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Reactions of Molybdenum(II) Xanthates with some Lewis Bases

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The reactions between molybdenum alkylxanthates and Lewis bases are described. Reactions with pyridine, methylpyridines, or dimethylsulfoxide give adducts $Mo_2(xanthate)_4L_2$ of the usual axial type. Acetone, nitriles, tetrahydrofuran, and dimethylsulfide form adducts in solution; these adducts decompose to starting materials at reduced pressure. Reaction of xanthate complexes with excess xanthate ion give a new complex $Mo_2(S_2COR)_5^-$. This complex is implicated as the intermediate in the production of neutral $Mo_2(S_2COR)_4$ from molybdenum acetate. Molybdenum alkylxanthates undergo only slight reaction with triphenylphosphine; with tributylphosphine, a complicated reaction ensues. Carbon monoxide and hexene do not react with molybdenum alkylxanthates at 1 atm, 25 °C. Spectroscopic data are provided for reaction products.

Introduction

A basic reaction of binuclear molybdenum(II) carboxylates and related complexes (thio- and dithiocarboxylates, xanthates, trithiocarbonates, sulfates, *etc.*) is the reaction with Lewis bases to form adducts. Until recently, the only known structural type was the 2:1 axial adduct as depicted in Fig. 1 [1]. Andersen [2] has recently reported that strongly basic phosphines with small cone angles can open carboxylate rings to produce unidentate carboxylate ligands and equatorially coordinated phosphines.

TABLE I. Infrared Spectra[a] of Molybdenum(II) Isopropylxanthate and Its Adducts.

$Mo[S_2COCH(CH_3)_2]_4$	1260(vw), 1215(sh), 1206(s), 1185(sh), 1137(m), 1090(s) 1049(m), 1027(w), 906(w), 898(w), 818(vw), 805(w), 530(w), 475(s), 460(w), 393(w), 371(w), 360(w), 336(w), 320(m), 296(w), 283(sh), 215(s).
pyridine adduct	1589(w), 1260(w), 1218(w), 1200(s), 1185(sh), 1140(w), 1090(s), 1050(s), 1030(w), 996(w), 906(w), 820(vw), 804(m), 754(w), 706(w), 532(w), 475(s), 410(m), 396(w), 383(w), 372(w), 345(w), 315(m), 296(w), 280(w), 220(m).
3-picoline adduct	1580(vw), 1261(m), 1193(s), 1178(w), 1142(w), 1092(s), 1056(m), 1046(w), 1033(w), 908(m), 820(w), 802(m), 788(m), 707(m), 636(w), 535(w), 471(s), 460(w), 398(m), 378(sh), 315(m), 300(sh), 280(sh), 220(m)
4-picoline adduct	1609(m), 1260(w), 1196(s), 1140(w), 1089(s), 1052(m), 1002(m), 907(m), 811(m), 523(m), 490(m), 470(s), 396(w), 375(w), 350(vw), 315(m), 295(w), 280(w), 217(m)
DMSO adduct	1290(vw), 1260(vw), 1194(s), 1180(sh), 1140(m), 1090(s), 1058(m), 1037(vw), 1010(s), 950(m), 906(w), 820(w), 802(sh), 537(w), 475(s), 385(s), 335(sh), 330(m), 317(m), 302(m), 220(s).
d^6-DMSO adduct	1190(s), 1176(sh), 1137(w), 1087(s), 1053(w), 1028(w), 1014(m), 992(s), 902(m), 817(m), 765(w), 737(vw), 536(w), 470(s), 398(w), 378(w), 347(s), 315(m), 305(m), 260(w), 215(s)
benzonitrile adduct	2238(w)[b], 1600(vw)[b], 1260(w), 1215(sh), 1198(s), 1183(sh), 1142(w), 1090(s), 1051(m), 1025(w), 906(m), 818(w), 805(w), 756(m)[b], 690(w)[b], 530(w), 475(s), 460(m), 393(w), 373(w), 396(w), 335(w), 320(m), 297(w), 281(sh), 218(m)

[a] Measured as Nujol mulls; frequencies in cm^{-1}. [b] These bands disappeared on extensive pumping of sample.

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TABLE II. Solution Electronic Spectra of Molybdenum(II) Isopropylxanthate.

