Inorganic Chemistry, Vol. 13, No. 9, 1974 2121

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Preparation and Characterization of Some Tetrahalodimolybdenum(II) Complexes[1]

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Received January 16, 1974

AIC40031H

The preparation of a variety of tetrahalodimolybdenum(II) complexes containing sulfur-, nitrogen-, and oxygen-donor ligands is described. The reaction of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ with diethyl sulfide, 2,5-dithiahexane, and other mono- and bidentate alkyl sulfides produces dinuclear complexes of the general formulas $Mo_2Cl_4L_4$ and $Mo_2Cl_4(LL)_2$. Reaction of $Mo_2Cl_4[S(C_2H_5)_2]_4$ and related complexes with pyridine or 2,2'-bipyridine yields the nitrogen-coordinated compounds $Mo_2Cl_4(C_5H_5N)_4$ (2), and $Mo_2Cl_4(bipy)_2$ (3), respectively. Complex 3 can also be prepared by the direct reaction of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ with 2,2'-bipyridine in methanol. The analogous reaction with pyridine does not afford 2, which can, however, be made by reduction of $Cs_3Mo_2Cl_8$ with pyridine. Similar reduction of $Cs_3Mo_2Br_8$ yields $Mo_2Br_4(C_5H_5N)_4$. The corresponding phosphine complex, $Mo_2Br_4[P(n\text{-}C_4H_9)_3]_4$, can be obtained from the reaction of $Cs_3Mo_2Br_8$ with tri-*n*-butylphosphine in methanol or by treating $Mo_2Br_4(C_5H_5N)_4$ with excess tri-*n*-butylphosphine. Reaction of $Mo_2Br_4(C_5H_5N)_4$ with excess dimethyl sulfide produces $Mo_2Br_4[S(CH_3)_2]_4$. Treatment of $Mo_2X_4[S(CH_3)_2]_4$ and related complexes with aceto- or benzonitrile yields tetrachlorotetrakis(nitrile)dimolybdenum(II) complexes while analogous treatment with dimethylformamide produces DMF-coordinated dinuclear molybdenum(II) complexes. Possible structures are discussed for these new complexes based on cogent spectral and chemical observations.

Introduction

The ability of molybdenum to form a variety of dinuclear complexes containing multiple metal-to-metal bonds has become apparent in recent years. By far the largest number of these compounds contain molybdenum in the oxidation state of +2. These include the carboxylates,[2] $[Mo_2(O_2CR)_4]$, dithiocarbonates,[3] $[Mo_2(S_2COR)_4]$, sulfate,[4,5] $[Mo_2(SO_4)_4]^{4-}$, and related complexes[4,6] such as $[Mo_2(en)_4]^{4+}$ and $[Mo_2(CH_3CO_2C_2H_5)_4]^{4+}$ as well as the halo complexes $[Mo_2Cl_8]^{4-}$ [7] and $Mo_2Cl_4(PR_3)_4$.[8] The principal interest in these compounds has been in their structural characterization; until recently, only brief consideration has been given to the investigation of their chemical reactivity.

We have previously described the reaction of pentaammonium nonachlorodimolybdenum(II) monohydrate with phosphines and phosphites.[8] Compelling spectral and physical evidence suggests that the resulting complexes are neutral derivatives of tetrachlorodimolybdenum(II) (Figure 1).

$$(NH_4)_5Mo_2Cl_9 \cdot H_2O \xrightarrow{R_3P\text{-}CH_3OH} \underset{1}{Mo_2Cl_4(PR_3)_4}$$

Here we wish to describe further reactions which provide convenient procedures leading to dinuclear molybdenum(II) complexes containing sulfur-, nitrogen-, and oxygen-donor molecules.

Experimental Section

Materials. Dimethyl sulfide, diethyl sulfide, 2,5-dithiahexane, 4,7-dithiadecane, 1,4-dithiane, tri-*n*-butylphosphine, pyridine, dimethylformamide, hexamethylphosphoric triamide, bipyridine, pyridine *N*-oxide, acetonitrile, benzonitrile, and dimethyl sulfoxide were commercial samples and, except where noted, were used without purification. 5,8-Dithiadodecane, prepared by reaction of sodium butylmercaptide with 1,2-dibromoethane, had a boiling point of 120–124° (1.5 Torr). *P,P,P',P'*-Tetramethylethylenediphosphine (TMEDP) was prepared by the desulfurization of *P,P,P',P'*-tetramethylethylenediphosphine disulfide[9] as described by Parshall.[10]

Spectra and Analyses. Raman spectra were recorded on a Cary Model 82 laser Raman spectrometer equipped with a rotating sample cell similar to that described elsewhere.[11] Unless otherwise noted, a slit width of 3 cm^{-1} and a scanning rate equal to the ratio of the slit width to time constant were employed. Blue (4880 Å) or green (5145 Å) excitation was provided by a Coherent Radiation Laboratory Model 52 argon ion laser. Reported frequencies are accurate to ±1 cm^{-1}. Infrared spectra were recorded on a Perkin-Elmer Model 225 spectrophotometer employing either KBr disks or Nujol mulls supported on polyethylene plates. Frequencies are accurate to ±1 cm^{-1}. Optical spectra were obtained on sealed samples using a Cary Model 14 spectrophotometer. Analyses and molecular weights were determined by Galbraith Laboratories, Knoxville, Tenn.

Dinuclear Molybdenum(II) Complexes. The molybdenum complexes $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, $Mo_2Cl_4(R_3P)_4$ ($R = n\text{-}C_4H_9$, CH_3O), and $Cs_3Mo_2Cl_8$ were prepared by established procedures.[7,8,12]

Tricesium Octabromodimolybdenum, $Cs_3Mo_2Br_8$.[13] Molybdenum(II) acetate (1.00 g, 2.34 mmol) was placed in a 250-ml flask equipped with a condenser capped with a rubber septum. The entire system was flushed with nitrogen before adding 100 ml of deoxygenated 48% hydrobromic acid. The resulting mixture was heated at 60° for 1 hr before adding a deoxygenated solution of cesium bromide (2.5 g in 50 ml of 48% hydrogen bromide). A yellow-brown precipitate formed immediately. It was collected by suction filtration, washed with 50 ml of absolute ethanol and 100 ml absolute ether, and then dried under reduced pressure. The isolated yield was 72%. *Anal.* Calcd for $Cs_3Mo_2Br_8$: Br, 51.98. Found: Br, 51.47.

Tetrachlorotetrakis(diethyl sulfide)dimolybdenum(II), $Mo_2Cl_4[S(C_2H_5)_2]_4$. Pentaammonium nonachlorodimolybdenum(II) monohydrate (2.0 g, 3.2 mmol) was placed in a 40-ml centrifuge tube containing a Teflon-coated stirrer bar. The tube was capped with a rubber septum and flushed with nitrogen before injecting a solution of diethyl sulfide (2.0 ml) in methanol (10 ml) by syringe. After stirring for 1 hr, the precipitated product was collected by suction filtration and washed once with methanol (5 ml) and then with three 10-ml portions of pentane. The yield of blue-green $Mo_2Cl_4[S(C_2H_5)_2]_4$ was 82%. This compound is readily soluble in a number of

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[1] Supported by the Research Corp., Uniroyal Foundation, and the Petroleum Research Fund, administered by the American Chemical Society.

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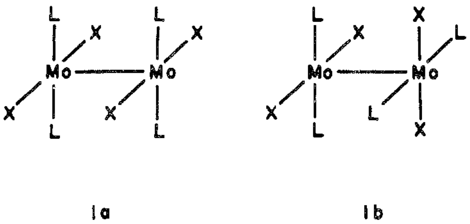

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Figure 1. Proposed idealized structures for the dinuclear complexes $Mo_2X_4L_4$ ($L = PR_3$, C_5H_5N, SR_2).

common organic solvents including diethyl ether, chloroform, and acetone. The resulting solutions are considerably more air-sensitive than the solid which can be handled in the laboratory atmosphere for brief periods with no obvious effect. *Anal.* Calcd for $C_{16}H_{40}Cl_4Mo_2S_4$: C, 27.67; H, 5.81; Cl, 20.42; S, 18.47. Found: C, 26.99; H, 5.73; Cl, 20.47; S, 17.83.

Tetrachlorotetrakis(dimethyl sulfide)dimolybdenum(II), $Mo_2Cl_4[S(CH_3)_2]_4$, was prepared in 87% yield from $(NH_4)_5Mo_2Cl_9\cdot H_2O$ (3.00 g, 4.84 mmol) and dimethyl sulfide (10 ml) by a procedure analogous to that used to prepare $Mo_2Cl_4[S(C_2H_5)_2]_4$. Its properties are similar to those of $Mo_2Cl_4[S(C_2H_5)_2]_4$. *Anal.* Calcd for $C_8H_{24}Cl_4Mo_2S_4$: C, 16.49; H, 4.12; Cl, 24.40. Found: C, 16.36; H, 4.17; Cl, 24.46.

Tetrachlorobis(2,5-dithiahexane)dimolybdenum(II), $Mo_2Cl_4(DTH)_2$. Pentaammonium nonachlorodimolybdenum(II) monohydrate (4.0 g, 6.5 mmol) was placed in a one-necked, 500-ml flask containing a Teflon-coated stirrer bar. The flask was stoppered with a rubber septum and the vessel flushed with nitrogen before adding methanol (200 ml) containing 2 ml of 12 *M* hydrochloric acid. 2,5-Dithiahexane (8.0 ml, 68 mmol) was injected by syringe. An immediate reaction occurred. The mixture was allowed to stir for 30 minutes and the resulting green product was isolated by suction filtration, washed with three 10-ml portions of absolute ethanol followed by three 10-ml portions of ether, and finally dried *in vacuo*. The blue-green complex was isolated in 90% yield. Tetrachlorobis(2,5-dithiahexane)dimolybdenum(II) is insoluble in most common organic solvents. It is, however, slightly soluble in dichloromethane. *Anal.* Calcd for $C_8H_{10}Cl_4Mo_2S_4$: C, 16.62; H, 3.49; Cl, 24.52; S, 22.19. Found: C, 16.57; H, 3.67; Cl, 24.21; S, 21.90.

