acetylacetonate[9] also has a grouping of three face-sharing octahedra. These octahedra are quite elongated, however, and the Ni–Ni distances are long (2.89 Å.).

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Reactions of Molybdenum(V) Chloride and Molybdenum(V) Oxotrichloride with Some Oxygen and Sulfur Donor Molecules

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Complexes of the types $MoOCl_3 \cdot 2L$ and $MoOCl_3 \cdot L'$ have been prepared by the reactions of molybdenum(V) chloride and molybdenum(V) oxotrichloride with the ligands L = tetrahydrofuran, pentamethylene oxide, tetrahydrothiophene, and pentamethylene sulfide, and L′ = 1,4-dioxane, 1,4-thioxane, ethylene glycol dimethyl ether, dimethyl sulfide, diethyl sulfide, and di-*n*-propyl sulfide. The compounds $MoO_2Cl_2 \cdot$2tetrahydrofuran and $MoCl_4 \cdot$2pentamethylene oxide have also been isolated. The visible and infrared spectra and the magnetic properties of these compounds have been examined and the results are discussed.

Introduction

Very few complexes of molybdenum(V) oxotrichloride have been reported, presumably because the halide is rather difficult to prepare. Those compounds that have been characterized have been prepared from molybdenum(V) chloride. Thus Horner and Tyree[1] recently treated molybdenum(V) chloride with the oxygen-containing ligands LO (where L = $(C_6H_5)_3P$, $(C_6H_5)_3As$, and $(CH_3)_2S$) and obtained the complexes $MoOCl_3 \cdot 2LO$. It seems that oxygen is extracted from the ligand, with the transient formation of molybdenum(V) oxotrichloride, which reacts with excess of the ligand. Mitchell[2] studied the reaction of bipyridyl with the pentahalide in moist carbon tetrachloride and noted the formation of the compound $MoOCl_3 \cdot$bipy.

Experimental

Analysis.—Molybdenum and chlorine were determined as described previously.[3] For sulfur determination, the compounds were fused with a Na_2O_2–Na_2CO_3 mixture in a bomb, and the sulfate formed was determined gravimetrically as $BaSO_4$. Carbon and hydrogen were determined by a professional analyst.

Spectra.—Visible spectra were determined on solutions in 1-cm. cells by means of a Unicam SP 600 spectrophotometer. Infrared spectra were examined on Nujol mulls with a Unicam SP 200 spectrophotometer.

Molecular Weight.—Determinations were made cryoscopically in benzene.[4]

Magnetic Susceptibility and Oxidation State.—Estimations were carried out in the usual manner.[5]

Materials.—$MoCl_5$ (Climax Molybdenum Co.) was purified by vacuum sublimation. $MoOCl_3$ was prepared as described by Edwards.[6] *Anal.* Calcd. for $MoOCl_3$: Cl, 48.7; Mo, 43.9. Found: Cl, 48.9; Mo, 43.8. The ligands were dried with calcium hydride and distilled several times from fresh potassium metal.

Reactions were carried out by standard procedures, using excess of ligand, without another solvent. Ampoules of the reactants were sealed at −80° and the contents allowed to react at room temperature. After a suitable reaction period the ampoule was opened under a nitrogen atmosphere and connected to an all-glass vacuum system incorporating a filtration unit. All compounds isolated were pumped under high vacuum for several hours prior to analysis.

(1) **Reactions of $MoCl_5$.** (i) **With C_4H_8O.**—The dark brown solution first formed slowly turned green and after 30 min. deposited a green solid. *Anal.* Calcd. for $MoOCl_3 \cdot 2C_4H_8O$: C, 26.5; H, 4.5; Cl, 29.4; Mo, 26.5. Found: C, 26.3; H, 4.6; Cl, 29.6; Mo, 25.9; μ, 1.68 B.M.; oxidation state, 5.0. Reaction for a really prolonged period (2 years) gave a dark brown solid. *Anal.* Calcd. for $MoO_2Cl_2 \cdot 2C_4H_8O$: C, 28.0; H, 4.7; Cl, 20.7; Mo, 28.1. Found: C, 27.5; H, 4.8; Cl, 21.1; Mo, 28.1; χ_M', -12×10^{-6} c.g.s.

