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Synthesis and Characterization of Molybdenum(IV) and -(V) Complexes of the Cyclopentadienedithiocarboxylate Ligand

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Much of the interest which has been generated over the past few years in transition element–sulfur systems has been stimulated by the ability of sulfur-containing ligands to stabilize unusual oxidation states and to induce unusual electronic effects at the transition element center.[2-6] Yet with the exception of dithioxanthates and dithiocarbamates, relatively few sulfur-liganded complexes of molybdenum are known[7-9] even though there exist strong arguments that molybdenum–sulfur sites play important roles in molybdenum metalloenzymes.[10] In particular, no dithioaromatic or dithioaliphatic acid derivatives of molybdenum are known.

Our interest in the cyclopentadienedithiocarboxylate ligand and its unusual effect on electronic properties at metal centers[11,12] coupled with our interest in molybdenum model systems prompted the preparation and subsequent study of a tris-molybdenum(IV) and a bis-molybdenyl(V) complex.

Experimental Section

Materials. Anhydrous solvents were prepared as before.[11,12] Molybdenum tetrachloride and molybdenum oxytrichloride were obtained from Research Organic/Inorganic Chemical Corp. $(C_2H_5)_4NBr$ was obtained from Aldrich Chemical Co.

$Na_2C_5H_4CS_2 \cdot C_4H_8O$. This complex was prepared as previously reported.[8]

$[(C_2H_5)_4N]_2Mo(C_5H_4CS_2)_3$. Due to the instability of the dithiolate ligand to hydrolysis, techniques similar to those employed in the preparation of the cobalt(II) complex were used here.[12] Typically, 2.00 g of $Na_2C_5H_4CS_2 \cdot C_4H_8O$ (7.75 mm) was added to a solution of 0.609 g of $MoCl_4$ (2.58 mm) in 200 ml of *anhydrous* acetonitrile at −70°. This frozen mass was slowly warmed to room temperature while stirring and allowed to react for 1 hr at room temperature. The solution was frozen again and 1.10 g of $(C_2H_5)_4NBr$ (5.20 mm) was added. After warming to room temperature, the reaction mixture was stirred for 1 additional hr. The mixture of NaBr and NaCl which formed was removed by filtration. The volume of the reaction mixture was reduced to 50 ml and a second fraction of precipitate was collected and discarded. Further reduction of the filtrate to 30 ml produced a dark brown powder. The yield was low since a significant portion of the product precipitated in the initial volume reduction. Anal. Calcd for $[(C_2H_5)_4N]_2Mo(C_5H_4CS_2)_3$: C, 52.55; H, 6.74; N, 3.60; S, 24.75. Found: C, 52.40; H, 6.94; N, 3.84; S, 24.45.

$[(C_2H_5)_4N]MoO(C_5H_4CS_2)_2$. Synthesis was carried using an analogous procedure to that employed above except $MoOCl_3$ served as the starting material. A black (or darkly colored) precipitate was isolated from the reddish brown reaction mixture. Anal. Calcd for $[(C_2H_5)_4N]MoO(C_5H_4CS_2)_2$: C, 45.96; H, 5.40; N, 2.68; S, 24.54. Found: C, 46.10; H, 5.39; N, 2.83; S, 24.28.

Several initial attempts to synthesize this compound yielded a green oil instead of the black crystalline material. While no analyses were obtained, it is possible that insufficient precautions were taken to maintain an inert atmosphere and that a Mo(VI) complex was obtained.

Analyses. Analyses were carried out by Galbraith Laboratories, Knoxville, Tenn.

Magnetic Susceptibility Determination. Susceptibilities were determined on solid samples at room temperature and diamagnetic corrections contributions made as before.[12]

Spectroscopic Measurements. Infrared, optical, ESR, and X-band spectra were obtained as before.[12] Second-order corrections were employed to correct for perturbations of the Zeeman transitions resulting from hyperfine interactions.[13]

Results and Discussion

The syntheses of tetraethylammonium bis(cyclopentadienedithiocarboxylato)oxomolybdenum(V) and tetraethylammonium tris(cyclopentadienedithiocarboxylato)molybdenum(IV) have been achieved.