Tetrachlorobis(4,7-dithiadecane)dimolybdenum(II), $Mo_2Cl_4(DTD)_2$, was prepared in 94% yield from $(NH_4)_5Mo_2Cl_9\cdot H_2O$ (2.0 g, 3.2 mmol) and 4,7-dithiadecane (4.0 ml, 21 mmol) by a procedure analogous to that used to prepare $Mo_2Cl_4(DTH)_2$. This complex is somewhat soluble in chloroform. Both $Mo_2Cl_4(DTH)_2$ and $Mo_2Cl_4(DTD)_2$ can be handled briefly in air. *Anal.* Calcd for $C_{16}H_{36}Cl_4Mo_2S_4$: C, 27.84; H, 5.26; Cl, 20.54; S, 18.57. Found: C, 26.93; H, 5.11; Cl, 20.98; S, 17.89.

Tetrachlorobis(5,8-dithiadodecane)dimolybdenum(II), $Mo_2Cl_4(DTDD)_2$, was prepared in 72% yield from $(NH_4)_5Mo_2Cl_9\cdot H_2O$ (2.0 g, 3.2 mmol) and 5,8-dithiadodecane (4 ml) in a manner similar to that described for the synthesis of $Mo_2Cl_4(DTH)_2$; however, an extended reaction time (2 hr) was necessary. The product is soluble in a number of organic solvents including acetone, methylene chloride, and chloroform. The resulting solutions decompose in laboratory atmosphere although the solid is moderately stable in air. *Anal.* Calcd for $C_{20}H_{44}Cl_4Mo_2S_4$: C, 32.18; H, 5.94; Cl, 19.00; S, 17.18. Found: C, 32.40; H, 5.86; Cl, 18.84; S, 17.24.

Reaction of 1,4-Dithiane with $(NH_4)_5Mo_2Cl_9\cdot H_2O$. Into a one-necked, 250-ml flask was placed pentaammonium nonachlorodimolybdenum(II) monohydrate (0.72 g, 1.2 mmol) and a Teflon-coated stirrer bar. The neck was stoppered with a rubber septum and the vessel was flushed with nitrogen before injecting a solution of 1,4-dithiane (0.56 g, 4.7 mmol) in methanol (70 ml). This mixture was stirred for 30 min and the resulting blue solid was collected by suction filtration, washed with three 10-ml portions of absolute ethanol, followed by three 10-ml portions of ether, and finally dried *in vacuo*. The isolated yield, calculated as $Mo_2Cl_4(S_2C_4H_8)_2$, was 92%. This compound is insoluble in most common organic solvents with the exception of CH_2Cl_2 in which it is sparingly soluble. *Anal.* Calcd for $C_8H_{16}Cl_4Mo_2S_4$: C, 16.74; H, 2.81; Cl, 24.70; S, 22.34. Found: C, 16.48; H, 2.84; Cl, 23.89; S, 20.32.

Tetrachlorotetrakis(pyridine)dimolybdenum(II), $Mo_2Cl_4(C_5H_5N)_4$. Tricesium octachlorodimolybdenum (1.00 g, 1.14 mmol) and pyridine (50 ml, freshly distilled from calcium hydride under nitrogen) were placed in a 100-ml flask equipped with a condenser capped with a rubber serum stopper. The system was flushed with nitrogen and then heated under reflux for 4 hr. Upon cooling, the red, crystalline solid which precipitated was collected by suction filtration and washed first with distilled water (10 ml), then absolute ethanol (20 ml), and finally absolute ether (20 ml) before drying *in vacuo*. The yield of $Mo_2Cl_4(C_5H_5N)_4$ was 68%. This substance appeared stable for long periods in air. *Anal.* Calcd for $C_{20}H_{20}Cl_4Mo_2N_4$: C, 36.95; H, 3.08; Cl, 21.82; N, 8.61. Found: C, 35.45; H, 2.94; Cl, 20.77; N, 8.26.

Tetrachlorotetrakis(pyridine)dimolybdenum(II) was also prepared by the following procedure. Tetrachlorobis(5,8-dithiadodecane)dimolybdenum(II) (0.66 g, 0.96 mmol) was placed in a 40-ml centrifuge tube equipped with a Teflon-coated stirrer bar. The vessel was capped with a serum stopper and flushed with nitrogen before injecting 1.0 ml of pyridine and 5.0 ml of methanol by syringe. The mixture was allowed to stir for 2 hr and the resulting red-brown solid which precipitated was collected by suction filtration, washed with two 10-ml portions of methanol followed by two 10-ml portions of ether, and finally dried *in vacuo*. The isolated yield was 90%. Solutions of tetrachlorotetrakis(pyridine)dimolybdenum(II) in pyridine are stable in the absence of air; decomposition accompanies dissolution in methylene chloride. *Anal.* Calcd for $C_{20}H_{20}Cl_4Mo_2N_4$: C, 36.95; H, 3.08; Cl, 21.82; N, 8.61. Found: C, 35.34; H, 2.96; Cl, 21.01; N, 8.10.

Tetrachlorobis(2,2′-bipyridine)dimolybdenum(II), $Mo_2Cl_4(bipy)_2$, was prepared by treating a suspension of $(NH_4)_5Mo_2Cl_9\cdot H_2O$ (0.50 g, 0.80 mmol) in methanol (30 ml) with 2,2′-bipyridine (2.0 g, 30 mmol) under a nitrogen atmosphere. After stirring for 90 min, the precipitated solid was collected by suction filtration, washed with one 10-ml portion each of water and methanol and then three 10-ml portions of ether, and finally dried *in vacuo*. The isolated yield was 87%. *Anal.* Calcd for $C_{20}H_{16}Cl_4Mo_2N_4$: C, 37.18; H, 2.50; Cl, 21.95; N, 8.67. Found: C, 35.00; H, 2.61; Cl, 22.43; N, 8.34.

The preparation of tetrachlorobis(2,2′-bipyridine)dimolybdenum(II) was also achieved by stirring 0.50 g (0.73 mmol) of $Mo_2Cl_4(DTD)_2$ in 50 ml of methanol with 2,2′-bipyridine (0.43 g, 2.8 mmol) under a nitrogen atmosphere for 2 hr. The gray product was collected by suction filtration, washed with one 10-ml portion of methanol and three 10-ml portions of diethyl ether, and then dried *in vacuo*. The isolated yield was 0.41 g (93%). *Anal.* Calcd for $C_{20}H_{16}Cl_4Mo_2N_4$: C, 37.18; H, 2.50; Cl, 21.95; N, 8.67. Found: C, 35.41; H, 2.67; Cl, 21.07; N, 8.10.

Tetrabromotetrakis(pyridine)dimolybdenum(II), $Mo_2Br_4(C_5H_5N)_4$, was prepared from tricesium octabromodimolybdenum (1.00 g, 0.810 mmol) and pyridine (30 ml) by a procedure analogous to that used to prepare $Mo_2Cl_4(C_5H_5N)_4$. The green, air-stable solid was obtained in 60% yield. Reaction times in excess of 1 hr led to reduced product yields. Although insoluble in most organic solvents, solutions of $Mo_2Br_4(C_5H_5N)_4$ can be obtained in pyridine. *Anal.* Calcd for $C_{20}H_{20}Br_4Mo_2N_4$: C, 29.02; H, 2.43; Br, 38.60; N, 6.77. Found: C, 28.83; H, 2.32; Br, 38.49; N, 6.70.

Tetrabromotetrakis(dimethyl sulfide)dimolybdenum(II), $Mo_2Br_4[S(CH_3)_2]_4$. Into a 400-ml flask was placed a Teflon-coated stirrer bar and 0.96 g (1.2 mmol) of $Mo_2Br_4(C_5H_5N)_4$. The flask was capped with a rubber serum cap and flushed with nitrogen before injecting 20 ml of dimethyl sulfide. After stirring for 24 hr, pentane (200 ml) was added. The precipitate which formed was collected by suction filtration and washed with three 10-ml portions of pentane. The isolated yield was 77%. *Anal.* Calcd for $C_8H_{24}Br_4Mo_2S_4$: C, 12.64; H, 3.18; Br, 42.05; S, 16.87. Found: C, 14.34, H, 3.02; Br, 41.05; S, 14.99.

Tetrabromobis(4,7-dithiadecane)dimolybdenum(II), $Mo_2Br_4(DTD)_2$, was prepared in 85% yield from $Mo_2Br_4(DMF)_4$ (0.25 g, 0.31 mmol) and DTD (1.0 ml, 5.0 mmol) by a procedure analogous to that used to prepare $Mo_2Cl_4(DTH)_2$. *Anal.* Calcd for $C_{16}H_{36}Br_4Mo_2S_4$: C, 22.14; H, 4.18; Br, 36.82; S, 14.75. Found: C, 22.03; H, 4.05; Br, 36.75; S, 14.64.

Tetrabromobis(2,2′-bipyridine)dimolybdenum(II), $Mo_2Br_4(bipy)_2$. Tetrabromotetrakis(pyridine)dimolybdenum(II) (0.70 g, 0.84 mmol) was placed in a 50-ml flask fitted with a condenser capped with a rubber septum. Bipyridine (1.0 g) was added to the flask and the system flushed with nitrogen before adding 30 ml of deoxygenated methanol by syringe. The resulting mixture was heated at reflux for 2 hr. After cooling, the blue-gray product was collected by suction filtration, washed with two 15-ml portions of methanol and then two 15-ml portions of ether, and air-dried. The isolated yield of $Mo_2Br_4(bipy)_2$ was 82%. This substance is insoluble in all common organic solvents. *Anal.* Calcd for $C_{20}H_{16}Br_4Mo_2N_4$: C, 29.16; H, 1.96; N, 6.80; Br, 38.80. Found: C, 28.94; H, 2.06; N, 6.77; Br, 38.69.

