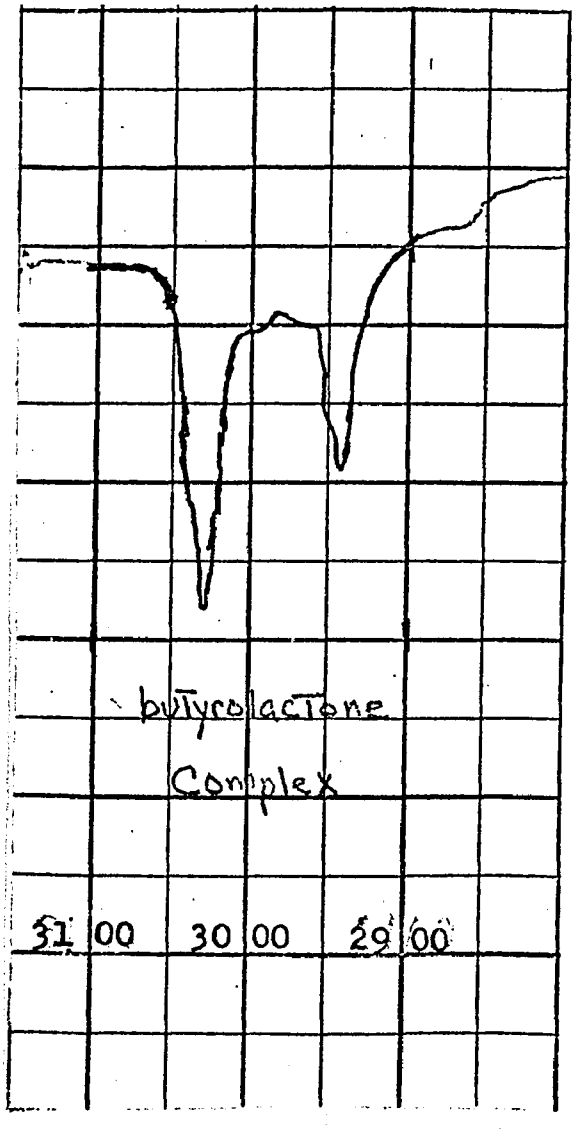
Peaks due mainly to $\nu asCH_3$ and νsCH_3 modes. Spectra taken as hexachlorobutadiene mulls on salt plates.



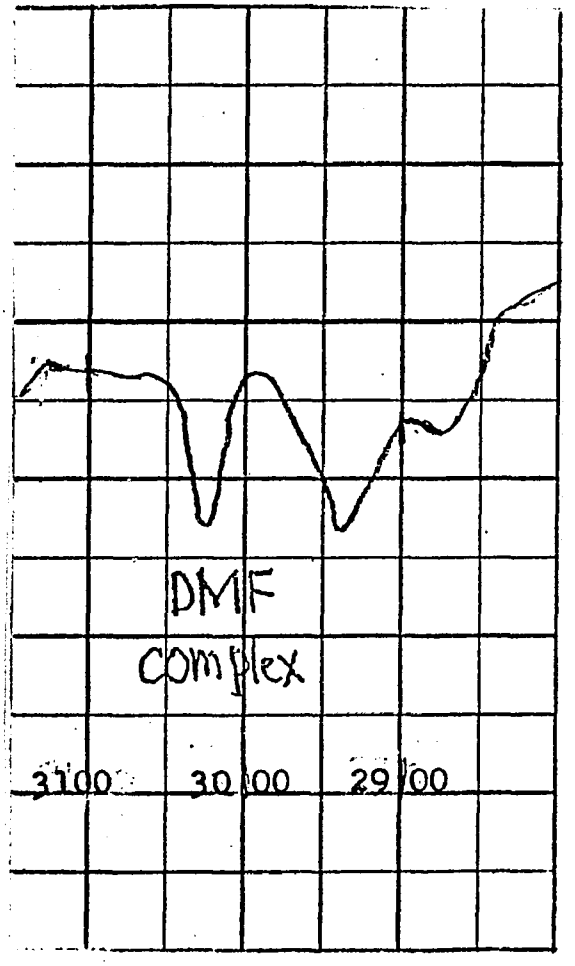
a



b



c



d

Figure 13

Observed infrared spectra in the region 1300-900 cm^{-1} for compounds:

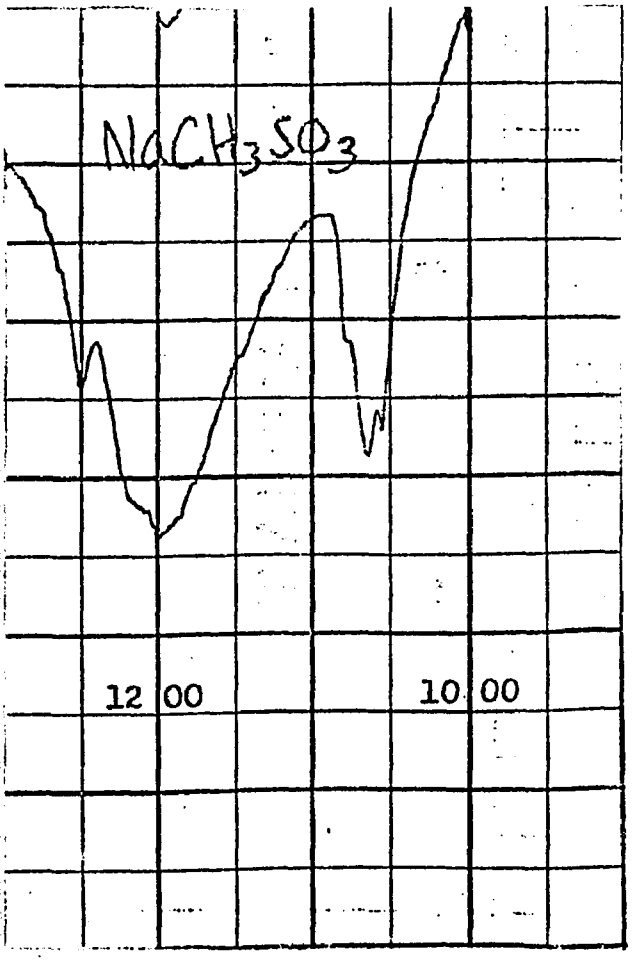
a) $NaCH_3SO_3$

b) $Mo_2(CH_3SO_3)_4$

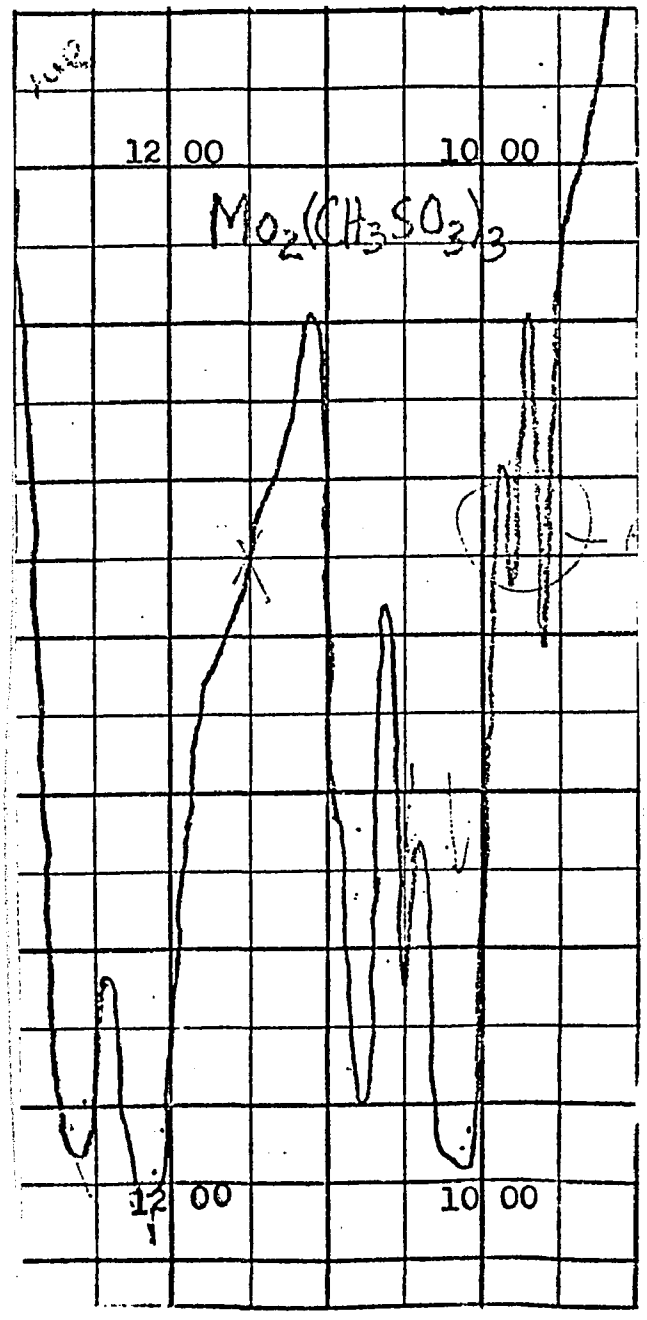
c) $Mo_2(CH_3SO_3)_4(C_4H_6O_2)_2$

d) $Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$

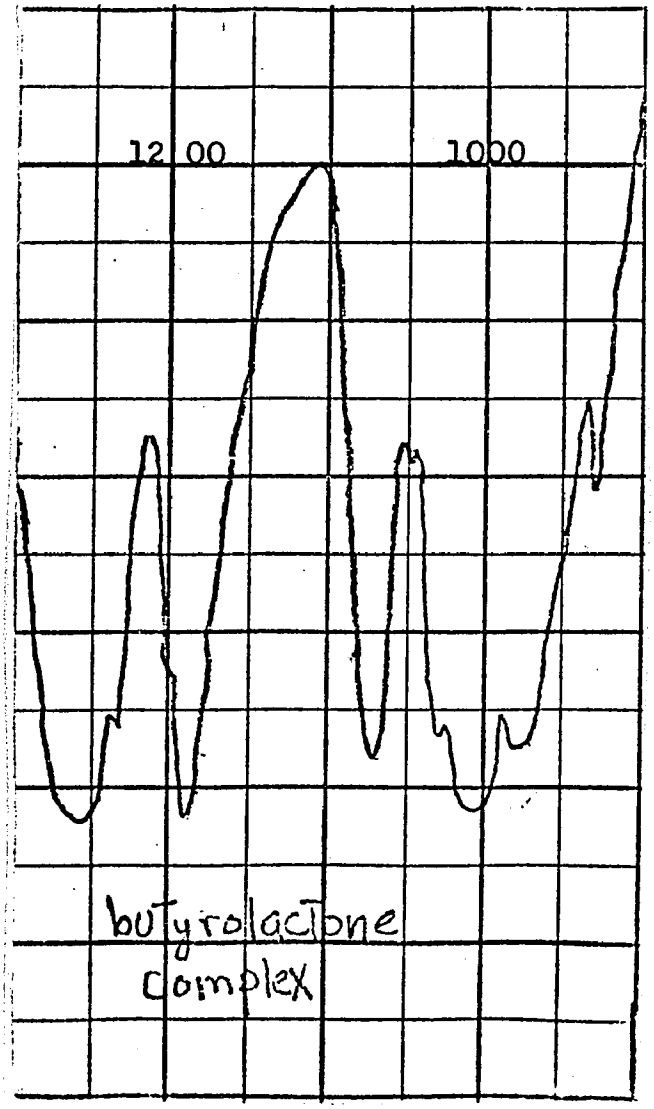
Peaks due mainly to $\nu asSO_3$ and νsSO_3 modes. Spectra taken as nujol mulls on salt plates.



