Molybdenum(II) Cluster Compounds Involving Alkoxy Groups[1]

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Molybdenum(II) halides readily react with alcoholic solutions of either sodium methoxide or ethoxide at room temperature to give crystalline coordination compounds of the type $Na_2[(Mo_6X_8)(OR)_6]$ in which the $Mo_6X_8{}^{4+}$ cluster behaves like a hexacoordinate coordination center. More vigorous treatment of molybdenum(II) chloride with sodium methoxide in methanol yields the crystalline compounds $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in which both ligand and cluster chloride ions are replaced by methoxy groups. This compound appears to contain the cluster $Mo_6(OCH_3)_8{}^{4+}$ analogous to the well-known $Mo_6X_8{}^{4+}$ on the basis of magnetic properties, oxidation state of the molybdenum, proton magnetic resonance, conductivity, molecular weight, and infrared spectra.

Introduction

Molybdenum(II) halides, perhaps the best known metal cluster compounds,[2] can be formulated as $(Mo_6\text{-}X_8)X_2X_{4/2}$ (where X = Cl, Br, I) to indicate that they consist of stable $Mo_6X_8{}^{4+}$ units surrounded by ligand halide ions, part of which bridge between clusters. A considerable amount of work has been done on their preparation,[3] structure,[4] bonding,[5-9] complex formation, and ligand-exchange reactions.[3,10-14] Indeed, the preparation of a large number of compounds containing molybdenum(II) halide clusters has been made possible by the readiness with which the ligand ions can be replaced by different ions or neutral ligands.

In all of the derivatives prepared the $Mo_6X_8{}^{4+}$ cluster is a persisting species which seems to be stable under a variety of conditions, and its halogen atoms have been considered virtually unreactive. However, the cluster is disrupted by strong bases, presumably through the formation of unstable substituted halomolybdenum(II) clusters. A controlled hydroxide attack gave products believed to contain hydroxide ions in the cluster in place of some halide ions.[15] The products were too unstable for a profitable study, but they were converted to more stable compounds by treatment first with hot hydrochloric or hydrobromic acid and then with tetraethylammonium halide. The resulting crystalline compounds appear to have one halogen in the cluster replaced by one hydroxyl group. Subsequent reports[16]

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deal with the kinetics of the alkaline hydrolysis. We are unaware of any other studies of the replacement of the halogen in the cluster with different groups. The purpose of the work reported here was to investigate the possibility of substituting alkoxide ions for halide ions inside the $Mo_6X_8{}^{4+}$ cluster.

Experimental Section

Materials.—Molybdenum powder and molybdenum(V) chloride were purchased from Climax Molybdenum Co. and used without further purification. Reagent grade sodium was also used as such. Methanol for reactions, conductivity, molecular weight, and proton magnetic resonance studies was dried by distillation over magnesium methoxide in a stream of nitrogen. Commercial absolute ethanol was further dehydrated by refluxing it with sodium and ethyl phthalate for a period of 2 hr and then distilling it in a stream of nitrogen. Ether and toluene were dried over sodium and distilled under nitrogen. The high-purity nitrogen used was sufficiently oxygen free that no further purification was required.

Molybdenum(II) Halides.—The preparation of molybdenum(II) chloride was based on known methods;[3a] however, some modifications were introduced in order both to simplify the procedure and to increase the yield of pure products to nearly theoretical. A typical preparation involves heating to red heat successive zones of a 125-cm Vycor tube containing an evenly distributed, intimate mixture of 150 g of 100-mesh molybdenum powder and 50 g of molybdenum(V) chloride as a stream of nitrogen is slowly passed through the tube. After the entire contents of the tube have been heated, the direction of the nitrogen stream is reversed, and the heating zone is passed back along the tube in that direction. The reaction is virtually complete after five or six heating cycles, and the mass in the reaction tube consists almost exclusively of molybdenum(II) chloride and excess molybdenum powder. The chloride is then purified by treating the entire mass with hot hydrochloric acid to dissolve the chloride, which separates as crystalline $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot 6H_2O$ on cooling the filtered solution. The excess molybdenum powder filtered off can be used in another run after it is washed and dried. Heating the chloro acid under vacuum at 200° gives up to 70 g of pure molybdenum(II) chloride.