Tetrabromotetrakis(tri-*n*-butylphosphine)dimolybdenum(II).

Into a 100-ml flask equipped with a reflux condenser and nitrogen inlet was placed tricesium octabromodimolybdenum (1.00 g, 0.810 mmol). The vessel was flushed with nitrogen and a deoxygenated solution of tri-*n*-butylphosphine (1 ml) in methanol (25 ml) was added by syringe. After refluxing for 6 hr, the resulting mixture was extracted with five 25-ml portions of ether. The combined extracts were concentrated to near-dryness under reduced pressure at room temperature. The blue solid which precipitated was collected by suction filtration under nitrogen, washed once with ~5 ml of cold (−50°) methanol, and finally dried *in vacuo*. The yield of $Mo_2Br_4[P(n\text{-}C_4H_9)_3]_4$ was 21%. *Anal.* Calcd for $C_{48}H_{108}Br_4Mo_2P_4$: C, 43.81; H, 8.21; Br, 24.29. Found: C, 44.21; H, 8.85; Br, 23.98.

A higher yield synthesis of tetrabromotetrakis(tri-*n*-butylphosphine)dimolybdenum(II) was achieved in the following manner. Tetrabromotetrakis(pyridine)dimolybdenum(II) (0.70 g, 0.85 mmol) was placed in a 50-ml flask fitted with a nitrogen inlet and a condenser. The vessel and its contents were flushed with nitrogen before introducing a deoxygenated solution of tri-*n*-butylphosphine (1 ml) in methanol (25 ml) by syringe. The resulting mixture was refluxed for 90 min and allowed to cool to room temperature. Blue crystals of $Mo_2Br_4[P(n\text{-}C_4H_9)_3]_4$ were isolated in 80% yield by suction filtration under nitrogen and dried *in vacuo*. *Anal.* Calcd for $C_{48}H_{108}Br_4Mo_2P_4$: C, 43.81; H, 8.21; Br, 24.29. Found: C, 43.56; H, 8.67; Br, 24.18.

Tetrachlorobis(tetramethylethylenediphosphine)dimolybdenum(II), $Mo_2Cl_4(TMEDP)_2$. Pentaammonium nonachlorodimolybdenum(II) monohydrate (1.0 g, 1.6 mmol) was placed in a 40-ml centrifuge tube equipped with a Teflon-coated stirrer bar. The tube was capped with a rubber serum stopper and flushed with nitrogen before injecting 15 ml of deoxygenated methanol and 1.0 ml of tetramethylethylenediphosphine (TMEDP) by syringe. This mixture was stirred for 12 hr and the resulting blue solid was collected by suction filtration, rinsed with two 15-ml portions of ether, and dried *in vacuo*. The yield was 92%. Tetrachlorobis(tetramethylethylenediphosphine)dimolybdenum(II) is sparingly soluble in CH_2Cl_2 and $CHCl_3$. Although the solid is stable to laboratory air for short exposure, solutions of $Mo_2Cl_4(TMEDP)_2$ decompose rapidly in air. *Anal.* Calcd for $C_{12}H_{32}Cl_4Mo_2P_4$: C, 22.88; H, 4.45; Cl, 22.55. Found: C, 21.72; H, 4.32; Cl, 22.93.

Tetrachlorotetrakis(acetonitrile)dimolybdenum(II), $Mo_2Cl_4(NCCH_3)_4$. Tetrachlorotetrakis(dimethyl sulfide)dimolybdenum(II) (0.48 g, 0.83 mmol) was placed in a 40-ml centrifuge tube containing a Teflon-coated stirrer bar. The tube was capped with a rubber septum and flushed with nitrogen before injecting 10 ml (190 mmol) of acetonitrile by syringe. After stirring for 12 hr, the mixture was concentrated to dryness at 20° under reduced pressure. The remaining solid was collected and washed with three 10-ml portions of diethyl ether affording 0.35 g (86% yield) of dark green, somewhat air-sensitive material. *Anal.* Calcd for $C_8H_{12}Cl_4Mo_2N_4$: C, 19.30; H, 2.43; Cl, 28.49; N, 11.25. Found: C, 19.08; H, 2.47; Cl, 28.37; N, 11.11.

Tetrachlorotetrakis(benzonitrile)dimolybdenum(II), $Mo_2Cl_4(NCC_6H_5)_4$. Tetrachlorotetrakis(dimethyl sulfide)dimolybdenum(II) (0.500 g, 0.857 mmol) was placed along with a Teflon-coated stirrer bar into a 50-ml flask which was then capped with a rubber septum and flushed with nitrogen before adding 5 ml of deoxygenated benzonitrile. The resulting deep green solution was stirred for 30 min before adding 40 ml of deoxygenated ether. The green, somewhat air-sensitive solid which precipitated was collected by suction filtration and washed with five 15-ml portions of ether and dried *in vacuo*. The yield was 66%. *Anal.* Calcd for $C_{28}H_{20}Cl_4Mo_2N_4$: C, 45.05; H, 2.68; Cl, 19.03; N, 7.50. Found: C, 44.81; H, 2.63; Cl, 18.86; N, 7.38.

Reaction of $Mo_2Cl_4(DTDD)_2$ with DMF. Tetrachlorobis(5,8-dithiadodecane)dimolybdenum(II) (0.38 g, 0.51 mmol) was placed in a 40-ml centrifuge tube containing a Teflon-coated stirrer bar. The vessel was stoppered with a rubber septum and flushed with nitrogen before injecting dimethylformamide (4.0 ml, 51 mmol). This mixture was stirred for 1 hr and the resulting red solid was collected by suction filtration under nitrogen and rinsed with three 10-ml portions of diethyl ether before drying under reduced pressure. The isolated yield, calculated as $Mo_2Cl_4(DMF)_4$, was 88%. *Anal.* Calcd for $C_{12}H_{28}Cl_4Mo_2N_4O_4$: C, 23.02; H, 4.51; Cl, 22.65; N, 8.95. Found: C, 22.58; H, 4.83; Cl, 22.16; N, 8.69.

Reaction of $Mo_2Br_4[S(CH_3)_2]_4$ with DMF. The above procedure was repeated using $Mo_2Br_4[S(CH_3)_2]_4$ (0.40 g, 0.53 mmol). The resulting red solid was obtained in 97% yield, calculated as $Mo_2Br_4(DMF)_4$. *Anal.* Calcd $C_{12}H_{28}Br_4Mo_2N_4O_4$: C, 17.93; H, 3.51; Br, 39.75; N, 6.97. Found: C, 18.81; H, 3.57; Br, 38.70; N, 7.24.

Table I. Absorption Spectra (~500–700 nm) for Some Dinuclear Molybdenum(II) Complexes

Species	Medium	Absorption maxima,[a] nm
$Mo_2(en)_4{}^{4+}$ [b]	Aq acid	474
$Mo_2{}^{4+}(aq)$[b]	0.5 *M* HTFMS[c]	498 (2.48 × 10^2)
$[Mo_2(SO_4)_4]^{4-}$ [b]	1 *M* HTFMS[c]	512
$[Mo_2Cl_8]^{4-}$ [b]	6 *M* HCl	518 (3.4 × 10^2)
$Mo_2Cl_4(DMF)_4$[d]	DMF	557 (~5 × 10^2)[e]
		519 (~4 × 10^2)[e]
	KBr	556
		519
$Mo_2Br_4(DMF)_4$[d]	DMF	530 (~6 × 10^2)[e]
		555 (~6 × 10^2)[e]
$Mo_2Cl_4[S(CH_3)_2]_4$	CH_2Cl_2	585 (1.1 × 10^3)
$Mo_2Cl_4[S(C_2H_5)_2]_4$	$(C_2H_5)_2S$	590 (1.8 × 10^3)
$Mo_2Cl_4(S_2C_4H_8)_2$	CH_2Cl_2	598 (1.5 × 10^3)
$Mo_2Cl_4(DTH)_2$	KBr	629
$Mo_2Cl_4(DTD)_2$	$CHCl_3$	634 (1.4 × 10^3)
$Mo_2Cl_4(DTDD)_2$	$CHCl_3$	634 (1.4 × 10^3)
$Mo_2Cl_4(C_5H_5N)_4$[f]	C_5H_5N	573 (1.3 × 10^3)
		635 (8.5 × 10^2)
$Mo_2Cl_4(bipy)_2$[f]	$CHCl_3$	530 (2.2 × 10^3)
$Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$	$(C_2H_5)_2O$	588 (1.3 × 10^3)
$Mo_2Cl_4(TMEDP)_2$	CH_2Cl_2	666 (2.5 × 10^3)
$Mo_2Cl_4[P(OCH_3)_3]_4$	$CH_3C(O)CH_3$	596 (1.2 × 10^3)
$Mo_2Cl_4(NCCH_3)_4$	CH_3CN	602 (1.8 × 10^3)
$Mo_2Cl_4(NCC_6H_5)_4$	C_6H_5CN	651 (3.0 × 10^3)
$Mo_2Br_4(C_5H_5N)_4$	C_5H_5N	656 (9.3 × 10^2)
		462 (6.2 × 10^2)
		417 (1.6 × 10^3)
$Mo_2Br_4(bipy)_2$	KBr	575
$Mo_2Br_4[S(CH_3)_2]_4$	CH_2Cl_2	597 (1.3 × 10^3)
$Mo_2Br_4(DTD)_2$	CH_2Cl_2	647 (2.5 × 10^3)

[a] Molar extinction coefficient, ϵ, in parentheses. [b] Data for this compound were taken from ref 4. [c] HTFMS is trifluoromethylsulfonic acid. [d] See text for discussion of this compound. [e] Molar extinction coefficients were calculated for this compound on the basis of the formulation $Mo_2X_4(DMF)_4$. Accurate determinations of extinction coefficients from observed spectra could not be carried out for this compound because of the considerable overlap between adjacent bands. The values given are approximate and may involve moderate error. [f] See Figure 2.