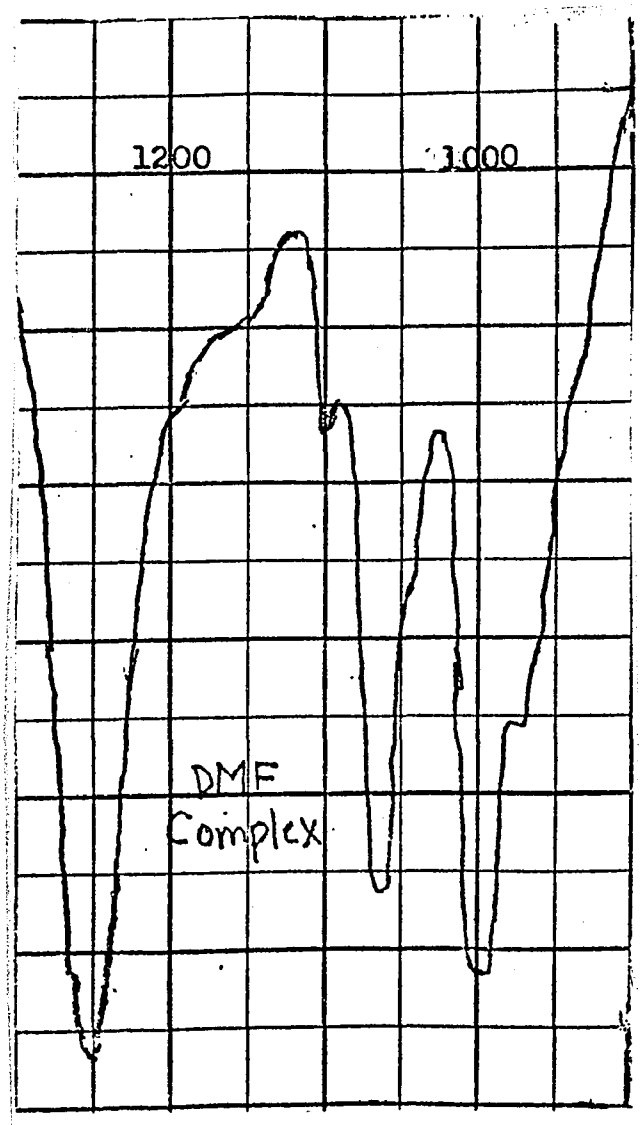
a



b



c



d

sulfonate. In Figure 13a the bands appear to be of similar intensity. However, this is not the case. The Perkin Elmer 521 spectrophotometer has a tendency to round off those bands whose intensity is very large. If the spectra are run with a screen, it can be seen that the band at 1190 cm^{-1} is several times more intense than the band at 1059 cm^{-1}. It is so intense that its absence would indicate the absence of ionic methanesulfonate in a compound. Furthemore, a band in approximately the same position is found in the spectra of $AgCH_3SO_3$ taken in nujol mull and in several kinds of pellets. Those spectra were taken by Burger et al.[52] This illustrates that the position of that band is fairly constant.

The spectra of the lactone and DMF complexes show large bands not readily assignable to ligand bands at 1260, 1072 and 1010 cm^{-1}. Smaller bands at 1055 and 980 cm^{-1}, similar to bands in $Mo_2(MS)_4$ are also found. The presence of the three large bands assignable to $\parallel SO_3$ suggests only one kind of methanesulfonate is present. The band at 1191 cm^{-1} in the lactone compound has already been assigned to $\parallel C_1O_2$ in the ligand. There is no such band in the DMF complex. These findings would tend to support the structure in Figure 10a.

Methanesulfonate has been coordinated to Mo^{+2} in the octahedral cluster $Mo_2Cl_4(DMF)_2(CH_3SO_3)_4$ synthesized by

Curtis and Cotton.[53] Here the methanesulfonate ligands are monodentate. Strong bands are seen at 1280, 1150, 980 and 950 cm^{-1}. The bands at 1280 and 1150 don't correspond well with the bands seen for the lactone and DMF complexes so it is doubtful that there is any monodentate methanesulfonate present in these compounds. This would tend to rule out the structure seen in Figure 10c.

In the above mentioned compound DMF bands were also recorded. Two major differences were noted. A band at 657 cm^{-1} in uncoordinated DMF and assigned to δOCN was found at 700 cm^{-1} in Curtis and Cotton's complex but at 660 cm^{-1} here. Secondly a band assigned to ν Mo-O was found at 420 cm^{-1} in Curtis and Cotton's complex while here the closest band is at 400 cm^{-1}.

San Filippo et al. has prepared the complexes $Mo_2Cl_4(DMF)_4$ and $Mo_2Br_4(DMF)_4$ in which the DMF bonds in the equatorial position in a monodentate fashion.[28] Most of the bands are similar to the ones here except he too saw the 657 band shifted to 698 cm^{-1}.

So far the infrared spectra tend to support the structure seen in Figure 10a. The most striking evidence for this choice comes from the far infrared spectra. The far infrared spectra of a very thick sample of $NaCH_3SO_3$ showed only one weak band at 344 cm^{-1}. Figures 14a-c show the spectra of the region 450-200 cm^{-1} for $Mo_2(MS)_4$ and the lactone and DMF complexes. Except for the ligand bands of

Figure 14

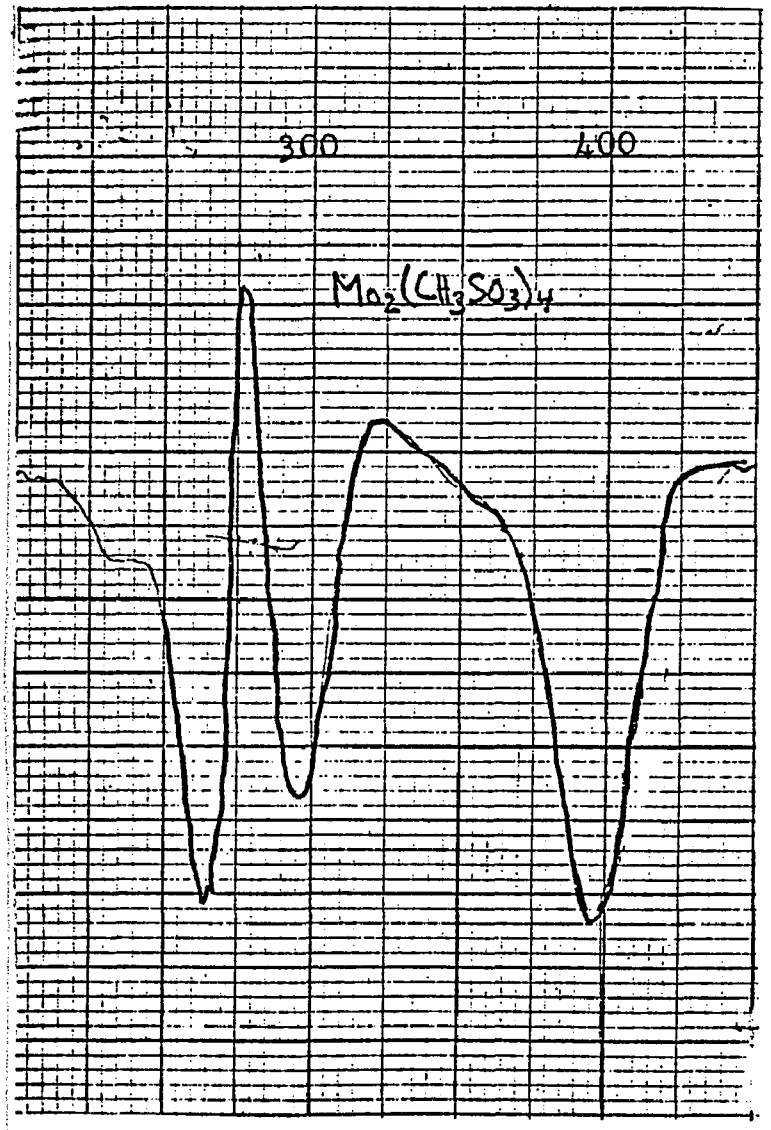
Observed far infrared spectra in region 450-200 cm^{-1} seen for compounds:

