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MASTER

SYNTHESIS OF TWO MERCAPTIDE-SUBSTITUTED HEXANUCLEAR MOLYBDENUM HALIDE CLUSTERS

John Byrne Michel

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Ames Laboratory, ERDA
Iowa State University
Ames, Iowa 50011

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Synthesis of two mercaptide-substituted hexanuclear molybdenum halide clusters

by

John Byrne Michel

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LIST OF SYMBOLS AND ABBREVIATIONS

DMF	Dimethylformamide, $(CH_3)_2NCOH$
DMSO	Dimethylsulfoxide, $(CH_3)_2SO$
L	A neutral ligand bound to a terminal position of the cluster
Ph	Phenyl, C_6H_5
py	Pyridine, C_5H_5N
SEt^-	Ethyl mercaptide, $SCH_2CH_3^-$
SR^-	Alkyl mercaptide
X^-, Y^-	Halides
ν	Symbol for stretching vibration

THESIS ABSTRACT*

John Michel

Two new derivatives of the $[(Mo_6Cl_8)Cl_4]$ cluster have been prepared. $Na_2[(Mo_6Cl_8)(SC_2H_5)_6]\cdot3(C_5H_5N)$ was made by first reacting molybdenum dichloride with sodium ethyl mercaptide (1:6 mole ratio) in refluxing methanol. The orange product was recovered in pure crystalline form by extraction of the solid residue with pyridine. This compound was characterized by its X-ray powder pattern, elemental analysis, and infrared and electronic spectra. It dissolves in most polar solvents, yielding reddish-orange solutions. Treatment of alcohol solutions with hydrochloric acid causes rapid conversion to $[(Mo_6Cl_8)Cl_6]^{2-}$, accompanied by the evolution of ethyl mercaptan.

$[(Mo_6Cl_8)(SC_2H_5)_4(C_5H_5N)_2]$ was prepared using the same procedure, starting with a 1:4 mole ratio of molybdenum dichloride and sodium ethyl mercaptide. This material was isolated as a red, amorphous solid. It was characterized by elemental analysis and infrared and electronic spectra. It is soluble in pyridine, DMSO, and DMF; other polar solvents

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must be acidified before it will dissolve. Treatment of this compound with a solution of concentrated hydrochloric acid in methanol again yielded $[(Mo_6Cl_8)Cl_6]^{2-}$. Its amorphism and insolubility in most polar solvents suggest this compound might be polymeric. Individual cluster units are probably linked in a random way by intercluster mercaptide bridges. More extensive characterization of this compound in its solid state is required to confirm this.

INTRODUCTION

The purpose of this research is the preparation and characterization of some new sulfur-derivatives of the hexanuclear molybdenum dichloride cluster. Recent developments reported in the chemical literature indicate that these compounds may be both interesting and synthetically accessible. Much research effort is currently being expended on a series of superconductors with high critical temperatures and fields. They are solid state compounds with the formulas Mo_6Y_8 and $M_xMo_6Y_8$ ($Y = S, Se, Te$; $0<x<2$). The metal cations M have been taken from all parts of the periodic table except the 5d-transition metals and elements of the actinide series (1-6). The choice of M determines the variable x, and whether a discrete phase or a solid solution is isolated.

The compounds are usually synthesized by mixing together molybdenum and chalcogen powders, and for the ternary phases, the metal chalcogenide MY. Alternately, a mixture of Mo_6Y_8 and M powders may be used to prepare the ternary phases. The mixture is then pressed into a pellet and heated at elevated temperature. The X-ray powder diffraction pattern is intermittently checked, and the reaction stopped as soon as the material proves to be homogeneous. Reaction temperatures and times are usually near 1000°C and twenty hours, respectively. Mo_6S_8 is a notable exception (7). It can be prepared only by reduction of a ternary sulfide. It is thermodynamically unstable above 468°C. The critical temperature of the superconducting transition for these materials is quite dependent on the sample's preparation (8,9). For $PbMo_6S_8$, T_c varied between 11.0 and 14.5 K. Very recently, crystalline $PbMo_6S_8$ was synthesized using an isothermal vapor transport process (9). This sample had the highest critical temperature yet reported for $PbMo_6S_8$, 14.7°K. The transport technique yielded crystalline material in useful quantity. Previously, the very small quantity of crystals available limited characterization to single crystal X-ray diffraction experiments. For other studies, less pure microcrystalline powder was used.

Correlation of structural features with the superconducting behavior is the area of greatest interest generated by these compounds (5,6,10-15). Clustering of the molybdenum atoms with intercluster distances short enough so that a three-dimensional metallic lattice is maintained is believed to be an important factor (11). These molybdenum chalcogenides are quite closely related structurally to the better-characterized molybdenum dihalides (7,16). Both have approximately octahedral metal-metal bonded cluster units of molybdenum atoms. The six molybdenum atoms occupy the face-centers of a surrounding cube of eight anions (chalcogenides or halides). These anions are the so-called "bridging ligands" since they are placed centrally above the molybdenum octahedron's triangular faces. In addition, the molybdenum dihalides have six "terminal ligands", each bound to a single molybdenum atom. They are located directly above the face centers of the cube. The chalcogenides have no terminal ligands. In molybdenum dichloride, all the intracluster metal-metal distances are 2.61 ± 0.01 Å, forming a perfect octahedron (17). In all the molybdenum chalcogenide compounds, the molybdenum octahedron, as well as the cube of anions, is trigonally distorted (7,15,16,18-21). Their symmetry is lowered to D_{3d}. Mo_6S_8, for example, has two intracluster metal-metal distances of 2.698 and 2.862 Å. All the crystal structures completed to date for this series of compounds have had similar distortions. Intercluster Mo-Mo distances are greater than 3.08 Å in all cases, indicating these are hexanuclear clusters.

Because of the basic structural similarity of the dihalides to the chalcogenides, it is tempting to apply existing bonding ideas to explain the differences in structural details. Both the Cotton and Haas (22) and the Guggenberger and Sleight (23) molecular orbital schemes indicate twenty-four electrons may be accommodated in the metal-metal bonding orbitals of the $(Mo_6Cl_8)^{4+}$ cluster. $[(Mo_6Cl_8)Cl_4]$ has the full complement of twenty-four.