(ii) **With $C_5H_{10}O$.**—A mixture of yellow and green solids was deposited from solution. The yellow compound was obtained pure by washing out the green solid (and various ligand decomposition products) with benzene. *Anal.* Calcd. for $MoCl_4 \cdot 2C_5H_{10}O$: C, 29.3; H, 4.9; Cl, 34.6; Mo, 23.4. Found: C, 29.3; H, 5.3; Cl, 34.7; Mo, 23.3; μ, 2.37 B.M.; oxidation state, 4.1. The green solid could not be isolated in a pure form.

(iii) **With $C_4H_8O_2$.**—After reaction for 20 days the brown solution deposited green crystals; the latter were isolated. *Anal.* Calcd. for $MoOCl_3 \cdot 1.5C_4H_8O_2$: C, 20.6; H, 3.5; Cl, 30.4; Mo, 27.4. Found: C, 20.1; H, 3.6; Cl, 30.5; Mo, 25.1; μ, 1.66 B.M.; oxidation state, 5.0.

(2) **Reactions of $MoOCl_3$.**—Reactions with oxygen ligands were carried out in the absence of a solvent; the product was

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[1] S. M. Horner and S. Y. Tyree, *Inorg. Chem.*, **1**, 122 (1962).

[2] P. C. H. Mitchell, *J. Inorg. Nucl. Chem.*, **25**, 963 (1963).

[3] D. A. Edwards and G. W. A. Fowles, *J. Chem. Soc.*, 24 (1961).

[4] G. W. A. Fowles and R. A. Hoodless, *ibid.*, 33 (1963).

[5] M. W. Duckworth, G. W. A. Fowles, and R. A. Hoodless, *ibid.*, 5665 (1963).

[6] D. A. Edwards, *J. Inorg. Nucl. Chem.*, **25**, 1198 (1963).