a) $Mo_2(CH_3SO_3)_4$

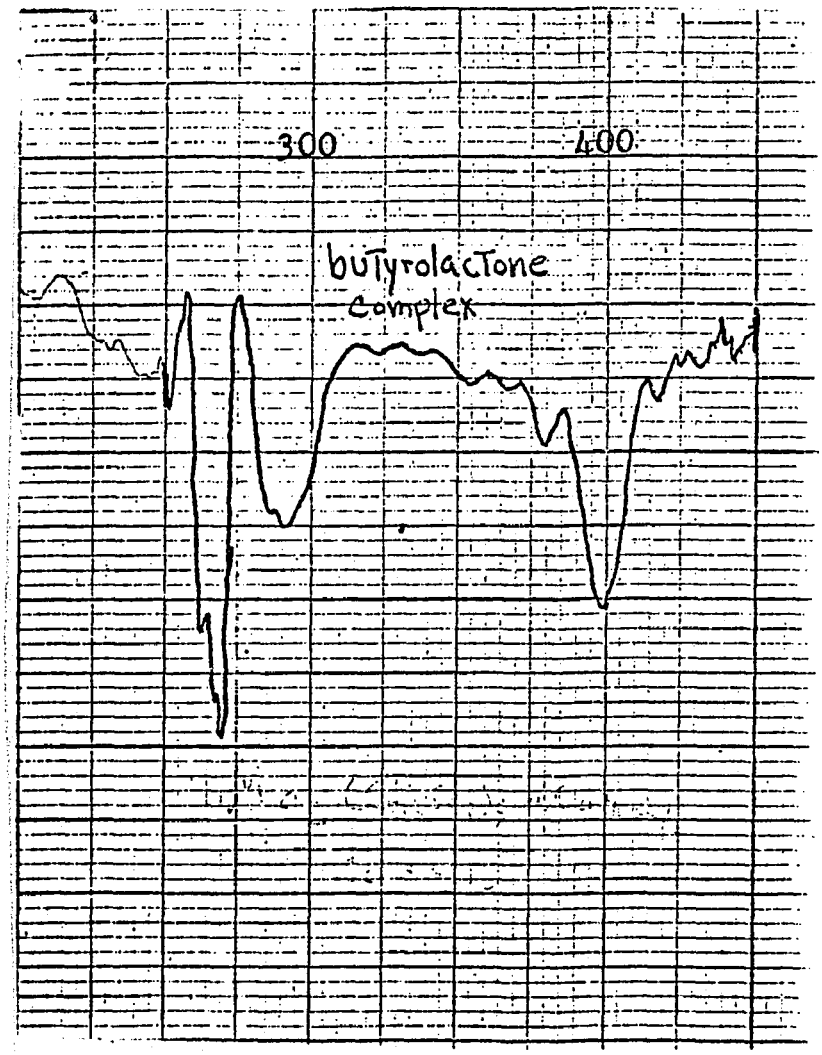
b) $Mo_2(CH_3SO_3)_4(C_4H_6O_2)_2$

c) $Mo_2(CH_3SO_3)_4((CH_3)_2NCHO)_2$

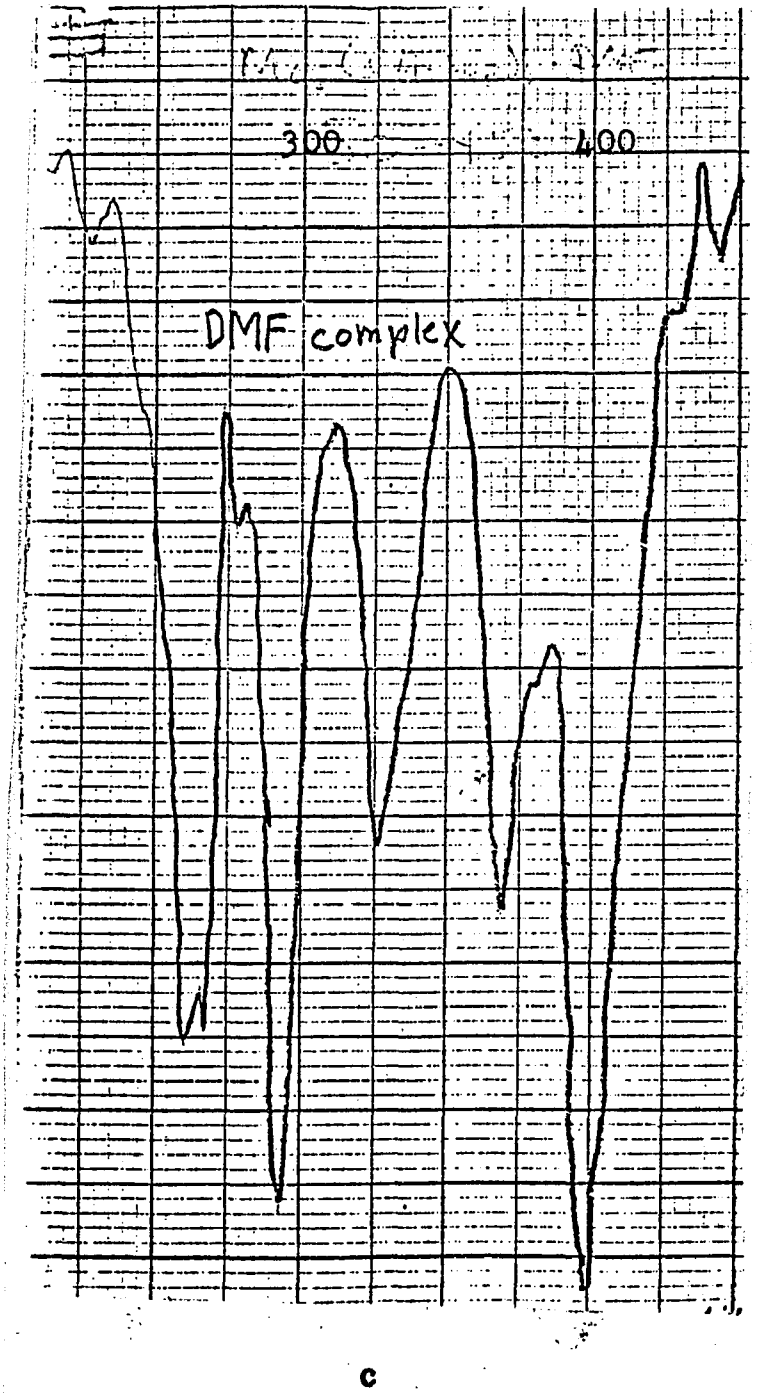
Peaks due mainly to Mo-O stretching modes and ligand peaks of DMF. Spectra were taken as nujol mulls on polyethylene plates.



a



b



c

DMF, the spectra are very similar. Spectra taken of pure DMF show the two ligand bands to be quite intense. All three compounds have three strong bands in the region expected for ν Mo-O. Structure 10a with the carbonyl ligands in the axial position has the same $Mo_2O_8O'_2$ skeleton established for the methanesulfonate complex.

The methanesulfonate ligand appears to be a stronger ligand than anticipated. Reaction with an ester and an amide did not produce a complex like the ethyl acetate complex with four bidentate ligands. Instead the coordination number is two. This is strongly suggestive of axial bonding. There is a precedent in the literature $Rh_2(Ac)_4 \cdot 2DMF$, in which one of the ligands binds axially in a binuclear compound.[50] Four possible structures were presented in Figure 10. Of these the structure in Figure 10a with four bidentate methanesulfonate ligands and two axial carbonyl ligands is most strongly supported by the evidence. Although solutions of these compounds in polar solvents are conducting, which would tend to support an ionic structure, solutions in nonpolar solvents are nonconducting. It would appear that these compounds tend to ionize in polar solvents. Furthemore, the infrared and far infrared data support the structure with axial bonding. If one considers the parent methanesulfonate compound as having eight equatorial and two axial metal ligand bonds then what has happened here is

is a substitution reaction of the axial sites by the carbonyl ligands.

Halide Compounds

As was previously stated these compounds are of the general formula $(R_4N)_2Mo_2X_4(CH_3SO_3)_2$ for X=Cl, Br, and I. These compounds are very similar in appearance being red-purple in color. They are fairly air stable but their methanolic solutions are very prone to oxidation. All three compounds are diamagnetic. Until recently this was the first case known of a homologous series of Mo_2^{+4} containing the three halides. This is the first case yet reported of a mixed ligand Mo_2^{+4} containing four monodentate and two bridging ligands.

The electronic spectra of these compounds were done on nujol mulls. The spectra of the visible region were also taken in methanol solution. The results are seen in Table 9. The spectra of the solid complexes is compared with that of $K_4Mo_2Cl_8 \cdot 2H_2O$ with spectra values and assignments by Norman and Kolari.[12] Certain things can be seen from the mull spectra. Changing the halide ligand causes a change in the position of the $\delta \rightarrow \delta^*$ band and confirms the assignment of a band in the ultraviolet region to a ligand to metal charge transfer band. It can be seen for the solution spectra that the wavelength values for the maxima are not the same. In the bromide case it goes from 542 to 525 nm and in the iodide case from 563 to 537 nm. The

Table 9

Electronic Spectra of the Tetrahalobis-μ-methanesulfonatodimolybdate (II) Compounds[a,b]

values are in nm

Nujol mulls

Cl	Br	I	$K_4Mo_2Cl_8 \cdot 2H_2O$	Assignment
525	542	563	532	$\delta \rightarrow \delta^*$
405 vw	420 vw	420 vw	417 w	$\pi \rightarrow \delta^*$
				$\delta \rightarrow d_{x^2-y^2}$
300	310	302	318	$\pi \rightarrow d_{x^2-y^2}$
267	272	270	<294	$\pi \rightarrow \pi^*$
218	235	252		$X \rightarrow \delta^*$

Methanol Solutions

510, 533	525	537
ϵ=790	ϵ=530	ϵ=570

a) The reference for the spectra and assignments for $K_4Mo_2Cl_8 \cdot 2H_2O$ is reference 12.

b) The spectra of the chloride compound in methanol solution appears to consist of two overlapping peaks.

chloride spectrum shows a broad band which appears to be the superposition of two different peaks. Apparently some kind of reaction is taking place. It is probably solvolysis or perhaps isomerization between cis and trans forms. The cis form is when two halide atoms are cis to each other on a molybdenum atom and the trans form is when they are trans to each other. This effect is somewhat enhanced by addition of extra $(CH_3)_4NCl$ and inhibited by addition of $NaCH_3SO_3$. Interaction of Mo_2^{+4} complexes with polar solvents is known to happen. San Filippo said his DMF complexes $Mo_2X_4(DMF)_4$ (X= Cl, Br) decomposed in polar solvents and Bowen and Taube remarked that the octachloride complex reacted with water.[28,32] Norman and Kolari recorded the spectra of the octachloride complex as a nujol mull because of solvent interference with water.[12] Therefore, the spectra of the halide complexes were taken as nujol mulls so that there would be no question of solvent interference.

The infrared spectra of the tetrahalobis-μ-methanesulfonatodimolybdate (II) compounds above 400 cm^{-1} are very similar. There are some differences due to the different cation in going from the chloride to the bromide and iodide compounds. The methanesulfonate peaks are less intense in the latter compoumds. This is because with larger halide ligands and larger cations the methanesulfonate ligands make up a smaller percentage by weight of the total compound. Therefore, equally large samples will show larger

peaks for the methanesulfonate in the chloride compound. Table 10 lists the peaks seen in the infrared spectra of these compounds above 400 cm^{-1}. Most of the peaks are due to the cation. These were determined by running spectra of the tetraalkylammonium halides and by referring to the article by Bottger and Geddes.[54] The few extra peaks seen in the iodide spectra are due to using a slightly thicker sample which allows some weak cation peaks to be seen. There are several areas where the assignments are due both to cation bands and the methyl group on the methanesulfonate. Note the three strong SO_3 bands. The average values at 1265, 1070 and 1013 cm^{-1} are very close to the values seen for the lactone and DMF complexes and support the argument that the only methanesulfonate ligands present in the lactone and DMF complexes are bidentate bridging ligands. For purposes of illustration the spectrum of the iodide complex in the region 1500-900 cm^{-1} is seen in Figure 15.

The far infrared spectra of these complexes were taken. The spectra in the region from 400-200 cm^{-1} are shown for the three complexes in Figure 16. When these spectra were run there was some interference from the beamsplitter of the interferometer. Later spectra obtained with a different beam splitter established the true peaks. Spectra run of the tetraalkylammonium halides howed negligible cation absorption in that region.

Because of the air stability of these compounds it was

Table 10

Infrared Spectra of the Tetrahalobis-μ-methanesulfonatodimolybdate (II) Compounds[a,b,c]

Values in cm^{-1}

Cl	Br	I	Assignment
3035 m,sh	3035 vw	3030 m	cation and $\nu asCH_3$
3030 m			
3015 m			
2970 w	2972 s	2971 s	cation and νsCH_3
2932 m	2960 s	2955 s	
	2945 m	2942 sh	
2863 w	2872 m	2888 m	cation
1491 s	1489 m	1482 m	cation
1482 sh	1460 w	1467 m	cation
1443 m		1445 w	cation and δdCH_3
	1372 w	1382 m	cation
1341 m	1335 w	1332 w	cation and δsCH_3
1289 msh			cation
1272 s	1260 vs	1265 s	$\nu asSO_3$
1069 s	1071 s	1070 m	$\nu asSO_3$
1013 s	1013 s	1013 s	νsSO_3
982 m	978 w	979 w	ρrCH_3, cation
972 vw			
956 m			cation

Table 10 cont.

Cl	Br	I	Assignment
950 m			cation
945 w			cation
	875 vw	874 w	cation
	786 vvw	799 w	cation
772 m	768 w	778 w	ν C-S
720 w	720 vw	719 w	
591 w	587 vw	583 vw)	δdSO_3 +
562 m	558 m	559 m)	δsSO_3
545 m	540 w	541 w)	

a) The methanesulfonate assignments are from reference 42.

b) The cation assignments come from spectra taken of tetraalkylammonium halides and reference 54.

c) A slightly thicker sample was used for the iodide complex than with the bromide complex allowing weak cation bands to be seen in one and not the other.

Figure 15

Infrared Spectra of the Compound $((C_4H_9)_4N)_2Mo_2I_4(CH_3SO_3)_2$ in the region 1500-900 cm^{-1}. Spectra taken as nujol mulls on salt plates. Peaks labeled N are due mainly to nujol.