Mo_6S_8, $PbMo_6S_8$, and $Ni_2Mo_6S_8$ may be regarded as having twenty, twenty-two, and twenty-four electrons, respectively. Thus, a decrease in the intracluster Mo-Mo distance is expected in this sequence. The average distances are 2.780, 2.702(1) and 2.72(8) Å, respectively (7,19,21). The Mo-Mo distances in the chalcogenides are significantly longer than that in molybdenum dichloride in all cases. This comparison is especially important for the pair $Ni_2Mo_6S_8$ (21) and $[(Mo_6Cl_8)Cl_4]$ (17) which may be regarded as isoelectronic. All three chalcogenides have trigonally distorted molybdenum octahedra. As a measure of this, the differences between the two Mo-Mo intracluster distances for Mo_6S_8 (7), $PbMo_6S_8$ (19), and $Ni_2Mo_6S_8$ (21) are 0.164, 0.048(0), and 0.07(4) Å, respectively. Using the Cotton and Haas scheme, Jahn-Teller distortion is predicted in the structures of Mo_6S_8 and $PbMo_6S_8$. This means a lowering of structural symmetry will occur to remove the electronic state's degeneracy. The Guggenberger and Sleight scheme predicts no such distortion for any of the three compounds. Neither scheme accounts for the deviation from ideal octahedral symmetry found in $Ni_2Mo_6S_8$. These considerations are necessarily of a qualitative, inconclusive nature. Solid state effects may be a primary force determining the chalcogenides' structures. Also, the noncluster components of the dihalide and chalcogenide compounds are very different. The application of these two molecular orbital schemes to clusters with nonhalogen bridging ligands is undocumented. Similarly, the usefulness of the two schemes in describing oxidized or reduced versions of the (M_6X_8) cluster is not known. $[Mo_6Cl_{11}(P(CH_2CH_3)_3)_3]$, recently reported by Hamer *et al.*, is the only such molybdenum cluster known (24). Evidence indicates it should be formulated as $[(Mo_6Cl_8)(PCH_2CH_3)_6]^{2+}[(Mo_6Cl_8)Cl_6]^{2-}$. If this is correct, the cation is a reduced 26-electron species. Its structure has not been solved. The isostructural tungsten dihalides are more susceptible to nondegradative oxidation than their molybdenum analogs. Reaction of tungsten dibromide, $[(W_6Br_8)Br_4]$, with bromine produced a series of oxidized, 22-electron clusters containing the $(W_6Br_8)^{6+}$ species (25,26). The structure of $[(W_6Br_8)Br_8]$ has been solved (27). Two of the terminal ligands are tetrabromide $(Br_4)^{2-}$ ions, shared between cluster units. The other four terminal ligands are bromide ions. The Cotton and Haas molecular orbital scheme predicts Jahn-Teller distortion for a 22-electron $(M_6X_8)^{6+}$ cluster. However, the cluster is octahedral, within experimental error. This agrees with the prediction of Guggenberger and Sleight's scheme. Chemical evidence indicated that oxidation of $[(W_6I_8)I_4]$ produced a $[W_6I_8]^{5+}$ cluster (28). This is a 23-electron species. No physical characterization was done.

In many cases, oxidation of a (M_6X_8) cluster yields a (M_6X_{12}) cluster. This is the common structural unit of low oxidation state niobium and tantalum halides (29). Kepert _et al._ (30) reported that oxidation of $[(Mo_6Cl_8)Cl_4]$ yielded $[(Mo_6Cl_{12})Cl_3]$. The average oxidation state of molybdenum has increased to +2.5. Oxidation of $[(W_6Cl_8)Cl_4]$ produced a W(III) cluster, $[(W_6Cl_{12})Cl_6]$ (30,31). The structure of the tungsten compound has been solved. $[(W_6Br_{12})Br_6]$ has also been made (32). These (M_6X_{12}) clusters cannot be directly compared to the (M_6X_8) units. The metal-metal bonding is significantly different in the two cases (22).

The apparent ease of reduction of Mo_6S_8 leads to speculation whether a hybrid, mixed sulfide-halide cluster would possess interesting oxidation-reduction properties. Holm's ferredoxin models, $[(Fe_4S_4)(SR)_4]^{n-}$ (n = 1, 2, 3, 4) (33), further support the suitability of sulfide ligands to clusters with extensive oxidation-reduction chemistry. It would be interesting to find whether a recognizable transition from solid state to molecular compound occurs in an envisioned series of compounds between Mo_6S_8 and $[(Mo_6Cl_8)Cl_4]$. Structural data would also be valuable, to better understand the bonding.

The obvious synthetic choice for a starting material is molybdenum dichloride. It will dissolve in several solvents, and the chemistry of the molybdenum dihalide clusters has been extensively studied. The bonding differences between the bridging and terminal halides, which are clearly indicated in the crystal structures, are just as clearly highlighted by a comparison of their reactivities.

Substitution of the six terminal ligands is a facile process. The $(Mo_6Cl_8)^{4+}$ cluster core is usually inert in solution. For example, if the terminal ligands are halides, they may be titrated argentometrically without decomposition of the cluster core (34). Lessmeister and Schaefer have recently measured the kinetics of terminal chloride substitution by bromide in aqueous solution (35). They found it is statistically controlled. The reaction involves two steps:

$$[(Mo_6Cl_8)Cl_6]^{2-} + H_2O \xrightarrow{slow} [(Mo_6Cl_8)Cl_5(H_2O)]^- + Cl^-$$

$$[(Mo_6Cl_8)Cl_5(H_2O)]^- + Br^- \xrightarrow{fast} [(Mo_6Cl_8)Cl_5Br]^{2-} + H_2O$$

The activation energy is only 18 kcal/mole. Some typical substitution reactions are described to illustrate the variety of species obtained using simple synthetic routes. $(H_3O)_2[(Mo_6Cl_8)X_6]\cdot 6H_2O$ with X = Cl, Br, or I may be prepared by recrystallizing $[(Mo_6Cl_8)Cl_4]$ from a one molar solution of the appropriate hydrohalic acid in ethanol (36). This may then be converted to $[(Mo_6Cl_8)X_4(H_2O)_2]$ by recrystallization from aqueous hydrohalic acid (37), or by heating at 200°C *in vacuo* (36). Further heating at 300°C produces anhydrous $[(Mo_6Cl_8)X_4]$. $[(Mo_6Cl_8)Cl_4(DMF)_2]$ and $[(Mo_6Cl_8)Cl_4(DMSO)_2]$ are prepared by dissolving $[(Mo_6Cl_8)Cl_4]$ in the respective liquid, followed by precipitation (38). Other bis-adducts are formed with such diverse ligands as acetone, ethanol, tetrahydrofuran, pyridine, and triphenylphosphine (39). $[(Mo_6Cl_8)(DMF)_6](ClO_4)_4$ and $[(Mo_6Cl_8)(DMSO)_6](ClO_4)_4$ are made by first precipitating the terminal chlorides of $[(Mo_6Cl_8)Cl_4]$ with alcoholic $AgClO_4$, followed by addition of the appropriate ligand (38).

Only very few nucleophiles are known which interact in solution with the bridging ligands of the $(Mo_6Cl_8)^{4+}$ cluster core. Controlled hydrolysis in weakly basic solution yielded $[(Mo_6Cl_8)(OH)_4]\cdot 14\ H_2O$. Attempts to promote further substitution led to intractable solids, and ultimately destroyed the cluster (40,41). Even under mild conditions, fluoride yields decomposition products. Both these reactions probably involve initial displacement of the bridging chlorides. Methoxide is the only ligand known which yields completely substituted derivatives from solution without destroying the cluster. Nannelli and Block prepared $[(Mo_6Cl_8)(OCH_3)_6]^{2-}$, and under very forcing conditions, $[(Mo_6(OCH_3)_8)(OCH_3)_6]^{2-}$ (42). This work suggested the sulfur analog of an alkoxide, a mercaptide, as a suitable sulfur ligand for the proposed investigation.

Although the reactivity of the bridging ligands is quite limited in solution, the situation is quite different in fused salt media. Sheldon first noted that in lithium halide melts, complete exchange occurred (43):

$$[(Mo_6Cl_8)Cl_4] + 12\ LiX \xrightarrow[500^\circ C]{LiX\ melt} [(Mo_6X_8)X_4] + 12\ LiCl$$

$$(X = Br,\ I)$$

Baumann *et al*. found that tempering of mixed halides $[(Mo_6Cl_8)Y_4]$ at 450°C for four weeks produced $[(Mo_6Cl_4Y_4)Cl_4]$ (40). Complete exchange of the bridging halides was accomplished by similar treatment of $[(Mo_6Cl_4Y_4)Y_4]$, where for both steps, Y = Br or I. In both Baumann's and Sheldon's experiments, the heavier halide moved preferentially to a bridging position, displacing the lighter halide to a terminal position. Baumann also found that similar tempering of $[(Mo_6Cl_8)(OH)_4]$ yielded $[(Mo_6Cl_7(OH))(OH)_3Cl]$ and $[(Mo_8Cl_6(OH)_2)Cl_2(OH)_2]$. Further substitution decomposed the cluster. In a separate study, Lesaar and Schaefer used mercuric halide melts for further exchange experiments (44):

$$[(Mo_6X_8)X_4] + 3\ HgY_2 \longrightarrow Hg[(Mo_6X_8)Y_6] + 2\ HgX_2$$

$$[(Mo_6X_8)X_4] + 7\ HgY_2 \longrightarrow Hg[(Mo_6Y_8)Y_6] + 6\ HgX_2$$

The anionic component of the melt, Y, displaced the cluster's terminal halides in all cases. However, there was a competition for each of the cluster's bridging positions between the halide X which originally occupied it and Y, the anionic component of the melt. The lighter halide of the two is thermodynamically preferred. This was a complete reversal of the cluster's behavior in lithium halide melts. Lesaar and Schaefer used a simple thermodynamic argument to explain this apparent anomaly.