Molybdenum(II) bromide was prepared by the method of Sheldon[3b] without substantial modifications.

$Na_2[(Mo_6Cl_8)(OCH_3)_6]$.—To a slurry of 60 g (59.9 mmol) of molybdenum(II) chloride in 50 ml of methanol a solution of sodium methoxide, prepared from 11.5 g (0.5 g-atom) of sodium in 150 ml of methanol, was added with stirring. The reaction mixture was heated to refluxing temperature and then filtered hot through a fritted glass. The yellow crystalline methoxy derivative, which separated when the clear solution cooled, was filtered and washed first with ether–methanol solution (9:1) and then with ether. After it was dried at 50° under vacuum, the com-

pound weighed 38.0 g (58%). During all of the operations care was taken to avoid contact with atmospheric moisture. *Anal.* Calcd for $C_6H_{18}Cl_8Mo_6Na_2O_6$: C, 6.60; H, 1.66; Cl, 25.99; Mo, 52.74; Na, 4.21. Found: C, 6.46; H, 1.66; Cl, 25.8; Mo, 52.5; Na, 4.1.

$Na_2[(Mo_6Br_8)(OCH_3)_6]$.—An identical experiment, starting from 2 g of sodium (87 mg-atoms) in 30 ml of methanol and 15 g of molybdenum(II) bromide (9.77 mmol) in 20 ml of methanol, gave 6.7 g (48%) of reddish yellow $Na_2[(Mo_6Br_8)(OCH_3)_6]$. *Anal.* Calcd for $C_6H_{18}Br_8Mo_6Na_2O_6$: C, 4.98; H, 1.25; Br, 44.18; Mo, 39.78; Na, 3.18. Found: C, 5.24; H, 1.43; Br, 43.06; Mo, 40.21; Na, 3.34.

$Na_2[(Mo_6Cl_8)(OC_2H_5)_6]$.—(a) A solution of sodium ethoxide made from 11.5 g of sodium (0.5 g-atom) in 175 ml of absolute ethanol was added, with mechanical stirring, to 60 g of molybdenum(II) chloride (59.9 mmol) in 50 ml of ethanol. The resulting yellow-orange suspension was stirred for about 1 hr and then filtered through a fritted-glass funnel. Addition of 600 ml of ether to the clear solution caused the yellow crystalline ethoxy derivative to precipitate. The product was filtered and washed with ether-ethanol solution (9:1 ratio) and then with ether. After it was dried under vacuum at 50°, the compound weighed 39.5 g (55.9%). During all operations care was taken to avoid contact with atmospheric moisture. *Anal.* Calcd for $C_{12}H_{30}Cl_8Mo_6Na_2O_6$: C, 12.26; H, 2.57; Cl, 24.13; Mo, 48.97; Na, 3.91. Found: C, 12.56; H, 2.82; Cl, 24.1; Mo, 48.2; Na, 4.0.

(b) A solution of 10.8 g of $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ in 250 ml of absolute ethanol was refluxed for 1 hr under a fractionation column, 48 cm long and 2.5 cm in diameter, packed with helices and vacuum insulated. Distillation was then started at the rate of about 20 ml of distillate/hr and continued until a total of 170 ml of solvent had been collected. The slightly cloudy reaction mixture was filtered, 200 ml of toluene was added, and the distillation was resumed until almost all of the alcohol solvent was removed as the azeotrope. The resulting yellow suspension was filtered, and the precipitate was washed with ether. After it had dried, the compound weighed 11.1 g (95.4%). *Anal.* Found: C, 12.81; H, 2.81.

$Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$.—A solution of sodium methoxide prepared from 13 g of sodium (0.565 g-atom) in 250 ml of methanol was added to a slurry of 30 g of molybdenum(II) chloride (29.9 mmol) in 50 ml of methanol with stirring under a slow stream of nitrogen. All of the subsequent operations were also performed under nitrogen. The reaction flask was then placed in an oil bath, and the methanol solvent was completely distilled off by raising the temperature of the oil bath to 150°. After the dry, brown residue cooled, it was treated with 80 ml of methanol, and 100 ml of ether was added to the resulting suspension. The suspension was stirred for about 0.5 hr and filtered to remove 20.15 g of NaCl (calcd, 20.97 g), and 500 ml of ether was added to the clear filtrate. Yellow-brown, crystalline $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ precipitated. It was collected on a fritted-glass funnel and washed with two 25-ml portions of ether containing 5% v/v methanol. The precipitate was then dissolved in a solution of 2 g of sodium in 50 ml of methanol, 50 ml of ether was added, and the reddish brown solution was filtered again. Additional ether (300 ml) gave crystals of the compound in the pure state, which was again collected on a fritted glass and washed with three 15-ml portions of ether containing 3% v/v methanol. After the product was dried at 80° under vacuum, it weighed 11.5 g (36.4%). *Caution: The compound, when dry, ignites if exposed to atmospheric oxygen. It should be handled and stored in dry, oxygen-free nitrogen.* *Anal.* Calcd for $C_{14}H_{42}Mo_6Na_2O_{14}$: C, 15.92; H, 4.01; Mo, 54.51; Na, 4.35; oxidation no., +2. Found: C, 15.63; H, 4.13; (Cl, 0.17); Mo, 55.15; Na, 4.28; oxidation no., +2.2.

The preceding preparation of $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ was repeated with double the amounts and gave 26.5 g of product (41.9%). *Anal.* Found: C, 15.67; H, 3.90; Mo, 54.4; Na, 4.66; oxidation no., +1.8.

Analytical Procedures.—Molybdenum was determined colorimetrically as the yellow peroxide complex in concentrated sulfuric

acid after fusion with sodium carbonate in platinum. The oxidation number of molybdenum was determined by dissolving the sample in acidified iron(III) sulfate solution and titrating the liberated iron(II) ion with dichromate. Halogens were determined by Volhard titration after fusion with sodium carbonate in platinum. Sodium was determined as sodium zinc uranyl acetate after solution of the sample and removal of any insoluble molybdenum oxide, which occasionally formed upon evaporation to dryness. Carbon and hydrogen were determined by standard procedures.

Spectra.—Infrared spectra, in the 800–3000-cm^{-1} range, were recorded with a Perkin-Elmer 337 grating spectrophotometer on either Nujol or hexachlorobutadiene mulls between KBr disks. The mulls were prepared and placed between the disks in a bag filled with dry nitrogen, and the spectra were then immediately recorded. This procedure was found to provide sufficient protection against both atmospheric moisture and oxygen.

Proton magnetic resonance spectra were recorded at 56.4 Mc/sec and 32° with a Varian DP-60 instrument. Samples were prepared and sealed under nitrogen. Tetramethylsilane was used as an internal standard.

Conductivity Measurements.—The conductivity values were measured with a Thomas–Serfass conductance bridge. The solutions were approximately 10^{-3} M and were prepared under nitrogen. Care was taken to avoid contact of the solutions with the atmosphere during the measurements.

Molecular Weight Measurements.—Molecular weights were determined in methanol at 40° with a Hitachi Perkin-Elmer Model 115 thermoelectric molecular weight apparatus calibrated with biphenyl. Concentrations of the solutions were in the range 10^{-2}–10^{-3} M. The solutions were prepared under nitrogen, and contact with the atmosphere was avoided during the measurements.

Magnetic Measurements.—Magnetic susceptibilities were measured by the Gouy method using a magnetic balance made from a Varian magnet and a modified Mettler H16 balance. Samples were prepared and sealed under nitrogen. The sample tube was calibrated with $Hg[Co(NCS)_4]$ and freshly distilled water.