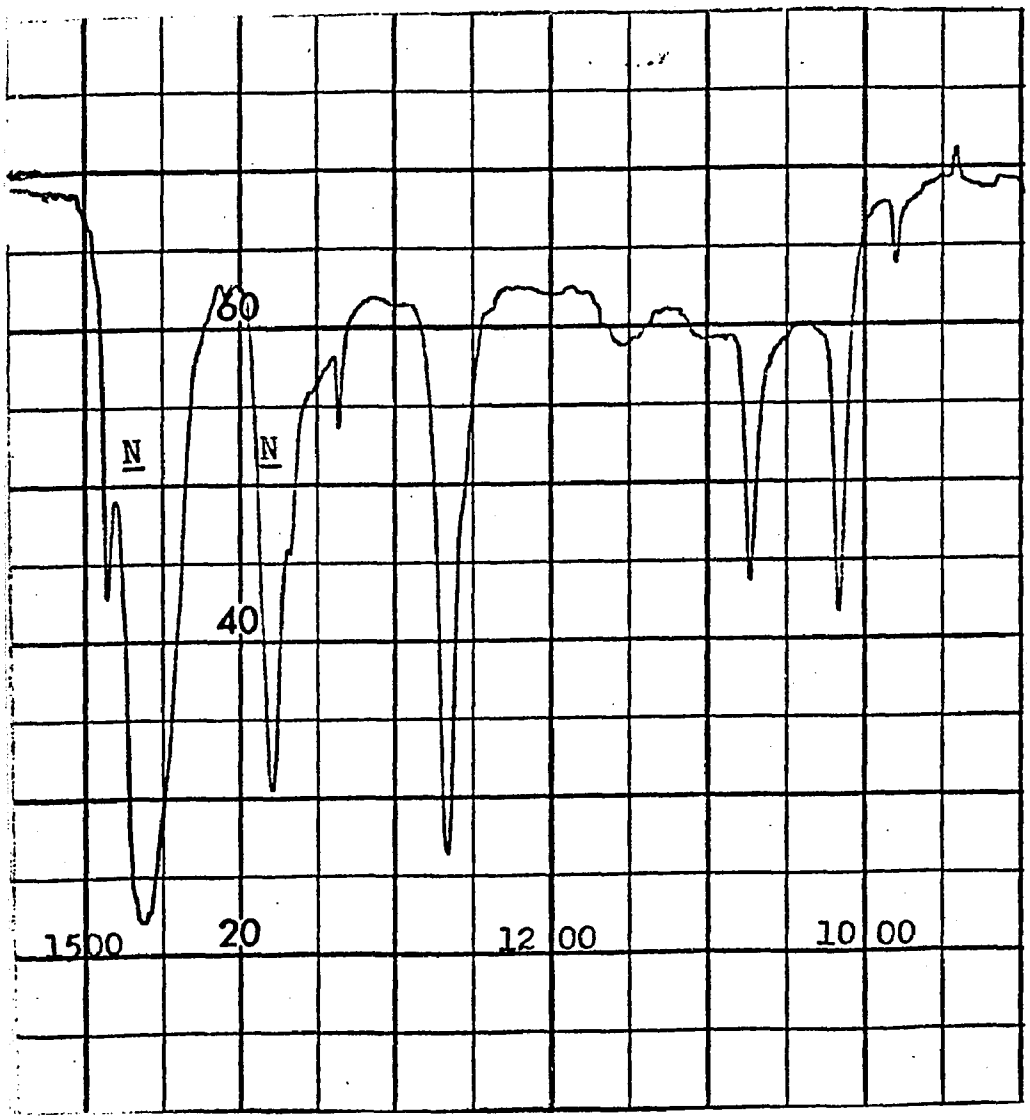

60
N
N
40
20
1500
12 00
10 00

Figure 16

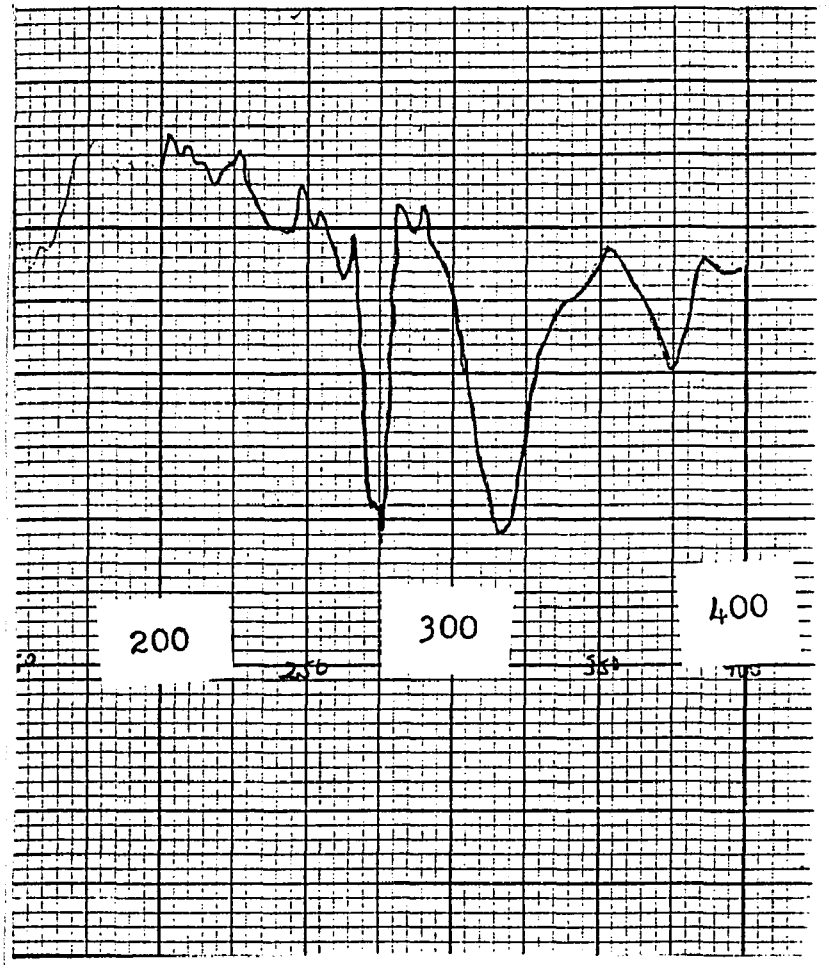
Far infrared spectra in the region 400-200 cm^{-1} of the compounds:

a) $((CH_3)_4N)_2Mo_2Cl_4(CH_3SO_3)_2$

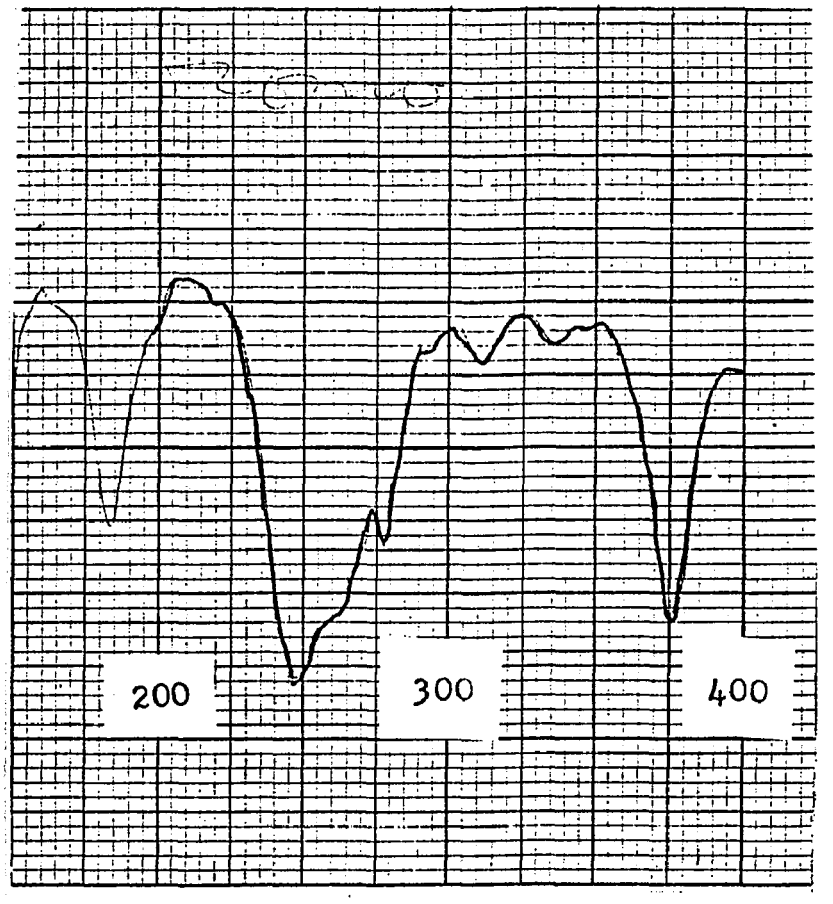
b) $((C_4H_9)_4N)_2Mo_2Br_4(CH_3SO_3)_2$

c) $((C_4H_9)_4N)_2Mo_2I_4(CH_3SO_3)_2$

Peaks due mainly to metal-ligand stretching modes. Some interference in the region around 270 cm^{-1} due to beamsplitter. Later spectra of iodide compound show this area to contain one peak. Spectra taken as nujol mulls on polyethylene plates.



a



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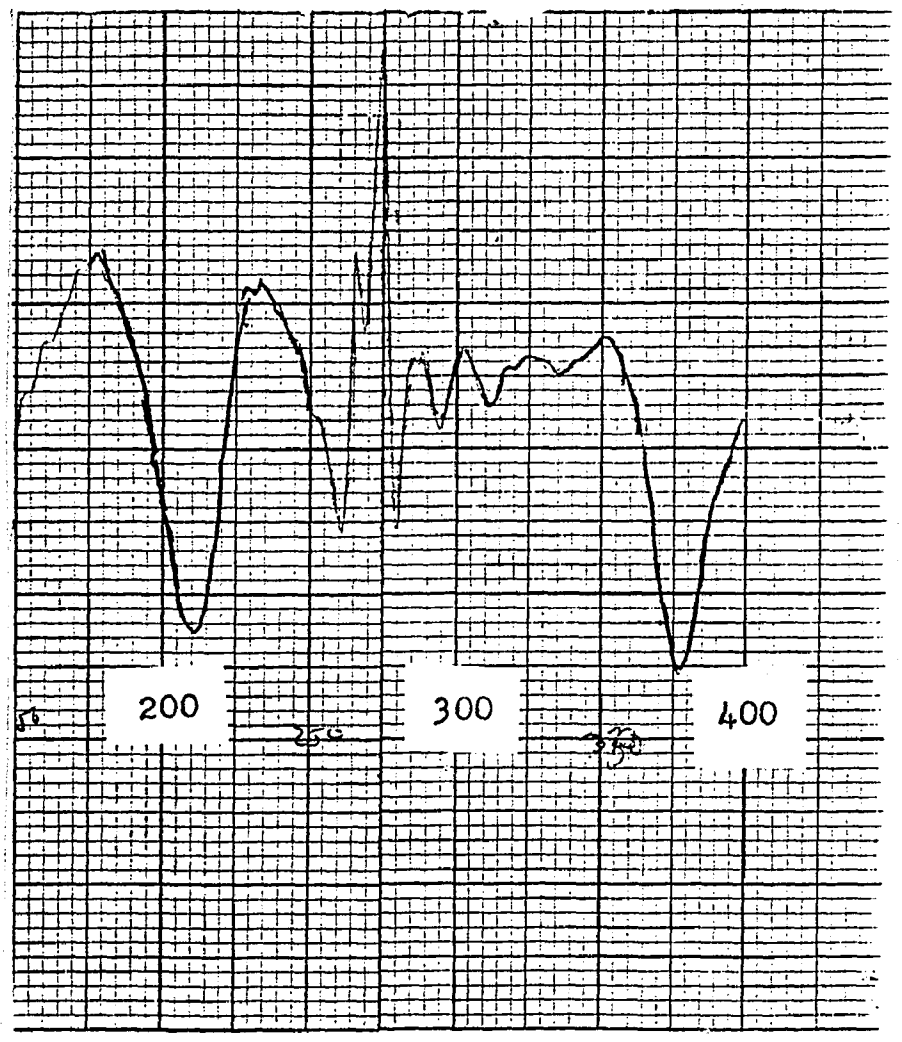


c

possible to make KBr pellets of them and use these pellets to take Raman spectra. The sample spinning technique was used to prevent thermal decomposition. In Figure 17 is seen the Raman spectra of the chloride compound in the region of the metal-metal stretching mode. There is another peak seen in this region. The presence of two peaks has been seen before in the Raman spectra of chloride complexes of Mo_2^{+4} and has been explained as the coupling of a_1 modes of ν Mo-Mo and ν Mo-Cl.[15,16] The Raman spectra of the bromide and iodide compounds are very similar and show only one prominent peak in the region expected for Mo-Mo stretching. The Raman spectra of the bromide compound in this region is seen in Figure 18. The bromide and iodide compounds show weak bands in the region around 450-440 cm^{-1}. It was believed that these bands might be due to cation bands so a Raman spectrum was taken of a nonspinning sample of $(C_4H_9)_4NI$. That compound also shows a weak band in this area. It also shows a stronger band at 267 cm^{-1} which is absent from the spectra of the molybdenum complexes. Perhaps these weak bands and the ones in the 245-230 cm^{-1} are due to metal-ligand stretching bands. The tabulated values for the far infrared and Raman spectra of the halide complexes are seen in Table 11.