The molybdenum(IV) complex is diamagnetic. While it is possible that some form of intermolecular interaction in the solid state might account for this diamagnetism, it is not likely.[8] The tris(1,2-dicyanoethylenedithiolato)molybdenum(IV) ion is also diamagnetic. The crystal structure of this system indicates an intermediate structure between a trigonal environment and an octahedral one at the molybdenum(IV) center.[14] Possibly in these systems (d^2), an orbitally nondegenerate level is lowest in energy. The molybdenum(V) complex also exhibits a magnetic moment characteristic of a diamagnetic complex. Since the molybdenyl complex is formally five-coordinate, it is not difficult to imagine a strong spin–spin interaction between molybdenum atoms through the sixth coordination site in the solid state. *Other monomeric MoO^{3+} systems which have magnetic moments characteristic of d^1 oxy cations are six-coordinate.*[15] The five-coordinate systems show greatly reduced susceptibilities.[16] It is also possible that in the solid the sixth site is occupied by a sulfur atom from another complex. Stacking of planar complexes of dithiolates to yield effective five- or six-coordinate complexes is known.[17]

In solution (CH_3CN) and in a frozen solution, however, the Mo(V) complex exhibits the ESR spectrum of a d^1 monomeric complex. Comparison of the intensity of this signal to that of a known $MoOCl_5^{2-}$ concentration indicates that essentially all of the Mo(V) compound is in solution. It is assumed that the sixth coordination site is occupied by a solvent molecule under these conditions. The ESR spectrum is that of a tetragonal (C_{4v}) Mo(V) complex (Figure 1). The spin hamiltonian parameters derived from this spectrum are given in Table I along with values for several other molybdenyl complexes for comparison.[18,19] Even though $g_\parallel$ and $g_\perp$ are almost perfectly coincident, it was possible to assign six of the parallel and five of the perpendicular components due to the molybdenum hyperfine splittings. The solution spectrum (Figure 2) is consistent with these assignments ($\langle a \rangle_{calcd} = 1/3(A_\parallel + 2A_\perp) \simeq \langle a \rangle_{obsd}$).

The ground state for a d^1 molybdenum complex with axial symmetry is $^2B_2$ (the unpaired electron is in an antibonding molecular orbital consisting primarily of a metal d_{xy} orbital which has π symmetry in this coordinate system[20]). It is possible to evaluate certain empirical parameters of the molecular orbitals for Mo(V) complexes by the approach introduced by McGarvey using the equations[21]

$$A_\parallel = -K - 4/7\beta^2 P + (g_\parallel - 2.0023)P + 3/7(g_\perp - 2.0023)P$$

$$A_\perp = -K + 2/7\beta^2 P + 11/14(g_\perp - 2.0023)P$$

where $A_\parallel$, $A_\perp$, $g_\parallel$, and $g_\perp$ represent the hyperfine splitting parameters parallel and perpendicular to the Mo=O bond and the components of the g tensor parallel and perpendicular to the Mo=O bond, respectively. K represents the Fermi contact

Table I. ESR Parameters for Some Molybdenum(V) Complexes

Complex	$g_\parallel$	$g_\perp$	$\langle g \rangle_{obsd}$	$\langle g \rangle_{calcd}$	$A_\parallel{}^a$	$A_\perp{}^a$	$\langle a \rangle_{obsd}{}^a$	$\langle a \rangle_{calcd}{}^a$
$MoOF_5{}^{2-\ c}$	1.874	1.911	1.905	1.899	92.93	45.13	62.2	61.1
$MoOCl_5{}^{2-\ b,c}$	1.963	1.940	1.948	1.948	74.7	32.6	46.6	46.6
$MoOBr_5{}^{2-\ d}$	2.09	1.944	1.944	1.99	55.0	30.0	41.5	42.0
$MoO(C_5H_4CS_2)^-$	1.980	1.981	1.980	1.981	52.61	23.35	32.40	33.10

^{a} Units in 10^{-4} cm^{-1}. ^{b} Single-crystal data. ^{c} Reference 18. ^{d} Reference 19.