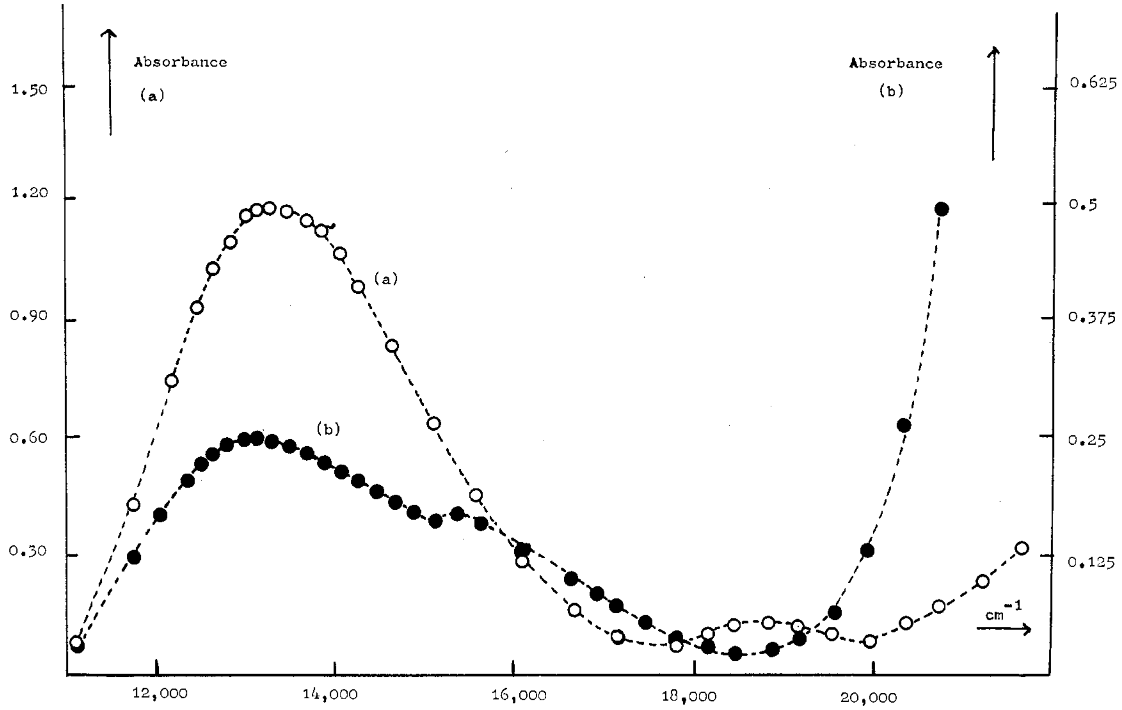

Figure 1.—Absorption spectra of (a) $MoOCl_3 \cdot 2C_4H_8O$ in C_4H_8O (2.8×10^{-2} *M*) and (b) $MoOCl_3 \cdot 2C_4H_8S$ in C_4H_8S.

either insoluble in the ligand (reactions iv and v) or was obtained by evaporation of the solution (reactions i, ii, and iii). Analogous reactions with sulfur ligands were carried out using benzene as solvent, the products being obtained by removal of volatiles at the pump. All complexes were green or yellow-green.

(i) **With C_4H_8O.**—*Anal.* Calcd. for $MoOCl_3 \cdot 2C_4H_8O$: C, 26.5; H, 4.5; Cl, 29.4; Mo, 26.5. Found: C, 26.5; H, 4.6; Cl, 29.3; Mo, 25.8; μ, 1.73 B.M.; oxidation state, 4.9.

(ii) **With $C_5H_{10}O$.**—*Anal.* Calcd. for $MoOCl_3 \cdot 2C_5H_{10}O$: C, 30.8; H, 5.2; Cl, 27.2; Mo, 24.6. Found: C, 30.5; H, 5.4; Cl, 27.7; Mo, 24.2; μ, 1.72 B.M.; oxidation state, 5.0.

(iii) **With $C_4H_{10}O_2$.**—*Anal.* Calcd. for $MoCl_3 \cdot C_4H_{10}O_2$: C, 15.6; H, 3.3; Cl, 34.5; Mo, 31.1; mol. wt., 309. Found: C, 15.9; H, 3.7; Cl, 33.7; Mo, 30.7; μ, 1.68 B.M.; oxidation state, 4.9; mol. wt., 321 (0.5% in C_6H_6).

(iv) **With $C_4H_8O_2$.**—*Anal.* Calcd. for $MoOCl_3 \cdot C_4H_8O_2$: C, 15.7; H, 2.6; Cl, 34.7; Mo, 31.3. Found: C, 15.9; H, 3.0; Cl, 34.7; Mo, 31.1; μ, 1.73 B.M.; oxidation state, 5.0.

(v) **With C_4H_8OS.**—*Anal.* Calcd. for $MoOCl_3 \cdot C_4H_8OS$: C, 14.9; H, 2.5; Cl, 33.0; Mo, 29.8; S, 9.9. Found: C, 15.8; H, 3.2; Cl, 32.4; Mo, 29.5; S, 9.2; μ, 1.70 B.M.