Results

Complexes with Alkyl Sulfides. The reaction of pentaammonium nonachlorodimolybdenum(II) monohydrate with a variety of mono- and bidentate alkyl sulfides is rapid in methanol. The resulting complexes show varying solubilities in organic solvents and, although relatively air stable in the solid state, are rapidly air oxidized in solution. Several lines of evidence suggest these compounds are derivatives of tetrachlorodimolybdenum(II).

First, dinuclear complexes of molybdenum(II) show a characteristic visible absorption between ~500 and 700 nm.[14] Table I summarizes the visible absorption data for the complexes prepared from the reaction of dimethyl sulfide, diethyl sulfide, 2,5-dithiahexane (DTH), 4,7-dithiadecane (DTD), and 5,8-dithiadodecane with $(NH_4)_5Mo_2Cl_9 \cdot H_2O$. The maxima and molar extinction coefficients are typical of those observed for dinuclear complexes of molybdenum(II).[4]

Second, the principal infrared bands observed for these complexes are listed in Table II. The moderate to strong bands appearing at 350 and 294 cm^{-1} in the spectrum of the dimethyl sulfide complex and 335 and 286 cm^{-1} in the spectrum of the diethyl sulfide complex are assigned as Mo–Cl stretching frequencies. Complexes involving the bidentate chelating ligands DTH, DTD, and DTDD reveal a strong

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(14) C. D. Cowman and H. B. Gray, *J. Amer. Chem. Soc.*, **95**, 8177 (1973), and references therein.

Table II. Selected Infrared Frequencies (cm^{-1}) of Some Tetrahalodimolybdenum(II) Complexes[a,b]

	Complex			Complex		Complex		Complex			Complex		Complex
Ligand $(CH_3)_2S$	Mo_2Cl_4-$[S(CH_3)_2]_4$	Mo_2Br_4-$[S(CH_3)_2]_4$	Ligand $(C_2H_5)_2S$	Mo_2Cl_4-$[S(C_2H_5)_2]_4$	Ligand DTH	Mo_2Cl_4-$(DTH)_2$	Ligand DTD	Mo_2Cl_4-$(DTD)_2$	Mo_2Br_4-$(DTD)_2$	Ligand DTDD	Mo_2Cl_4-$(DTDD)_2$	Ligand $C_4H_8S_2$	Mo_2Cl_4-$[S_2C_4H_8]_2$
1434 vs	1431 s	1440 sh	1451 m	1454 sh	1320 m	1312 m	1457 s	1457 s	1457 s	1466 s	1465 s	1408 s	1424 s
	1422 sh	1429 s		1446 m	1283 sh		1437 m	1442 sh		1457 s	1457 s		1401 m
1331 sh	1388 w	1413 sh	1427 w	1426 m	1270 m	1250 w	1424 m	1416 s	1416 s	1437 s	1445 sh		1390 m–w
1308 m	1319 m	1316 m	1375 m	1381 m	1206 s		1377 m	1379 m	1377 s	1424 s	1416 s	1298 m	1285 w
	1297 w	1296 w	1267 sh	1284 w		1175 w	1338 w	1337 m	1336 m	1380 m	1380 m	1278 s	1267 vw
1027 s	1030 s	1026 s	1258 m	1258 m	1134 m		1296 m	1292 m	1291 m	1355 w, br	1361 w		1252 w
972 s	976 s	978 s	1073 w	1075 m	1120 sh	1129 m	1270 w	1262 vw	1261 w		1347 w	1183 m	1199 w
906 vw	908 w	915 vw	1043 vw	1049 w	1027 vw	1024 w	1239 m	1233 m	1231 m	1303 m	1305 sh	1152 s	1160 m
742 w	730 w, br	757 w	973 m	973 m	1010 vw			1203 w	1218 w	1293 m	1293 m		1124 w
692 m	681 w	676 m	779 w	782 w	975 sh	972 sh	1199 s		1177 w	1272 m	1278 m		1020 w
	350 m	669 m	763 w		960 s	960 s	1128 w	1129 w	1129 m	1265 sh		997 w	977 w
	294 m		737 vw	744 w		909 w	1088 w	1089 w	1091 m		1254 m	941 w	913 w
282 w, br	280 sh	*265 s*	690 w	680 vw	840 w	841 w	1047 w	1035 w	1080 sh	1224 m	1222 m	902 vs	900 w
				620 w	738 m			933 m	932 m	1198 s	1198 vw	888 m	870 w
				335 s	686 s		897 w	898 w	902 w		1175 w		793 m
				286 m	650 vw	652 vw	888 sh	884 sh	885 w	1128 w	1129 m		726 w
						634 w	833 vw	835 w, br	845 w	1097 w	1095 m		698 w
						454 w	785 m	787 m	768 m	1070 w	1073 w		691 w
						339 sh	740 m	735 m	735 m	1050 w	1049 w	663 vs	651 w
						312 s	716 w	716 w		997 vw	992 w	650 vw	623 w
							695 w			969 vw	969 w		509 w
								611 w	610 w		939 m	477 w	
								465 vw	464 w	915 w	914 w	470 mw	
								341 sh		895 w		456 vw	
								311 s	*238 m*	876 w	874 w		*327 s*
											846 w, br		*285 m*
										786 w	779 w, br		
										745 m	742 m		
										730 m	725 sh, br		
										718 m			
										696 m	685 vw		
											615 w		
											487 vw		
											464 w		
											338 sh		
											310 s		

	Complex			Complex			Complex		Complex		Complex		Complex		Complex			Complex
Ligand C_5H_5N	Mo_2Cl_4-$(C_5H_5N)_4$	Mo_2Br_4-$(C_5H_5N)_4$	Ligand bipy	Mo_2Cl_4-$(bipy)_2$	Mo_2Br_4-$(bipy)_2$	Ligand $P(n\text{-}C_4H_9)_3$	Mo_2Cl_4-$[P(n\text{-}C_4H_9)_3]_4$	Mo_2Br_4-$[P(n\text{-}C_4H_9)_3]_4$	Mo_2Cl_4-$(TMEDP)_2$	Ligand CH_3CN	Mo_2Cl_4-$(NCCH_3)_4$	Ligand C_6H_5CN	Mo_2Cl_4-$(NCC_6H_5)_4$	Ligand DMF	Mo_2Cl_4-$(DMF)_4$	Mo_2Br_4-$(DMF)_4$	Ligand $(CH_3O)_3P$	Mo_2Cl_4-$[P(OCH_3)_3]_4$
1030 vs	1043 s	1044 s	989 m			897 m, br			948 vs	2300 m	2305 m	2225 s	2245 s	1672 vs	1637 vs, br	1642 vs, br	1016 vs, br	1030 vs, br
991 vs	1007 s	1008 s	973 sh	957 m	962 m	783 w, br	793 m	790 m	903 s	2259 s	2275 s	1595 m	1601 s	1506 sh	1495 sh		975 sh	978 sh
981 w	983 w	987 w	881 m	897 w	895 w	765 sh	769 sh	769 sh	872 m	1442 s	1405 s, br		1583 m	1495 m	1486 w	1486 w		803 s
938 vw	965 w	949 w	754 vs	772 vs	769 vs		749 sh	757 m	840 w	1373 s	1359 s	1489 m	1490 s	1437 m	1436 m	1434 m	769 s	780 s
883 vw	879 m	873 vw	739 sh	726 vs	723 vs	721 m, br	740 sh	738 m	736 m		1352 sh	1447 m	1446 s		1419 s	1420 sh	751 s	740 s

810 vw			667 w	667 w	665 w	718 m	714 m	712 w		1225 w		1390 w	1405 m	1406 m	1407 vw	534 sh	546 sh
749 vs	756 vs	759 vs	662 w	658 w	659 w	459 w	460 m	630 vw		1124 w		1332 w	1386 s	1377 s	1374 s	512 s	522 s
703 vvs	695 vs	700 vs	653 m	651 w		*326 m*		440 w		1080 sh	1288 w	1287 m		1359 s	1361 s	454 w	430 vw
	691 sh	696 vs	650 m	643 m	641 w	*278 m*	*260 m*	*335 sh*	1032 m	1020 m		1218 w	1256 m	1251 m	1250 w	396 sh	382 w
675 w	677 sh	678 m	617 m					*300 s*	920 m	950 w	1199 w	1190 m	1092 s	1117 s	1116 m	370 w	*344 m*
653 w	666 sh	667 w	426 w					269 w		914 vw	1178 m	1178 m		1108 s		287 w	*295 m*
		652 w	400 s	422 m	420 m			234 w	750 w	700 m, br	1161 m	1163 w	1061	1058 w	1057 vw		
	636 m	636 s		*304 s*	*270 m*					545 m, br	1066 w	1097 m	865 w		759 w		
	633 m									420 vw	1028 s	1028 w		704 s	700 s		
604 s	607 vw	608 vw								*344 w–m*	1000 m	998 w	657 m	698 s	682 sh		
	442 w									*297 s*	972 vw	985 sh		412 m, br	405 m, br		
	437 mw	436 w								282 sh	925 m	937 vw		397 s	396 m		
405 s	397 vw	396 vw								252 m	888 vw	846 vw		370 m	372 w		
	342 s										842 w			*297 s, br*			
	280 m										760 m	762 sh			*240 m*		
		267 m[c]										754 s					
	244 m	*259 m*[c]									686 m	682 s					
											621 w						
											545 w	548 s					
												402 vw					
												347 m					
												301 w					
												289 m					

[a] Qualitative intensities: vs, very strong; s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad. The spectra of uncoordinated ligands were recorded as neat liquids or melts unless otherwise noted. [b] The frequencies assigned to molybdenum–halogen stretching vibrations are shown in italics. Assignments are based on position (see ref 17), intensity, and, where possible, comparison of analogous bromo and chloro complexes. [c] The equal intensity and the symmetry of the band envelope suggest that this doublet arises from the splitting of a single band centered at ~263 cm^{-1}.