Solvent	λ_{max} [a]	ϵ [a]	λ_{max}	ϵ	λ_{max}	ϵ
Acetone	555	600	434	6000	364	13000
Acetonitrile	559	500	434	5000	366	11000
[b] $CHCl_3/Cl^-$	565	500	437	5500	364	11000
[b] $CHCl_3/Br^-$	565	500	434	5800	366	11000
DMSO	561	600	445	6000	359	9100
Pyridine	570	500	442	5500	362	9600
THF	556	500	434	5200	366	11000

[a] λ_{max} (nm); ϵ (M^{-1} cm^{-1}). [b] 0.10 *M* solutions of halide salts.

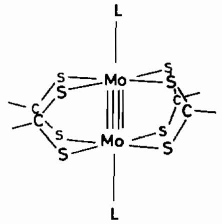

Fig. 1. Type structure for axial adducts $Mo_2(S_2COR)_4 \cdot 2L$. The -OR groups are omitted for clarity; the sites of their attachment are shown.

TABLE III. ^{1}H-nmr Spectra[a] of Adducts of Molybdenum(II) Isopropylxanthate.

^{1}H-nmr Spectra	
Pyridine adduct	1.54 (doublet, J = 7 Hz, 24 H), 5.67 (heptet, J = 7 Hz, 4 H), 7.28 (multiplet, 4 H), 7.70 (multiplet, 2 H), 8.42 (multiplet, 4 H)
3-picoline adduct	1.52 (doublet, J = 7 Hz, 24 H), 2.27 (singlet, 6 H), 5.63 (heptet, J = 7 Hz, 4 H), 7.10 (multiplet, 2 H), 7.44 (multiplet, 2 H), 8.21 (multiplet, 4 H)
4-picoline adduct	1.51 (doublet, J = 7 Hz, 24 H), 2.30 (singlet, 6 H), 5.62 (heptet, J = 7 Hz, 4 H), 7.02 (multiplet, 4 H), 8.30 (multiplet, 4 H)
Dimethylsulfoxide adduct	1.53 (doublet, J = 7 Hz, 24 H), 2.55 (singlet, 12 H), 5.63 (heptet, J = 7 Hz, 4 H)
Dimethylsulfide adduct	(prepared *in situ*) 1.53 (doublet, J = 7 Hz), 2.43 (singlet), 5.61 (heptet, J = 7 Hz). Integral ratio (double:heptet) 6:1

[a] Shifts in δ relative to internal TMS; measured in $CDCl_3$.

As part of studies into electronic structures and reaction rates of binuclear molybdenum complexes, we have examined the reactions of molybdenum xanthates with several Lewis bases. Previous workers have reported the structure of the molybdenum exthylxanthate–THF adduct [1b] and spectroscopic data for the corresponding pyridine adduct [3]. This report describes axial adducts of molybdenum isopropylxanthate, a typical xanthate, and the reactions with xanthate and carboxylate ions, as well as reactions with two phosphines, 1-hexene, and carbon monoxide.

Experimental

Infrared spectra were obtained on a Perkin-Elmer Model 580 recording spectrophotometer. Nmr spectra were obtained on a Varian EM-390 spectrometer with variable-temperature capability. Electronic spectra were obtained on a Cary 17 spectrophotometer. Spectroscopic data for molybdenum(II) isopropylxanthate and the adducts are given in Tables I–III. Analyses were obtained from Galbraith Laboratories, Knoxville, Tennessee. Decomposition temperatures are uncorrected.

Preparation of Molybdenum(II) Xanthates

Samples of molybdenum(II) xanthates were prepared as described by reaction 1 [3, 4]. To a solution of the appropriate potassium xanthate [5]

$$Mo_2(O_2CCH_3)_4 + 4\,KS_2COR \rightarrow Mo_2(S_2COR)_4 + 4KO_2CCH_3 \qquad (1)$$

(4.8 mmol) in 25 ml of methanol under nitrogen was added 0.50 g (1.2 mmol) of molybdenum acetate [6]. The yellow mixture turned orange-red, then dark green. After a few minutes, the red product precipitated. The mixture was filtered, and the solid was washed with two 20-ml portions each of methanol and ether and then vacuum-dried for two hours. Yields were typically 90%. The xanthate complexes are typically insoluble in hydrocarbons, halocarbons, alcohols, ethyl ether, and water, but dissolve in such donor solvents as DMSO, pyridine, acetonitrile, and acetone. Solids are stable for weeks in air. Analysis for molybdenum isopropylxanthate: for $C_{16}H_{28}Mo_2O_4S_8$, calc. C 26.22, H 3.85, S 35.0; found C 26.11; H, 3.86, S 34.8. Molybdenum(II) xanthates typically decompose at 140–150 °C without melting.

