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# Synthesis and Chemical and Structural Investigation of Molybdenum(IV) Thioxanthate Complexes. An Unusual Example of $\eta^3$ Coordination for a Dithio Acid Ligand

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The synthesis of the compounds $MoO(S_2CSR)_2$, R = $i\text{-}C_3H_7$ and $t\text{-}C_4H_9$, is reported. The electronic, IR, and proton NMR spectra are discussed and compared to those obtained for the parent dimers $[Mo_2O_3(S_2CSR)_2]$. The molecular structure of $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ was revealed in a single-crystal x-ray diffraction study. The compound crystallizes in the triclinic crystal system, space group $P\bar{1}$, with $a$ = 6.14 (1) Å, $b$ = 10.24 (1) Å, $c$ = 12.924 (8) Å, $\alpha$ = 109.71 (1)°, $\beta$ = 93.25 (1)°, and $\gamma$ = 99.80 (1)°, giving a density of 1.76 g cm$^{-3}$ on the basis of two molecules per unit cell, in agreement with the measured density of 1.74 (2) g cm$^{-3}$. The structure was solved using 1450 independent, statistically significant reflections collected on a full-circle automated diffractometer. The structure was solved by the usual Patterson and Fourier series methods to give a final value of the discrepency factor $R_1$ of 0.059. The molecule is a pseudo-square-pyramidal monomer with two distinct ligand coordination types: one thioxanthate group exhibits the usual bidentate geometry, with Mo–S distances of 2.438 (4) and 2.454 (5) Å and a chelate ring angle S–Mo–S of 72.2 (1)°, while the second thioxanthate group displays unusual nonclassic coordination, with the Mo significantly displaced from the $S_2CS$ plane such that the Mo–central carbon bond distance is 2.25 (1) Å and the Mo–S distances are 2.375 (5) and 2.365 (4) Å, with a chelate ring angle S–Mo–S of 77.9 (2) Å. The oxo group completes the coordination about the Mo atom [Mo–O distance 1.66 (1) Å] which is displaced 0.86 Å from the plane generated by the four sulfur donors toward this approximately apical oxygen. Voltammetric studies of the monomers indicate an irreversible oxidation and a quasi-reversible reduction as the major electrode processes. Comparison of the voltammetric behavior of the monomers with that of the dimer complexes $[Mo_2O_3(S_2CSR)_4]$ establishes the importance of dimer disproportionation into monomeric species in determining the overall electrochemical characteristics of these complexes. Oxidation–reduction mechanisms are proposed on the bases of these electrochemical studies, spectroscopic measurements, and isolation of electrode reaction products.

## Introduction

The coordination chemistry of molybdenum in the higher oxidation states (IV–VI) continues to draw a growing interest, in view of the possible relevance of these complexes to the redox-active molybdoenzymes.[1] In particular, the nitrogenase iron–molybdenum protein component from a number of bacterial sources[2–4] contains two molybdenum atoms per mole of enzyme. It has been proposed that the two molybdenum atoms are present at this enzyme-active site and function in a concerted fashion in the catalytic process.[5] The vital importance of molybdenum to the function of these enzymes and the speculation of a dimeric metal site involving coordination to sulfur-donor ligands have prompted a number of chemical,[5–7] electrochemical,[8] and structural studies[9–26] of molybdenum–oxo complexes enjoying some degree of coordination to sulfur-containing ligands. The chemical and structural aspects of the molybdenum dithiocarbamates have been extensively investigated, and the interrelationship of the dimeric and monomeric species has been established. The chemical[5,6]

and electrochemical[8] behavior of these complexes is dictated by the disproportionation of the molybdenum(V) dimer into monomeric Mo(IV) and Mo(VI) species:

$$Mo_2O_3(dtc)_4 \rightleftarrows MoO(dtc)_2 + MoO_2(dtc)_2 \qquad (1)$$
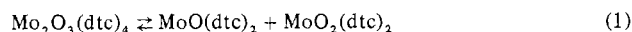
In a series of parallel investigations[12,27,28] we have studied the chemistry of molybdenum with the analogous thioxanthate ligand. This choice was dictated by the ability of the ligand to stabilize redox-active complexes[29,30] and to produce unique structural types through ligand dissociation or rearrangement.[31] In this paper, we describe the synthesis of a new type of molybdenum(IV) dithio acid monomer $MoO(S_2Cs\text{-}i\text{-}C_3H_7)_2$ and its relationship to the previously reported dimers.[12] The infrared and visible spectra are presented and discussed. The structure of the complex, determined by x-ray crystallography, is contrasted to the geometry of other monomeric square-pyramidal molybdenum compounds.