It can be seen from Table 11 that there are similar-

Figure 17

Raman spectrum of $((CH_3)_4N)_2Mo_2Cl_4(CH_3SO_3)_2$ showing Mo-Mo and Mo-Cl A_1 stretching modes. Spectrum was taken on spinning KBr pellet of this compound.

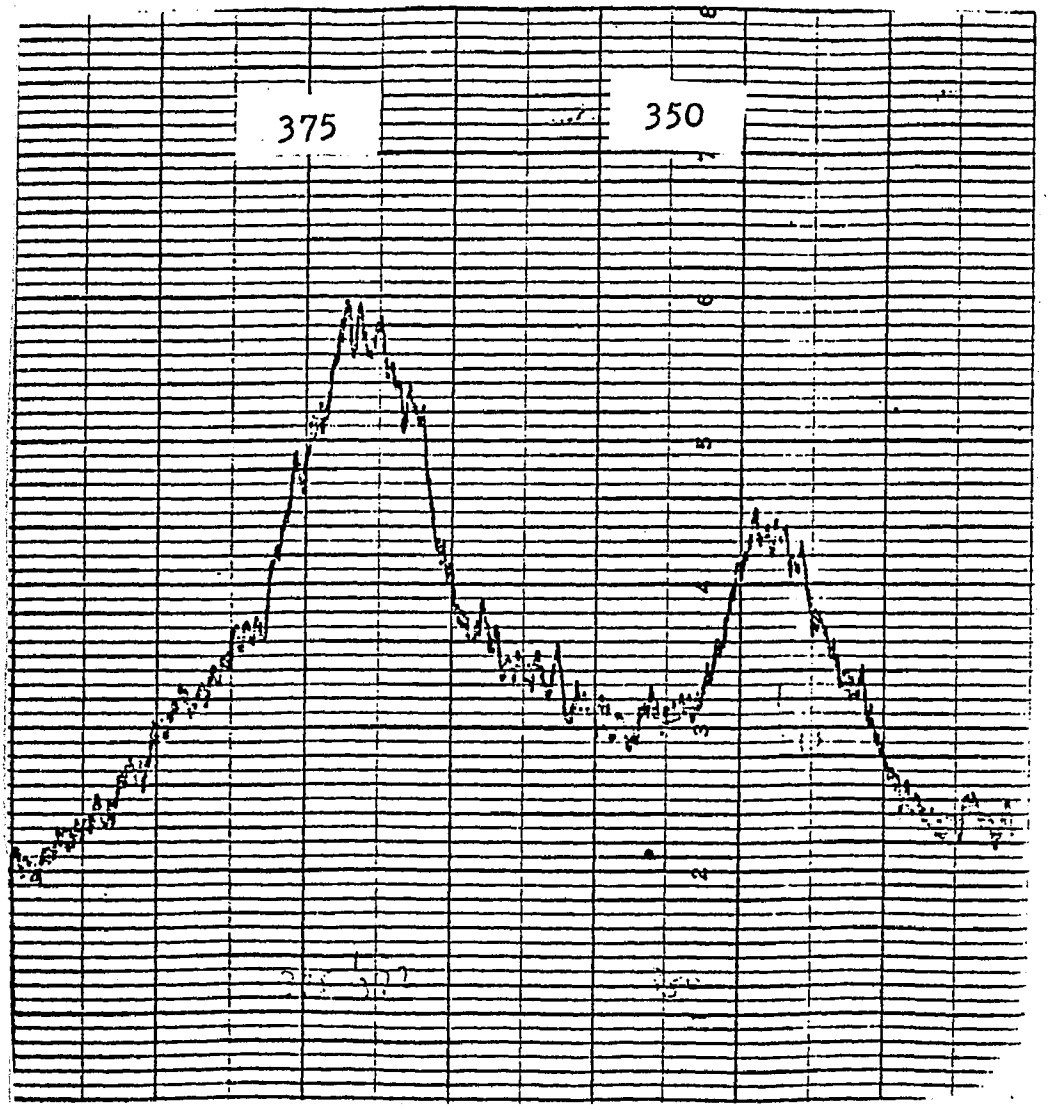

375
350

Figure 18

Raman spectrum of $((C_4H_9)_4N)_2Mo_2Br_4(CH_3SO_3)_2$ showing Mo-Mo A_1 stretching mode. Spectrum for iodide compound was very similar. Spectrum was taken on spinning KBr pellet of this compound.

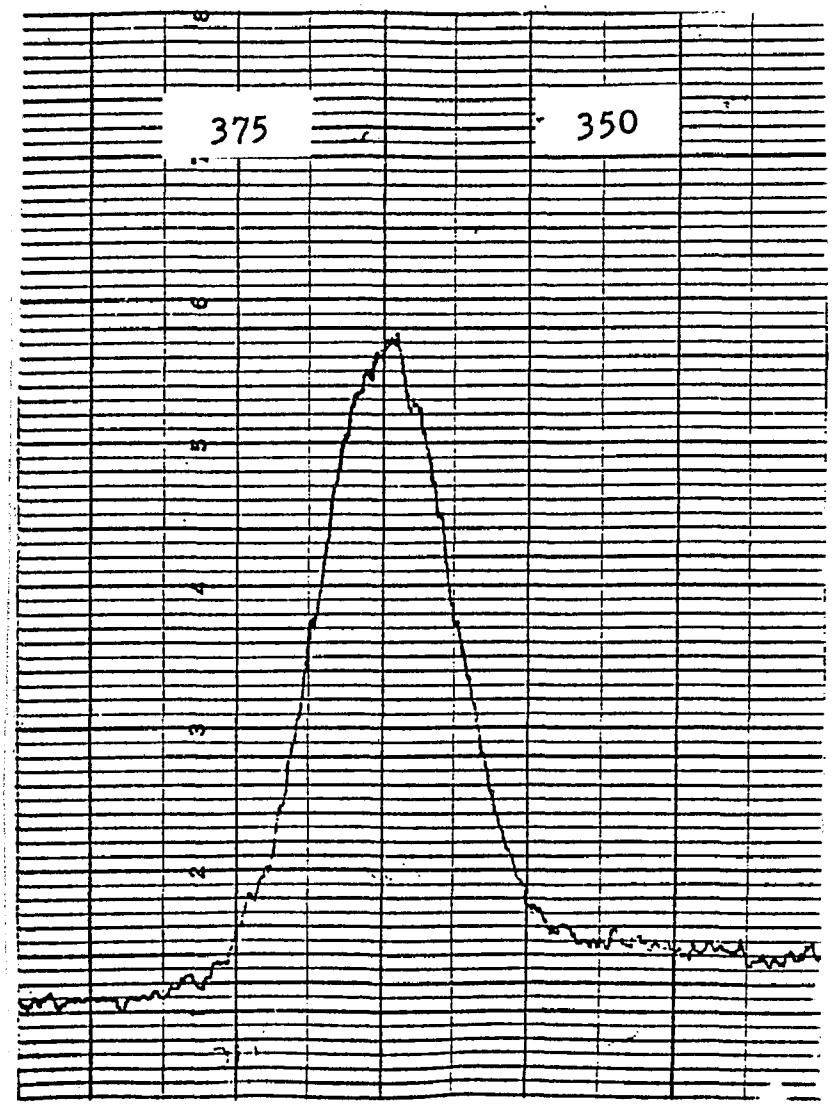

375
350

Table 11

Far Infrared and Raman Spectra of the Tetrahalo-bis-μ-methanesulfonatodimolybdate (II) Compounds

Values in cm^{-1}

Cl		Br		I	
IR	Raman	IR	Raman	IR	Raman
			440 w		447 w
375 m		374 m		377 m	
	372 vs		364 vs		362 vs
	343 s				
317 s					
270 s		275 s		265 s	
		245 s			
			233 w		241 w
				212 s	
160 m		183 m		145 m	
132 w		138 w		138 w	
115 w					

ities in the spectra of these compounds. In the far infrared spectra all three compounds have peaks in the regions of 377-374 cm^{-1} and 275-265 cm^{-1}. These peaks are probably due to Mo-O stretching modes. It is seen that there is one large band which changes position when the halide is changed. This would seem to be due to a Mo-X stretching band. Calculations done on these bands assuming them to be due to Mo-X stretching and using a simple diatomic formula give very similar force constants. Although the motions of these complexes are undoubtedly coupled and the assumption of simple stretching is a great simplification the point is proven. The results of these calculations are in Table 12. The Raman spectra of these compounds show the presence of one large band due to Mo-Mo stretching at 372, 364 and 362 cm^{-1} for the three compounds, and the Mo-Cl stretching band at 343 cm^{-1}. Oldham and Ketteringham reported that Mo-Br coupling did not take place with Mo-Mo in their Raman spectra of bromide complexes of Mo_2^{+4} compounds.[15] There are no reports on Raman spectra of Mo_2^{+4} iodide compounds in the literature.

It is obvious that in these complexes a binuclear Mo_2^{+4} ion is coordinated by two methanesulfonate and four halide ligands. There does not seem to be any axial coordination and none is expected. From Figure 2 it is seen that the chloride ligands are bent back out of the plane perpendicular to the metal-metal axis. It would be

Table 12

Force Constant Calculations for the Mo-X Bands of the Tetrahalobis-μ-methanesulfonatodimolybdate (II) Anions Assuming Simple Diatomic Behavior[a]

Bond	μ amu	ν cm^{-1}	k mdyne/A°
Mo-Cl	25.9	317	1.53
Mo-Br	43.6	245	1.54
Mo-I	54.7	212	1.44

a) Use is made of the diatomic stretching formula:

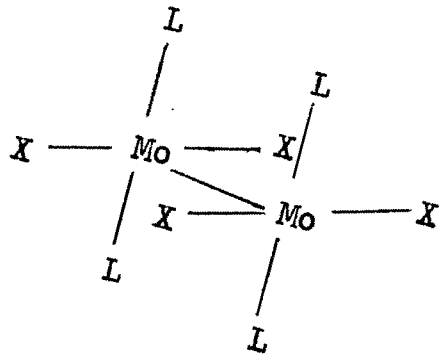
$$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$$

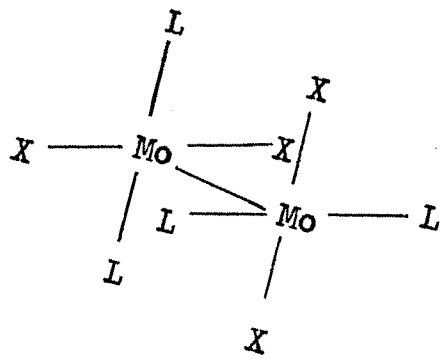
sterically difficult to have any kind of axial coordination. There is no precedent in the literature for a Mo_2^{+4} compound with equatorial halide ligands to have axial ligands. The compounds are, therefore, eight coordinate. The one remaining question is the arrangement of the ligands. A major problem with structural characterization of binuclear complexes is that there are many isomeric possiblities. Frequently the compounds are noncrystalline and cannot be structured by X ray diffraction. For compounds of the general formula $Mo_2X_4L_4$ assuming that there are two X and two L ligands per Mo atom there are at least five isomeric possibilities as seen in Figure 19. For compounds of the general formula $Mo_2X_4(LL)_2$ assuming two X and one LL ligand per Mo atom there are three isomeric possibilities as seen in Figure 20. There is the possibility that more than one isomer is present after a synthesis. For the compounds synthesized here with the anion formula $Mo_2X_4(CH_3SO_3)_2^{-4}$ there are two possibilities, the cis and the trans shown in Figure 21. Binuclear compounds showing both forms have been synthesized for Re_2^{+6} compounds. There are the trans $Re_2I_4(O_2CPh)_2$[55] and cis $Re_2Cl_4(O_2CCH_3)_2 \cdot H_2O$[56]. The references cited are crystal studies and contain no spectroscopic data.