This proposed research is not the first attempt to prepare sulfur derivatives of the molybdenum dihalide clusters. Molybdenum dichloride has been reacted with both sulfur and selenium powders yielding products of the composition $Mo_3Cl_4Y_7$ (Y = S, Se) (45). Similar products were obtained using molybdenum dibromide. The structure of these amorphous materials is unknown. In another study, Perrin _et al_. reacted molybdenum dibromide with the chalcogen powders at 1150°C for twenty-four hours in a silica tube (46). This procedure produced $Mo_6Br_{10}Y$ (Y = S, Se). Using molybdenum diiodide yielded $Mo_6I_{10}Y$. These compounds are crystalline, and are isostructural with Nb_6I_{11}. Neither of these efforts adequately employed the synthetic possibilities presented by the molybdenum dihalide clusters.

For this project, organic mercaptides, SR^-, have been chosen as the sulfur ligands. They offer a number of advantages. Reactions may be carried out in solution. They are uninegative anions, like the chloride ions they will displace. As was already mentioned, they are closely related to the alkoxide ligands used by Nannelli and Block (42,47,48). These workers' success leads to the expectation that it should be possible to introduce mercaptide ligands into both the bridging and terminal positions of the cluster. Strictly by analogy to the alkoxides, the two compounds $Na_2[(Mo_6Cl_8)(SR)_6]$ and $Na_2[(Mo_6(SR)_8)(SR)_6]$ should be synthetically accessible. Modifications might yield their neutral congeners $[(Mo_6Cl_8)(SR)_4]$ and $[(Mo_6(SR)_8)(SR)_4]$. Thermal tempering experiments similar to those of Baumann et al. (40) would be of interest to determine whether migration of mercaptide from a bridging to a terminal position, or vice-versa, might occur.

EXPERIMENTAL

Handling and Purification Procedures

Most of the compounds handled in this project are moisture sensitive. To prevent their hydrolysis, all reactions were performed either on a standard Pyrex high-vacuum line (working vacuum of 10^{-4} to 10^{-6} torr), a small combination vacuum-nitrogen (Schlenk) line, or in a nitrogen atmosphere dry box (dew point ca. -80°C). All nitrogen gas used for this work was prepurified nitrogen (99.995% pure from Air Products Corp.).

Reagents

Ethyl mercaptan (CH_3CH_2SH, practical grade) was obtained from Matheson, Coleman, and Bell. Due to its high vapor pressure and stench, a great deal of discretion and care was required in its handling. The liquid was transferred to a round-bottom Pyrex flask. After attachment to the vacuum line, it was outgassed during several freeze-thaw cycles. The main fraction of the liquid was then vacuum distilled into a similar flask, where it was stored over Linde 4A molecular sieves. The flask was frozen with liquid nitrogen and evacuated during thawing prior to each use.

Aluminum trichloride ($AlCl_3$, certified anhydrous) was obtained from Fisher Scientific Co. Before use, it was resublimed at ca. 125°C under dynamic vacuum. The purified material was stored in the dry box.

Molybdenum pentachloride ($MoCl_5$, nominal purity 99.5%) was obtained from Research Organic-Inorganic Corp. Sodium chloride (NaCl, cert. ACS reagent) was obtained from Fisher Scientific Co. Both compounds, packed under vacuum, were opened in the dry box and stored there without further purification.

Aluminum metal was obtained in the form of small chips machined from laboratory stock. Nominal purity is 99.5%. No further purification was required. Sodium metal was obtained from Fisher Scientific Co. It was stored in air under oil. Immediately prior to use, an appropriate quantity was sliced off and placed in a beaker of hexane. It was then transferred directly to the reaction vessel. A blanket of nitrogen was maintained over this flask during the transfer. The flask was then capped, attached to the vacuum line, and evacuated. Some tarnishing of the metallic surface was visible during these manipulations.

Solvents

Pyridine (C_5H_5N, Boiling Range 115.0-115.3°C) was obtained from Fisher Scientific Co. The handling procedure was identical to that used for ethyl mercaptan.

Methanol (CH_3OH, cert. ACS reagent, Boiling Range 64.5-64.8°C) was obtained from Mallinckrodt, Inc. It was transferred to a round-bottom Pyrex flask with a standard taper 24/40 ground glass joint. Nitrogen was bubbled through the liquid for thirty minutes. While continuing the purging, chunks of sodium metal were carefully added to the methanol. After the reaction was completed, and the flask had cooled, it was capped. The sodium methoxide solution was then attached to the vacuum line, and outgassed during several freeze-thaw cycles. The flask was frozen and re-evacuated prior to each use.

Ethanol (absolute) was obtained from Commercial Solvents Corp. It was used without further purification.

Starting materials

Molybdenum dichloride (Mo_6Cl_{12}) was prepared by the method of Dorman and McCarley (36). In this procedure, aluminum was used to reduce molybdenum pentachloride in a slightly acidic sodium tetrachloroaluminate melt. The reaction is:

$$6\ MoCl_5 + 6\ Al \xrightarrow{NaAlCl_4} Mo_6Cl_{12} + 6\ AlCl_3\ .$$

The purification procedure was slightly modified to produce large crystals of the acid hydrate, $(H_3O)_2(Mo_6Cl_{14})\cdot 6\ H_2O$. Although this required more time, it was done to ensure a pure product. An unidentified brown impurity had solubility properties similar to those of the acid hydrate. The crystals of $(H_3O)_2[Mo_6Cl_{14}]\cdot 6\ H_2O$ were then pulverized using a mortar and pestle, added to a Pyrex reaction tube, and attached to the vacuum line. Under a dynamic vacuum, the tube's temperature was increased to 350°C over a period of four to five hours. The solid was maintained *in vacuo* at this temperature for *ca*. twenty hours. While cooling, the compound's color changed from a deep reddish-brown back to a dull yellow, characteristic of amorphous molybdenum dichloride. The tube was opened in the dry box, and the sample stored there. Its purity was occasionally checked by elemental analysis and infrared spectroscopy.

Sodium ethyl mercaptide ($NaSCH_2CH_3$) was prepared by reacting excess ethyl mercaptan with sodium metal in a nitrogen atmosphere. This reaction required extreme care. An apparatus having two Pyrex round-bottom flasks interconnected at the base of the neck was used. Using a blanket of nitrogen gas, sodium metal was introduced into one of the flasks. The apparatus was quickly capped, attached to the vacuum line, and evacuated. Ethyl mercaptan was vacuum distilled into the other flask. After replacing the apparatus on the Schlenk line, nitrogen was bled into the system. A slight positive pressure was maintained during the reaction by means of a mercury bubbler. This also served as an exit for the hydrogen gas evolved during the reaction. The flask containing the sodium was kept immersed in a Dry-Ice acetone bath. Small quantities of ethyl mercaptan were intermittently poured over into the sodium flask. Unless great care was exercised, the reaction became too vigorous, even at the bath temperature of -78°C. When this occurred, the flask was temporarily immersed in a liquid nitrogen bath. The reaction product was a large quantity of white powder. Excess ethyl mercaptan was distilled off on the vacuum line. Due to its stench and sensitivity to moisture, the solid was stored in the dry box.