In addition, the present investigation has attempted to elucidate the electrochemical properties of the oxomolybdenum

**Table I.** Analytical Data for Molybdenum Thioxanthate Complexes

| Compd | % calcd | | | | % found | | | | Mol wt | |
|---|---|---|---|---|---|---|---|---|---|---|
| | C | H | S | Mo | C | H | S | Mo | Calcd | Found |
| $Mo_2O_3(S_2CSC_2H_5)_4$ | 18.3 | 2.54 | 48.7 | | 18.3 | 2.37 | 48.4 | | | |
| $Mo_2O_3(S_2CS-i-C_3H_7)_4$ | 22.8 | 3.32 | 45.5 | 22.7 | 22.8 | 3.50 | 45.3 | 22.4 | 844 | 850 |
| $Mo_2O_3(S_2CS-t-C_4H_9)_4$ | 26.7 | 4.00 | 42.7 | | 26.7 | 3.94 | 42.4 | | | |
| $MoO(S_2CS-i-C_3H_7)_2$ | 23.2 | 3.38 | 46.4 | 23.2 | 23.3 | 3.43 | 46.2 | 23.0 | 414 | 426 |
| $MoO(S_2CS-i-C_3H_7)_2PPh_3$ | 46.2 | 4.29 | 28.4 | | 46.1 | 4.14 | 28.2 | | | |
| $Mo_2O_4(S_2CS-i-C_3H_7)_2$ | 17.2 | 2.51 | 34.4 | 34.4 | 16.9 | 2.43 | 33.9 | 34.0 | 558 | 549 |

thioxanthate complexes in methylene chloride. The behavior of these complexes is contrasted to that observed for the analogous oxomolybdenum dithiocarbamate complexes in the same solvent and to the observations of De Hayes et al.[8] in acetonitrile and dimethylformamide solvent systems.

## Experimental Section

**Preparations.** All compounds were prepared from commercially available materials in a well-ventilated fume cupboard. All solvents were rigorously degassed, and all subsequent reactions and measurements were carried out in an atmosphere of purified nitrogen unless otherwise indicated. Microanalyses and molecular weight determinations were performed by Galbraith Laboratories, Knoxville, Tenn., and Instranal Laboratories, Rensselaer, N.Y. Melting points were obtained using a Thomas-Hoover capillary melting point apparatus. Melting points are uncorrected.

**Ammonium Oxopentachloromolybdate(V), $(NH_4)_2(MoOCl_5)$.** This compound was generally used as a starting material in order to avoid the large amount of contaminant present in commercial grade molybdenum pentachloride. The compound was prepared by a previously described method.[32] Molybdenum pentachloride (27.1 g, 0.1 mol) was dissolved in 100 mL of concentrated hydrochloric acid containing 27.7 g of ammonium chloride (0.5 mol). Hydrogen chloride, generated in a Brown hydrogenator by the action of sulfuric acid on ammonium chloride, was passed through the solution at 0 °C until a copious green precipitate formed. The precipitate was collected by filtration, washed with ether containing 5% thionyl chloride, and dried and stored in a vacuum desiccator.

**Sodium Salts of the Thioxanthate Ligands, $NaS_2CSR$ ($R = C_2H_5$, $i$-$C_3H_7$, $t$-$C_4H_9$, $CH_2C_6H_5$).** The sodium salts were prepared by the dropwise addition of the corresponding alkyl mercaptan (1 mol) to a saturated aqueous solution of NaOH at 0 °C, followed by the addition of excess carbon disulfide (1.2 mol). The yellow precipitate which formed immediately was collected by filtration and twice recrystallized from ethanol/ether or water/acetone. The salts are characterized by their unpleasant odor and are best stored in a vacuum desiccator over phosphorus pentoxide.

**Preparation of $Mo_2O_3(S_2CSR)_4$ Complexes ($R = C_2H_5$, $i$-$C_3H_7$, $t$-$C_4H_9$).** (a) A solution of $(NH_4)_2MoOCl_5$ (3.25 g, 0.01 mol) in 50 mL of water was added to a solution of the thioxanthate salt (0.025 mol) in 25 mL of water cooled to 4 °C in an ice bath. The dark precipitate which formed immediately was collected by filtration and washed with 50 mL of water and 50 mL of ethanol/ether. Thin-layer chromatrography of a benzene solution of this material showed it to be a mixture of a purple complex and a small amount of a blue material. The mixture was dissolved in benzene/petroleum ether (1:2) and chromatographed on Bio-Sil A 200–400 mesh silica (BioRad Laboratories), using benzene/petroleum ether as eluent. The purple eluate fraction was then evaporated in a stream of dry nitrogen, and the purple complex was recrystallized three times from carbon disulfide/pentane (1:1) to yield purple crystalline plates (yields were in the range 20–25% *after* recrystallization). Table I lists the analytical data for these complexes.