Mo–Cl stretching vibration at ~312 cm^{-1}, exhibiting a shoulder at ~340 cm^{-1}. The assignment of these bands as ν(Mo–Cl) is supported by their absence in the bromo compounds $Mo_2Br_4[S(CH_3)_2]_4$ and $Mo_2Br_4(DTD)_2$ (*vide infra*). A comparison of the spectrum of the DTH complex with the spectrum of uncoordinated DTH reveals that the strong band at 1206 cm^{-1} and the somewhat weaker bands at ~738 and ~686 cm^{-1}, assigned respectively as the methylene wagging mode and the C–S stretching vibrations of the trans conformer of the free ligand,[15a] are absent in the coordinated ligand. As previously noted by Cotton in an analysis of the 2,5-dithiahexane complexes of rhenium(III)[15b] and McCarley in an investigation of the DTH complexes of Nb(IV) and Zr(IV) halides,[15c] this observation suggests that the coordinated DTH ligand exists in a gauche conformation.

Third, earlier studies[16] have shown that the Raman spectra of complexes of tetrachlorodimolybdenum(II) exhibit an intense band at ~345 cm^{-1} attributable to ν(Mo–Mo). Table III summarizes the Raman spectra of the complexes prepared from dimethyl and diethyl sulfide, DTH, DTD, and DTDD. The strong, relatively invariant band present at ~345 cm^{-1} in all spectra establishes the dinuclear nature of these sulfur-coordinated complexes. The moderate to strong Raman band appearing at 327 ± 5 cm^{-1} in some spectra is tentatively assigned as a molybdenum–sulfur stretching vibration. This assignment is consistent with the position of ν(M–S) observed in other transition metal–alkyl sulfide complexes[17] and with the fact that the same band appears in $Mo_2Br_4(DTD)_2$. The failure to observe a molybdenum–sulfur stretching vibration in some spectra and a ν(Mo–Cl) in all these spectra is presumably the result of preferred intensity enhancement, a phenomenon frequently observed in spectra such as these where a strong resonance Raman effect prevails.

Analogous mono- and bidentate alkyl sulfide derivatives of tetrabromodimolybdenum(II) can be prepared by procedures discussed in later sections.

Complexes with Pyridine and Bipyridine. Complexes of the empirical formula $MoCl_2(C_5H_5N)_2$, **2**, and $MoCl_2$(bipy), **3**, can be obtained by refluxing $Mo_2Cl_4(DTH)_2$ or a related alkyl sulfide complex in pyridine or bipyridine–methanol. The same bipyridine complex can also be made from the direct reaction of pentaammonium nonachlorodimolybdenum(II) monohydrate with bipyridine–methanol. Treatment of $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ with pyridine under analogous conditions yielded products of ill-defined stoichiometry.

The infrared spectra of **2** and **3** are presented in Table II. In addition to revealing those bands characteristic of coordinated pyridine and bipyridine, two Mo–Cl stretching vibrations appear at 342 and 280 cm^{-1} in the spectrum of the pyridine complex while the spectrum of the bipyridine complex displays a single metal–chlorine stretching vibration at 304 cm^{-1}. The Raman spectra of both complexes (Table III) show an intense band at ~343 cm^{-1} which is assigned as the Mo–Mo stretching frequency. A less intense band which appears at 324 cm^{-1} in the spectrum of the bipyridine compound may be either a Mo–Cl or Mo–N stretching frequency since such vibrations typically[17] occur in this region.

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(15) (a) M. Hayashi, Y. Shiro, T. Oshima, and M. Murata, *Bull. Chem. Soc. Jap.*, **39**, 118 (1966); (b) F. A. Cotton, C. Oldham, and R. A. Walton, *Inorg. Chem.*, **6**, 214 (1967); (c) J. B. Hamilton and R. E. McCarley, *ibid.*, **9**, 1339 (1970).

(16) J. San Filippo, Jr., and H. J. Sniadoch, *Inorg. Chem.*, **12**, 2326 (1973).

(17) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

Table III. Summary of Selected Solid-State Raman Frequencies (cm^{-1}) Observed for Some Tetrahalodimolybdenum(II) Complexes[a,b]

$Mo_2Cl_4[S(CH_3)_2]_4$	$Mo_2Br_4[S(CH_3)_2]_4$	$Mo_2Cl_4[S(C_2H_5)_2]_4$	$Mo_2Cl_4(DTH)_2$	$Mo_2Cl_4(DTD)_2$	$Mo_2Br_4(DTD)_2$	$Mo_2Cl_4(DTDD)_2$
1073 vw (ν_3)	1040 vw (ν_3)	1035 vw (ν_3)	1420 w	1557 vw	764 w, br	1558 w
975 vw	1016 vw	692 m (ν_2)	980 w	858 vw	714 vw	1535 w, br
714 m (ν_2)	725 vw	625 w	767 m	806 w	686 m (ν_2)	779 m
685 w	696 m (ν_2)	514 vw	754 m	770 m	660 w	771 m
618 w	684 sh	370 w	712 m	710 w	642 w	698 m
358 vs	609 vw	*348 vs*	696 m	681 w	626 vw	680 m
285 w	*350 vs*	279 w	657 m	647 vw	613 w	620 w
261 m	299 vw	202 vw	637 m	620 w	*345 vs*	425 w
	261 w	132 vw	458 vw	432 w	318 m	*351 vs*
	183 w		430 vw	375 sh	178 w	329 m
			359 vs	*353 vs*		225 vw
			331 vs	332 s		143 w
			288 m	285 vw		
			215 m	224 vw		
			158 m	206 vw		
				142 w		

$Mo_2Cl_4(S_2C_4H_8)_2$	$Mo_2Cl_4(C_5H_5N)_4$[c]	$Mo_2Br_4(C_5H_5N)_4$	$Mo_2Cl_4(bipy)_2$	$Mo_2Br_4(bipy)_2$
1063 vw (ν_3)	1015 w	1653 vw	1604 m	1603 w
712 w (ν_2)	693 w (ν_2)	1609 s	1565 m	1568 m
677 w	*348 vs*	1567 vw	1498 s	1498 s
632 w		1492 vw	1321 m	1333 w
423 vw		1452 vw	1286 w	1288 w
357 vs		1347 vw	1177 w	1175 w
322 m		1236 s	1111 vw	1110 vw
286 w		1224 w	1030 s	1028 m
277 w		1088 vw	963 vw	987 w, br
169 vw		1073 m	785 w, br	780 w
		1016 vs	771 m	770 w
		1012 sh	670 m	660 w
		764 w	660 m	423 w
		703 vw	424 w	370 w
		665 w	370 m	*330 vs*
		640 m	*338 vs*	299 w
		520 w	324 m	230 vw
		442 m	262 w	183 vw
		439 sh	213 w	172 vw
		335 s		
		260 vw		
		216 vw		
		189 m		
		158 m		

$Mo_2Cl_4(NCCH_3)_4$	Mo_2Cl_4-$(NCC_6H_5)_4$	Mo_2Br_4-$[P(n\text{-}C_4H_9)_3]_4$[d]	Mo_2Cl_4-$(TMEDP)_2$	$Mo_2Cl_4(DMF)_4$	$Mo_2Br_4(DMF)_4$
412 w	1492 m	1089	695 m (ν_2)	1048 w (ν_3)	1375 vw (ν_4)
347 vs	1208 m	1020 vw, br	*349 vs*	704 m (ν_2)	1097 vw
330 sh	1183 s	683 w (ν_2)		406 w	1033 w (ν_3)
294 w	1003 m	*342 vs*		*352 vs*	752 vw
268 w	804 w	170 w			691 m (ν_2)
	778 m				406 vw
	768 w				*348 vs*
	550 w				
	522 s				
	400 w				
	352 vs				
	296 m				
	158 m				

[a] Qualitative intensities are the same as those described in Table II. ν_2 and ν_3 are respectively the first and second overtone bands. [b] Unless otherwise stated all spectra were recorded using 5145-Å exciting radiation. Frequencies in italic type denote those bands assigned as ν(Mo–Mo). [c] Recorded using 4880-Å exciting radiation. [d] The Raman spectrum of $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$ has been reported elsewhere.[16]

The visible spectra of **2** and **3** are shown in Figure 2. The comparative complexity which the spectrum of **2** exhibits is surprising. By contrast, the spectrum of **3** reveals a single band at 532 nm.

Reduction of $[Mo_2X_8]^{3-}$. The treatment of dimolybdenum(II) tetraacetate with warm hydrochloric acid has been shown to yield the octachlorodimolybdenum ion $[Mo_2Cl_8]^{3-}$, a binuclear species with strong metal-metal bonding (Mo–Mo = 2.38 Å).[12] The ease with which certain dinuclear molybdenum(III) compounds can be reduced to give dinuclear molybdenum(II) complexes[18] suggested to us that a similar reduction might also occur with $[Mo_2Cl_8]^{3-}$. Such a reaction would, of course, provide an alternative route to the preparation of dimolybdenum(II) compounds. Indeed, we have found that $[Mo_2Cl_8]^{3-}$ is readily reduced by pyridine to tetrachlorotetrakis(pyridine)dimolybdenum(II) under relatively mild conditions

$$[Mo_2Cl_8]^{3-} \xrightarrow{C_5H_5N,\ 110^\circ} \underset{\mathbf{2}}{Mo_2Cl_4(C_5H_5N)_4}$$

(18) W. Mowat, A. Shortland, G. Yagupsky, N. J. Hill, M. Yagupsky, and G. Wilkinson, *J. Chem. Soc. A*, 533 (1972).