Physical Characterization Methods

Analytical procedures

The procedure used for sample decomposition was nearly identical for the determinations of both molybdenum and chloride. A sample was removed from the dry box in a screw cap vial. The vial was quickly weighed, the sample emptied into a flask, and the recapped vial weighed. Two pellets of potassium or sodium hydroxide were added to the sample. Then 100 ml of water was added, followed by 2-3 ml of 30% hydrogen peroxide. The analytical solutions turned dark reddish-brown whenever hydrogen peroxide was added to them. The color disappeared after a few minutes. Gentle heating was used initially. When the hydrogen peroxide had nearly all reacted, the rate of heating was increased so as to boil the solution nearly to dryness. The residue was allowed to cool. Another small portion of 30% hydrogen peroxide was added to this small volume. The sample was left at room temperature until bubbling stopped. The volume was increased to 100 ml. This process was repeated until a colorless residue was obtained after boiling to dryness. With this completed, the sample solution was adjusted to 100 ml and heated to expel remaining peroxide. The resulting solution was left overnight at room temperature prior to analysis. Sample decomposition for a chloride determination differed slightly. The solution was never heated to dryness. Sample volume was maintained at *ca*. 100 ml during two or three cycles of hydrogen peroxide addition and subsequent expulsion.

The solutions used for molybdenum determinations were analyzed according to the method of Yagoda and Fales (49). The molybdate was precipitated and collected as the sulfide, MoS_3. This was ignited to molybdenum oxide, and weighed. The sample was reweighed at hourly intervals until weights were constant within 0.2 mg.

The pH of the solutions used for chloride analysis was adjusted to *ca*. 4 with nitric acid. The volume was increased to 150 ml. The solution was then titrated with standardized 0.1 N silver nitrate solution. A silver/silver chloride electrode was used with a double junction reference electrode obtained from Orion Research, Inc.

Analysis for carbon and hydrogen was done by Mr. John Richard of the Ames Laboratory analytical group, or by Galbraith Laboratories. Samples were removed from the dry box and sealed under vacuum prior to analysis.

Infrared spectra

Infrared spectra were recorded using a Beckman IR 4250 recording spectrometer in the 4000-200 cm^{-1} region. All spectra were calibrated with the 906.9 cm^{-1} absorption of polystyrene. Peak locations are estimated to be accurate to within two cm^{-1}. Spectral samples were nujol mulls pressed between cesium iodide windows. Since most of the compounds are moisture sensitive, the nujol was stored over sodium sand in the dry box. The mulled samples were prepared in the dry box and were removed in screw-cap bottles which were left sealed until the spectrum was recorded. The sample holder also provided some protection from the atmosphere.

The spectra of these two mercaptide cluster complexes were closely compared to similarly recorded spectra of sodium ethyl mercaptide, pyridine, and molybdenum dichloride. No attempt was made to assign all the absorptions to specific vibrational modes.

Electronic absorption spectra

Electronic absorption spectra were scanned on a Cary 14 recording spectrometer. Silica sample cells with a one-centimeter path length were used. The experimental conditions were considered sufficient to prevent sample decomposition. The spectrum of $Na_2[(Mo_6Cl_8)(SCH_2CH_3)_6]\cdot 3(C_5H_5N)$ in methanol was recorded using a vacuum-tight sample cell equipped with a Teflon needle valve. The sample was loaded into the cell in the dry box. The cell was then closed, attached to the vacuum line, and evacuated. Dry methanol solvent was vacuum-distilled into the cell. The needle valve was then closed, and the cell was removed from the vacuum line and the spectrum recorded. Conventional, capped cells were used for the spectra of samples dissolved in DMSO. Pre-purified nitrogen was bubbled through the DMSO for thirty minutes immediately prior to its use. Exposure of the solutions to air was minimized. None of the solutions became cloudy during the experiment as would be expected if decomposition had occurred. The capped cells were also used for spectra of samples dissolved in methanol/hydrochloric acid (ca. 1.2 M). No attempt was made to avoid exposure of these solutions to air.

SYNTHESES

Preparation of $[(Mo_6Cl_8)(SCH_2CH_3)_4(C_5H_5N)_2]$ - Compound I

The equation for this preparation is:

$$[(Mo_6Cl_8)Cl_4] + 4\ NaSCH_2CH_3 \longrightarrow Mo_6Cl_8(SCH_2CH_3)_4 + 4\ NaCl$$

1.00 g Mo_6Cl_{12} and 0.34 g $NaSCH_2CH_3$ (1:4 mole ratio) were weighed out in the dry box. These reagents were added to a reflux flask along with a magnetic stirring bar. The reflux flask was a one-piece combination of a round-bottom flask and water-cooled condenser, equipped with a 24/40 ground glass joint and a vacuum-tight Teflon needle valve. The flask was capped, brought out of the dry box and attached to the vacuum line. After evacuating the flask, dry methanol was vacuum distilled into it. The flask was warmed to room temperature, closed off, and attached to the Schlenk line. Nitrogen was bled in and was maintained at a slight positive pressure by using a mercury bubbler. The reaction slurry was magnetically stirred, and heated to refluxing temperature with a mineral oil bath. The reactants were refluxed ca. eight hours. During this time, the color changed from yellow to orange. Sometimes sodium chloride precipitated from the reaction mixture, depending on the volume of solvent used. After refluxing, the reaction mixture was cooled to room temperature and filtered under a nitrogen atmosphere. The flask containing the orange filtrate was capped and attached to the vacuum line. Methanol was removed by vacuum distillation, leaving a solid orange residue in the flask. This evacuated flask was taken into the dry box and attached to a modified Soxhlet extractor. The entire apparatus was attached to the vacuum line and evacuated. Some dry pyridine (ca. 30 ml) was vacuum distilled into the extractor. Separation was achieved since sodium chloride is insoluble in pyridine; the product dissolved forming a deep red solution. Continuous extraction was not possible since the sodium chloride was so finely divided that it always clogged the sintered glass filter. After most of the product had been extracted away from the solid reaction residue, the pyridine was distilled off under vacuum. The product was isolated as a shiny red glass.

X-ray powder photographs of several samples of the product invariably indicated that they were amorphous. Calculated and experimentally observed elemental compositions are:

	Found	Calculated Values	
		$[(Mo_6Cl_8)(SCH_2CH_3)_4(C_5H_5N)_2]$	$[(Mo_6Cl_8)(SCH_2CH_3)_4(C_5H_5N)_2]\cdot(C_5H_5N)$
Mo	44.65	45.62	42.92
Cl	21.77	22.48	21.15
C	18.90	17.13	20.60
H	2.16	2.40	2.63

The experimental Cl/Mo ratio is 1.32 (1.33 calculated).