Reactions with Lewis Bases

Reactions of molybdenum(II) xanthates with Lewis bases were carried out under a nitrogen atmosphere or *in vacuo*, using methylene chloride, chloroform, or benzene solvent as received. Check experiments showed that the reactions were unaffected by nitrogen, by the solvent used, by further purification of solvent, or by the order of mixing reactants. Benzyltriethylammonium chloride was prepared from benzyl chloride and triethylamine; samples of other bases were obtained commercially. In typical experiments, 0.20 g (0.27 mmol) of the isopropylxanthate complex was mixed with base in 25 ml of solvent. Typically 0.54 mmol of solid base or tributylphosphine was used; with the other liquid bases, larger amounts of base were used, with no effect on the reaction. Other molybdenum xanthates (methyl, ethyl, n-propyl, n-butyl, and benzyl) undergo similar chemistry to that described below for the isopropylxanthate.

Pyridine, Methylpyridines, and DMSO

When molybdenum isopropylxanthate was mixed with pyridine in DMSO in solvent, a red solution formed at once. The solutions were stirred for 15 minutes and filtered. The solvent was removed *in vacuo*; rusty-red solids remained. The adducts $Mo_2[S_2COCH(CH_3)_2]_4 \cdot 2L$ (L-pyridine or DMSO) formed quantitatively. Each dissolves in methylene chloride, chloroform, benzene, and an excess of appropriate base, from which it may be recovered unchanged. The solids are air-stable for weeks; solutions may be handled in air briefly but decompose overnight. The adducts may be pumped at 0.005 torr at room temperature for at least one hour without losing the base. Analyses: for $C_{26}H_{38}Mo_2N_2O_4S_8$, calc. C 35.05, H 4.27, found C 35.05, H 4.55; for $C_{20}H_{40}Mo_2O_6S_{10}$, calc. C 27.02, H 4.54, found C 27.28, H 4.97. Both adducts decompose at *ca.* 145 °C without melting.

The reactions with 3- or 4-picoline proceed in similar fashion. However, no solution forms when 2-picoline and molybdenum isopropylxanthate are mixed in solvent; the solid recovered after removal of solvent was the original complex, as deduced from the nmr spectrum (d^6-acetone). Lutidine isomers with 2-methyl groups were also unreactive.

Nitriles, Dimethylsulfide, Acetone, and THF

Reaction of molybdenum isopropylxanthate with acetonontrile, dimethylsulfide, acetone, or THF also produced red solutions. The red solid recovered after removal of solvent was insoluble in non-donor solvents. Infrared (Nujol mull) and nmr (d^6-acetone) spectra identified the solid as starting material. The xanthate was only slightly soluble in the reaction mixture with benzonitrile. The red solid recovered after removal of solvent gave the infrared spectrum described in Table I. When the solid was pumped on the vacuum line, the bands at 2238, 1600, 756, and 690 cm^{-1} disappeared; the infrared spectrum of the residue was identical to that of starting material.

Bromide and Chloride Ions

Mixtures of molybdenum(II) isopropylxanthate and tetrabutylammonium bromide or benzyltriethylammonium chloride gave red solutions in chloroform or acetone. The solids recovered from these reactions were intimate mixtures of red and white solids; their infrared spectra could be assigned as mixtures of starting materials. The solids were not further characterized.

Xanthate and Carboxylate Ions

Reactions of molybdenum isopropylxanthate with potassium isopropylxanthate in acetone, acetonitrile, DMSO, or pyridine yielded green solutions with absorption maxima at *ca.* 475 and 600 nm in the electronic spectra and complex nmr spectra consisting of overlapping multiplets centered at *ca.* 5.6 and 5.2 δ and overlapping doublets in the 1.5–1.2 δ region. The electronic and nmr spectra of solutions of molybdenum and potassium isopropylxanthates and ethylxanthates were examined as functions of concentrations. Reactions with carboxylate ions also give green solutions; reactions were studied by nmr spectroscopy.