(vi) **With R_2S (R = CH_3, C_2H_5, and *n*-C_3H_7).**—*Anal.* Calcd. for $MoOCl_3 \cdot S(CH_3)_2$: C, 8.6; H, 2.2; Cl, 37.9; Mo, 34.2; S, 11.4. Found: C, 8.7; H, 2.4; Cl, 38.2; Mo, 34.1; S, 10.9; μ, 1.69 B.M. Calcd. for $MoOCl_3 \cdot S(C_2H_5)_2$: C, 15.6; H, 3.3; Cl, 34.5; Mo, 31.1; S, 10.4; mol. wt., 309. Found: C, 15.9; H, 3.5; Cl, 34.4; Mo, 30.8; S, 9.9; μ, 1.70 B.M.; mol. wt., 315, 287 (0.5% solution in C_6H_6). Calcd. for $MoOCl_3 \cdot S(n\text{-}C_3H_7)_2$: C, 21.4; H, 4.2; Cl, 31.6; Mo, 28.5; S, 9.5. Found: C, 21.5; H, 4.3; Cl, 30.4; Mo, 27.5; S, 9.2.

(vii) **With C_4H_8S.**—*Anal.* Calcd. for $MoOCl_3 \cdot 2C_4H_8S$: C, 24.3; H, 4.1; Cl, 27.0; Mo, 24.3; S, 16.3. Found: C, 21.6; H, 3.9; Cl, 27.4; Mo, 23.8; S, 15.3; μ, 1.75 B.M.

(viii) **With $C_5H_{10}S$.**—*Anal.* Calcd. for $MoOCl_3 \cdot 2C_5H_{10}S$: C, 28.4; H, 4.8; Cl, 25.2; Mo, 22.7; S, 15.2. Found: C, 28.6; H, 4.9; Cl, 24.9; Mo, 22.0; S, 15.0; μ, 1.70 B.M.

Results and Discussion

In this paper we report the complexes $MoOCl_3 \cdot 2L$, where L = C_4H_8O, $C_5H_{10}O$, C_4H_8S, and $C_5H_{10}S$, and $MoOCl_3 \cdot L'$, where L' = $C_4H_8O_2$, C_4H_8OS, $C_4H_{10}O_2$, and several dialkyl sulfides. These formed readily in the direct reaction of molybdenum(V) oxotrichloride with excess of the appropriate ligand at room temperature. The tetrahydrofuran compound also formed upon reaction of excess of ligand with molybdenum(V) chloride, but we found that prolonged reaction periods (2 years) resulted in the formation of the diamagnetic sexivalent compound $MoO_2Cl_2 \cdot 2C_4H_8O$. Reaction of pentamethylene oxide with molybdenum(V) chloride yielded a mixture of the quadrivalent complex $MoCl_4 \cdot 2C_5H_{10}O$ and a green solid which could not be obtained in a pure form but appeared to be $MoOCl_3 \cdot 2C_5H_{10}O$. Dioxane and molybdenum(V) chloride yielded a complex of over-all composition $MoOCl_3 \cdot 1.5C_4H_8O_2$.

All the complexes of quinquevalent molybdenum had magnetic moments quite close to the spin-only value. This was to be expected, since the strong π-bonding between the molybdenum and oxygen atoms reduces the spin–orbit coupling constant from 1030 to 240 cm.$^{-1}$.(7)

Visible and Ultraviolet Spectra of $MoOCl_3 \cdot 2L$ Complexes.—These complexes are best considered as octahedral with a strong tetragonal distortion resulting from the molybdenum–oxygen bond. The visible spectrum of each of the four complexes (measured in solution in excess of the ligand) shows two weak peaks with extinction coefficients below 50. The first peak is observed around 13,000 cm.$^{-1}$ in every case, but the second is found at 19,000 cm.$^{-1}$ for the oxygen ligand complexes and around 15,000 cm.$^{-1}$ for the sulfur analogs (*cf.* Figure 1). Horner and Tyree(8) also found

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(7) H. B. Gray and C. R. Hare, *Inorg. Chem.*, **1**, 363 (1962); C. R. Hare, I. Bernal, and H. B. Gray, *ibid.*, **1**, 831 (1962).

(8) S. M. Horner and S. Y. Tyree, *ibid.*, **2**, 568 (1963).