Preparation of $Na_2[(Mo_6Cl_8)(SCH_2CH_3)_6]\cdot 3(C_5H_5N)$ - Compound II

The equation for the first step of this preparation is:

$$[(Mo_6Cl_8)Cl_4] + 6\ NaSCH_2CH_3 \longrightarrow Na_2[(Mo_6Cl_8)(SCH_2CH_3)_6] + 4\ NaCl$$

1.00 g Mo_6Cl_{12} and 0.51 g $NaSCH_2CH_3$ (1:6 mole ratio) were used for the preparation. Except for the amount of sodium ethyl mercaptide, the synthesis was identical to that of compound I until the isolation of the product from the pyridine extraction. This compound is also quite soluble in pyridine. However, slow removal of the pyridine under vacuum yielded a red, crystalline product. Some ether was distilled in with the product and the remaining pyridine solution to improve the yield. $Na_2[(Mo_6Cl_8)(SCH_2CH_3)_6]\cdot 3(C_5H_5N)$ was isolated as an orange powder. Calculated and observed elemental compositions are:

	Found	Calculated Values $Na_2[(Mo_6Cl_8)(SCH_2CH_3)_6]\cdot 3(C_5H_5N)$
Mo	38.34	38.14
Cl	18.51	18.79
C	21.78	21.49
H	3.02	3.01

The Cl/Mo ratio is 1.31 (1.33 calculated). X-ray powder photographs indicate this derivative is crystalline. A listing of the estimated intensities and calculated d-spacings is presented in Table 1.

Table 1. X-ray powder pattern data for $Na_2[(Mo_6Cl_8)(SC_2H_5)_6]\cdot 3(C_5H_5N)$[a,b]

d-spacing (Å)	Est. Intensity	d-spacing	Est. Intensity
11.04	vvs	2.55	vvw
9.95	vvs	2.50	vvw
8.82	vs	2.39	vvw
6.16	vs	2.35	vw
5.45	s	2.28	vvw
4.81	m	2.23	vvw
4.64	m	2.18	vw
4.41	vvw	2.14	w
4.11	w	2.05	vw
3.42	vvw	2.00	vvw
3.32	vvw	1.95	vw
3.08	w	1.88	vvw
3.01	w	1.86	vvw
2.79	vvw		

[a] Data obtained with Cu K_α radiation.

[b] Abbreviations (in this and subsequent tables): s, strong; m, medium; w, weak; v, very; br, broad; sh, shoulder.

RESULTS AND DISCUSSION

Infrared Spectra

The infrared spectra were studied with the intent of obtaining the maximum amount of characterizing data for the two compounds. Table 2 lists the absorptions of compounds I and II in the range from 2000 to 200 cm^{-1}. Figure 1 is a reproduction of the spectral traces of both compounds. The spectra indicate pyridine is a component of both compounds. Gill <u>et</u> <u>al</u>. have shown that it is possible to deduce from the infrared spectra of complexes containing pyridine whether pyridine is coordinated to the metal (50). One indicator is a shift of the unbound molecule's strong absorption at 1578 cm^{-1} to <u>ca</u>. 1600 cm^{-1}. In compound I, this band appears at 1601 cm^{-1}. This indicates that pyridine is coordinated to the molybdenum cluster. In compound II, the cluster of peaks between 1570 and 1611 cm^{-1} resembles the corresponding peaks of compound I more closely than those of free pyridine. This may be caused by lattice effects. However, the major band's location at 1588 cm^{-1} is not significantly shifted from the free molecule. It may be concluded that pyridine is not bound to the cluster in compound II. Other criteria support these conclusions. A band occurring at 601 cm^{-1} in pyridine is shifted to <u>ca</u>. 625 cm^{-1} upon coordination. In compound I, this strong band

Table 2. Infrared data for $[(Mo_6Cl_8)(SC_2H_5)_4(C_5H_5N)_2]$ - compound I, and $Na_2[(Mo_6Cl_8)(SC_2H_5)_6]\cdot3(C_5H_5N)$ - compound II (2000 - 200 cm^{-1})

I	II	Comments
	1611 w	
1601 w-m	1588 m-s	(1593)[a] 1598 py
1572 sh	1570 w-m	(1578) 1582 py
1560 sh		
1482 sh	1482 w	(1478) 1484 py
1460 w	1455 m,br	Nujol
1443 m	1440 s	(1436) 1439 py
1375 m-s	1375 m-s	Nujol
1309 vw,br(?)		1309 NaSEt
1246 s	1249 s	1258 NaSEt
1214 m-s	1213 w	(1217) 1218 py
1152 w,br	1146 w-m	(1145) 1146 py
1109 vw(?)		
1062 s	1062 w-m	(1067) 1068 py
1041 m-s	1040 sh	1033 NaSEt
1024 m-s	1029 s	(1031) 1030 py
1009 m-s	1014 sh	1015 NaSEt
988 vw	993 w-m	(991) 990 py
964 m	963 m	968 NaSEt
874 vw(?)	879 w	
854 w(?)		
805 vw(?)	797 w(?)	
754 vs	744 s	(747) 747 py
		745 NaSEt

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[a] Values in parentheses are published values; all others were recorded in this work.

Table 2. (Continued)

I	II	Comments
720 vw	715 vw,sh	
694 vs	701 vs	(700) 702 py
678 sh		
664 vw,sh		
640 m-s	654 m-s	660 NaSEt
600 vw,br	610 m-s	(601) 603 py
	403 m	(403) 406 py
390 w-m		ν(Mo-S)
380 } doublet	375 m-s	ν(MO-S)
362 vw,sh		
340 sh	340 s	(350) (Mo_6Cl_8)
319 s	302 s	(300) (Mo_6Cl_8)
294 sh	292 sh	
282 sh		
275 sh		
236 vw(?)	222 w	(220) (Mo_6Cl_8)