Phosphines

The reaction of molybdenum isopropylxanthate with triphenylphosphine gave a dark red suspension and, after removal of solvent, a dirty red solid. Extraction with ether gave a green solution and left a rusty-red solid. The infrared spectrum of the solid was that of the original xanthate except for weak bands at 760 and 690 cm^{-1}; under 15X magnification, the solid was seen to be a mixture of red and white solids. The green solution, on removal of solvent, gave a white solid contaminated with traces of a green solid. The infrared spectrum was identical to that of triphenylphosphine except for a weak band at 645 cm^{-1}.

Reaction of the xanthate with tributylphosphine immediately produced a green solution, which left a dark green tar on removal of solvent. Extraction with pentane gave a dark green solid and left a red solid spectroscopically (ir) identical with the starting xanthate. Typical recoveries of this solid were 20% of the original mass. Removal of pentane from the green solution again left a green tar; its infrared spectrum contained bands at 1940(m), 1910(sh), 1890(m), 1860(m), 1800(w), 1720(w), 1235(s), 1194(s), 1140(m), 1096(s), 1032(s), 970(w), 909(s), 802(s), 734(m), 596(m–w), 590(m–w). The nmr spectrum ($CDCl_3$) contained two overlapping multiplets at 5.6 and 5.3 δ and complex multiplets at 1.37 and 0.94 δ.

Carbon Monoxide and 1-Hexene

When carbon monoxide was bubbled through a suspension of molybdenum isopropylxanthate in chloroform, no change was observed. The recovered solid was spectroscopically (ir) identical to the original complex. The xanthate also did not react with 1-hexene in chloroform.

Results and Discussion

Molybdenum(II) Xanthates

The reaction of molybdenum(II) acetate with potassium isopropylxanthate proceeds readily to give molybdenum(II) isopropylxanthate in high but not quantitative yield. Other molybdenum xanthates can be prepared analogously; in addition to ethyl and isopropyl, we have also examined briefly the methyl, n-propyl, n-butyl, and benzyl derivatives. These derivatives have quite similar chemical and spectroscopic properties; they are not further considered here.

The infrared spectrum of the isopropylxanthate in the 4000–600 cm^{-1} region agrees with that reported [3, 7] before except that we do not observe the bands at 1001 and 995 cm^{-1}. The two intense bands at *ca.* 1200 and 1100 cm^{-1} appear to be analogous to the antisymmetric and symmetric C–O–C stretching modes of esters and ethers [8]; we assign them as C–O–C stretching modes of the ligands. In the 600–180 cm^{-1} region, we observe more bands than reported previously, possibly because of better resolution of our spectrophotometer [9]. We assign the band at 475 cm^{-1} as a bending mode of the ligands, and the band at 320 cm^{-1} as a Mo–S stretching mode.

Reactions with Lewis Bases

Three classes of reactions may be conveniently considered here: (a) those which yield simple adducts, (b) those which disrupt the molybdenum xanthate core, and (c) those in which no reaction occurs.

a. Simple Adducts

The analytical data and integrated ^{1}H-nmr spectra of the pyridine and DMSO adducts support their formulation as 1:2 adducts $Mo_2[S_2COCH(CH_3)_2]_4 \cdot 2L$. The integrated nmr spectra of the picoline adducts support the same formulation. These results are consistent with the structures of molybdenum ethylxanthate–THF adducts and molybdenum(II) trifluoroacetate–pyridine adduct [10, 1b]. We propose similar structures for these adducts, as depicted in Fig. 1, with the Mo_2^{4+} unit bound equatorially to four xanthate ligands and axially to the added base. The infrared spectra of the adducts are very similar to the spectrum of molybdenum isopropylxanthate itself. This suggests that the core remains intact. The isopropyl resonances in the nmr (1.7 and 5.6 δ) show only the expected spin–spin coupling, implying that these ligands are equivalent.