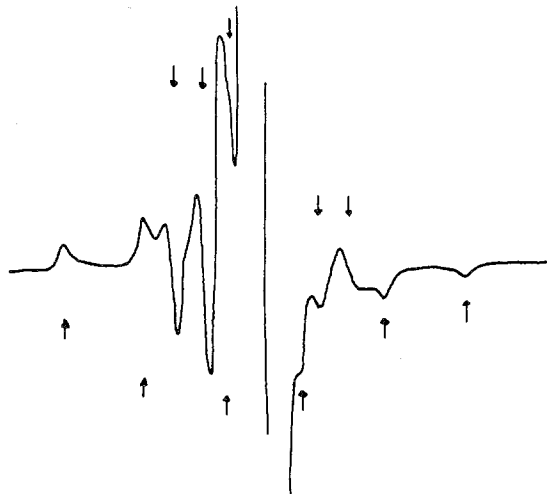**Figure 1.** Electron spin resonance spectrum of $MoO(C_5H_4$-$CS_2)_2{}^-$ in CH_3CN at 100°K. Upward arrows indicate parallel lines, downward arrows indicate perpendicular lines, and magnetic field increases from left to right.
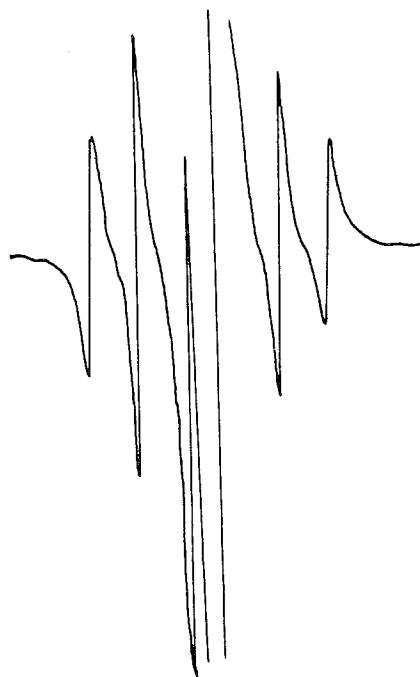

Figure 2. Electron spin resonance spectrum of $MoO(C_5H_4$-$CS_2)_2{}^-$ in CH_3CN at 290°K. Magnetic field increases from left to right.

term and $P = g_e g_n \beta_e \beta_n \langle r^{-3} \rangle$. P is given the free-ion value of -0.0055 cm^{-1} of the Mo(III) ion which represents the effective nuclear charge for Mo(V) in the MoO^{3+} unit.[22]

In other molybdenyl systems, the interpretation has been offered that transfer of paired electron density from oxygen to molybdenum results in the effective reduction of the oxidation state of the central metal (to Mo^{3+}) with concomitant expansion of the atomic wave functions in the complex.[23] This phenomenon is reflected in a decrease in the spin–orbit coupling

Table II. Molecular Orbital Coefficients and Fermi Contact Terms for Some Molybdenum(V) Complexes

Complex	β	$-K^a$	χ^b	$-P_{complex}{}^a$
$MoOF_5{}^{2-}$	0.9499	0.00554	7.09	0.0050
$MoOCl_5{}^{2-}$	0.9346	0.00436	5.58	0.0048
$MoOBr_5{}^{2-}$	0.8281	0.00383	4.90	0.0038
$MoO(C_5H_4CS_2)_2{}^-$	0.7769	0.00319	4.08	0.0033

^{a} Units in 10^{-4} cm^{-1}. ^{b} In atomic units.