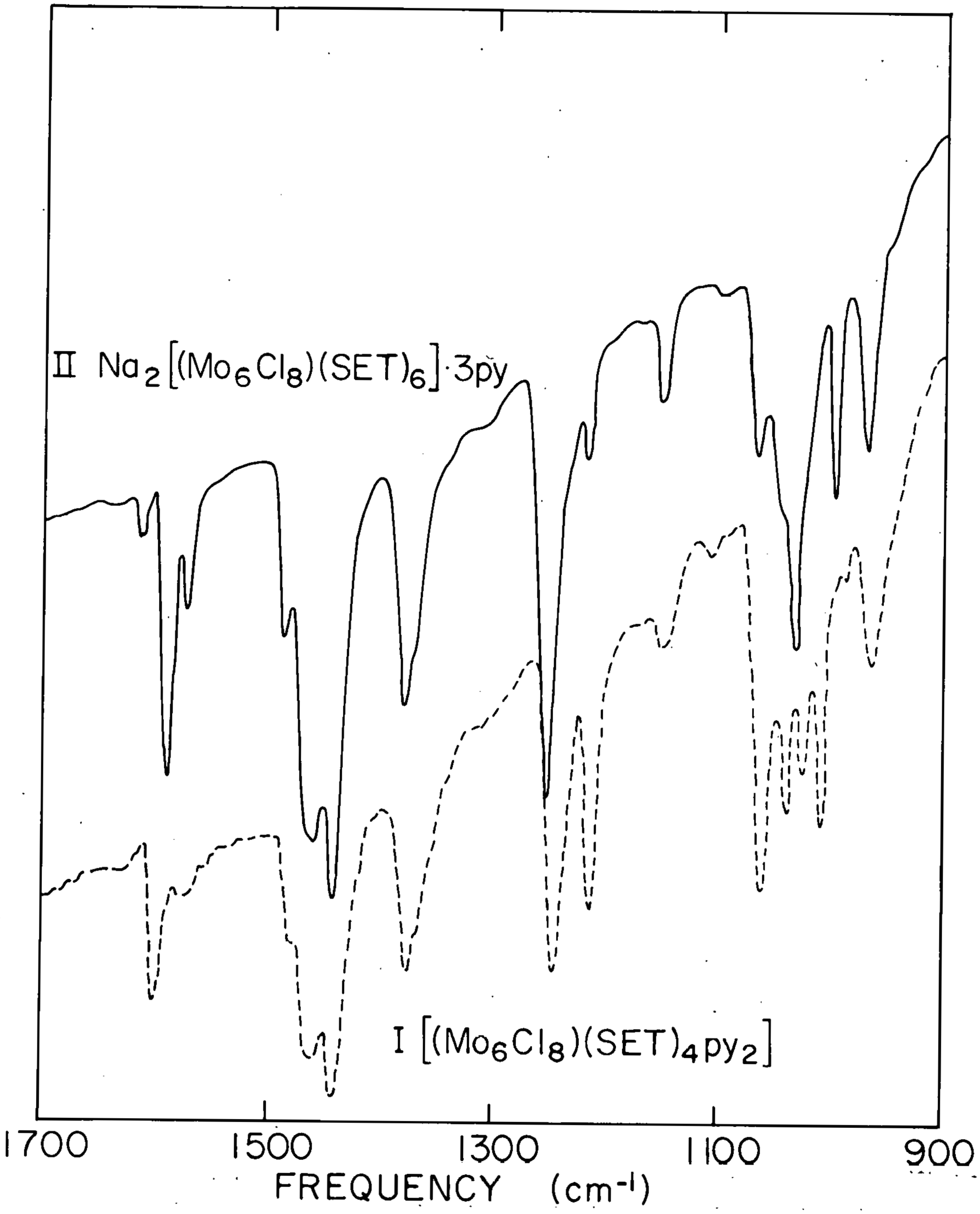

Figure 1. Infrared spectra of compounds I and II

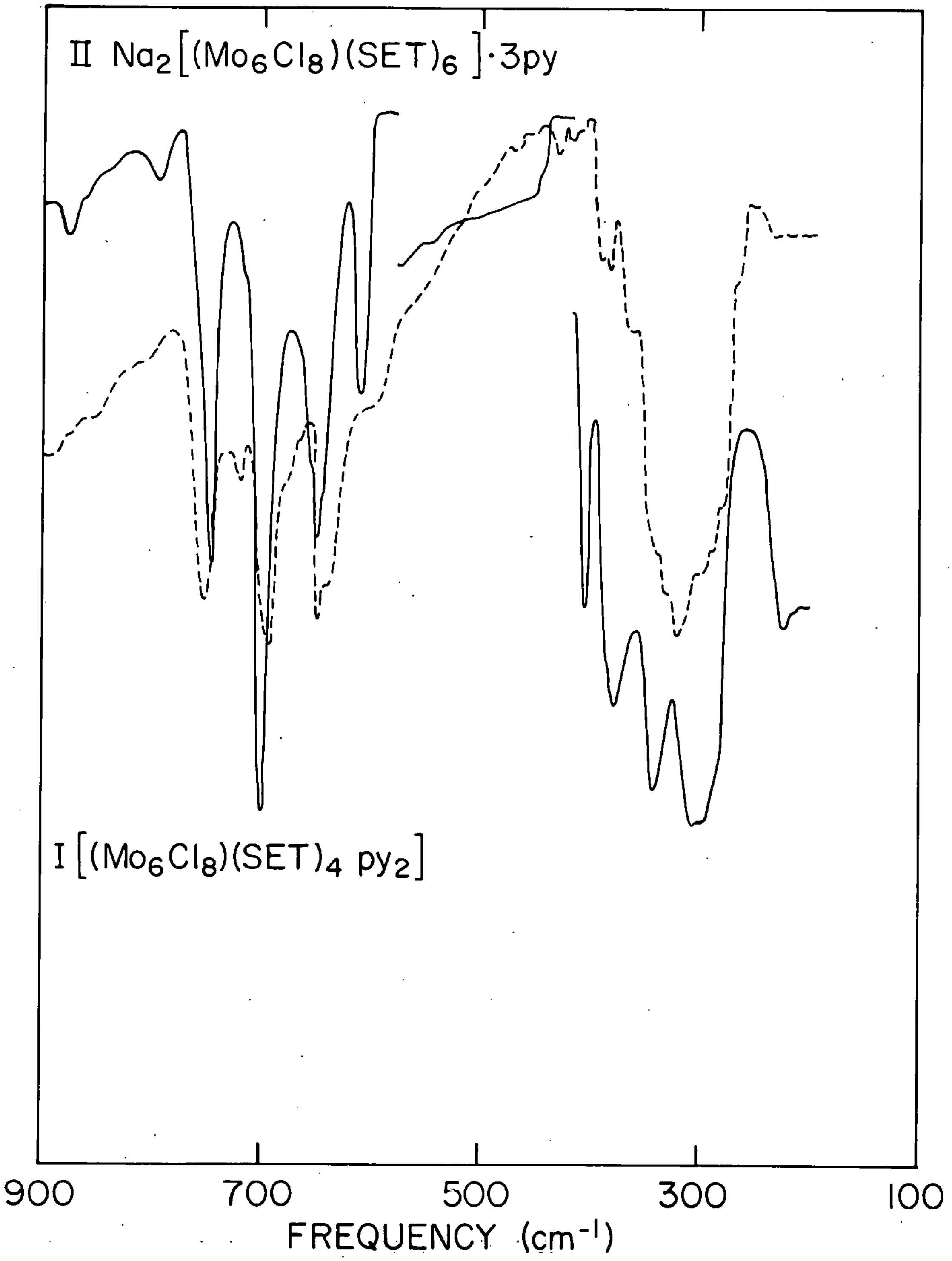

Figure 1. (Continued)

is not seen. In compound II, a strong band is found at 610 cm^{-1}. Also, a medium strength band at 403 cm^{-1} in pyridine shifts to ca. 420 cm^{-1} after coordination. A strong band occurs at 403 cm^{-1} in compound II; no comparable band is found for compound I.

Several studies of the vibrational spectra of the hexanuclear molybdenum and tungsten dihalides have been made (51,52). They compared the spectra of a large number of closely related derivatives to aid in making specific assignments. No such scheme is possible here. Instead, these authors' assignments and data were compared with the spectra of the two mercaptide cluster complexes. The purpose of this was to determine whether the $(Mo_6Cl_8)^{4+}$ cluster is intact in these complexes. The spectra of compounds I and II are quite complex between 300 and 400 cm^{-1}. (Mo_6Cl_8) absorptions, as well as a ν(Mo-S) stretching band are expected in this region. Therefore, the assignments for these bands are very tentative.

Five vibrational modes are expected to be infrared-active for an octahedral $[(Mo_6Cl_8)Y_6]$ cluster. There are two (Mo_6Cl_8) stretches, a (Mo-Y) stretch, a (Mo-Mo) stretch, and a (Cl-Mo-Y) bend. None of these modes are completely independent. Some mixing does occur (51). Nevertheless, bands occur consistently near 330 and 220 cm^{-1} in a variety of $[(Mo_6Cl_8)L_6]$ complexes (52). These two absorptions have been designated as the two (Mo_6Cl_8) stretching modes. The band at *ca*. 330 cm^{-1} is often split into two strong bands at *ca*. 300 and 350 cm^{-1}. This is due to a reduction in symmetry usually caused by interaction with ions in the lattice. In these two mercaptide derivatives of the cluster, the alkyl tails of the mercaptide ligands could conceivably lower the overall symmetry to C_1. As in previous studies, the contribution of nonlinear terminal ligands to the cluster's overall symmetry is neglected. In compound II, $Na_2[(Mo_6Cl_8)(SCH_2CH_3)_6]\cdot 3py$, the cluster unit should have octahedral symmetry. However, the two Na^+ ions and three pyridine molecules in the lattice may lower this symmetry. Compound I, $[(Mo_6Cl_8)(SEt)_4py_2]$, has at most D_{4h} symmetry. This lower symmetry should cause splitting of the infrared bands. In a series of $[(W_6Cl_8)L_4]$ complexes, this splitting was observed in the spectra of crystalline samples (51). However, it was not in the spectra of amorphous samples of the same compounds. Apparently, the terminal ligands surrounding the cluster core in the amorphous samples are disordered, resulting in closer approach to octahedral symmetry. All samples of compound I were amorphous.