The spectroscopic data in Tables I–III suggest that acetonitrile, benzonitrile, acetone, THF, and dimethylsulfide generate similar adducts *in situ*. These bases are less strongly bound than pyridine or DMSO and are easily lost at reduced pressure. By contrast, rhodium acetate adducts with acetonitrile, THF, and dimethylsulfide are stable at reduced pressure [10]. The difference reflects the relatively weak bonding between binuclear molybdenum(II) complexes and axial ligands. An axial Mo–ligand bond is some 0.5–0.7 Å longer than a corresponding equatorial bond [1, 11] and some 0.3–0.5 Å longer than a rhodium–axial ligand bond [12]. The greater stabilities of the pyridine and DMSO adducts probably results from the greater basicity of the pyridine and DMSO ligands [13]. A preference for basic donors was noted in a related rhenium carboxylate [14]. The failure of 2-picoline to form an adduct probably relates to steric hindrance; interactions between the methyl group and the sulfurs of the xanthate ligand prevent approach to the hindered [16] molybdenum site. The failure to isolate solid adducts with the halide ions may reflect solubility of the xanthate, relative lattice energies, or both.

The infrared spectra of the DMSO and d^6-DMSO adducts imply [15] that these ligands bond through oxygen, and that the 1010 cm^{-1} band is the S–O stretching frequency. The far-infrared spectrum should contain the Mo–ligand stretching vibration and two DMSO bending modes. We observe a new band at 385 cm^{-1} and enhanced absorption in the 330 and 300 cm^{-1} regions. The presence of xanthate absorptions in this general region complicates any consideration of assignments. In any case, the metal–oxygen vibration comes at lower frequency than is usual (444–415 cm^{-1}) [16] for this mode. A similar low-frequency shift occurs for the metal–ligand vibration in the pyridine and picoline adducts from the 200–300 cm^{-1} region to below 180 cm^{-1}. These low-frequency shifts of metal–ligand vibrations are consistent with the long Mo–axial ligand bonds observed crystallographically [1, 11].

The absorbance of all solutions in Table II obey Beer's law over the 10^{-3}–10^{-4} concentration range. Solutions of the solid pyridine or DMSO adducts in chloroform do not; the absorbances are always less in the more dilute solutions than expected. These results suggest that, in dilute solutions, dissociation of the insoluble isopropylxanthate occurs. Anderson [2] has inferred

TABLE IV. ^{1}H-nmr[a] and Electronic[b] Spectra for $Mo_2(S_2COR)_5^-$.

NMR	
R = C_2H_5	4.66, 4.64, 4.19 (quartets, J = 8 Hz, intensity 4:2:4); 1.46, 1.43, 1.19 (triplets, J = 8 Hz, 6:3:6)
R = i-C_3H_7	5.60, 5.54, 5.20 (multiplets, J = 7 Hz, intensity 2:1:2), 1.50, 1.47, 1.20 (doublets, J = 7 Hz, intensity 12:6:12)

Electronic	λ_{max}	ϵ	λ_{max}	ϵ	λ_{max}	ϵ
R = C_2H_5	604	1500	480	3000	358	7500
R = i-C_3H_7	603	1500	480	3100	357	7400

[a] Measured in δ relative to internal TMS; d^6-acetone solvent. [b] λ_{max} (nm); ϵ (M^{-1} cm^{-1}); in acetone solution.

dissociation of adducts of molybdenum trifluoroacetate from nmr data.

An nmr study of the pyridine adduct provides information into the rate of axial substitution of the adducts. The spectrum of the pyridine adduct (Table III) is typical of the spectra of adducts. The spectrum contains signals for the isopropylxanthate ligands (1.7 and 5.6 δ) and signals from the pyridine. These peaks are shifted slightly (less than 0.2 ppm) from their positions in the spectra of the free base. When extra pyridine is added to the sample, the pyridine resonances shift to average, concentration-dependent positions. These results indicate that free and coordinated pyridine undergo rapid exchange; this process remains rapid at –80 °C. The Beer's law studies suggest that the exchange involves an equilibrium

$$Mo_2[S_2COCH(CH_3)_2]_4 \cdot 2C_5H_5N \rightleftharpoons [Mo_2[S_2COCH(CH_3)_2]_4 \cdot C_5H_5N + C_5H_5N$$

It is possible that at the concentrations in the nmr experiments (0.1 *M*), the adduct may dissociate sufficiently so that the resonance positions given in Table III are average values instead of true positions for coordinated ligand.

