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Coordination Chemistry of Molybdenum Oxochlorides

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The coordination chemistry of molybdenum(VI) dioxodichloride, molybdenum(VI) oxotetrachloride, and molybdenum(V) oxotrichloride was studied, and considerable emphasis was placed on derivatives of acetylacetone. From MoO_2Cl_2 it was found possible to synthesize the yellow molybdenyl bisacetylacetonate, $MoO_2(C_5H_7O_2)_2$, and the air-stable amide complexes, $MoO_2Cl_2 \cdot 2L$, where L = N,N-dimethylformamide, N,N-dimethylacetamide, and N,N-dibutylacetamide. Molybdenum(V) oxotrichloride was readily prepared by reduction of $MoOCl_4$ with refluxing chlorobenzene. This oxychloride reacted with acetylacetone to give the benzene-soluble acetylacetonate, $MoOCl(C_5H_7O_2)_2$. Dimethyl sulfoxide and pyridine reacted wth $MoOCl_3$ to form $MoOCl_3 \cdot 2(CH_3)_2SO$ and $MoOCl_3 \cdot 2C_5H_5N$. Molybdenum(VI) oxotetrachloride was found to be readily reducible in solution to form adducts containing the $MoOCl_3$ nucleus. Reaction with acetylacetone formed the neutral acetylacetone adduct, $MoOCl_3 \cdot C_5H_8O_2$, and a similar reaction with benzophenone allowed the formation of $MoOCl_3 \cdot (C_6H_5)_2CO$. Also, the molybdenum(V) complex, $MoOCl_3 \cdot 2C_5H_5N$, was formed by the reaction of $MoOCl_4$ with pyridine. Molybdenum(VI) oxotetrachloride was found to oxidize aromatic compounds with specific coupling in the *para* position: refluxing phenol formed 4,4′-dihydroxybiphenyl and refluxing benzene reacted to give poly-*p*-phenylene.

Introduction

Much has been reported on the coordination chemistry of molybdenum(VI) dioxodichloride. Krauss and Huber[1] described complexes of MoO_2Cl_2 with a large number of aprotic, largely oxygen-donor ligands (acid anhydrides, esters, ethers, ketones, aldehydes, and nitriles). These hexacoordinate complexes, $MoO_2Cl_2 \cdot 2$(ligand), are colorless, very moisture-sensitive crystals which were monomeric in benzene solutions. An interesting and pertinent compound was the neutral acetylacetone solvate, $MoO_2Cl_2(C_5H_8O_2)$, formed by the reaction of acetylacetone with a benzene suspension of MoO_2Cl_2 after gentle warming. Long standing at room temperature causes esterification with the apparent formation of acetylacetonate coordination.[2] A number of additional complexes of the type $MoO_2Cl_2 \cdot 2L$ (L = $(C_6H_5)_3PO$, $(CH_3)_2SO$, $(C_6H_5)_3AsO$, and C_5H_5NO) have been prepared by Horner and Tyree.[3] These complexes have limited organic solubility and possess resistance to hydrolysis by comparison with the carbonyl donor complexes of Krauss and Huber.[1]

Coordination complexes of molybdenum(V) oxotrichloride were first synthesized *in situ* in crude form by using moist ether solutions of $MoCl_5$. This allowed Wardlaw and Webb to obtain the etherates $MoOCl_3 \cdot (C_2H_5)_2O$ and $MoOCl_3 \cdot 2(C_2H_5)_2O$.[4] Horner and Tyree used ethanol solutions of $MoCl_5$ to produce $MoOCl_3 \cdot 2(C_6H_5)_3PO$, $MoOCl_3 \cdot 2(C_6H_5)_3AsO$, and $MoOCl_3 \cdot 2(CH_3)_2SO$.[3] The use of a slightly moist carbon tetrachloride solution of $MoCl_5$ allowed the synthesis of $MoOCl_3 \cdot 2,2'$-bipyridyl.[5] This *in situ* generation of $MoOCl_3$ was employed because of the lack of a convenient synthetic procedure for $MoOCl_3$. Recently, solid $MoOCl_3$ has been used to prepare the octahedral nitrile complexes, $MoOCl_3 \cdot 2RCN$, where R is CH_3, C_2H_5, and *n*-C_3H_7.[6] Reaction of the acetonitrile complex with $(C_6H_5)_3P$ formed $MoOCl_3 \cdot 2(C_6H_5)_3P$ and reaction with 2,2′-bipyridyl and 1,10-phenanthroline formed complexes of the type $MoOCl_3 \cdot L$.

Some additional coordination chemistry of MoO_2Cl_2 and $MoOCl_3$ as well as that of $MoOCl_4$, a new molybdenum oxochloride with no previously described coordination chemistry, has been studied, and this paper reports the preparation and characterization of various complexes derived from these oxychlorides. The oxidative reactions of $MoOCl_4$ with some aromatic compounds are also described.

Experimental Section

The experiments were performed in a prepurified nitrogen atmosphere. All material transfers of air-unstable compounds were conducted in nitrogen in a controlled atmosphere glove box. All melting points were corrected and were determined in nitrogen-filled, flame-sealed capillaries.