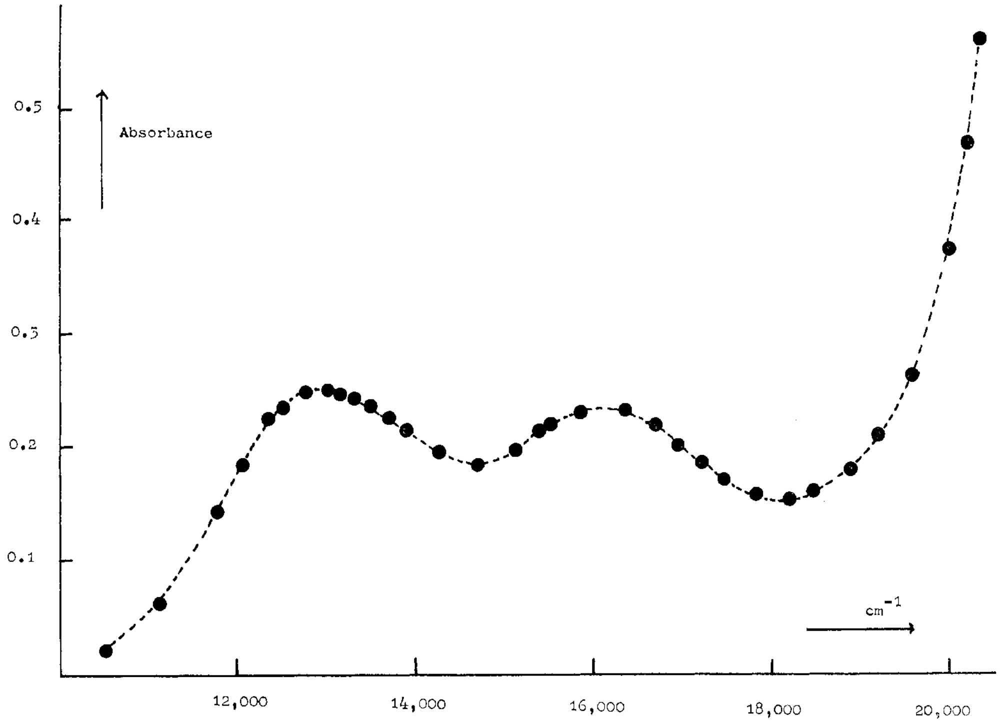

Figure 2.—Absorption spectrum of $MoOCl_3 \cdot S(CH_3)_2$ in C_6H_6–$S(CH_3)_2$ mixed solvent (1.3×10^{-2} *M*).

two peaks, one between 13,500 and 13,800 cm.$^{-1}$ and the other between 22,300 and 23,800 cm.$^{-1}$, and assigned these peaks to the transitions $^2E_g \leftarrow {}^2B_{2g}$ and $^2B_{1g} \leftarrow {}^2B_{2g}$, respectively. There is some doubt about the validity of these assignments, since they are based on the orbital scheme proposed by Ballhausen and Gray[9] for the analogous vanadyl systems and subsequently extended by Gray and Hare[7] to molybdenum. Recently, controversy has arisen[10] over the vanadyl assignments, and it has been shown[11] that the molybdenum scheme put forward for $[MoOCl_5]^{2-}$ does not account for the spectrum of $[MoOBr_5]^{2-}$ or the tungsten analogs.