constant, λ, as indicated by the small values for the observed g shifts $[g_\parallel - g_0 = -8\lambda/\Delta E(^2B_2 \rightarrow {}^2E)$ and $g_\perp - g_0 = -2\lambda/\Delta E(^2B_2 \rightarrow {}^2B_1)]$ when compared to those calculated using the free-ion spin–orbit coupling constant.[24] In the above two equations, β^2 is the coefficient for the ground-state b_2 molecular orbital. It is assumed, therefore, that a β value near 1 represents an ionic system and a β value near 0.5 represents a covalent system. The values of β and K obtained for the molybdenum(V) dithiolate system are given in Table II along with values for several other Mo(V) complexes for comparison. It must be recognized that the absolute value of β has little meaning and that only a comparison between systems has merit when a crude approximation such as outlined here is used. The calculations of P and K for the halide complexes $MoOF_5{}^{2-}$ and $MoOCl_5{}^{2-}$ were carried out using data obtained by others.[18,19] The values reported here for the $MoO(C_5H_4CS_2)_2{}^-$ system were obtained in acetonitrile glass at 100°K while those for $MoOX_5{}^{2-}$ were obtained in HX glasses.

Previous studies have shown that the $C_5H_4CS_2{}^{2-}$ ligand interacts with appropriate metal orbitals to form very covalent out-of-plane π molecular orbitals.[11,12] The trend in β (Table II) indicates that at least in comparison to the molybdenyl halide systems, a significantly covalent in-plane π molecular orbital is also present. Despite the crudeness of this approach, the trend is not a result of the limitations of the calculations.

A more refined calculation by Manoharan and Rogers[20] for the $MoOF_5{}^{2-}$ and $MoOCl_5{}^{2-}$ species gave values for β of 0.956 and 0.905, respectively, compared to the results here of 0.950 and 0.935. The unavailability of values for the effective spin–orbit coupling constant for sulfur in this complex and for effective overlap integrals for the Mo–S bonds precludes a similar approach in the dithiolate system. A consistent fit can only be obtained for positive values of $A_\parallel$ and $A_\perp$. (It is known that $A_\parallel$ and $A_\perp$ have the same sign since the isotropic $\langle a \rangle$ value observed is near the calculated value.)

Values for the isotropic contact term K (in cm^{-1}) and χ (in atomic units) where

$$\chi = -\frac{3}{2}\left(\frac{hca_0{}^3}{2.0023 g_n \beta_e \beta_n}\right)K$$

are also listed in Table II. To determine g_n an average value for the two isotopes of molybdenum was employed

$$g_n = \frac{{}^1/_2(-0.9099 - 0.9290)}{{}^5/_2}$$

To a first approximation, the isotropic contact term should decrease as the covalency increases.[20] This is evidenced by the paralleled decrease in β and K. $P_{complex}$ is taken as $\beta^2 P_{ion}$.

An unusual feature of the ESR data listed in Table I is that for the chloride and bromide system $g_\parallel$ is larger than $g_\perp$. Manoharan and Rogers[20] attributed this to the large value of

Table III. Infrared^a and Optical^b Data (cm^{-1}) for (1)
[(C$_2$H$_5$)$_4$N]MoO(C$_5$H$_4$CS$_2$)$_2$ and (2) [(C$_2$H$_5$)$_4$N]$_2$Mo(C$_5$H$_4$CS$_2$)$_3$

Ir

(1) 1188 m, 1178 s, 1080 s, 1015 sh, 1004 m, *942 s, br*,
897 m, 808 s, 787 w, 756 m, 728 m, 640 m, 382 m, br

(2) 1380 m, 1345 m, 1170 br, 1063 m, 1022 m, 1000 sh,
947 m, 816 s, 790 sh, 744 m, 643 w, 342 m, 336 sh

Optical

(1) 23,256, 26,316, 27,248, 31,446 (ϵ 7)

(2) 22,727, 26,455, 29,851, 35,714, 37,453, 40,816

^{a} Obtained in Nujol mulls. ^{b} Obtained in CH$_3$CN solution.

the one-electron spin–orbit coupling constants for chlorine and bromine [587 and 2460 cm^{-1}, respectively (λ_F is only 272 cm^{-1} [25])].