Analytical Procedures.—The elemental analyses of all organic molybdenum complexes and molecular weight determinations were performed by Huffman Laboratories, Inc., Wheatridge, Colo. Inorganic molybdenum oxochlorides were analyzed by the Climax Molybdenum Co. of Michigan Analytical Laboratory. The analytical procedure involved digestion with alkaline hydrogen peroxide, followed by potentiometric titration for chloride, and by α-benzoinoxime precipitation with subsequent ignition to MoO_3 for molybdenum.

Oxidation states of several compounds were determined by cerimetric titration and/or measurement of magnetic moments (μ_{eff}). In the case of acetylacetone derivatives of molybdenum, these were dissolved in concentrated hydrochloric acid and extracted with chloroform prior to the cerimetric titration. Magnetic moments were determined using the Gouy technique.[7] In calculating μ_{eff}, a Curie temperature of 0 °K was assumed.

The infrared spectra were determined using a Perkin-Elmer Corp. Model 21 instrument. Samples were prepared as potassium bromide and chloride disks[8] and Nujol mulls inside the nitrogen box. The visible-ultraviolet spectra were determined using a Beckman Instruments, Inc., Model DU spectrophotometer. Solid samples were run by the diffuse-reflectance tech-

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[1] H. L. Krauss and W. Huber, *Chem. Ber.*, **94**, 2864 (1961).

[2] H. L. Krauss, private communication, 1964.

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

[4] W. Wardlaw and W. H. Webb, *J. Chem. Soc.*, 2103 (1930).

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

[6] D. A. Edwards, *ibid.*, **27**, 303 (1965).

[7] We are indebted to Lew Hryhorczuk, Wayne State University, for determination of the magnetic moments.

[8] W. H. Price and R. H. Maurer, *Appl. Spectry.*, **17**, 106 (1963).

nique,[9] sometimes using anhydrous LiF or SiO_2 as diluent. Solution spectra were determined using sealed cells filled in the nitrogen box.

Materials.—Commercially available reagent grade chemicals were used without further purification, except in the cases noted.

Molybdenum(VI) dioxodichloride and molybdenum(VI) oxotetrachloride are Climax Molybdenum Co. research products.[10] The molybdenum(VI) oxotetrachloride was purified by repeated vacuum (0.03- 0.05 mm) sublimation at 70–80°.

Acetylacetone, Eastman White Label grade, was purified according to a literature procedure.[11] Dimethyl sulfoxide, pyridine, methylene chloride, chloroform, carbon tetrachloride, chlorobenzene, and phenol were carefully dried by standard procedures and fractionally distilled under nitrogen.

Synthesis and Properties of Some Coordination Derivatives of Molybdenum(VI) Dioxodichloride. $MoO_2(C_5H_7O_2)_2$.—A solution of 1.62 g (0.00815 mole) of MoO_2Cl_2 in 10 ml (9.76 g, 0.0976 mole) of acetylacetone was prepared, and while stirring, 150 ml of water was added, resulting in the formation of a yellow-orange solid. After stirring for 30 min, the solid was filtered, washed with water, and dried to a constant weight *in vacuo*. The product weighed 2.21 g (84% yield) and melted at 184–185° (lit.[12] mp about 185°). *Anal.* Calcd for $MoO_2(C_5H_7O_2)_2$: C, 36.82; H, 4.33; Mo, 29.42. Found: C, 37.00; H, 4.28; Mo, 28.67.

This compound has limited solubility and generally decomposes in common organic solvents. Methylene chloride and chloroform solutions soon deposit solids and liberate acetylacetone as demonstrated by ultraviolet absorption. Long exposure to atmospheric moisture causes hydrolysis with liberation of acetylacetone. A cryoscopic molecular weight in biphenyl gave values of 355 and 321 (calcd 326.17). The following infrared absorptions were obtained in the 1600–650-cm^{-1} region: 1597 (s), 1515 (s), 1418 (m), 1364 (s), 1266 (s), 1183 (w), 1026 (s), 935 (s), 904 (s), 800 (w).

$MoO_2Cl_2 \cdot 2HCON(CH_3)_2$.[13]—To 8.96 g (0.0451 mole) of MoO_2Cl_2 was added 40 ml of refrigerated N,N-dimethylformamide (DMF). This caused immediate formation of white solid. This solid, 5.21 g, mp 162–164°, was filtered, washed with ether, and vacuum dried. The same melting point was obtained on recrystallization from DMF–ether. An additional 8.85 g of product, mp 162–164°, was separated from the original filtrate, to give a total yield of 90%. *Anal.* Calcd for $MoO_2Cl_2 \cdot 2HCON(CH_3)_2$: C, 20.88; H, 4.90; Cl, 20.55; Mo, 27.81; N, 8.12. Found: C, 21.92; H, 4.45; Cl, 20.26; Mo, 27.41; N, 8.23.

The following peaks were observed in the 1700–650-cm^{-1} region of the infrared spectrum: 1653 (s), 1488 (w), 1429 (s), 1374 (s), 1247 (m), 1117 (m), 1055 (w), 1007 (w), 939 (s), 905 (s), 858 (w), 680 (s). The carbonyl frequency of DMF at 1670 cm^{-1} was lowered to 1653 cm^{-1} on coordination. Nonligand absorptions of the complex were found at 1007 (w), 939 (s), 905 (s), and 858 (w) cm^{-1}.