Results and Discussion

General.—At room temperature both molybdenum(II) chloride and bromide react with excess sodium methoxide in methanol to yield mixtures from which crystalline $Na_2[(Mo_6X_8)(OCH_3)_6]$ eventually separates. The chloride undergoes an analogous reaction with sodium ethoxide, and it appears likely that this kind of reaction will take place between any molybdenum(II) halide and a variety of alkoxides in appropriate alcohols. In some cases alcohol interchange represents a convenient synthetic route to alkoxides of this type as indicated by the preparation of $Na_2[(Mo_6Cl_8)(OC_2H_5)_6]$ from the methoxide analog and ethanol.

When a mixture of molybdenum(II) chloride and excess sodium methoxide in methanol is heated to dryness at 150°, however, the reaction product is completely free of chloride ions and appears to be $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$. It can be obtained in yields of pure, recrystallized product as high as 50%.

The relatively easy replacement of the ligand halide ions with alkoxide ions is not surprising in view of their known lability. The resulting halocluster alkoxides possess most of the chemical properties of typical metal alkoxides.[17] They are sensitive to moisture and react with hydrohalic acids to re-form molybdenum(II) hal-

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ides. The molar conductivities of approximately 10^{-3} M solutions in either methanol or ethanol given in Table I are appropriate for 2:1 electrolytes, and the molecular weights of the methoxy derivatives in methanol (Table I) are about one-third of the formula weight. These data in conjunction with the diamagnetism of the compounds are strong evidence that the halocluster alkoxides reported here should be formulated $Na_2[(Mo_6X_8)(OR)_6]$ to represent a structure in which the cluster acts as a coordination center with six ligands bonded to it. Supporting infrared and proton magnetic resonance data will be presented later.

TABLE I
CONDUCTIVITY AND MOLECULAR WEIGHT DATA
FOR $Na_2[(Mo_6X_8)(OR)_6]$ IN ROH

X	R	Λ_M	Mol wt	Form. wt/mol wt
Cl	CH_3	144	424	2.6
Br	CH_3	154	453	3.2
OCH_3	CH_3	142	347	3.0
Cl	C_2H_5	53		

Under more rigorous conditions all of the halide ions, both in ligand form and in the cluster, are replaced by methoxide ions, and a product which is pyrophoric when dry is formed. It can be handled in a nitrogen atmosphere, stored without appreciable decomposition, and appears to possess some of the chemical and physical properties of the other methoxides. It is diamagnetic, and the molybdenum is in the $+2$ oxidation state. The conductivity and molecular weight reported in Table I are comparable to those of the halocluster alkoxides and suggest that the compound should be formulated Na_2-$[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ with methoxy groups integral to the cluster. Infrared and proton magnetic resonance, as will be seen, also support this formulation. In addition, some methoxy groups in the compound appear more reactive than others, in agreement with the two kinds of methoxy groups, ligand and cluster, in the proposed formula.

Reaction between molybdenum(II) chloride and sodium ethoxide in ethanol under conditions similar to those employed for the synthesis of $Na_2[\{Mo_6(OCH_3)_8\}$-$(OCH_3)_6]$ gave a product which appears to be its ethoxide analog. However, the product was not obtained in sufficient purity for definitive study.