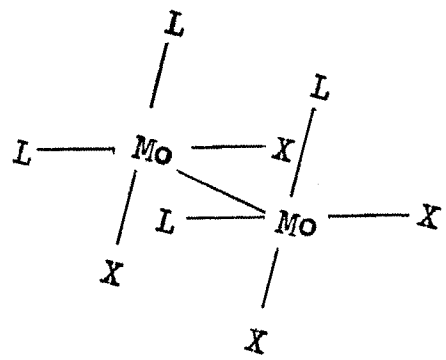
An attempt can be made to determine structure from the vibrational spectra. Bratton et al. attempted a normal coordinate analysis of the $Mo_2Cl_8^{-4}$ anion which has D_{4h}

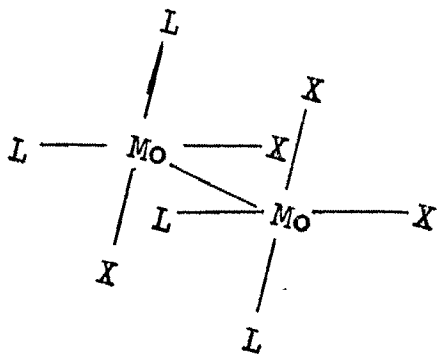
Figure 19

Possible isomeric structures for compounds of formula $Mo_2X_4L_4$ assuming 2 X and 2 L ligands per Mo atom.


L
L
X
Mo
X
X
Mo
X
L
L


L
X
X
Mo
X
L
Mo
L
L
X


L
L
L
Mo
X
L
Mo
X
X
X


L
X
L
Mo
X
L
Mo
X
X
L

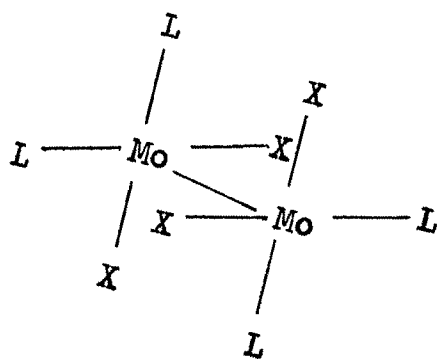
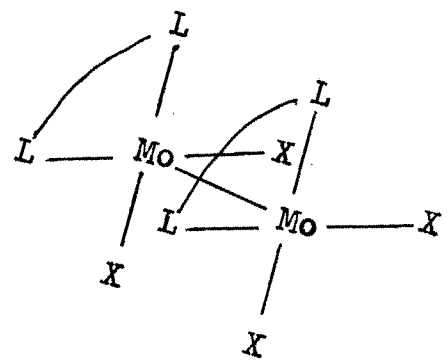
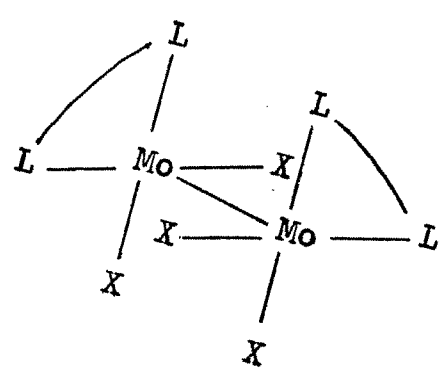

L
X
L
Mo
X
X
Mo
L
L

Figure 20

Possible isomeric structures for compounds of formula $Mo_2X_4(LL)_2$ assuming 2 X and 1 LL ligand per Mo atom.


L
L
Mo
X
L
L
Mo
X
X
X


L
L
Mo
X
L
X
Mo
L
X

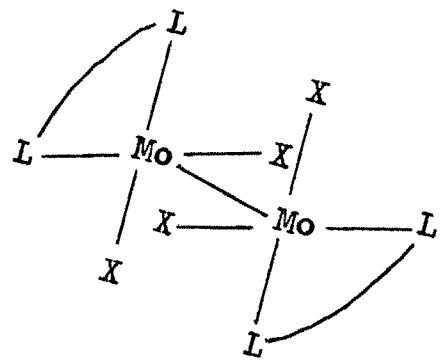
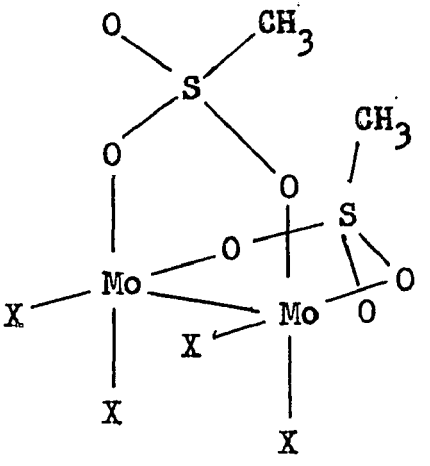
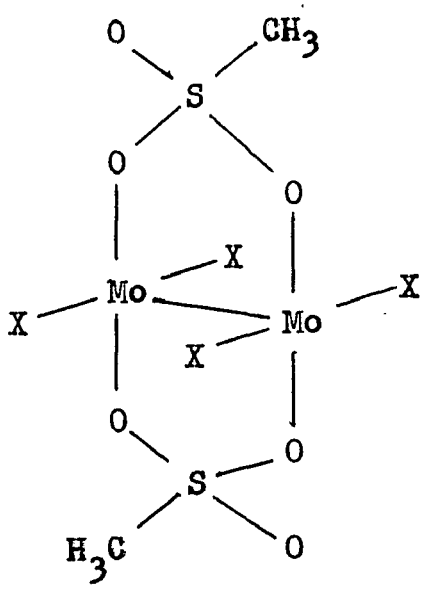

L
X
L
Mo
X
X
Mo
L
X
L

Figure 21

Cis and trans structures for the $Mo_2X_4(CH_3SO_3)_2^{-2}$ ions. Cis has C_{2v} symmetry. Trans has C_{2h} symmetry.



cis



trans

symmetry. Assignments were made from the basic stretches and bends of the complex.[14] The results are seen in Table 13. Clark and Franks used these results in their Raman study of the same compound.[16] It can be seen that in D_{4h} symmetry that for metal-metal and metal-ligand stretches the infrared and Raman spectra should be mutually exclusive. In the anions considered here of the formula $Mo_2X_4(CH_3SO_3)_2^{-4}$ the symmetry is necessarily lowered from D_{4h}. Consider Figure 21. For the cis structure the basic $Mo_2X_4O_4$ skeleton has C_{2v} symmetry and the trans structure has D_{2h} symmetry which is actually closer to C_{2h} when the whole molecule is considered. For C_{2v} symmetry the selection rules are different from C_{2h} symmetry. The effect of lowering the symmetry from D_{4h} to C_{2v} and C_{2h} is shown in Table 14. In principle, one could expect to differentiate between the cis and trans forms. In C_{2v} symmetry all the infrared modes are expected to be Raman active and all but a_2 Raman modes are expected to be infrared active. For C_{2h} symmetry mutual exclusivity of infrared and Raman spectra is still expected. Examining Table 11 it would seem that a case could be made for the trans structures. The infrared and Raman spectra of these compounds do seem to be mutually exclusive. There is a Raman band for the chloride complex at 372 cm^{-1} and an infrared band at 375 cm^{-1}. However, the former is undoubtedly due to Mo-Mo

Table 13

The Distribution of the Normal Modes of Vibration of Ions of the Type $Mo_2Cl_8^{-4}$ of D_{4h} Symmetry[a,b,c,d]

Approximate Description

	a_{1g}	b_{1g}	b_{2g}	e_g
	R_p	R	R	R
ν(MoMo)	1			
ν(MoCl)	1	1		1
δ(MoMoCl)	1[b]	1		1
δ(ClMoCl)	1[b]		1	1
MoMo torsion				

	a_{1u}	a_{2u}	b_{1u}	b_{2u}	e_u
		ir			ir
ν(MoMo)					
ν(MoCl)		1		1	1
δ(MoMoCl)		1[b]		1	1
δ(ClMoCl)		1[b]	1		1
MoMo torsion	1				

Vibration Modes = $3a_{1g} + 2b_{1g} + 1b_{2g} + 3e_g + 1a_{1u} + 2a_{2u} + 1b_{1u} + 2b_{2u} + 3e_u$

a) The average bond parameters are Mo-Mo= 2.14 A°, Mo-Cl= 2.45 A°, and $\angle$(MoMoCl)= 105°.

Table 13 cont.

b) The symmetry species a_{1g} and a_{2u} each contain one redundancy in the angle bending coordinates.

c) R stands for Raman active. ρ stands for polarized. ir stands for infrared active.

d) The source of this table is reference 14.

Table 14

Effect of Lowered Symmetry on Mo-Mo and Mo-L Stretching Modes of Mo_2^{+4} Complexes[a]

D_{4h} for $Mo_2Cl_8^{-4}$

Mo-Mo	a_{1g} R
Mo-L	a_{1g} R + b_{1g} R + e_g R + a_{2u} ir + b_{2u} + e_u ir.

C_{2v} for cis $Mo_2X_4(CH_3SO_3)_2^{-2}$

Mo-Mo	a_1 R,ir
Mo-L	$2a_1$ R,ir + $2a_2$ R + $2b_1$ R,ir + $2b_2$ R,ir.

C_{2h} for trans $Mo_2X_4(CH_3SO_3)_2^{-2}$

Mo-Mo	a_g R
Mo-L	$2a_g$ R + $2b_g$ R + $2a_u$ ir + $2b_u$ ir.

a) L stands for ligand. R stands for Raman active. ir stands for infrared active.

stretching and since the latter band is found at approximately the same location in all three complexes it would seem to be due to Mo-O stretching. Therefore, these two bands would seem to be fundamentally different. Also the strong 343 cm^{-1} band, also a_1, seems to be absent except possibly as a weak shoulder from the infrared spectra. So far it seems that the evidence favors the trans structure. However, caution must be taken. Firstly for the cis structure six metal ligand stretching bands are predicted for the infrared while for the trans structure four are predicted. Only three strong bands are seen in any of these compounds. San Filippo took infrared and Raman spectra of a number of mixed ligand complexes. Some were of the formula $Mo_2X_4L_4$. For the chloride complexes in which L= PR_3, R_2S, C_6H_5CN, and py, two strong bands were observed in the infrared spectra which were assigned to Mo-Cl stretches. One was at 337 ± 15 cm^{-1} and the other was at 285 ± 10 cm^{-1}. The latter band was less intense than the former. For L= CH_3CN and DMF and for compounds of the formula $Mo_2X_4(LL)_2$ there was one intens e band at 305 ± 10 cm^{-1} with a shoulder at 340 cm^{-1}.[28] From Figure 20 it can be seen that complexes with chelating ligands must have the chloride ligands cis to each other. The spectra of the complex $((CH_3)_4N)_2Mo_2Cl_4(CH_3SO_3)_2$ seen in Figure 16a looks more like the spectra San Filippo saw with the chelating ligands. Also a look at his Raman results shows that the

compounds with the chelating ligands, $Mo_2Cl_4(LL)_2$, have two strong Raman bands while those without chelating ligands do not. Therefore, it appears that although the mutual exclusivity of the infrared and Raman spectra favor the trans structure shown in Figure 20, comparison with San Filippo's results point towards the cis structure as being more likely for the chloride compound and probably the others as well.