The blue eluate fraction was also collected, evaporated, and recrystallized. The properties of this side product are consistent with the formulation $Mo(S_2CSR)_4$. The chemical and structural properties of this complex have been described in a previous publication.[27]

(b) The complexes were also prepared by a method reported by Jowitt and Mitchell for the analogous dithiocarbamate complexes.[33] To a filtered solution of molybdenum trioxide (4.3 g, 0.03 mol) in 20 mL of hot concentrated hydrochloric acid was added an aqueous solution of hydrazine hydrochloride until reduction to molybdenum(V) was complete.[34] Sodium carbonate was added until a precipitate formed which was subsequently redissolved by acidification with dilute

hydrochloric acid. This solution was added to an aqueous solution of the sodium thioxanthate (0.12 mol) whereupon a dark precipitate formed immediately. The product was filtered and washed with 50 mL of water and 50 mL of ether. Thin-layer chromatography once again indicated the presence of substantial amounts of the blue side product. The mixture was chromatographed as previously described; the purple fraction was evaporated to dryness, and the residue was recrystallized from carbon disulfide/pentane (1:1) three times to give large purple plates of the complex.

Attempts to prepare these complexes by sulfur dioxide reduction of sodium molybate/ligand solutions[35] or by direct reaction of molybdenum pentachloride and the thioxanthate ligand resulted in the formation of brown intractable materials or materials which gave unsatisfactory analytical results.

**$\mu$-Dioxo-bis[oxo(isopropyl thioxanthato)molybdenum(V)], $Mo_2O_4(S_2CS-i-C_3H_7)_2$.** (a) A benzene solution of $\mu$-oxo-bis[oxo-bis(isopropyl thioxanthato)molybdenum(V)], $Mo_2O_3(S_2CS-i-C_3H_7)_4$ (0.5 g in 50 mL), was refluxed for 2 h; the original purple color was discharged and a light tan precipitate was formed. This material was filtered, washed with water, acetone, and ethyl ether, and then dried in vacuo at room temperature.

(b) A solution containing $(NH_4)_2MoOCl_5$ (1.62 g, 0.005 mol) and the thioxanthate salt $NaS_2CSC_3H_7$ (0.87 g, 0.005 mol) in 20 mL of water was refluxed for 3 h resulting in a tan precipitate which was filtered, washed, and then dried in a stream of dry nitrogen (yield was typically 80%).

**Oxobis(isopropyl thioxanthato)molybdenum(IV), $MoO(S_2CS-i-C_3H_7)_2$.** The dimeric molybdenum(V) complex $Mo_2O_3(S_2CS-i-C_3H_7)_4$, prepared as previously described, was dissolved in carbon disulfide (0.5 g in 15 mL) and chromatographed on a silica column (Macherey Nagel, 0.05–0.2 mm/70–270 mesh; Brinkmann Instruments Inc., distributor), using $CS_2$ as eluent. The purple color was rapidly discharged and three bands developed on the column: a leading yellow band, an intermediate blue region, and a sharp red band. The red eluate fraction was collected and evaporated in a stream of dry nitrogen. Recrystallization from carbon disulfide/pentane (1:1) produced red needles (yield 20% after recrystallization) analyzing as $MoO(S_2CS-i-C_3H_7)_2$.

The yellow eluate was also collected and evaporated in a stream of nitrogen to produce a yellow oil. Elemental analysis and mass spectrometry indicated that the isolated compound was $C_3H_7SC$-$S_2$-$S_2CSC_3H_7$. Anal. Calcd for $C_8H_{14}S_6$: C, 31.8; H, 4.64; S, 63.6. Found: C, 31.9; H, 4.54; S, 63.4. Mass spectral data, $m/e$ (% of parent peak p): 302 (100, p), 304 (26, p + 2).

The blue fraction proved to be a mixture of the eight-coordinate monomer $Mo(S_2CSC_3H_7)_4$, which is produced as a side product in the reaction, and $Mo_2O_4(S_2CSC_3H_7)_2$ (infrared spectroscopy). Thin-layer chromatography on a silica plate using methylene chloride resulted in successful separation of a blue band from a yellow-tan fraction which exhibited an infrared spectrum identical with that of $Mo_2O_4(S_2CSC_3H_7)_2$ as synthesized by conventional techniques.

The $t$-$C_4H_9$ analogue $MoO(S_2CS-t-C_4H_9)_2$ was prepared by the same reaction sequence.