This compound rapidly turns blue on exposure to ultraviolet radiation. Although hydrolyzed in water, exposure to air in the dark caused very slow decomposition. It is soluble only in polar oxygenated solvents and chloroform. A methanol solution rapidly reacted with 8-hydroxyquinoline (oxine) to give the highly insoluble, yellow-orange molybdenyl oxinate complex.

$MoO_2Cl_2 \cdot 2CH_3CON(CH_3)_2$.—The experimental procedure was very similar to that described for the synthesis of $MoO_2Cl_2 \cdot 2DMF$. Machine shaking was required to dissolve 8.01 g (0.0428 mole) of MoO_2Cl_2 in 35 ml of N,N-dimethylacetamide (DMA). A large excess of anhydrous diethyl ether was added to obtain 13.64 g (86% yield) of light green, crystalline solid, mp 122–123°. A portion of this product was recrystallized from the DMA–ether solvent pair to obtain light yellow, needlelike crystals, mp 120–123°. *Anal.* Calcd for $MoO_2Cl_2 \cdot 2CH_3CON(CH_3)_2$: C, 25.75; H, 4.86; Cl, 19.01; Mo, 25.72; N, 7.51. Found: C, 26.34; H, 4.93; Cl, 19.34; Mo, 25.61; N, 7.43. The ebullioscopic molecular weight in benzene was 325, 333; calcd 373.10.

The C=O stretching frequency of ligand DMA was shifted from 1653 to 1605 cm^{-1}. In the 650–1700 cm^{-1} region, the following nonligand absorptions were obtained: 968 (m), 948 (s), 909 (s), and 741 (s) cm^{-1}.

This compound has approximately 5% solubility in hot benzene, accompanied by some decomposition. It was found to be fairly stable in air (1.19% weight loss in 3 weeks), but exposure to ultraviolet light caused rapid formation of blue color.

$MoO_2Cl_2 \cdot 2CH_3CON(n\text{-}C_4H_9)_2$.—To 25 ml of refrigerated N,N-di-*n*-butylacetamide (DBA) was added all at once 10.87 g (0.0547 mole) of MoO_2Cl_2. There was immediate, gentle exothermic reaction, and a greasy yellow-brown solid adhered to the flask bottom. Trituration, shaking, and heating did not appreciably dissolve this solid.

The supernatant liquor was decanted, and an excess volume of anhydrous diethyl ether was added without appreciable phase separation. This solution became greenish upon exposure to light. Diethyl ether was removed by distillation up to a maximum bath temperature of 132°. Unreacted DBA was removed by vacuum distillation to yield a dark blue oil, 19.19 g (65% yield). *Anal.* Calcd for $MoO_2Cl_2 \cdot 2CH_3CON(n\text{-}C_4H_9)_2$: C, 44.36; H, 7.82; Cl, 13.10; Mo, 17.72; N, 5.17. Found: C, 43.82; H, 7.72; Cl, 13.20; Mo, 18.16; N, 5.14.

This compound is readily soluble in tetrahydrofuran, acetone, chloroform, and benzene; it is insoluble in carbon tetrachloride, petroleum ether, and ligroin.

The infrared absorption shows a doublet (1639 and 1613 cm^{-1}) in the C=O region, whereas DBA absorbs around 1653 cm^{-1}. The only strong nonligand absorptions are found at 943 and 909 cm^{-1}, essentially identical with the frequencies of the other amide complexes.

Properties of Molybdenum(VI) Oxotetrachloride.—Triply sublimed $MoOCl_4$, green crystals, mp 101–103°, demonstrates slight paramagnetism: $\chi_m^{cor} = 47.6 \times 10^{-6}$ cgs, spin only μ_{eff} of 0.339 BM at 25° corresponding to 0.05 unpaired electron. Cerimetric titration of a dilute HCl solution of $MoOCl_4$ demonstrated an oxidation state of +5.95 in agreement with the magnetic moment data. It is readily attacked by atmospheric moisture and reacts with bulk water to give solid "molybdenum blue," the indistinct molybdenum oxide hydrate with an oxidation state between molybdenum(V) and molybdenum(VI). Furthermore, $MoOCl_4$ is photolytically decomposed by ultraviolet radiation to form $MoOCl_3$ and Cl_2. Green $MoOCl_4$ dissolves in CCl_4 or $CHCl_3$ to form deep red-brown solutions similar to those formed by $MoCl_5$.

The values found for the ebullioscopic molecular weight determination of $MoOCl_4$ in CCl_4 were 261 and 279, compared to the calculated value of 253.78. This indicates the lack of dissociation of $MoOCl_4$ in CCl_4 solution. Furthermore, vacuum evaporation of a CCl_4 solution allowed recovery of the starting $MoOCl_4$. A crystalline film of $MoOCl_4$, deposited by evaporation from a CCl_4 solution, has strong infrared absorption due to Mo=O at 997 cm^{-1} (weaker absorption at 820 cm^{-1}), whereas a CCl_4 solution of $MoOCl_4$ shows strong, single absorption at 1009 cm^{-1}. A Nujol mull spectrum could not be obtained because $MoOCl_4$ reacts with Nujol. Also, the KBr and KCl disk spectra exhibit multiple peaks similar to spectra of $MoOCl_4^-$ salts[14] implying interaction.