What has been accomplished here is the synthesis of a homologous series of compounds of the general formula $(R_4N)_2Mo_2X_4(CH_3SO_3)_2$ with X= Cl, Br, and I. These compounds are very similar in appearance, are all diamagnetic and have very similar infrared spectra. Changing the halide ligand causes two changes in the electronic spectra. The position of the $\delta \rightarrow \delta^*$ shifts slightly. Lower wavelengths are found in the order I Br Cl which is in the order of the spectrochemical series. Also a band is seen to shift in the ultraviolet and confirms the assignment of Norman and Kolari of a band in this region to a ligand to metal charge transfer band. Again more energy is needed for the Cl to metal than the I to metal transfer. Changing the halide also shifts a band in the far infrared. Simple calculations show that the force constants of these bands assuming simple Mo-X stretching behavior are very close in value. Finally, a comparison of the results here with those of San Filippo favor the

assignment of the cis rather than the trans structure seen in Figure 20.

If one makes the reasonable assumption that the halide ligands would block out any axial ligands then the complexes must be eight coordinate. These compounds illustrate partial substitution in which the axial bonding of methanesulfonate is eliminated and four of the equatorial methanesulfonate bonds have been replaced by four halide ligands. This is also the first example in Mo_2^{+4} chemistry of mixed ligand compound with four halide and two bridging ligands.

The Thiocyanate Compound

Thiocyanate is sometimes considered a pseudohalide ligand but the thiocyanate compound made here greatly differs in appearance from the halide compounds. Full substitution of methanesulfonate has taken place. The blue-green color is unlike that of the other compounds mentioned here in this work but is not unknown for Mo_2^{+4} chemistry. San Filippo reported several greenish Mo_2^{+4} compounds.[28] The oxidation state of Mo here is +2 and the compound is diamagnetic so that the compound appears to be binuclear. Further evidence comes from the existence of octathiocyanato complexes of binuclear rhenium, Re_2^{+6}, which have been prepared and studied.[57,58] Reference 58 is a study of such a complex by photoelectron spectroscopy which showed only one kind of thiocyanate nitrogen to be present.

A solution electronic spectra of this compound was taken in DME. There is a visible peak at 667 nm with $\epsilon = 2.8 \times 10^3$. The ultraviolet peaks were so intense that very dilute solutions were prepared. These discolored rapidly, however. Therefore, a spectrum was taken of a nujol mull. The sample had to be prepared in a glove bag and the sample compartment of the spectrophotometer was flushed with argon beforehand. Broad, poorly defined bands were seen at 690, 375, 325 and 275 nm.

The infrared spectra of the compound was taken as hexachlorobutadiene and nujol mulls. In addition a solution spectrum was taken of the compound in DME in the region around 2000 cm^{-1} to confirm the presence of the two large bands in that area. Frequently it is observed that the presence of several thiocyanate bands in solid spectra is due to crystal packing effects and that most bands disappear in solution spectra.[59] The two large bands were found to be present in solution spectra also. The far infrared spectrum was also taken. The infrared and far infrared spectra are tabulated in Table 15. Figure 22 shows the spectrum in the region of the two C-N stretching bands. Note the spacing between the frequencies is not equal because expanded scale paper was used in this run.

The presence of the two ν C-N which persisted in solution was puzzling at first. Furthemore, the value of 1920 cm^{-1} is very low for ν C-N.[59] However, if the structure is binuclear as in $Mo_2Cl_8^{-4}$, then the symmetry is D_{4h}. There should be two νC-N, νC-S, and νMo-N. For some reason only one νC-N was reported for the thiocyanate complex of the rhenium binuclear ion.[57]

Since thiocyanate is an ambidentate ligand the question of the mode of bonding is important. In a recent review of the infrared spectra of many thiocyanate coordination compounds several guidelines for judging struc-

Table 15

Infrared and Far Infrared Spectra of the Thiocyanate Compound $(NH_4)_4Mo_2(NCS)_8 \cdot 4(C_4H_{10}O_2)$[a-c]

Values are in cm^{-1}

Bands	Assignment
3300-2700 br	NH_4^+ and DME
2095 vs	ν C-N
1960 m	NH_4NCS in DME
1920 s	ν C-N
1655-1550 br	NH_4NCS in DME
1410 m	DME
1271 w	DME
1239 w	DME
1191 w	DME
1116 m	DME
1071 s	DME
1020 m	DME
948 w	2 δ NCS
895 w	DME
851 s	DME
830-810 m, br	ν C-S
720 w	ν C-S ?
471 w	δ NCS
380 w	NH_4^+

Table 15

Band	Assignment
295 vs	ν Mo-N
200 vs	ν Mo-N ?
100 w	

a) The spectra were taken as nujol and hexachlorobutadiene mulls. Spectra below 400 cm^{-1} were taken as nujol mulls on the interferometer so that the intensities given in this region are relative only to that region.

b) NH_4NCS in DME means that these peaks were seen in the solution spectra of NH_4NCS in DME and could not be due to NCS coordination to Mo.

c) Literature references are as follows:

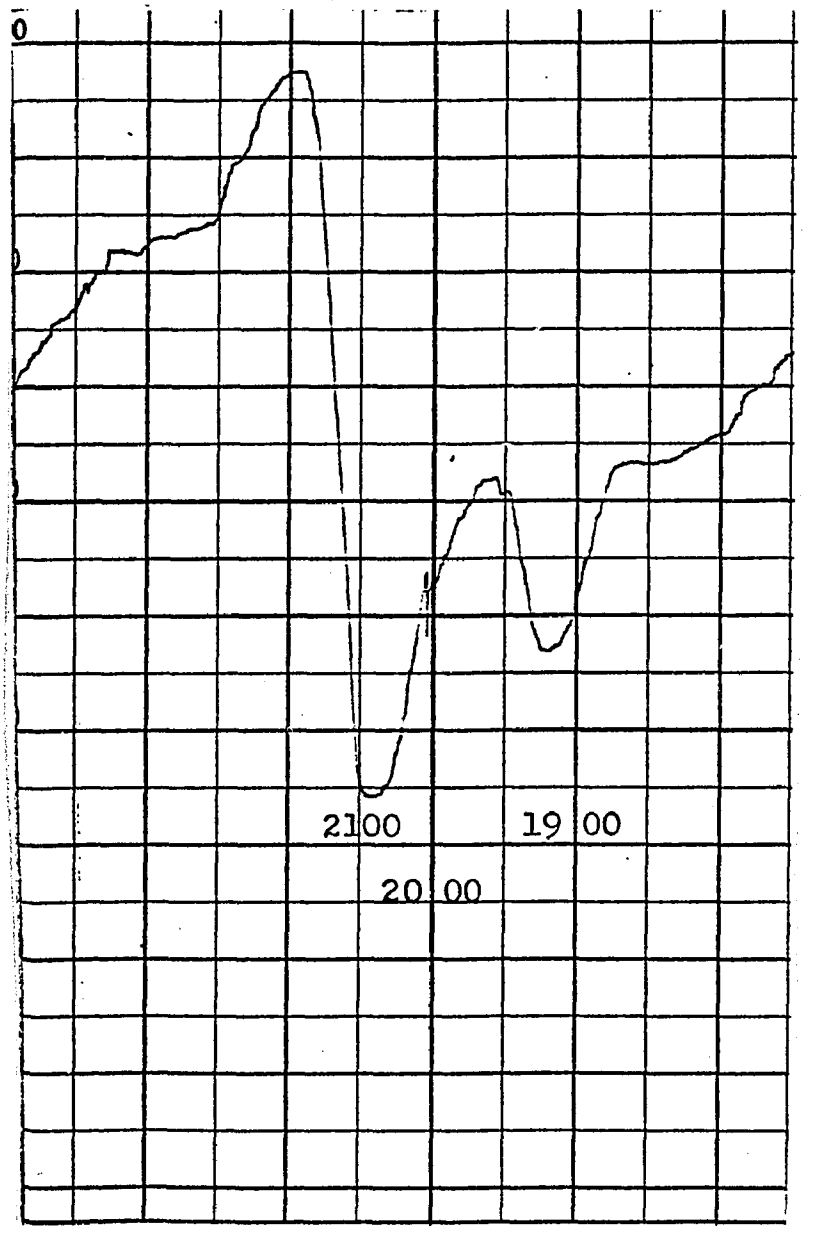
coordinated thiocyanate- references 59-60

NH_4NCS- references 61-62

DME- references 63-64.

Figure 22

Infrared spectra of $(NH_4)_4Mo_2(NCS)_8 \cdot 4(C_4H_{10}O_2)$ in the region 2100-1900 cm^{-1}. Note the unevenness of the scale due to using expanded scale chart paper. The two large peaks are due to ν C-N stretching modes. Spectra taken on hexachlorobutadiene mulls on salt plates.


0
2100
19 00
20 00

ture were laid down.[59] The main thiocyanate band here is at 2095 cm^{-1}. Bridging thiocyanate complexes have considerably higher values. S bonded thiocyanate usually absorbs over 2100 cm^{-1}. The value at 2095 cm^{-1} is typical for N bonded thiocyanate. N bonded thiocyanate also is expected to have νC-S at about 820 cm^{-1} while S bonded has this band at 700 cm^{-1}. The strong band in the 830-810 region favors the N assignment although a weak band at 720 is questionable. Perhaps it is the second ν C-S band allowed by D_{4h} symmetry. δNCS is about 490 cm^{-1} for N bonded and 450 cm^{-1} for S bonded cases. 2δNCS is about 950 cm^{-1} for N bonded and about 910 cm^{-1} for S bonded cases. From what is seen here the argument is stronger for N bonding. The peak at 295 cm^{-1} is due to Mo-N stretching. It is similar to the value seen for $Cs_3Mo(NCS)_6$ of 303 cm^{-1}.[59] The band at 200 cm^{-1} seems very low for a Mo-N stretching mode. It is in the same area as a band seen by Durig and Pate for NH_4NCS.[62] It was assigned as a translational mode in the crystal.

Inspection of the stretching and bending modes shows that the assignment to N bonded thiocyanate has more support than assignment to S bonded thiocyanate. Comparison with spectral results for Mo (III) thiocyanate compounds show great similarities. These compounds are known to be N bonded.[59,60] It was observed that KNCS had limited solubility in DME and it appears that the DME is not coordi-

to the molybdenum. It may be hydrogen bonded to the ammonium, enhancing some of the weaker infrared modes by distortion from symmetry. Therefore, it appears that there is a binuclear Mo_2^{+4} ion with eight N bonded thiocyanate ligands. Being N bonded they are properly called isothiocyanate ligands.

An attempt was made to take the Raman spectra of this compound. Since the compound is very delicate and air sensitive, and since the exciting line of the Raman is not found within the electronic spectral maxima of this compound, the spectrum was taken of a nonspinning sample. However, there were no bands seen in the region of metal-metal stretch between 400-300 cm^{-1}. It is likely that the compound decomposed.

Despite the disappointment of not obtaining good Raman spectra there is still much evidence that this compound contains the octaisothiocyanatodimolybdate (II) anion. The oxidation state of Mo is +2, the compound is diamagnetic, there are only four isothiocyanate ligands per Mo atom and there is the analogy of the known Re_2^{+6} compounds.

This case illustrates full substitution of the methanesulfonate complex. There is apparently no axial bonding and all the methanesulfonate has been replaced.