b. Reactions which Disrupt the Core

Electronic and nmr spectroscopy (new bands at *ca.* 600 and 475 nm; overlapped features near 5.4 and 1.4 δ) indicate that the reaction between molybdenum and potassium isopropylxanthates does not give a simple 1:2 adduct with an intact $Mo_2[S_2COCH(CH_3)_2]_4$ core. Spectrophotometric (electronic and nmr) titrations of the ethyl and isopropylxanthate systems indicate that the green solutions contain complexes $Mo_2(S_2COR)_5^-$, formed via reaction 2, for which K > 10^5 M^{-1} in acetone solution at 25 °C [17]. Spectroscopic data for $Mo_2(S_2COR)_5^-$, with R ethyl or isopropyl, are given in Table IV.

$$Mo_2(S_2COR)_4 + ROCS_2^- \rightleftharpoons Mo_2(S_2COR)_5^- \qquad (2)$$

Similar reactions occur in acetonitrile, DMSO, and pyridine. At room temperature, the $Mo_2(S_2COR)_5^-$ complex undergoes neither rapid ligand exchange nor net chemical reaction with added xanthate ion; on heating to 80 °C, irreversible changes occur in the nmr spectrum (d^6-DMSO). The only identified product is the ester $ROCS_2R$. Reactions between free and coordinated xanthates have been reported to produce dithiocarbonate complexes [18]; a molybdenum dithiocarbonate complex could be a product of the high-temperature reaction.

The complex $Mo_2(S_2COR)_5^-$ has no analog in previously reported chemistry of the Mo_2^{4+} unit. Molybdenum carboxylates undergo ligand exchange with carboxylate salts (to be reported later) [19] but do not produce an nmr-detected $Mo_2(O_2Cr)_5^-$ complex. Molybdenum xanthates do react with carboxylate salts; studies of the reaction between molybdenum ethylxanthate and potassium pivalate in acetone solution show that reaction 3 occurs. Electronic spectra of the green solutions obtained in the reparation of molybdenum xanthates (reaction 1)

$$5\ Mo_2(S_2COEt)_4 + 4\ Me_3CCO_2^- \rightarrow 4\ Mo_2(S_2COEt)_5^- + Mo_2(O_2CCMe_3)_4 \qquad (3)$$

implicate $Mo_2(S_2COR)_5^-$ as the green intermediate; this complex is probably the "green impurity" reported by Cotton [4] when excess xanthate ion is used in the preparation. Even when stoichiometric amounts of materials are used, the intermediate forms readily, probably because molybdenum acetate is so insoluble in organic solvents that solutions always contain excess xanthate ions initially. Reaction 1 shifts to the left only when the neutral complex $Mo_2(S_2COR)_4$ can precipitate.

The structure of the $Mo_2(S_2COR)_5^-$ complexes is naturally of interest. We are currently attempting to crystallize salts of the complexes with large cations for crystallographic studies. Physical and chemical data do suggest some structural features. The nmr

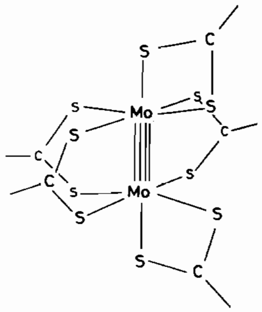

Fig. 2. Proposed structure of the $Mo_2(S_2COR)_5^-$ ion. The sites of attachment of the -OR groups are indicated.

spectra of solutions (Table IV) indicate that three structurally distinct types of xanthate ligands are present (2:1:2 ratio). Similarities of chemical shift suggest that two types (2:1) are very similar to each other and to the ligands in $Mo_2(S_2COR)_4$, while the last type (2) is somewhat different. We suggest the structure shown in Fig. 2, in which three ligands serve as bridging ligands (and account for the lowest-field portions of each region of absorption in the nmr spectrum) and two bond as chelates to only one metal center (and produce the highest-field portions of each region of nmr absorption) by using both axial and equatorial coordination sites.