Reactions of Molybdenum(VI) Oxotetrachloride. $MoOCl_3 \cdot C_5H_8O_2$ ($C_5H_8O_2$ = Neutral Acetylacetone).—In a flask equipped with a glass filtering frit and a stopcock attached to the bottom,

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[9] R. J. H. Clark, *J. Chem. Soc.*, 417 (1964); *J. Chem. Educ.*, **41**, 488 (1964).

[10] A. K. Mallock, "Preparation of Molybdenum Dioxydichloride (MoO_2Cl_2) and Molybdenum Oxytetrachloride ($MoOCl_4$)," presented at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

[11] J. Steinbach and H. Frieser, *Anal. Chem.*, **25**, 882 (1953).

[12] W. C. Fernelius, K. Terada, and B. E. Bryant, *Inorg. Syn.*, **6**, 147 (1960).

[13] Unpublished work of Mark M. Chamberlain, Western Reserve University, has revealed the earlier preparation of this complex, using $MoO_2Cl_2 \cdot H_2O$ as the intermediate.

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

a solution of $MoOCl_4$ (7.31 g, 0.0288 mole) in 90 ml of chloroform was prepared, and then acetylacetone (3.2 ml, 0.0312 mole) was added. The solution was heated to reflux over a 30-min period and then allowed to cool. The green crystals were filtered, washed with chloroform, and vacuum dried to obtain 6.30 g (69% yield), mp 176–177° dec.

This compound had a magnetic moment (μ_{eff}) of 1.55 BM at 24°. Cerimetric titration confirmed the presence of pentavalent molybdenum. The infrared spectrum determined as a Nujol mull showed the following peaks in the 1700–650-cm^{-1} region: 1695 (vs), 1634 (s), 1550 (w), 1527 (w), 1408 (w), 1357 (w), 1227 (w), 1190 (m), 1166 (m), 1053 (m), 990 (vs), 870 (w), 763–769 (w). The Nujol mull shows one strong Mo=O band at 990 cm^{-1}, whereas the KBr disk shows two absorptions, 1020 and 975–990 cm^{-1}, indicating interaction with KBr. *Anal.* Calcd for $MoOCl_3 \cdot C_5H_8O_2$: C, 18.86; H, 2.53; Cl, 33.40; Mo, 30.12. Found: C, 18.99; H, 2.78; Cl, 33.30; Mo, 30.02.

This compound is insoluble in chloroform, methylene chloride, carbon tetrachloride, and benzene. It is soluble in water to give a brown solution and in concentrated hydrochloric acid to give a bright green solution; in both instances, displacement of acetylacetone occurs. The same result was obtained using dimethyl sulfoxide to obtain crude $MoOCl_3 \cdot 2(CH_3)_2SO$.[3]

Some attempts were made to determine the nature of the oxidation accompanying the formation of the product. Although no chlorine was detected, HCl was found to be evolved, and gas–liquid partition chromatographic (glpc) analysis of the reaction mixture filtrate revealed the presence of 3-chloro-2,4-pentanedione.

$MoOCl_3 \cdot (C_6H_5)_2CO$.—To a solution of 6.06 g (0.0239 mole) of $MoOCl_4$ in 80 ml of CCl_4 was added 4.28 g (0.0235 mole) of benzophenone. The resultant solution was refluxed for 6 hr, and then it was allowed to stand overnight. The resulting crystals were filtered and washed with CCl_4. After vacuum drying, 5.5 g of green crystals (56% yield), mp 156–161° dec, was obtained. *Anal.* Calcd for $MoOCl_3 \cdot (C_6H_5)_2CO$: C, 38.98; H, 2.52; Cl, 26.56; Mo, 23.95. Found: C, 39.55; H, 2.55; Cl, 26.21; Mo, 24.10.

Vacuum concentration of the combined reaction mixture filtrate and CCl_4 wash allowed the isolation of an additional 0.41 g of green crystals, mp 151–161° dec. Cerimetric titration demonstrated that the molybdenum was pentavalent. The ebullioscopic molecular weight in benzene was 545 and 567 (calcd 400.53) indicating association, which is consistent with this apparently five-coordinate species attempting to achieve six-coordination. Its Nujol mull infrared absorption spectrum was identical with that of the product obtained by the equimolar condensation reaction of benzoic acid with $MoCl_5$ in refluxing benzene.[15] This spectrum showed carbonyl stretching at 1527 cm^{-1}, a negative shift of 138 cm^{-1} from that of the noncoordinated ligand. The molybdenyl group was found to absorb strongly at 990 cm^{-1}.