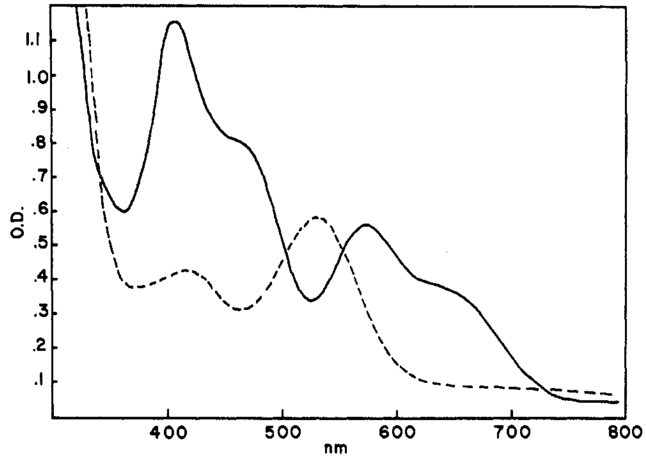

Figure 2. The visible spectra of $Mo_2Cl_4(C_5H_5N)_4$, **2**, and $Mo_2Cl_4(bipy)_2$, **3**, prepared from $Mo_2Cl_4(DTDD)_2$ and $(NH_4)_5Mo_2Cl_9·H_2O$, respectively: $[2] = 1.0 \times 10^{-4}$ *M* in C_5H_5N (——); $[3] = 8.2 \times 10^{-5}$ *M* in $CHCl_3$ (- - - -).

The identity of this material was confirmed by comparison of its physical and spectral properties with those observed for $Mo_2Cl_4(C_5H_5N)_4$ prepared from $Mo_2Cl_4(DTH)_2$ by ligand replacement. Attempts to carry out a similar reduction of $[Mo_2Cl_8]^{3-}$ with bipyridine yielded nonstoichiometric products.

The study of dinuclear molybdenum(II) halides has centered primarily on the investigation of the chloro complex $[Mo_2Cl_8]^{4-}$ and compounds derived from it. In our hands, numerous attempts to prepare the bromide analog, *i.e.*, $[Mo_2Br_8]^{4-}$, either by direct reaction of $Mo_2(O_2CCH_3)_4$ with hydrogen bromide under conditions similar to those used to prepare $[Mo_2Cl_8]^{4-}$ or by halide exchange between $[Mo_2Cl_8]^{4-}$ and hydrobromic acid, were unsuccessful. The principal product obtained from both procedures is $[Mo_2Br_8]^{3-}$, isolated as its tricesium salt.[19] This conclusion is sustained by product elemental analysis, chemical reactivity, and the visible spectrum of this substance [435 (2200) and 772 nm (167) in 6 *M* HBr] which shows a close similarity to that of $Cs_3Mo_2Cl_8$ [402 (1500) and 753 nm (97) in 6 *M* HCl].

Like tricesium octachlorodimolybdenum, $Cs_3Mo_2Br_8$ can be readily reduced. For example, treatment of $Cs_3Mo_2Br_8$ with pyridine yields tetrabromotetrakis(pyridine)dimolybdenum(II), **4**. The vibrational spectra of this and the related complex $Mo_2Br_4(bipy)_2$, **5**, prepared by reaction of $Mo_2Br_4(C_5H_5N)_4$ with 2,2′-bipyridine, are tabulated in Tables II and III. The infrared spectra of $Mo_2Br_4(C_5H_5N)_4$ and $Mo_2Br_4(bipy)_2$ display several bands which may be attributed to Mo–Br stretching vibrations. Thus, the spectrum of **4** shows an intense doublet centered at ~263 cm^{-1} while a strong band appears at 270 cm^{-1} in the spectrum of **5**. The Raman spectra of both these compounds are characterized by a very strong band at ~333 cm^{-1}, assigned to ν(Mo–Mo). Like the visible spectrum of $Mo_2Cl_4(C_5H_5N)_4$, that of $Mo_2Br_4(C_5H_5N)_4$ reveals two principal maxima, whereas the visible spectrum of $Mo_2Br_4(bipy)_2$, like that of $Mo_2Cl_4(bipy)_2$, shows only one.

In addition to pyridine, alkylphosphines also effect reduction of $[Mo_2X_8]^{3-}$, *i.e.*

$$[Mo_2X_8]^{3-} \xrightarrow{R_3P\text{-MeOH, }70°} Mo_2X_4(PR_3)_4$$

Higher yields of $Mo_2X_4(PR_3)_4$ are obtained, however, from the ligand replacement reaction between $Mo_2X_4(C_5H_5N)_4$ and excess phosphine. As a representative example, the visible, infrared, and Raman spectra of $Mo_2X_4[P(n\text{-}C_4H_9)_3]_4$ are summarized in Tables I-III. A similar reaction between $Mo_2Br_4(C_5H_5N)_4$ and alkyl sulfides provides a synthetically useful means of preparing sulfur-coordinated complexes of tetrabromodimolybdenum(II). The spectral properties of one such complex, $Mo_2Br_4[S(CH_3)_2]_4$, are summarized in Tables I-III.

Nitrile Complexes. Several complexes of tetrachlorodimolybdenum(II) give solutions in acetonitrile which exhibit equivalent visible spectra with maxima at 602 nm. Upon concentrating an acetonitrile solution of $Mo_2Cl_4[S(CH_3)_2]_4$, a dark green solid is obtained, the Raman spectrum of which displays an intense spike at 347 cm^{-1}. The infrared spectrum of this material shows a moderately strong band at 2275 cm^{-1}. The carbon-nitrogen stretching vibration in free acetonitrile occurs at 2254 cm^{-1}.[20] The shift of ν(C–N) to higher frequency is consistent with the presence of coordinated acetonitrile.[21] The strong band appearing at 297 cm^{-1} and the weaker band at 344 cm^{-1} are assigned as Mo–Cl stretching vibrations. These data suggest the formation of an acetonitrile complex of tetrachlorodimolybdenum(II), a conclusion that is supported by analytical data which are in agreement with the formulation $Mo_2Cl_4(NCCH_3)_4$. Similar complexes can be prepared with other nitriles, *e.g.*, benzonitrile. The spectral properties of $Mo_2Cl_4(NCCH_3)_4$ and $Mo_2Cl_4(NCC_6H_5)_4$ are presented in Tables I-III. In light of what is known[22] about the nature of metal-nitrile coordination in a variety of transition metal-nitrile complexes, it is likely that nitrile coordination in these new complexes, as in others, occurs through the nitrogen atom.

Oxygen-Bonded Complexes. The ability of dimethylformamide (DMF), dimethyl sulfoxide (DMSO), hexamethylphosphoric triamide (HMPA), pyridine *N*-oxide (PyO), and related compounds to form coordination complexes with a variety of metals including Mo(II) is well-known.[23] Attempts to prepare complexes of tetrachlorodimolybdenum(II) by direct reaction of DMF, DMSO, HMPA, and PyO with $(NH_4)_5Mo_2Cl_9·H_2O$ were largely unsuccessful. By contrast, $Mo_2Cl_4(DTDD)_2$ and related complexes of tetrachlorodimolybdenum(II) undergo a rapid reaction with DMF. The resulting compound, formulated as $Mo_2Cl_4(DMF)_4$ (**6**), is only sparingly soluble in a limited number of polar organic solvents. In most instances, dissolution is accompanied by rapid decomposition of the complex.

The infrared data for $Mo_2Cl_4(DMF)_4$ are listed in Table II. For comparison, the corresponding bands of the uncoordinated ligand are also listed. Two observations are apparent from these data. First, a strong band appears at 297 cm^{-1}. Based on its intensity and frequency, this band is assumed to be ν(Mo–Cl). Second, it is obvious that the carbonyl stretching vibration of the uncoordinated DMF occurs at 1670 cm^{-1} while in the spectrum of the coordinated

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(19) See also ref 13b.

(20) P. Venkateswarlu, *J. Chem. Phys.*, 19, 293 (1951).

(21) R. A. Walton, *Spectrochim. Acta*, 21, 1795 (1965), and references therein.

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(23) J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 11, 1280 (1972); W. Kitching, C. J. Moore, and D. Doddrell, *ibid.*, 9, 541 (1970); F. A. Cotton and N. F. Curtis, *ibid.*, 4, 241 (1965), and references therein; W. L. Reynolds, *Progr. Inorg. Chem.*, 12, 1 (1971).

ligand this band is shifted to 1637 cm^{-1}. Since it is generally acknowledged that the decreased carbon-oxygen stretching frequencies observed for coordinated DMF are indicative of metal-ligand coordination through the ligand oxygen, the above observations, therefore, not only confirm the presence of coordinated ligand but also suggest that their coordination involves oxygen-bonded structures.

The Raman data observed for **6** are summarized in Table III. The appearance of an intense band at 352 cm^{-1} is typical of dinuclear complexes of molybdenum(II).

The reaction of $Mo_2Br_4[S(CH_3)_2]_4$ with DMF affords a compound **7** which analyzes for $Mo_2Br_4(DMF)_4$ and whose spectral properties parallel those of **6**. Thus, **7** exhibits an intense Raman band at 348 cm^{-1} and an infrared spectrum indicative of oxygen-coordinated DMF as well as a Mo-Br stretching vibration at 240 cm^{-1}. Collectively, these data support the formulation of **6** and **7** as dinuclear complexes of molybdenum(II). As seen in Table I, the visible spectra of **6** and **7**, like those of $Mo_2Cl_4(C_5H_5N)_4$ and $Mo_2Br_4(C_5H_5N)_4$, reveal two distinct maxima.