TABLE I

VISIBLE SPECTRA OF $MoOCl_3$ COMPLEXES

Compound	Solvent	Peak positions, cm.$^{-1}$ [a]	
$MoOCl_3 \cdot 2C_4H_8O$	C_4H_8O	13,400 (40)	19,050
$MoOCl_3 \cdot 2C_5H_{10}O$	$C_5H_{10}O$	13,160	19,050
$MoOCl_3 \cdot 2C_4H_8S$	C_4H_8S–C_6H_6	13,160	15,150 sh
$MoOCl_3 \cdot 2C_5H_{10}S$	$C_5H_{10}S$–C_6H_6	13,160 (14)	15,380 sh (11)
$MoOCl_3 \cdot C_4H_8O_2$	$C_4H_8O_2$	13,070	18,350
$MoOCl_3 \cdot C_4H_{10}O_2$	$C_4H_{10}O_2$	13,160	...
$MoOCl_3 \cdot C_4H_8OS$	C_4H_8OS–C_6H_6	13,510	17,540
$MoOCl_3 \cdot S(CH_3)_2$	$S(CH_3)_2$–C_6H_6	12,990 (20)	16,390 (18)
$MoOCl_3 \cdot S(C_2H_5)_2$	$S(C_2H_5)_2$–C_6H_6	13,160 (14)	15,620 (11)
$MoOCl_3 \cdot S(C_2H_5)_2$	C_6H_6	13,070 (21)	
$MoOCl_3 \cdot S(n\text{-}C_3H_7)_2$	$S(n\text{-}C_3H_7)_2$–C_6H_6	13,160	15,150 sh

[a] ϵ_{max} values given in parentheses.

The ^2E_g and $^2B_{2g}$ terms arise through the splitting of the T_{2g} term as a result of the axial asymmetry (almost exclusively due to the molybdenum–oxygen multiple bond), and the extent of the splitting should not vary significantly from compound to compound. For this reason the peak found around 13,000 cm.$^{-1}$ is clearly associated with the $^2E_g \leftarrow {}^2B_{2g}$ transition. The peak associated with the $^2B_{1g} \leftarrow {}^2B_{2g}$ transition, however, should depend to a greater extent on the ligands associated with $MoOCl_3$, but it would be surprising if this should shift from 23,000 cm.$^{-1}$ for LO ligands, to 19,000 for ether ligands, and to 15,000 cm.$^{-1}$ for thioether ligands, even though this is the general ligand field order.

The ultraviolet spectrum of the adduct $MoOCl_3 \cdot 2C_4H_8O$ measured in tetrahydrofuran solution shows three peaks, at 28,400, 32,400, and 40,400 cm.$^{-1}$, the latter two peaks being much more intense than the first. These values are very close indeed to those observed for the oxychloride ion $[MoOCl_5]^{2-}$ [11] (28,010, 32,260, and 40,000 cm.$^{-1}$).

Infrared Spectra.—The ether complexes show the expected infrared spectra (*cf.* Table II) with molybdenum–oxygen stretching frequencies in the 980–1000

TABLE II

INFRARED SPECTRA

Compound	ν C–O–C (asym.)	ν Mo=O
C_4H_8O	1075	...
$MoOCl_3 \cdot 2C_4H_8O$	1050	1000; 985
$MoO_2Cl_2 \cdot 2C_4H_8O$	1035	990 br
$C_5H_{10}O$	1095	...
$MoOCl_3 \cdot 2C_5H_{10}O$	1070	995; 985
$C_4H_{10}O_2$	1125	...
$MoOCl_3 \cdot C_4H_{10}O_2$	1075	1000; 985
$C_4H_8O_2$	1125	...
$MoOCl_3 \cdot C_4H_8O_2$	1095	995 br
C_4H_8OS	1105	...
$MoOCl_3 \cdot C_4H_8OS$	1090 br	990 br

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(9) C. J. Ballhausen and H. B. Gray, *Inorg. Chem.*, **1**, 111 (1962).

(10) J. Selbin and T. R. Ortolano, *J. Inorg. Nucl. Chem.*, **26**, 37 (1964); T. R. Ortolano, J. Selbin, and S. P. McGlynn, *J. Chem. Phys.*, **41**, 262 (1964).