Synthesis of $MoOCl_3$ by Chlorobenzene Reduction of $MoOCl_4$.—A stirred mixture of $MoOCl_4$ (40.00 g, 0.158 mole) and 160 ml (177.6 g, 1.58 moles) of chlorobenzene was refluxed while titrating the effluent gas with standard NaOH. After 3.5 hr of reflux, 0.0753 mole of HCl had been titrated. The reaction mixture was filtered, and the solid was washed with chlorobenzene. After vacuum drying, 32.32 g of brown powder (93.9% yield) was obtained which had mp 301.5–303.5° (lit.[16] mp 295°). A black melt was obtained which froze to black needles, which is characteristic of $MoOCl_3$.[16] *Anal.* Calcd for $MoOCl_3$: Cl, 48.72; Mo, 43.95. Found: Cl, 48.76; Mo, 43.16.

The Nujol mull infrared absorption spectrum shows only one peak, 1007 (s) cm^{-1}, whereas the KBr and KCl disk spectra show peaks at 1005 (s), 974 (s), and 930 (w) cm^{-1}, indicating interaction with the medium.

The glpc analysis of the filtrate indicated that 0.0684 mole of dichlorobenzenes with a *para*:*ortho* isomer ratio of 9.6:1 was obtained.

Reaction of $MoOCl_4$ with Benzene.—Benzene (60 ml) was added to $MoOCl_4$ (10.00 g, 0.0394 mole) with immediate evolution of HCl and formation of a brown solid. After refluxing for 8 hr, 9.70 g of brown powder was isolated by filtration, washed with benzene, and vacuum dried. The filtrate, washed with water and concentrated by fractionation, contained 0.35 mole % chlorobenzene by glpc analysis. The brown solid had a composition equivalent to $C_{2.4}H_{3.2}Cl_{3.5}O_{2.0}Mo$ and contained 86% of the starting Mo. On treatment of this solid with hot, concentrated hydrochloric acid, a dark brown solid (1.2 g, 40% yield, based on $MoOCl_4$) and a dark green molybdenum(V) solution were obtained. After repeated washings with aqueous NaOH and concentrated HCl, this solid had the infrared spectrum and X-ray diffraction pattern characteristic of poly-*p*-phenylene.[17] *Anal.* Found: C, 84.04; H, 4.42; Cl, 4.46; Mo, 3.64. This analysis indicates some polymeric organic molybdenum impurity as well as some chlorinated polymer.

Reaction of $MoOCl_4$ with Phenol.—A stirred mixture of $MoOCl_4$ (6.56 g, 0.0258 mole) and phenol (30.00 g, 0.318 mole) was heated to 182° over a 40-min period and maintained at 182–185° for 2.5 hr, at which time the evolution of HCl was insignificant. After cooling, the reaction mixture was stirred with methanol, and on filtration a black, insoluble solid (2.41 g) was isolated. This solid had an empirical formula of $C_{4.2}H_{4.6}Cl_{0.87}O_{3.0}Mo$ and contained 40.6% of the starting molybdenum. Alkaline hydrolysis of this material afforded polyphenol resins. Treatment of the filtrate gave 0.94 g (19.6% yield based on $MoOCl_4$) of 4,4′-dihydroxybiphenyl, and glpc analyses revealed a small amount of chlorophenols.

Reaction of $MoOCl_4$ with *o*- and *p*-Cresols.—Using conditions similar to those described for the phenol oxidation, the reactions of $MoOCl_4$ with *o*- and *p*-cresol were studied. Only polycresol resins could be isolated from the reaction mixtures, and all of the starting molybdenum was present as a black, intractable polymer similar to that obtained for the phenol oxidation.

Coordination Complex Derivatives of Molybdenum(V) Oxotrichloride. $MoOCl(C_5H_7O_2)_2$.—The technique employed for this synthesis was similar to that described above for $MoOCl_3 \cdot C_5H_8O_2$. Addition of acetylacetone (7.81 g, 0.0781 mole) to a suspension of $MoOCl_3$ (4.67 g, 0.0214 mole) in 80 ml of benzene caused immediate evolution of HCl, and after refluxing 6.5 hr, a dark red solid (0.73 g) was isolated by filtration. This material had an empirical formula of $C_{7.8}H_{11.7}Cl_{2.1}Mo_{1.0}O_{3.3}$, which approximates the formula of the monoacetylacetonate, $MoOCl_2(C_5H_7O_2)$. Its organic insolubility indicates that it is polymeric to achieve six-coordination. The combined reaction mixture filtrate and benzene wash was vacuum evaporated to obtain 6.17 g (83% yield) of green-brown solid, mp 164.5–166.5° dec. *Anal.* Calcd for $MoOCl(C_5H_7O_2)_2$: C, 34.75; H, 4.08; Cl, 10.26; Mo, 27.76. Found: C, 35.48; H, 4.32; Cl, 10.29; Mo, 27.55. The molecular weight, determined cryoscopically in benzene, was 339, 344; calcd 345.6. Cerimetric titration revealed that the molybdenum was pentavalent in this compound.

The Nujol mull and KBr disk spectra were found to be essentially identical. The following peaks were obtained in the 1700–650-cm^{-1} region: 1550 (s, sh), 1527 (s), 1414 (s), 1333 (s), 1276 (s), 1189 (w), 1026 (s), 962 (s), 938–930 (s, d), 800 (s).