Conclusion

Part Two of this thesis deals with the synthesis of $Mo_2(CH_3SO_3)_4$, its characterization, and the reactions it undergoes. This compound was first synthesized by way of the following reaction:

$$Mo_2(CH_3COO)_4 + 4\ CH_3SO_3H \xrightarrow{\text{diglyme}} Mo_2(CH_3SO_3)_4 + 4\ CH_3COOH \qquad (32)$$

It was thought that the methanesulfonate might be a labile ligand and be easily removed in substitution reactions. Instead it was discovered that the methanesulfonate complex undergoes a variety of reactions ranging from partial to complete substitution.

Study of the infrared and far infrared spectra of the methanesulfonate complex shows it can be considered as a ten coordinate compound with the eight equatorial sites taken up by four bridging methanesulfonate ligands and the two axial sites being bonded to by oxygens on methanesulfonates bonded to other binuclear ions. It thus resembles the sulfate complex.[33] (See Figure 7). The methanesulfonate complex undergoes reactions in which the axial ligands are replaced, in which half the methanesulfonate ligands are replaced with no evidence for axial bonding and in which all the methanesulfonate ligands are replaced.

It was found that the methanesulfonate complex would react with the carbonyl ligands γ-butyrolactone and DMF

to form complexes in which two carbonyl ligands have added on.

$$Mo_2(CH_3SO_3)_4 + 2\ C_4H_6O_2 \xrightarrow{\text{heat}} Mo_2(CH_3SO_3)_4 \cdot 2C_4H_6O_2 \qquad (35)$$

$$Mo_2(CH_3SO_3)_4 + 2\ (CH_3)_2NCHO \longrightarrow Mo_2(CH_3SO_3)_4 \cdot 2(CH_3)_2NCHO \qquad (36)$$

Many different structures were considered for the products of equations 35 and 36. It was found that the DMF complex in DMF and both compounds in methanol had conductivities like univalent electrolytes but that the γ-butyrolactone complex in γ-butyrolactone and both compounds in diglyme had nonconducting solutions. Examination of the infrared and far infrared spectra of these compounds showed that the structure which best accounted for the spectra seen consisted of a binuclear ion with four bridging methanesulfonate groups and two axially bonded carbonyl ligands. This would explain the similarity of the far infrared spectra of these compounds to that of the methanesulfonate compound because all three would have the same $Mo_2O_8O'_2$ skeleton. These are covalent compounds which can apparently ionize in polar solvents. In these cases substitution of the axial ligands has occurred with the equatorial ligands unchanged.

The methanesulfonate complex will react with the halide ligands Cl, Br, and I to form a homologous series of anions

of the formula $Mo_2X_4(CH_3SO_3)_2^{-2}$. There seems to be no evidence of axial bonding. Partial substitution of the equatorial ligands has taken place.

$$Mo_2(CH_3SO_3)_4 + 4\,R_4NX \longrightarrow 2\,R_4NCH_3SO_3 + (R_4N)_2Mo_2X_4(CH_3SO_3)_2 \qquad (33)$$

These compounds are very similar in appearance and physical properties. Changing the halide does cause some changes, however. The $\delta \rightarrow \delta^*$ in the visible spectra and a ligand to metal charge transfer band in the ultraviolet spectra are halide dependent. Norman and Kolari's assignment of the latter band were confirmed by the results here.[12] The chloride compound has a somewhat different Raman spectrum because of coupling of the a_1 νMo-Mo and νMo-Cl modes. In the other compounds this isn't observed. A band in the far infrared spectra was shown to be due to Mo-X stretching with very similar force constants in all three cases.

There are two isomeric possibilities for these compounds as shown in Figure 21, the cis and the trans structures. Although the observed spectra seem to fit the selection rule requirements of the C_{2h} trans structure better than the C_{2v} cis structure, comparison of the observed spectra with the experimental results of San Filippo point to the cis structure as being more likely.[28]

Finally, the methanesulfonate compound will react with thiocyanate ion to yield a compound in which there is no axial bonding and in which thiocyanate has completely substituted for the methanesulfonate.

$$Mo_2(CH_3SO_3)_4 + 8\ NH_4NCS \xrightarrow{DME} 4\ NH_4CH_3SO_3 + (NH_4)_4Mo_2(NCS)_8 \cdot 4DME \qquad (34)$$

Examination of the infrared spectra of this compound shows that the thiocyanate is N bonded giving an isothiocyanate complex.

$Mo_2(CH_3SO_3)_4$ did not prove to be as susceptible to complete substitution as originally believed. Rather it undergoes a variety of reactions with different degrees of substitution. It is a good illustration of the complexity to be expected when studying the coordination chemistry of binuclear systems.

BIBLIOGRAPHY

BIBLIOGRAPHY

1. F. A. Cotton, Chem. Soc. Reviews, 4, 27 (1975).
2. E. W. Abel, A. Singh and G. Wilkinson, J. Chem. Soc., 3097 (1959).
3. E. Bannister and G. Wilkinson, Chem. and Ind., 319 (1960).
4. T. A. Stephenson, E. Bannister and G. Wilkinson, J. Chem. Soc., 2538 (1964).
5. G. Holste and H. Schafer, Z. Anorg. Allg. Chem., 391, 263 (1972).
6. D. Lawton and R. Mason, J. Amer. Chem. Soc., 87, 921 (1965).
7. J. V. Brencic and F. A. Cotton, Inorg. Chem., 8, 7 (1969).
8. J. V. Brencic and F. A. Cotton, Inorg. Chem., 8, 2698 (1969).
9. J. V. Brencic and F. A. Cotton, Inorg. Chem., 9, 346 (1970).
10. J. V. Brencic and F. A. Cotton, Inorg. Chem., 9, 351 (1970).
11. F. A. Cotton, Inorg. Chem., 4, 334 (1965).
12. J. G. Norman Jr., and H. J. Kolari, J. Amer. Chem. Soc., 97, 33 (1975).
13. J. San Filippo Jr., Inorg. Chem., 11, 3140 (1972).
14. W. K. Bratton, F. A. Cotton, M. Debeau and R. A. Walton, J. Coord. Chem., 1, 121 (1971).
15. C. Oldham and A. P. Ketteringham, J. Chem. Soc. Dalton, 2304 (1973).
16. R. J. H. Clark and M. L. Franks, J. Amer. Chem. Soc., 97, 2691 (1975).

17. G. Holste, Z. Anorg. Allg. Chem., 414, 81 (1975).

18. F. A. Cotton and J. G. Norman Jr., J. Coord. Chem., 1, 161 (1971).

19. E. Hochberg, P. Walks and E. H. Abbott, Inorg. Chem., 13, 1824 (1974).

20. L. E. Orgel, An Introduction to Transition Metal Chemistry 2nd. ed., Methuen & Co., London, 1966 p. 178

21. L. Ricard, P. Karagiannidis and R. Weiss, Inorg. Chem., 12, 2179 (1973).

22. D. F. Steele and T. A. Stephenson, Inorg.Nucl. Chem. Letters, 9, 777 (1973).

23. F. A. Cotton, T. Inglis, M. Kilner and T. R. Webb, Inorg. Chem., 14, 2023 (1975).

24. F. A. Cotton, J. M. Troup, T. R. Webb, D. H. Williamson and G. Wilkinson, J. Amer. Chem. Soc., 96, 3824 (1974).

25. W. Oberkirch, Dissertation, Technische Hochschule, Aachen (1963).

26. F. A. Cotton and J. R. Pipal, J. Amer. Chem. Soc., 93, 5441 (1971).

27. B. Heyn and H. Still, Z. fur Chemie, 13, 191 (1973).

28. J. San Filippo Jr., H. J. Sniadoch and R. L. Grayson, Inorg. Chem., 13, 2121 (1974).

29. J. V. Brencic, D. Dobcnik and P. Segedin, Monatsh. Chem., 105, 142 (1974).

30. J. V. Brencic, D. Dobcnik and P. Segedin, Monatsh. Chem., 105, 944 (1974).

31. J. V. Brencic, D. Dobcnik and P. Segedin, Monatsh. Chem., 107, 395 (1976).

32. A. R. Bowen and H. Taube, Inorg. Chem., 13, 2245 (1974).

33. F. A. Cotton, B. A. Frenz, E. Pedersen and T. R. Webb, Inorg. Chem., 14, 391 (1975).

34. F. A. Cotton and J. G. Norman Jr., J. Amer. Chem. Soc., 94, 5697 (1972).

35. E. H. Abbott, F. Schoenewolf Jr., and T. Backstrom, J. Coord. Chem., 3, 255 (1974).

36. A. B. Brignole and F. A. Cotton, Inorg. Syn., 13, 88 (1972).

37. L. Dubicki and R. L. Martin, Aust. J. Chem., 22, 1571 (1969).

38. Handbook of Preparative Inorganic Chemistry Vol. II 2nd. ed., Georg Brauer Ed., Academic Press, New York, 1965 p.1367

39. D. D. Perrin, W. L. F. Armarego and D. R. Perrin, Purification of Laboratory Chemicals, Pergamon Press, New York, 1966

40. D. F. Shriver, The Manipulation of Air Sensitive Compounds, McGraw Hill Book Co., New York, 1969

41. ibid. p. 195-200

42. M. G. Miles, G. Doyle, R. P. Cooney and R. S. Tobias, Spectrochim. Acta, 25A, 1515 (1969).

43. R. B. Penland, S. Mizushima, C. Curran and J. V. Quagliano, J. Amer. Chem. Soc., 79, 1575 (1957).

44. A. Loewenschuss, J. Shamir and M. Ardon, Inorg. Chem., 15, 238 (1976).

45. R. Mecke, R. Mecke and A. Luttringhaus, Chem. Ber., 90, 975 (1957).

46. K. Nakanishi, Infrared Absorption Spectroscopy, Nankodo Co. Ltd., Tokyo, 1969 p. 44

47. J. R. Durig, G. L. Coulter and D. W. Wertz, J. Molec. Spectr., 27, 285 (1968).

48. R. L. Jones, J. Molec. Spectr., 11, 411 (1963).

49. J. E. Katon, W. R. Flairkeller Jr., and J. V. Pustinger, Anal. Chem., 36, 2126 (1964).

50. V. R. Shafranskii and T. A. Malkova, J. of Gen. Chem. of the U. S. S. R., 45, 1051 (1975).

51. M. F. Lappert, J. Chem. Soc., 817 (1961).

52. H. Burger, K. Burcyk and A. Blaschette, Monatsh. Chem., 101, 102 (1970).

53. F. A. Cotton and N. F. Curtis, Inorg. Chem., 4, 241 (1965).

54. G. L. Bottger and A. L. Geddes, Spectrochim. Acta, 21, 1701 (1965).

55. K. W. Bratton and F. A. Cotton, Inorg. Chem., 8, 1299 (1969).

56. P. A. Koz'min, M. D. Surazhskaya and V. G. Kuznetov, Zhur. Strukt. Khim., 11, 313 (1970).

57. F. A. Cotton, W. R. Robinson, R. A. Walton and R. Whyman, Inorg. Chem., 6, 929 (1967).

58. D. G. Tisley and R. A. Walton, J. Chem. Soc. Dalton, 1039 (1973).

59. R. A. Bailey, S. L. Kozak, T. W. Michelsen and W. N. Mills, Coord. Chem. Reviews, 6, 407 (1971).

60. J. Lewis, R. S. Nyholm and P. W. Smith, J. Chem. Soc., 4590 (1960).

61. F. Am Miller and C. H. Wilkens, Anal. Chem., 24, 1253 (1952).

62. J. R. Durig and C. B. Pate, Spectrochim. Acta., 28A, 1031 (1972).

63. R. G. Snyder and G. Zerbi, Spectrochim. Acta, 23A, 391 (1967).

64. R. Iwamoto, Spectrochim. Acta, 27A, 2385 (1971).