(11) E. A. Allen, B. J. Brisdon, D. A. Edwards, G. W. A. Fowles, and R. G. Williams, *J. Chem. Soc.*, 4649 (1963).

cm.$^{-1}$ region.[12] The asymmetric C–O–C stretching frequencies of the tetrahydrofuran and pentamethylene oxide are lowered by 25 cm.$^{-1}$ upon coordination. The infrared spectrum of the complex ($MoOCl_3 \cdot C_4H_{10}O_2$) formed by the potentially chelating ether, ethylene glycol dimethyl ether, indicates that both oxygen atoms are donated to molybdenum; thus, whereas the free ligand shows an asymmetric C–O–C stretching frequency at 1125 cm.$^{-1}$, the complex shows a single modified peak at 1075 cm.$^{-1}$; it has been observed previously[13] that in the titanium complex $TiCl_3 \cdot 1.5C_4H_{10}O_2$ both the modified and unmodified peaks were present, indicating that some at least of the ligands were not coordinated through both oxygen atoms. Since the molybdenum complex is monomeric in benzene solution, it must be six-coordinate unless a molecule of solvent is also coordinated. The complex shows the usual peak in the visible spectrum around 13,000 cm.$^{-1}$.

The infrared spectrum of the dioxane complex also shows a single asymmetric C–O–C stretching frequency at 1095 cm.$^{-1}$, indicating the coordination of both oxygen atoms, but we suggest that as the complex is insoluble in the usual solvents, it is likely to be dimeric or polymeric with the dioxane molecules linking neighboring molybdenum atoms. A similar structure suggested for the mercury complexes $HgCl_2 \cdot C_4H_8O_2$[14] has been confirmed by X-ray studies.[15] An analogous structure is proposed for the thioxane adduct, on the basis of its general insolubility and infrared spectrum, although it is not possible to show that the sulfur atom is coordinated (as well as oxygen) since the C–S–C vibration is very weak and difficult to observe with certainty.[16] In the titanium complexes $TiX_4 \cdot 2C_4H_8OS$ (X = Cl and Br),[17] proton resonance studies have confirmed the infrared evidence that thioxane coordinates through sulfur and not oxygen, however, so it is reasonable to assume that the sulfur atom will coordinate to molybdenum. The visible spectra of both the dioxane and thioxane complexes show two peaks, one at 13,000 and the other around 18,000 cm.$^{-1}$.

$MoOCl_3 \cdot L'$ Complexes.—Whereas the cyclic thioethers gave 1:2 adducts, only 1:1 adducts could be isolated from reactions between $MoOCl_3$ and dialkyl sulfides. The green complexes, $MoOCl_3 \cdot SR_2$, were soluble in benzene, and a molecular weight study of the diethyl sulfide adduct showed it to be monomeric. In the solvent mixture SR_2–C_6H_6, the green solutions formed showed two peaks, but benzene solutions were brown, and their spectra no longer showed the second peak. We tentatively suggest that in the solid the complexes may be six-coordinate (through chlorine bridging), and that in benzene solution dissociation may occur to give the monomeric species; when dialkyl sulfide is added to the benzene solution a molecule of the ligand may then coordinate to re-establish six-coordination. Similar proposals have been made[4] to explain changes in the spectra of the titanium complexes $TiX_3 \cdot 2N(CH_3)_3$ (X = Cl and Br) as solids and in solution.

One yellow quadrivalent complex, $MoCl_4 \cdot 2C_5H_{10}O$, was formed in the reaction of molybdenum(V) chloride with pentamethylene oxide, apparently as a mixture with the expected adduct $MoOCl_3 \cdot 2C_5H_{10}O$. A similar behavior (with the formation of a quinquevalent oxychloride derivative and a quadrivalent complex) was observed[7] in the reaction of the pentachloride with alkali metal chlorides in liquid sulfur dioxide, when a mixture of the salts $M_2[MoCl_6]$ and $M[MoOCl_4]$ was formed. The magnetic moment of 2.37 B.M. is typical of that found for quadrivalent molybdenum complexes and is reasonably close to the value (2.45 B.M.) obtained for the same compound synthesized[18] by displacing *n*-propyl cyanide by pentamethylene oxide from the adduct $MoCl_4 \cdot 2n\text{-}C_3H_7CN$.[18]

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