This product undergoes slow hydrolytic and/or oxidative decomposition in air. It was readily soluble in chloroform but underwent solvolytic decomposition. Hydrolysis in water causes slow and complete dissolution. An aqueous acetylacetone solution caused precipitation of the brown, binuclear molybdenyl bisacetylacetonate, $Mo_2O_3(C_5H_7O_2)_4$.[18] Attempted vacuum (0.1 mm) sublimation up to a maximum temperature of 138° caused thermal decomposition.

$MoCl_3 \cdot 2(CH_3)_2SO$.—A reaction mixture of 0.70 g (0.00321 mole) of $MoOCl_3$ and 0.4 ml (0.44 g, 0.00563 mole) of dimethyl

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[15] M. L. Larson, *J. Am. Chem. Soc.*, **82**, 1223 (1960).

[16] I. A. Glukhov and S. S. Eliseev, *Izv. Akad. Nauk Tadzh. SSR, Otd. Geol. Khim. i Tekhn. Nauk*, 79 (1959).

[17] P. Kovacic and R. M. Lange, *J. Org. Chem.*, **28**, 968 (1963).

[18] M. L. Larson and F. W. Moore, *Inorg. Chem.*, **2**, 881 (1963).

sulfoxide in 80 ml of methylene chloride was stirred for approximately 1 hr to obtain a dark green solution. This solution was filtered and vacuum evaporated to obtain a blue solid, indicating some decomposition.[3] This blue impurity was dissolved by vigorous stirring with absolute ethanol. The resultant green solid was separated by filtration and vacuum dried to obtain 0.36 g (34% yield), mp 137–138° (lit.[3] mp 140–142°). *Anal.* Calcd for $MoOCl_3 \cdot 2(CH_3)_2SO$: C, 12.82; H, 3.23; Cl, 28.40; Mo, 25.61; S, 17.12. Found: C, 13.30; H, 3.22; Cl, 28.18; Mo, 26.01; S, 18.17.

$MoOCl_3 \cdot 2C_5H_5N$.—Anhydrous pyridine (26 ml, 25.5 g, 0.323 mole) was added dropwise to 5.00 g (0.0229 mole) of $MoOCl_3$ with the exothermic formation of solid. This was filtered and washed once with pyridine and twice with CCl_4. After vacuum drying, 7.16 g (83% yield) of tan solid, mp 255–256° dec, was obtained. *Anal.* Calcd for $MoOCl_3 \cdot 2C_5H_5N$: C, 31.90; H, 2.68; Cl, 28.25; Mo, 25.48; N, 7.44. Found: C, 32.09; H, 3.11; Cl, 29.08; Mo, 24.04; N, 7.20.

The Nujol mull infrared absorption spectrum shows that the ligand is pyridine.[19] Nonligand molybdenum–oxygen peaks are found at 966 (m, sh), 952 (s), and 938 (s) cm^{-1}.

It is insoluble in acetone, benzene, and chloroform but does have some solubility in pyridine. Exposure to atmospheric moisture causes slow hydrolysis.

A somewhat less pure product was obtained by the reaction of a CCl_4 solution of $MoOCl_4$ with pyridine. A solution of 4.75 g (0.0187 mole) of $MoOCl_4$ in 80 ml of CCl_4 was prepared. To this solution was added 3.0 ml (2.96 g, 0.0374 mole) of pyridine dissolved in 10 ml of CCl_4. This caused immediate formation of solid, and, after stirring for 45 min at room temperature, the system was filtered to isolate the product. After washing with CCl_4 and vacuum drying, 6.16 g (88% yield) of tan solid, mp 244–248° dec, was obtained. *Anal.* Calcd for $MoOCl_3 \cdot 2C_5H_5N$: C, 31.90; H, 2.68; Cl, 28.25; Mo, 25.48; N, 7.44. Found: C, 31.03, H, 2.86; Cl, 29.37; Mo, 25.42; N, 7.20.

The Nujol mull infrared absorption is identical with that of the product derived from $MoOCl_3$. The pentavalent character of molybdenum in this compound was confirmed by its magnetic moment (μ_{eff}) of 1.63 BM (25°).

Discussion

It was found that MoO_2Cl_2 can act as a source of the MoO_2^{2+} cation since the reaction of MoO_2Cl_2 with acetylacetone–water gives a high yield of $MoO_2(C_5H_7O_2)_2$. The N,N-dialkylamide complexes of MoO_2Cl_2 are thermally stable and stable to atmospheric moisture, in contrast to the hydrolytic instability of the neutral ligand carbonyl donor complexes of MoO_2Cl_2 prepared by Krauss and Huber.[1] The infrared spectra of these amide complexes confirm that the coordination is through the carbonyl group, as has been found for other complexes of DMF[20,21] and DMA.[22] Furthermore, the N—C═O bending frequency of DMF is raised from 657 to 680 cm^{-1} on coordination to MoO_2Cl_2, in agreement with the observations of Jungbauer and Curran.[23]