Compound I has a very strong, broad absorption at 319 cm^{-1}, with many shoulders on it. It resembles the 332 cm^{-1} band in a spectrum of amorphous Mo_6Cl_{12}. No well-defined absorption occurs in the 220 cm^{-1} region for compound I. Compound II has a much sharper spectrum in this region. Two strong, completely resolved bands at 302 and 340 cm^{-1} are probably due to (Mo_6Cl_8) stretching. The splitting in this case may be due to the previously mentioned lattice effects. A well-defined band occurs at 222 cm^{-1} in the spectrum of compound II, and is assigned to the other (Mo_6Cl_8) vibration. It resembles the 221 cm^{-1} band in a spectrum of an amorphous Mo_6Cl_{12} sample. The infrared spectra support the retention of the $(Mo_6Cl_8)^{4+}$ cluster core in these mercaptide complexes.

Assignment of the bands arising from ethyl mercaptide absorptions is based primarily on the spectrum of a mulled sample of $Na^+SCH_2CH_3^-$. Bands due to ethyl mercaptide are clearly visible in the spectra of compounds I and II. Several $(Mo_6Cl_8)^{4+}$ compounds containing anions not coordinated to the cluster are known (38). It is not possible to determine from the frequencies associated with ethylmercaptide's absorptions whether it is coordinated. Nevertheless, the infrared spectra do provide shaky proof that these mercaptide ions are coordinated. After all the other major bands have been assigned, a band in the spectrum of each compound remains to be accounted for. In II, this band occurs at 375 cm^{-1}; in I, it is split and occurs at 390 and 380 cm^{-1}. These are tentatively assigned to the (Mo-S) stretching mode. These frequencies are somewhat lower than ν(Mo-S) = 450 cm^{-1} in Mo(SCH$_3$)$_3$ (53). In this latter compound, molybdenum is in the 3+ oxidation state; in compounds I and II, it is in the 2+ state. The frequency assigned to the terminal chloride-Mo stretch in Mo_6Cl_{12} should also be a good standard for comparison. A band at 250 cm^{-1} is usually designated as ν(Mo-Cl$_t$). However, there is some question of the validity of this assignment. This frequency is quite low when compared with ν(Mo-Cl$_t$) = 340 cm^{-1} in $[(Mo_6Br_8)Cl_4]$ (52) and ν[W-Cl$_t$] = 305 cm^{-1} in $[(W_6Cl_8)Cl_4]$ (51). There is reason to believe ν(Mo-Cl)$_t$ in Mo_6Cl_{12} may be hidden by the (Mo_6Cl_8) absorption at 330 cm^{-1}. If a value of <u>ca</u>. 330 cm^{-1} is assumed for ν(Mo-Cl$_t$), the assigned values for ν(Mo-S) in compounds I and II seem too high.

This analysis of the infrared spectra of these two compounds indicates:

a) both compounds probably contain the $(Mo_6Cl_8)^{4+}$ cluster;

b) pyridine is coordinated to the cluster in compound I but not in II;

c) both compounds contain ethyl mercaptide;

d) ethyl mercaptide is probably coordinated to the cluster in both cases.

Electronic Spectra

The electronic spectra were studied with the intent to provide additional support for the presence of the $(Mo_6Cl_8)^{4+}$ cluster in both compounds. Fergusson et al. observed bands at 317, 342, and 359 nm in a solid state reflectance spectrum of a $[(Mo_6Cl_8)Cl_6]^{2-}$ salt (39). After comparing the spectra of a variety of cluster derivatives, substituted in the terminal and/or bridging positions, he concluded that the 317 nm band may be assigned to the $(Mo_6Cl_8)^{4+}$ cluster core; its position changes only when the bridging halides are exchanged. The other two bands depend on the terminally bound halides. Nonhalo terminally bound ligands seem to have no effect on any of the bands. The mode of bonding of the terminal halides (bridging between two clusters or bound to one cluster) also has no effect on the spectrum. Thus, $Cs_2[(Mo_6Cl_8)Cl_6]$, $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$ and $[(Mo_6Cl_8)Cl_4py_2]$ all have essentially identical spectra. Mackay found bands at 224, 312, and 336 nm in the spectrum of an ethanol solution of $Cs_2[(Mo_6Cl_8)Cl_6]$ (52). The molar absorptivity of the band at 224 nm indicates it probably is a terminal ligand-cluster charge transfer band.

Since solid samples of compounds I and II decompose in the air, all spectra were recorded of samples in solution. Compound I, $[(Mo_6Cl_8)(SEt)_4py_2]$, is insoluble in methanol. It dissolved in DMSO, forming a clear yellow solution.

Compound II, $Na_2[(Mo_6Cl_8)(SEt)_6]\cdot 3py$, dissolved in both solvents, yielding clear yellow solutions. All three sample solutions gave identical results in scans from 600 to 300 nm. They began to absorb at 480 nm; the absorbance kept increasing all the way to 300 nm. However, no discrete peaks appeared. Since DMSO itself absorbs strongly below 300 nm, only the methanol solution of compound I was scanned further. Absorbance was still increasing below 300 nm. There is probably a charge transfer band here. None of the cluster's characteristic absorptions between 300 and 350 nm showed up in any of these spectra.

Although these efforts were discouraging, another approach was taken to show that the $(Mo_6Cl_8)^{4+}$ cluster is intact in these compounds. Samples of both compounds were weighed out from the dry box and dissolved in 1.2 M hydrochloric acid in methanol. Gentle heating was required to get compound II into solution. A sample of $[(Mo_6Cl_8)Cl_4]$ was similarly treated. All three solutions were clear yellow. Their spectra were scanned from 600 to 300 nm. As the data in Table 3 show, all three spectra were identical. Since it is known $[(Mo_6Cl_8)Cl_4]$ is converted to $[(Mo_6Cl_8)Cl_6]^{2-}$ under these conditions, compounds I and II reacted with the hydrochloric acid yielding this same species. The spectra are quite similar to those reported by Mackay (52) and Fergusson *et al.* (39) for $[(Mo_6Cl_8)Cl_6]^{2-}$ salts, except the band at

Table 3. Electronic absorption band parameters (300 - 600 nm)[a]

$[(Mo_6Cl_8)Cl_4]$		$[(Mo_6Cl_8)(SC_2H_5)_4(C_5H_5N)_2]$		$Na_2[(Mo_6Cl_8)(SC_2H_5)_6]\cdot 3(C_5H_5N)$	
λ, nm	ε^b	λ, nm	ε^b	λ, nm	ε^b
345	2.9	345	2.8	345	3.1
315	3.1	308	3.2	311	3.4

[a] Spectra obtained in methanol/hydrochloric acid solutions.

[b] Molar extinction coefficients are in units of 10^3 liter mole^{-1} cm^{-1}.

359 nm observed in Fergusson's study was not found. However, the band which Fergusson et al. noted as characteristic of the $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster was observed in these spectra. The slight discrepancies between these sets of data can probably be attributed to solvents and procedures used in recording the spectra.