Finally, tetrachlorobis(2,5-dithiahexane)dimolybdenum(II) also reacts with DMSO, HMPA, and PyO. Infrared and Raman spectra of the resulting air-sensitive substances are consistent with a dinuclear molybdenum(II) structure in which the DMSO, HMPA, and PyO molecules are coordinated through their oxygen atoms. However, repeated elemental analyses indicated these products were not stoichiometrically well-defined compounds.

Discussion

Figure 1 illustrates the structures proposed for $Mo_2Cl_4(PR_3)_4$. As demanded by the ^1H nmr data,[8] the phosphine and phosphite ligands coordinated to the same metal center are disposed trans to one another.[24,25] The extension of this conclusion to the general family of complexes $Mo_2X_4L_4$, barring certain exceptions (*vide infra*), is supported by two additional considerations. First, the infrared metal-chlorine vibrational spectra of the monodentate phosphine, phosphite, sulfide, benzonitrile, and pyridine complexes of tetrachlorodimolybdenum(II) all bear strong similarities. In particular, each is characterized by the presence of two distinct Mo-Cl stretching vibrations: a strong band occurring at 337 ± 15 cm^{-1} and a less intense band appearing at 285 ± 10 cm^{-1}. A typical spectrum is seen in Figure 3.

Second, the appearance of two Mo-Cl stretching vibrations is also consistent with the proposed structure **1b** (point group D_{2d}) for which group theory considerations predict a total of two infrared-active M-X stretching vibrations (B_2 and E). Similar considerations for structure **1a** (point group D_{2h}) also predict two Mo-X stretching modes (B_{1u} and B_{2u}).[26]

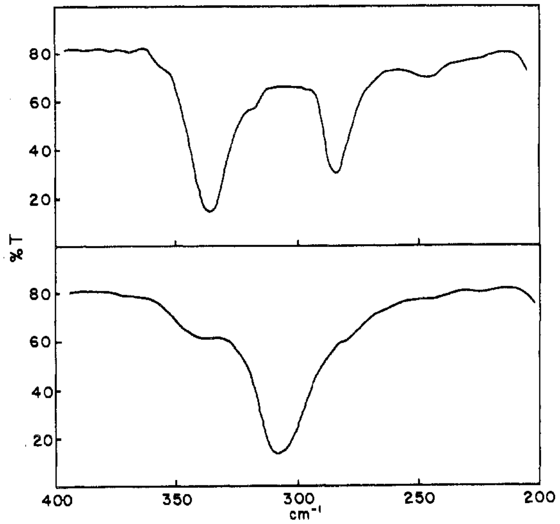

Figure 3. Infrared spectra (400–200 cm^{-1}) of $Mo_2Cl_4[S(C_2H_5)_2]_4$ (top) and $Mo_2Cl_4(DTDD)_2$ (bottom).

The structure(s) of those complexes involving the bidentate ligands DTH, DTD, DTDD, TMEDP, and bipyridine is not as readily inferred as that of $Mo_2X_4L_4$; however, several key structural characteristics can be deduced from existing spectral data, particularly from the infrared-active metal-halogen stretching frequencies. Comparison of the Mo-Cl stretching frequencies in Table II reveals that they fall into two distinct regions. As discussed above, complexes involving monodentate ligands exhibit two Mo-Cl stretching vibrations with the higher frequency band occurring at 337 ± 15 cm^{-1}; complexes which involve the bidentate chelating ligands DTH, DTD, DTDD, TMEDP, and bipy are characterized by a single intense Mo-Cl stretching vibration at 305 ± 10 cm^{-1} with a shoulder appearing in most instances at ~340 cm^{-1} (*cf.* Figure 3).

The marked dependence of ν(M-Cl) on the nature of the trans ligand in square-planar complexes is contrasted by the relative insensitivity of ν(M-Cl) to the nature of the cis ligands.[17,26] Thus, for example, the intense, asymmetric Pt-Cl stretching vibration in *cis*-PtL_2Cl_2 is sometimes equal to but generally at a significantly lower frequency than ν(Pt-Cl) observed in the corresponding trans complex.[17] Extending this observation to the fused square-planar geometry of the dinuclear molybdenum(II) systems, it follows, in view of the preferred trans orientation demonstrated for monodentate phosphine and phosphite and presumably also sulfide and pyridine, that the significantly different molybdenum-chlorine vibrational spectra observed for complexes involving bidentate chelating ligands arise because the halogen centers coordinated to the same metal center are situated cis to each other. Despite this boundary condition there remains a minimum of three geometries (Figure 4), all of which represent reasonable structures for tetrahalodimolybdenum(II) complexes of the general formulation $Mo_2X_4(LL)_2$.[27]

The electronic spectra of $Mo_2X_4L_4$ and $Mo_2X_4(LL)_2$ also reveal several structure-related correlations. For example,

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(24) A single-crystal X-ray study[25] has established the dinuclear complex $Re_2Cl_4[P(C_2H_5)_3]_4$ as isostructural with **1b** shown in Figure 1. Although of lower symmetry than **1a**, structure **1b** is presumably preferred for steric reasons.[25] In view of the likely probablility that the Mo–Mo bond distance in $Mo_2X_4L_4$ will prove, as it has in all other dinuclear Mo(II) complexes, to be ~2.1 Å, comparable if not greater steric crowding than that experienced in $Re_2Cl_4[P(C_2H_5)_3]_4$, where the Re–Re bond distance is ~2.2 Å, seems probable. The obvious implication is that the same geometry is therefore likely to be preferred by $Mo_2X_4L_4$.

(25) F. A. Cotton, B. A. Frenz, J. R. Ebner, and R. A. Walton, *J. Chem. Soc., Chem. Commun.*, 4 (1974).

(26) Unfortunately, the number of Raman-active M–X stretching modes observed for $Mo_2X_4L_4$ and $Mo_2X_4(LL)_2$ cannot be deduced from the Raman data (Table III) because of preferential intensity enhancement resulting from resonance effects.

(27) Group theory considerations predict the following ir-active metal-halogen stretching vibrations for the structures: (a) point group C_{2v}, three bands (A_1, B_1, B_2); (b) point group C_2, four bands (2 A, 2 B); (c) point group C_{2h}, two bands (A_u, B_u). The discrepancy between the number of bands predicted for structures (a) and (b) and the number of bands observed for $Mo_2Cl_4(LL)_2$ suggests, but does not require, structure (c) to be the preferred geometry for these complexes. This conclusion is also consistent with apparent steric considerations[24] in that structure (c) would appear to provide the least steric repulsion between ligand molecules coordinated to adjacent molybdenum centers.

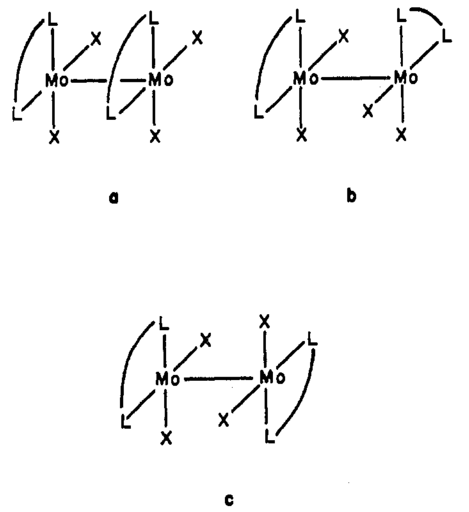

Figure 4. Suggested structures for the bidentate complexes of tetrahalodimolybdenum(II), $Mo_2X_4(LL)_2$.

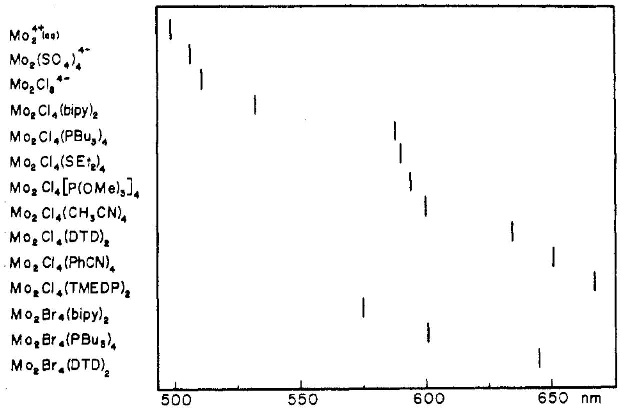

Figure 5. The relationship between the position of the visible absorption band and the ligand character in some dimolybdenum(II) complexes.

it is apparent from the data summarized in Table I and Figure 5 that a noticeable enhancement in intensity and red-shift in position of the characteristic visible band occurs as the π-acceptor character of the coordinating ligands increases. Such observations are consistent with an increasing delocalization of the electron density from the metal-metal bond, presumably as a result of enhanced ligand nephelauxetic character. A close comparison of the individual entries in Table I reveals the additional observation that this transition occurs at a significantly higher frequency in the trans-coordinated phosphine and sulfide complexes $Mo_2Cl_4L_4$ [$L = P(n\text{-}C_4H_9)_3$, $S(CH_3)_2$, $S(C_2H_5)_2$] than in the related cis-coordinated complexes $Mo_2Cl_4(LL)_2$, involving chelating ligands TMEDP, DTH, DTD, and DTDD. These observations are summarized by the following spectrochemical series expressing the relative order of the frequency of this transition as a function of the coordinating ligand for a variety of tetrachloro- and tetrabromodimolybdenum(II) complexes: X = Cl: $Cl > bipy > P(n\text{-}C_4H_9)_3 \sim P(OCH_3)_3 \sim S(C_2H_5)_2 > DTD > TMEDP$. X = Br: $bipy > S(CH_3)_2 \sim P(n\text{-}C_4H_9)_3 > DTD$. A clearer understanding of the origins of these relationships must await the further investigation and structural characterization of these compounds; nonetheless, it appears that the characteristic visible band in tetrahalodimolybdenum(II) compounds is likely to provide a sensitive, convenient probe of structural differences in these systems.