Molybdenum(V) oxotrichloride can be readily prepared by reducing $MoOCl_4$ with refluxing chlorobenzene. This reduction is accompanied by formation of HCl and dichlorobenzenes according to the equation

$$2MoOCl_4 + C_6H_5Cl \longrightarrow 2MoOCl_3 + C_6H_4Cl_2 + HCl$$

This reduction is analogous to the chlorobenzene or benzene reduction of $MoCl_5$ to $MoCl_4$[24] and is more convenient than earlier methods of preparing $MoOCl_3$.[25,26] Like $NbOCl_3$,[27] $MoOCl_3$ is presumed to be polymeric in the solid state.[26] While $NbOCl_3$ reacts with acetylacetone to form polymeric $NbOCl_2(C_5H_7O_2)$,[28] $MoOCl_3$ mainly reacts to form six-coordinate $MoOCl(C_5H_7O_2)_2$ with formation of only a small amount of crude, presumably polymeric $MoOCl_2(C_5H_7O_2)$. The complexes $MoOCl_3 \cdot 2(CH_3)_2SO$ and $MoOCl_3 \cdot 2C_5H_5N$ were readily prepared by reaction of $MoOCl_3$ with the appropriate ligand, indicating that complexes of $MoOCl_3$ can be prepared from the oxychloride, despite its polymeric character and organic insolubility.

Molybdenum(VI) oxotetrachloride is a readily reduced compound, and thermodynamic studies[29] indicate that thermal decomposition of $MoOCl_4$ to $MoOCl_3$ and Cl_2 takes place even at room temperature. Therefore, the slight paramagnetism found for $MoOCl_4$ may be due to the presence of $MoOCl_3$ impurity. Attempts to prepare pure complexes containing the $MoOCl_4$ or $(MoOCl_3)^+$ nucleus were unsuccessful, and only complexes containing the molybdenum(V) group $MoOCl_3$ could be isolated. Reaction with acetylacetone under carefully controlled conditions formed the interesting compound, $MoOCl_3 \cdot C_5H_8O_2$, which contains neutral acetylacetone ligand as does $MoO_2Cl_2 \cdot C_5H_8O_2$.[1] During the reaction, no chlorine was detected, but HCl was evolved and 3-chloro-2,4-pentanedione was found in the reaction mixture filtrate. This indicates that the reduction takes place in a manner similar to the chlorobenzene reduction of $MoOCl_4$

$$2MoOCl_4 + 3C_5H_8O_2 \longrightarrow 2MoOCl_3 \cdot C_5H_8O_2 + HCl + C_5H_7ClO_2$$

Benzophenone and pyridine also react with $MoOCl_4$ to form the molybdenum(V) complexes, $MoOCl_3 \cdot (C_6H_5)_2CO$ and $MoOCl_3 \cdot 2C_5H_5N$, respectively.

In its reactions with aromatic derivatives, $MoOCl_4$ was found to be strongly *para* directing and to cause some specific oxidations. With refluxing chlorobenzene mainly *p*-dichlorobenzene was formed while with refluxing benzene a 40% yield of poly-*p*-phenylene was isolated. This polymer has previously been isolated in low yield from the reaction of benzene with $MoCl_5$–H_2O.[17] Phenol at reflux temperature (185°) reacts with $MoOCl_4$ to form the coupling product, 4,4′-dihydroxybiphenyl. It appears that $MoOCl_4$ is a unique oxidizing agent for certain aromatic compounds and that it sometimes reacts to form specific products.

Infrared Spectra.—Table I summarizes the molybdenum-to-oxygen absorptions found for the various compounds. Those compounds possessing a single molybdenyl oxygen absorb strongly in the region expected for a compound possessing a Mo═O group,[30] but those compounds containing the MoO_2^{2+} group

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absorb at much lower frequencies. A similar lowering of frequency has been observed for complexes containing the *trans* ReO_2^+ group, and this lowering has been found to be due to a mutual weakening of the Re-to-O bond by the *trans* effect.[31] It is proposed, in the absence of X-ray evidence, that the MoO_2^{2+} group of the present compounds contains *trans* (linear) oxygens because of the low frequency of the Mo-to-O absorption. This proposal is further supported by the suggestion that the oxygens in the MoO_2^+ group in $[MoO_2C_2O_4]^+$ are *cis* since this compound absorbs strongly at 980 cm^{-1}.[32]

TABLE I

MO-TO-O INFRARED ABSORPTIONS[a]

Compd	Mo=O frequency, cm^{-1}	Compd	O=Mo=O frequency, cm^{-1}
$MoOCl_4$[b]	1010	MoO_2Cl_2[c]	905
$MoOCl_3$	1007	$MoO_2(C_5H_7O_2)_2$	904
$MoOCl_3 \cdot C_5H_8O_2$	990	MoO_2(oxinate)$_2$[d]	903
$MoOCl_3 \cdot (C_6H_5)_2CO$	990	$MoO_2Cl_2 \cdot 2DMF$	939, 905
$MoOCl_3 \cdot 2C_5H_5N$	966	$MoO_2Cl_2 \cdot 2DMA$	948, 909
$MoOCl_3 \cdot 2(CH_3)_2SO$	970	$MoO_2Cl_2 \cdot 2DBA$	943, 909
$MoOCl(C_5H_7O_2)_2$	962		

[a] Nujol mulls. [b] CCl_4 solution. [c] See ref 10. [d] J. P. Phillips and J. F. Deys, *Anal. Chim. Acta*, **17,** 231 (1957).