Infrared Spectra.—Infrared spectra for $Na_2[(Mo_6$-$Cl_8)(OCH_3)_6]$ and $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in two regions are reproduced in Figures 1 and 2. The CO stretching absorptions of both compounds appear as strong peaks in the 1000–1100-cm^{-1} range, and the CH_3 rocking absorptions, as weaker peaks between 1100 and 1200 cm^{-1} in Figure 1. The splitting of these absorption bands on passing from $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ to $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ is corroboration for the presence of methoxy groups in different bonding situations in the latter and suggests that only one type of methoxy group is present in the former. For both compounds the CH deformations appear at about 1450 cm^{-1} in Figure 2, and there is a series of peaks between
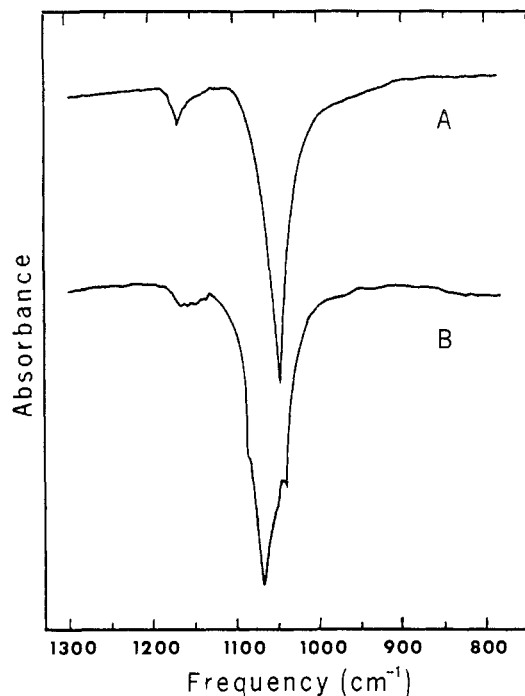
Figure 1.—Infrared spectra in Nujol mull: A, $Na_2[(Mo_6Cl_8)$-$(OCH_3)_6]$; B, $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$.
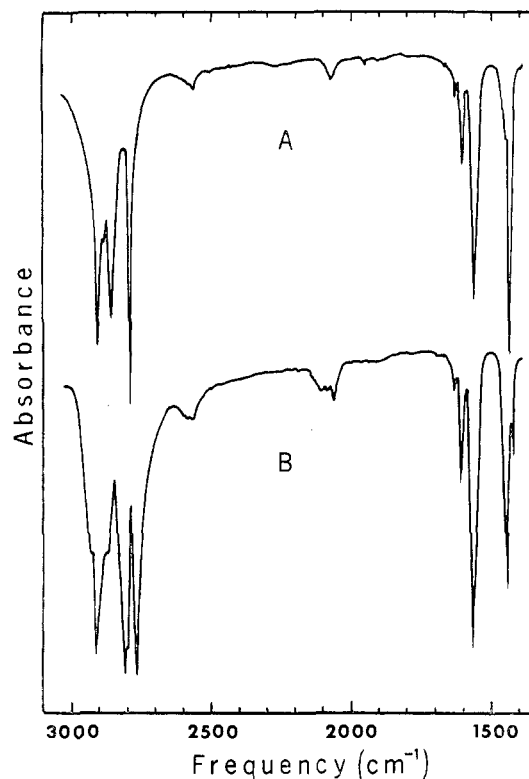
Figure 2.—Infrared spectra in hexachlorobutadiene mull: A, $Na_2[(Mo_6Cl_8)(OCH_3)_6]$; B, $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$.

2700 and 3000 cm^{-1} due to CH stretching modes and overtones of the deformations. Again splitting is observed on passing from $Na_2[(Mo_6Cl_8)(OCH_3)_6]$ to Na_2-$[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$, although perhaps to a more limited extent. In both ranges the spectrum of Na_2-$[(Mo_6Br_8)(OCH_3)_6]$ is identical with its chlorine analog.

Proton Magnetic Resonance Spectra.—Figure 3

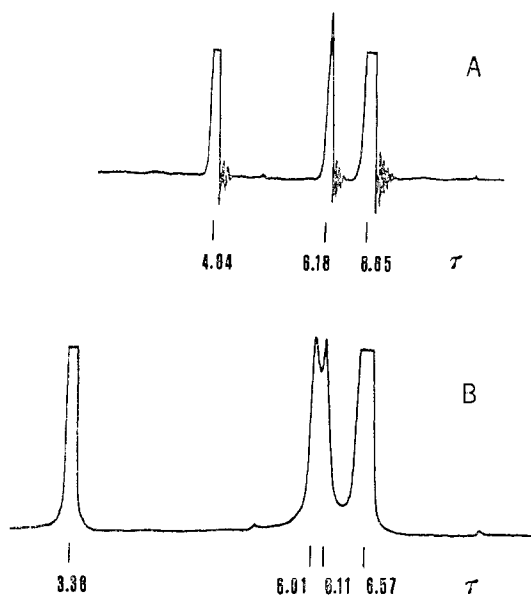Figure 3.—Proton magnetic resonance spectra: A, Na_2-[$(Mo_6Cl_8)(OCH_3)_6$], 40.9% solution in methanol; B, $Na_2[\{Mo_6$-$(OCH_3)_8\}(OCH_3)_6]$, 58.8% solution in methanol.