The structure of the 1,4-dithiane complex $Mo_2Cl_4(S_2C_4H_8)_2$ merits brief individual discussion at this point. Infrared spectral studies of p-dithiane-metal complexes ($C_4H_8S_2 \cdot MCl_2$, M = Cu, Hg, Cd, Pt) suggest that the coordinated ligand in these complexes, like the free ligand, exists in the chair form.[28] It follows that p-dithiane does not serve as a chelating bidentate ligand in such instances but rather as an intermolecular bridging ligand, yielding polymeric chains. The infrared and electronic spectral characteristics of $Mo_2Cl_4(S_2C_4H_8)_2$, which are distinctly different from those exhibited by $Mo_2Cl_4(DTH)_2$ and related complexes involving the bidentate sulfur-containing ligands shown in Table I, become reasonable when viewed in this context. Thus, as a nonchelating ligand, p-dithiane might be expected to coordinate to Mo_2Cl_4 much as any monodentate alkyl sulfide. This contention is supported by the similarity observed between the number and frequency of the ir-active Mo-Cl stretching vibrations as well as the position of the characteristic visible absorption in $Mo_2Cl_4(S_2C_4H_8)_2$ and the corresponding values exhibited by $Mo_2Cl_4(SR_2)_4$ ($R = CH_3$, C_2H_5). Indeed, the internal consistency of this result argues for the correctness of the aforecited spectroscopic correlations and conclusions.

Several anomalies persist in the above spectral correlations when applied to the complexes $Mo_2Cl_4(NCCH_3)_4$ and $Mo_2Cl_4(DMF)_4$. For example, the recognized position of nitrile ligands in the π-acidity scale (*i.e.*, $R_3P \sim R_2S > RCN$) is not reflected, as it is for other trans-coordinated monodentate ligands, in the position of the visible absorption band.[29]

A more serious anomaly results from a close comparison of infrared vibrational spectra. Consonant with the metal-chlorine vibrational spectra observed for monodentate phosphine, phosphite, sulfide, and pyridine complexes of tetrachlorodimolybdenum(II), the infrared spectrum of $Mo_2Cl_4(NCC_6H_5)_4$ exhibits two distinct Mo-Cl stretching vibrations (347 (s) and 289 (m) cm^{-1}). By contrast, the infrared spectrum of $Mo_2Cl_4(NCCH_3)_4$ shows a metal-chlorine vibrational spectrum typical of cis-coordinated complexes, *i.e.*, a strong, somewhat broadened band at 297 cm^{-1} accompanied by a medium to weak band at 344 cm^{-1}. Parallel anomalies arise from a similar comparison of the metal-halogen vibrational spectrum of $Mo_2Cl_4(DMF)_4$. It is not clear whether these combined considerations reflect actual anomalies or rather result from a difference between the structure(s) of $Mo_2Cl_4(NCCH_3)_4$ and $Mo_2Cl_4(DMF)_4$ and the structure **1b** suggested for other complexes of the family $Mo_2X_4L_4$.

The central purpose of this study was to survey the reactivity of octa- and tetrahalodimolybdenum(II) complexes. We have found that under mild conditions $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ serves as a useful precursor to a variety of dinuclear molybdenum(II) complexes containing sulfur donor molecules. In turn, these complexes can themselves be used to prepare a number of additional dinuclear complexes which cannot be prepared from $(NH_4)_5Mo_2Cl_9 \cdot H_2O$ directly.

Several questions are raised by these results. For example, the mechanism of substitution now becomes a matter of some interest. The preparation of trans-coordinated complexes from cis-coordinated precursors involves geometrical isomerism. Are dissociative or displacement (or both) path-

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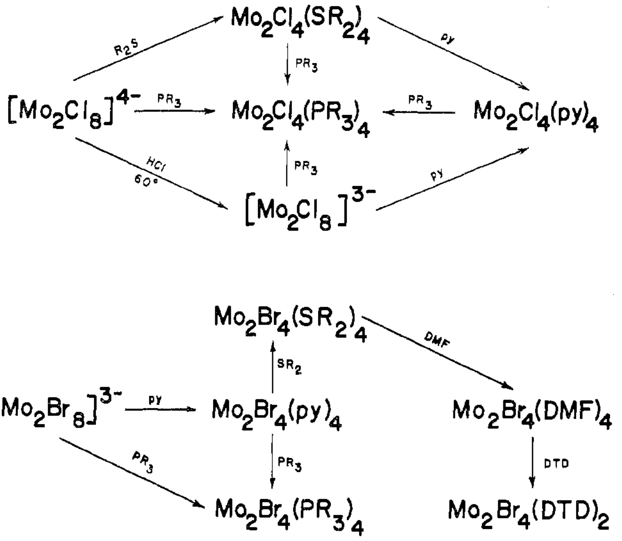
(28) P. J. Hendra and D. B. Powell, *J. Chem. Soc.*, 5105 (1960).

(29) The fact that this band occurs at a considerably lower frequency in $Mo_2Cl_4(NCC_6H_5)_4$ than the corresponding band in $Mo_2Cl_4(NCCH_3)_4$ is presumably in part a consequence of the ability of the phenyl ring to participate in extended conjugation, thereby enhancing the delocalization of electron density from the metal-metal bond.

Scheme I. Some Reactions of Tetra- and Octahalodimolybdenum Complexes



ways involved? To what degree do electronic and steric factors manifested in ligands coordinated to the same molybdenum center affect substitution and other processes at the adjacent metal center? These and related questions now under investigation will be discussed more fully in forthcoming papers.

Finally, we have observed that the $[Mo_2X_8]^{3-}$ ion can be reduced to $Mo_2X_4L_4$ by excess pyridine or tri-*n*-butylphosphine to produce the respective complexes of tetrahalodimolybdenum(II). The reaction, which may proceed with retention of the metal-metal bond, provides a convenient and at present the only procedure for preparing derivatives of tetrabromodimolybdenum(II) compounds. These and some related chemical relationships are summarized in Scheme I.

Acknowledgments. We are grateful to Professor R. A. Walton for communicating the results of related investigations prior to publication and to Professor M. Francia of Barnard College for helpful discussions.

Registry No. $Cs_3Mo_2Br_8$, 39469-89-1; $Mo_2Cl_4[S(C_2H_5)_2]_4$, 51731-32-9; $Mo_2Cl_4[S(CH_3)_2]_4$, 51731-33-0; $Mo_2Cl_4(DTH)_2$, 51731-34-1; $Mo_2Cl_4(DTD)_2$, 51731-35-2; $Mo_2Cl_4(DTDD)_2$, 51731-36-3; $Mo_2Cl_4(S_2C_4H_8)_2$, 51731-38-5; $Mo_2Cl_4(C_5H_5N)_4$, 51752-03-5; $Mo_2Cl_4(bipy)_2$, 51731-39-6; $Mo_2Br_4(C_5H_5N)_4$, 51731-40-9; $Mo_2Br_4[S(CH_3)_2]_4$, 51731-41-0; $Mo_2Br_4(DTD)_2$, 51731-42-1; $Mo_2Br_4(bipy)_2$, 51731-43-2; $Mo_2Br_4[P(n\text{-}C_4H_9)_3]_4$, 51731-44-3; $Mo_2Cl_4(TMEDP)_2$, 51731-45-4; $Mo_2Cl_4(NCCH_3)_4$, 51731-46-5; $Mo_2Cl_4(NCC_6H_5)_4$, 51731-47-6; $Mo_2Cl_4(DMF)_4$, 51731-48-7; $Mo_2Br_4(DMF)_4$, 51731-49-8; $Mo_2Cl_4[P(n\text{-}C_4H_9)_3]_4$, 38832-72-3; $Mo_2Cl_4[P(OCH_3)_3]_4$, 38832-74-5; $(NH_4)_5Mo_2Cl_9 \cdot H_2O$, 51794-31-1; 2,2′-bipyridine, 366-18-7; pyridine, 110-86-1; acetonitrile, 75-05-8; DMF, 68-12-2; $Cs_3Mo_2Cl_8$, 51795-65-4.

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A Nuclear Magnetic Resonance Study of the Conformations of Six-Membered Chelate Rings in Manganese Carbonyl Halide Complexes of Di(tertiary arsines)

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Received April 15, 1974 AIC402402

The complexes $XMn(CO)_3As(CH_3)_2CH_2CHRCH_2As(CH_3)_2$ (R = H, $C(CH_3)_3$; X = Cl, Br, I) which contain six-membered chelate rings were prepared and their nmr spectra investigated. Selectively deuterated analogs were prepared in order to solve the spectra. The locked-chair configuration found when R = H shows the least interaction between the axial methyl group of the arsenic atoms and the axial halogen atom. When R = $C(CH_3)_3$, two isomers were observed for each complex; both have rings with locked-chair configurations and R equatorial. The more stable isomer has the same configuration as a complex with R = H except the *tert*-butyl group is in an equatorial position.

Introduction

The stereochemistry of metal complexes that contain six-membered rings has been of recent interest.[2-16] In contrast to five-membered ring systems which have a number of equal-energy conformers,[3-17] theoretical[18] and X-ray[8,12,14,16] studies of six-membered ring systems, containing an octahedral site, indicate the symmetrical chair conformer (a) (Figure 1) is favored over the symmetrical boat (b) or skew-boat conformers (c).

In an earlier publication[2] we discussed the nmr spectra of chromium, molybdenum, and tungsten tetracarbonyl com-

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