As was stated above, the $[(Mo_6Cl_8)Cl_6]^{2-}$ cluster is present in methanolic solutions of compounds I and II which have been acidified with hydrochloric acid. The smell of liberated ethyl mercaptan is apparent as the compounds are dissolving; the mercaptide ligands are replaced by chloride, and are converted to ethyl mercaptan in the acidic solution. It may be concluded that some form of the $(Mo_6Cl_8)^{4+}$ cluster is a structural unit of compounds I and II. It is very unlikely that the $(Mo_6Cl_8)^{4+}$ cluster should be formed from a noncluster entity in methanol/hydrochloric acid solution with gentle heating. The absence of any bands characteristic of $(Mo_6Cl_8)^{4+}$ in the spectra of compounds I and II in dry DMSO or methanol has two possible explanations:

1) The peaks have been shifted to wavelengths below 300 nm, where they are hidden by a charge transfer band.
2) The charge transfer band is shifted to lower energy in compounds I and II than in previous cluster compounds. The tail between 300 and

400 nm is intense enough to obscure the $(Mo_6Cl_8)^{4+}$ bands there.

The first explanation is less likely. Since it is believed the band at 317 nm is characteristic of the $(Mo_6Cl_8)^{4+}$ cluster and is independent of the terminal ligands, this implies the cluster has been altered. For example, one or more of the bridging halides may have been substituted by a mercaptide. The other peaks may be shifted due to the mercaptide ligands in terminal positions. When reacted with methanol/hydrochloric acid, the hypothesized cluster's bridging mercaptides are replaced by chloride. The characteristic spectrum of $[(Mo_6Cl_8)Cl_6]^{2-}$ would then be observed. Much harsher reaction conditions and/or much stronger nucleophiles up to now have been required to replace a bridging halide in nonbasic media (40,42). However, nothing is known about the reactivity of a mercaptide in a bridging position. Nannelli and Block were able to replace four bridging methoxide ligands with phenoxide ligands at 120°C in solution.

The second explanation is more plausible. The shift of the charge transfer band to lower energy might be caused by the terminal mercaptide ligands. They are softer bases than chloride, and so they might cause such a shift. The molar absorptivity of a spectrum of compound I in DMSO between 300 and 350 nm is an order of magnitude larger than found by Mackay in this region. This suggests the characteristic cluster bands are covered. In methanol/hydrochloric acid solution, the mercaptide ligands would be displaced by chloride; the absorbing species would be $[(Mo_6Cl_8)Cl_6]^{2-}$. Further support for the formulation of compounds I and II as $(Mo_6Cl_8)^{4+}$ clusters is provided by their elemental analysis, which consistently indicate a Cl/Mo ratio of 1.33, and their infrared spectra.

CONCLUSION

Additional insight into the structures of compounds I and II can be gained from consideration of their chemical behavior. The solubility of compound I in a variety of solvents was checked in a futile attempt to prepare crystalline samples. It is insoluble in weakly polar and nonpolar solvents. However, compound I dissolves in the strongly donating solvents pyridine, DMSO and DMF, and also in acidified polar solvents. For example, although it is insoluble in neat methanol or acetonitrile, compound I dissolves in both if they are acidified with nitric or hydrochloric acids. Compound II is soluble in these solvents, and also dissolves in neat methanol or acetonitrile. Although compound II dissolves in water, compound I is not even wetted by it.

Its amorphism and insolubility in most common solvents suggest compound I might be polymeric. There are several points of similarity between compound I and $[(Mo_6Cl_8)Cl_4]$. $[(Mo_6Cl_8)Cl_4]$ dissolves in a limited number of solvents, but its solubility in methanol is greatly enhanced by the addition of hydrochloric acid. This behavior reflects a polymeric structure where each $(Mo_6Cl_8)^{4+}$ cluster is linked to other clusters through four doubly-bridging terminal chlorides. For this reason, the structural formula is best writted as $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$ (17). Unless $[(Mo_6Cl_8)Cl_4]$

is formed or annealed at high temperature, it is amorphous. Its amorphism is attributed to disorder caused by the random formation of the intercluster bridges. By analogy, it seems likely that the clusters of compound I are linked in a disordered way by mercaptide bridges. Attempts to promote crystallization by annealing lead to decomposition of this compound. However, mercaptides do frequently serve as doubly-bridging ligands, as for example in $[Ni_6(SR)_{12}]$ (54) and $((CH_3)_4N)_2](CoSPh)_4(SPh)_6]$ (55). This propensity for bridging can lead to more extensive polymerization, as in the case of $Mo(SCH_3)_3$ (53).

Extending the analogy, amorphous $[(Mo_6Cl_8)Cl_{4/2}Cl_2]$ reversibly absorbs moisture from the air to form $[(Mo_6Cl_8)Cl_4(H_2O)_2]$, a crystalline compound (37). This amorphous to crystalline transformation is probably facilitated by a more ordered arrangement of the cluster units in the dihydrate, permitted by the destruction of the intercluster bridges. Compound I also absorbs moisture from the air. However, this process is irreversible, and the product is amorphous. The obvious smell of ethyl mercaptan during exposure of compound I to air indicates hydrolysis as in the process

$$Mo\text{-}SCH_2CH_3 + H_2O \longrightarrow Mo\text{-}OH + CH_3CH_2SH\ .$$

It is not necessary to postulate intercluster mercaptide bridges to rationalize the amorphism of compound I. If the known structural features of compound I are contrasted with those of crystalline compound II, another explanation is apparent. Pyridine is coordinated to the cluster in compound I. This bulky ligand probably hinders efficient packing. In compound II, the uncoordinated pyridine molecules are free to occupy optimal lattice positions. However, this rationalization does not account for the differing solubility characteristics of compounds I and II as well as the postulated intercluster mercaptide bridges.

The analytical data indicate there are two pyridine molecules per cluster in compound I. The infrared spectrum indicates both these pyridine molecules are coordinated. To accommodate these facts, and the possibility of intercluster mercaptide bridges, compound I should be formulated as $[(Mo_6Cl_8)(C_5H_5N)_2(SC_2H_5)_{x/2}(SC_2H_5)_{4-x}](SC_2H_5)_{x/2}$; $x = 0,2,4$. The existing data are not sufficient to suggest the exact formula. More extensive characterization of the compound in the solid state would be required. Since compound I is amorphous, it is doubtful whether this would be worthwhile.

It can be confidently stated that the correct formula of compound II is $Na_2[(Mo_6Cl_8)(SC_2H_5)_6]\cdot 3(C_5H_5N)$.

SUGGESTIONS FOR FUTURE WORK

The most important goal for any extension of this work is the preparation of a series of crystalline, mercaptide-substituted clusters. Mercaptides with alkyl chains shorter than ethyl might be the key. Preparation of cluster compounds with CH_3S^- or HS^- ligands might be accomplished by a route similar to the one used in this work. Reaction of compounds I and II with these two ligands might also lead to the desired result.

Synthetic efforts should also include attempts to prepare clusters more mercaptide-rich than compounds I and II. Preliminary attempts to make $[(Mo_6(SEt)_8)(SEt)_6]$ produced an amorphous brown solid. This material still contained _ca_. 12 percent chloride. A solvent with a boiling point higher than that of methanol was required.

The oxidation state of molybdenum in all of the hexanuclear molybdenum chalcogenide phases is greater than 2+. For this reason, reactions between a molybdenum dihalide cluster and an oxidizing "mercaptide" ligand, such as CH_3SSCH_3, would be interesting.

Thermal exchange of the bridging and terminal ligands (halide-mercaptide, mercaptide-mercaptide') of a mercaptide-substituted cluster might lead to more new and potentially interesting compounds.

More extensive characterization of all these compounds in the solid state would be necessary. Far infrared, Raman, and photoelectron spectroscopy might all provide valuable assistance.

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