The nmr chemical shifts are consistent with this structure. The resonances assigned to the non-bridging ligand of $Mo_2(S_2COEt)_5^-$ (4.21 and 1.19 δ) lie upfield from those of $Mo_2(S_2COEt)_4$ (4.68 and 1.48 δ), the xanthate ion (4.37 and 1.23 δ) and the ester $EtOCS_2Et$ (4.68 and 1.42 δ for the EtO group). San Filippo [20] has observed an appreciable diamagnetic anisotropy associated with the quadruple metal–metal bond. McConnell [21] has described the approximate shielding by an axially symmetric group of electrodes. In this case, r would be the distance between the protons of interest and the

$$\sigma = \frac{3\cos^2\theta - 1}{3r^3}(X_L - X_T)$$

molecular center, θ the acute angle between r and the metal–metal bond, and X_L and X_T the longitudinal and transverse magnetic susceptibilities of the metal–metal bond. For the bridging ligands, θ is essentially 90°. A comparison of the shifts for the methylene protons with those of the free ion suggests that θ for the non-bridging ligands is somewhat less than the "magic angle" 55°44′. By comparison, the angle to the equatorial sulfur atoms is approximately 60° [22]. This qualitative consideration suggests that the non-bridging chelated structure is reasonable.

The polar solvents used in these studies have precluded solution infrared spectroscopy. Solids isolated with K^+, Et_4N^+, or Bu_4N^+ counterions have produced red mulls whose infrared spectra are those of the starting materials. We presume that reaction 2 shifts to the left, because $Mo_2(S_2COR)_4$ is the least soluble component of the mixture. With Ph_4As^+, green mulls were obtained. Their spectra are similar but not identical to the spectra of reactants. We see no bands assignable to unidentate xanthate [23]. This result suggests that unidentate xanthate groups are not present in the $Mo_2(S_2COR)_5^-$ complexes. This result is consistent with the proposed structure.

Several chemical features are also consistent with this structure. Particularly we note that $Mo(S_2COR)_5^-$ does not react readily with either carboxylate ions or pyridine. This result would be natural if all coordination sites – equatorial and axial – were occupied. Chelation would reduce the reactivity associated with the axial sites by preventing the axial ligand from leaving the complex. We also note that xanthate ligands are more commonly bidentate than unidentate [24].

Why does the $Mo_2(S_2COR)_5^-$ complex form? The large 'bite' of the xanthate ligand, allowing it to span axial and equatorial sites may be an important factor; the nucleophilic behavior of the sulfur-donating ligand may also contribute to formation of the new complex. Further studies with sulfur-donating ligands are in progress.

Andersen [2] observed that triethylphosphine react with molybdenum trifluoroacetate to give equatorially bound phosphine and unidentate carboxylate. We might anticipate a similar course for the reaction between tributylphosphine (of similar basicity and cone angle to triethylphosphine) and a molybdenum xanthate. Although some of the ir bands are reminiscent of bridging xanthates, the green color of the mixture and the complex nmr spectrum suggests that the $Mo_2(S_2COR)_4$ core has indeed been disrupted. The xanthate reaction, unlike that of the trifluoroacetate, does not follow the simple 2:1 stoichiometry. It is tempting to assign the bands at 596 and 590 cm^{-1} to tributylphosphine sulfide [25] and the bands around 1900 cm^{-1} to one or more metal carbonyl derivatives. If these assignments are corect, they would suggest that additional reactions between the phosphine and the ligand has occurred. Again we see no evidence for formation of a xanthate ester, a reaction noted by Fackler and Seidel [18] for reaction of a platinum xanthate with phosphines.

Andersen [2] observed that triphenylphosphine react with molybdenum trifluoroacetate to form an axial adduct. We observe no such adduct here, almost certainly because the phosphine is too bulky to bind at the axial site. The small amount of green material suggests that core disruption has occurred, in a very minor reaction. The weak band at 645 cm^{-1} may be from the phosphine sulfide [25]; perhaps some reaction with the ligand has again occurred.

c. Systems in Which no Reaction Occurs

The failure of carbon monoxide and hexene to react with the xanthate suggests that ligands which depend largely on pi-acidity for their effectiveness will not bond strongly to Mo_2^{4+}. The di-orbitals suitable for back-bonding are already strongly involved in the metal-metal bond in these systems [26]. Appreciable back-bonding could only come at the expense of metal–metal bonding; our results indicate that this is not favorable.

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