The infrared spectrum of $MoOCl_3 \cdot C_5H_8O_2$ confirms that this compound, like $MoO_2Cl_2 \cdot C_5H_8O_2$,[2] contains neutral acetylacetone. Both complexes absorb strongly at 1695 cm^{-1}, while uncoordinated acetylacetone has strong C=O and C=C absorption at 1709 to 1739 cm^{-1} and metal acetylacetonates do not have C=O or C=C absorption above 1600 cm^{-1}.[33] This lowering of the C=O frequency by 30 cm^{-1} is of the same order of magnitude as found for $MoOCl_3 \cdot (C_6H_5)_3AsO \cdot (CH_3)_2CO$ (-48 cm^{-1})[3] and aliphatic ketone complexes of gallium and indium chlorides (-40 to -60 cm^{-1}).[34] Similarly, the C=O frequency of benzophenone is lowered 138 cm^{-1} on coordination with $MoOCl_3$, and the magnitude of the shift is in agreement with that found for other aromatic ketone complexes.[34,35]

Visible Spectra.—The visible spectra are summarized in Table II. The spectra of $MoOCl(C_5H_7O_2)_2$, $MoOCl_3 \cdot C_5H_8O_2$, $MoOCl_3 \cdot (C_6H_5)_2CO$, and $MoOCl_3 \cdot 2C_5H_5N$ can be assigned by using the assignments of Edwards,[6] and of Horner and Tyree[36] for $MoOCl_3$ complexes which are based on the studies of the visible spectrum of $MoOCl_5^{2-}$ by Gray and Hare.[37] The weak peak in the 13,000–14,000 cm^{-1} region is assigned to the $^2B_2 \rightarrow {}^2E(I)$ transition involving the π orbitals of the molybdenyl oxygen, and the second weak peak is due to the ligand-field transition $^2B_2 \rightarrow {}^2B_1$. The band near 27,000 cm^{-1} found for $MoOCl_3 \cdot 2C_5H_5N$ is assigned to the charge-transfer band $^2B_2 \rightarrow {}^2E(II)$ despite the fact that it appears to be a ligand-field band from its intensity.[38] It has been found that the intensities of ligand-field and charge-transfer bands are much closer in magnitude for diffuse-reflectance spectra as compared to solution spectra.[9] These spectra confirm the conclusion of Horner and Tyree[36] that the tetragonal distortion due to the molybdenyl group is the most important feature of the molecular orbital scheme and that substitution of various ligands for the chlorines of $MoOCl_5^{2-}$ does not greatly affect the visible spectrum.

TABLE II

VISIBLE SPECTRA

Compd	Media	Cm^{-1}	A or ϵ	Assignment
$MoOCl_3 \cdot C_5H_8O_2$	Solid	14,290	0.33	$^2B_2 \rightarrow {}^2E(I)$
	(LiF diluent)	27,780	0.68	$^2B_2 \rightarrow {}^2E(II)$
$MoOCl_3 \cdot (C_6H_5)_2CO$	C_6H_6	14,490 sh	88	$^2B_2 \rightarrow {}^2E(I)$
		21,050 sh	518	$^2B_2 \rightarrow {}^2B_1$
$MoOCl_3 \cdot 2C_5H_5N$	Solid	13,800	0.31	$^2B_2 \rightarrow {}^2E(I)$
	(LiF diluent)	20,830	0.48	$^2B_2 \rightarrow {}^2B_1$
		26,667 sh	0.70	$^2B_2 \rightarrow {}^2E(II)$
$MoOCl(C_5H_7O_2)_2$	C_6H_6	13,510 sh	50	$^2B_2 \rightarrow {}^2E(I)$
		16,810 sh	83	$^2B_2 \rightarrow {}^2B_1$
		26,320	3320	$^2B_2 \rightarrow {}^2E(II)$
$MoCl_5$	CCl_4	14,810	165	
		20,750	4870	
		32,570	2790	
		38,170	3280	
$MoOCl_4$	CCl_4	14,430	315	
		20,750	2820	
		37,170	2920	

The visible spectrum of a CCl_4 solution of $MoCl_5$ is similar to that found for $MoCl_5$ vapor.[39] The similarity of the spectra may imply that in dilute CCl_4 solution (1.5×10^{-4} to 2×10^{-3} M) $MoCl_5$ is monomeric and possesses a trigonal bipyramidal structure as assumed by Bader and Westland for the vapor state. Molybdenum pentachloride was found by cryoscopy to be monomeric in dilute (0.15%) benzene solution.[40] The visible spectrum of $MoOCl_4$ cannot be assigned at present, but, since $MoOCl_4$ is a molybdenum(VI), d^0, compound, the spectrum should contain only charge-transfer bands. The weak peak at 14,430 cm^{-1} may possibly be due to a molybdenum(V) species formed by solvolytic dissociation since a band in this region is characteristic of the presence of Mo^V=O.[36,37] No resolvable bands were found in the diffuse reflectance spectrum of $MoOCl_4$.

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