shows proton magnetic resonance spectra of both Na_2-[$(Mo_6Cl_8)(OCH_3)_6$] and $Na_2[\{Mo_6(OCH_3)_8\}(OCH_3)_6]$ in methanol as a solvent. The sharp peak at 6.18 ppm in the spectrum of the first compound is due to the protons of the ligand methoxide ions, the strong peak at 6.65 ppm, to the methyl protons of the methanol, and the other, at 4.84 ppm, to the hydroxyl protons of the methanol. The area of the peak at 6.18 ppm corresponds to six methoxy groups. This estimate is made possible by the high concentration of the solution, which allows a fairly accurate comparison of the areas of the peaks. Furthermore, the fact that the peak is so sharp

clearly indicates equivalency among the methoxide ions. A similar spectrum is given by a solution of $Na_2[(Mo_6$-$Br_8)$ $(OCH_3)_6]$ in methanol.

In the spectrum of the solution of $Na_2[\{Mo_6$-$(OCH_3)_8\}(OCH_3)_6]$ the peak due to the methoxy groups of the compound has become a well-defined doublet with maxima at 6.01 and 6.11 ppm. The splitting leaves little doubt about the existence in the molecule of two types of methoxy groups, in complete agreement with the proposed structure.

The peaks at 6.57 and 3.38 ppm are due to the methyl and hydroxyl protons of the solvent, respectively. The areas under the peaks of the doublet cannot be determined separately because of overlap; however, the total area of the doublet corresponds to 14 methoxy groups. There are indications that the maximum at 6.01 ppm may be due to the ligand methoxide ions. When traces of water are added to the methanol solution of Na_2-[$\{Mo_6(OCH_3)_8\}(OCH_3)_6$], the peak at 6.01 ppm slowly decreases in intensity and eventually disappears, leaving the peak at 6.11 ppm unchanged. The ligand methoxide ions presumably are the first to be hydrolyzed, with consequent weakening and eventual disappearance of their pmr signal.

Complexes of Nickel(II) with Cyclic Tetradentate Schiff Bases Derived from 2-Mercaptoaniline[1]

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The synthesis, electrical conductivity, and electronic spectra are described for a number of complexes of nickel(II) with the new cyclic planar tetradentate ligands S,S'-*o*-xylyl-2,3-butanedione bis(2-mercaptoanil) and S,S'-*o*-xylyl-1,2-cyclohexanedione bis(2-mercaptoanil) and the related noncyclic ligand S,S'-dibenzyl-2,3-butanedione bis(2-mercaptoanil). The complexes are prepared by the action of α,α'-dibromo-*o*-xylene or α-bromotoluene on the nickel(II) complexes of the Schiff base of the appropriate α-diketone and 2-mercaptoaniline. Bromide, iodide, and thiocyanate salts have been isolated. All of the complexes show high-spin magnetic moments and are 1:1 electrolytes in acetonitrile. Their electronic spectra have been assigned on the basis of a model of tetragonally distorted octahedral symmetry, and the ligand field strengths of the new ligands and the tetragonal splitting parameters have been estimated and compared with those of related ligands.

Introduction

A survey[2] of complexes of nickel(II) with cyclic tetradentate ligands reveals that the great majority involve

(1) Presented at the 154th National Meeting of the American Chemical Society, Chicago, Ill., 1967.

(2) D. H. Busch, *Helv. Chim. Acta*, Fasciculus Extraordinarius Alfred Werner, 174 (1967).

ligands which have either a double negative charge or no charge at all, giving neutral or doubly positively charged complex species, respectively. In the latter class, the charge on the cation usually is compensated by two mononegative anions which may, or may not, be coordinated. Considerable interest is attached to the