For the dithiolate system studied here, $g_\perp$ is greater than $g_\parallel$ as for most other MoO^{3+} systems. However, $g_\perp$ is larger than $g_\parallel$ by a much smaller margin for the dithiolate than for the fluoride complex. Employing Manoharan and Rogers' argument, then a reasonable spin–orbit coupling constant for the sulfur in this dithiolate system would be that for the sulfhydryl sulfur (382 cm^{-1}).

Infrared and uv–visible spectral data for MoO(C$_5$H$_4$CS$_2$)$_2$$^-$ and Mo(C$_5$H$_4$CS$_2$)$_3$$^{2-}$ are given in Table III. All the electronic transitions for the molybdenyl complex are of sufficient intensity to be charge transfer in origin. The low-energy $^2B_2 \rightarrow {}^2E$ transition, normally found near 14,000 cm^{-1} in MoO systems, is not observed here apparently because of its low intensity. The intense bands found above 26,000 cm^{-1} for MoOCl$_5$$^{2-}$ have all been accounted for by Gray and Hare[26] in terms of excitation of an electron from filled π orbitals on oxygen to empty d orbitals on the metal. This scheme however, fails fully to account for the spectrum of the somewhat more covalent MoOBr$_5$$^{2-}$ system where it is probable that π interactions of the bromine atoms contribute to the charge-transfer bands.[27]

On the basis of the electron spin resonance spectrum of bis(cyclopentadienedithiocarboxylato)oxomolybdate(V), it is obvious that the in-plane π-donor ability of the dithiolate ligand plays an important part in the electronic character of the system. Certainly, some of the charge-transfer peaks must arise from dithiolate ligand to metal transitions.

Registry No. 1, 54517-07-6; 2, 54517-09-8; MoOF$_5$$^{2-}$, 18040-31-8; MoOCl$_5$$^{2-}$, 17523-68-1; MoOBr$_5$$^{2-}$, 17523-72-7.

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Surface-Supported Metal Cluster Carbonyls. I. Decarbonylation and Aggregation Reactions of Rhodium Clusters on Alumina

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The adsorption of carbon monoxide on supported metal particles has been an area of interest in the chemistry and physics of surfaces for some time. Such factors as metal particle size, methods of reduction and sintering, and the type of support used often appear to affect the details of CO adsorption on the surface of these particles. The interest in CO adsorption on metals and obvious parallels with metal carbonyl compounds suggest that surface-supported metal carbonyls, especially polynuclear carbonyls, might have interesting and important properties as catalysts and as models of metal particles.

The interactions of nickel carbonyl with alumina and silica have been reported by Parkyns;[1] on the silica surface the carbonyl appears simply to physisorb while the alumina surface catalyzes a reaction yielding materials which have an ir spectrum typical of CO adsorbed on nickel metal. Studies of catalyst systems formed from molybdenum hexacarbonyl supported on a variety of oxide supports have also been reported.[2-6] In addition, there have been recent studies in which metal carbonyls, including polynuclear carbonyls, were bonded to modified polymer supports such as chemically modified polystyrene.[7-9] However, we are not aware of any studies reporting the interaction of polynuclear cluster carbonyls with simple oxide surfaces.

Because of our interest in metal cluster carbonyls and the belief that, under appropriate conditions, such metal cluster species should exhibit unique catalytic properties and perhaps model the behavior of very small metal particles, we have begun an investigation of oxide-supported metal cluster carbonyls. We report here the reactions which occur when the rhodium carbonyls Rh$_6$(CO)$_{16}$, Rh$_4$(CO)$_{12}$, and Rh$_2$(CO)$_4$Cl$_2$ are adsorbed on alumina.

Experimental Section

Materials. The three rhodium carbonyls were prepared by literature methods[10-12] starting from RhCl$_3$·nH$_2$O purchased from Engelhard Industries. Aluminas and silicas were from a variety of sources and of purity varying from chromatographic grade to high-purity materials.