**Oxobis(isopropyl thioxanthato)triphenylphosphinomolybdenum(IV), $MoO(Ph_3P)(S_2CS-i-C_3H_7)_2$.** Addition of 2.3 g (9 mmol) of $PPh_3$ to a solution of 2.5 g (3 mmol) of the dimeric complex $Mo_2O_3$-$(S_2CS-i-C_3H_7)_4$ in 150 mL of thoroughly degassed $CS_2$, followed by 2 h of vigorous stirring, resulted in a deep red solution. The solution volume was reduced to 30 mL on a rotary evaporator and 20 mL of pentane added. The resulting orange crystals were washed with 70/30 ethanol/water to remove $OPPh_3$. Repeated recrystallization from carbon disulfide/pentane yielded yellow crystals. Analysis indicated that the compound isolated is $MoO(S_2CS-i-C_3H_7)_2(PPh_3)$.

**Reactions of $MoO(S_2CS-i-C_3H_7)_2$.** (a) $MoO(S_2CS-i-C_3H_7)_2$ (1 g, 2.4 mmol) was added to a solution of $OPPh_3$ (2 g, 7.2 mmol) in

$CH_2Cl_2$ (100 mL). The red reaction mixture underwent no color change over a period of 7 days. After evaporation of the solvent, analysis of the product mixture (IR and NMR) indicated that no reaction had occurred.

(b) Under both aerobic and anaerobic conditions, solutions of $MoO(S_2CS-i-C_3H_7)_2$ (0.30 g) in $CHCl_3$ (40 mL) or $CH_2Cl_2$ (40 mL) were found to be stable over a 5-day period.

(c) Treatment of $MoO(S_2CS-i-C_3H_7)_2$ (0.4 g, 0.97 mmol) with bromine (0.16 g, 0.97 mmol) in dry, degassed benzene results in precipitation of fine yellow needles. Recrystallization from carbon disulfide/pentane yielded a complex analyzing as $MoOBr_2(S_2CS-i-C_3H_7)_2$.

(d) Reaction of $MoO(S_2CS-i-C_3H_7)_2$ (0.3 g, 0.7 mmol) in 40 mL of degassed $CH_2Cl_2$ with $MoO_2(S_2CNEt_2)_2$ (0.31 g, 0.72 mmol) in 30 mL of $CH_2Cl_2$ produces an immediate color change, giving a purple solution characteristic of the molybdenum(V) dimers. The solution was concentrated by rotary evaporation and chromatographed on a silica column (200–400 mesh), using carbon disulfide/methanol eluent. Two purple fractions were collected individually and evaporated in a stream of dry nitrogen. The first was identified as an impure preparation of $Mo_2O_3(S_2CNEt_2)_4$ and the second, after recrystallization from carbon disulfide/pentane to give shiny purple plates, was found to analyze as $Mo_2O_3(S_2CS-i-C_3H_7)_4$ (IR and NMR).

**Bis(*N,N*-diethyldithiocarbamato)dioxomolybdenum(VI) and Analogues, $MoO_2(S_2CNR_2)_2$ (R = $C_2H_5$, $C_3H_7$, $C_6H_5$).** The $MoO_2(dtc)_2$ complexes were synthesized according to the procedure of Jowitt and Mitchell.[33]

**μ-Oxo-bis[bis(*N,N*-diethyldithiocarbamato)oxomolybdenum(V)], $Mo_2O_3(S_2CNR_2)_4$.** The complex was prepared as described by Newton et al.[5]

**Bis(*N,N*-diethyldithiocarbamato)oxomolybdenum(IV), MoO-$(S_2CNR_2)_2$.** The compound was prepared from the molybdenum(VI) species $MoO_2(S_2CNR_2)_2$ using oxo abstraction by $PPh_2Et$.[6]

**Magnetic, Spectroscopic, and Electrochemical Measurements.** The gram magnetic susceptibilities of the crystalline solids were measured at room temperature by the Gouy technique.[36] The Gouy tubes were calibrated with $Hg[Co(NCS)_4]$, prepared as described in the literature.[37]

Proton nuclear magnetic resonance spectra were recorded on a Varian Associates A-60 spectrometer. Electronic spectra of chloroform solutions were obtained on a Cary 14 spectrophotometer at concentrations of $10^{-3}$–$10^{-5}$ M using 1-cm matched quartz cells. Infrared spectra were taken on a Beckman IR-12 instrument in the range 4000–200 $cm^{-1}$ using KBr plates and polyethylene strips. The spectra were calibrated against polystyrene.

Normal-pulse polarography, ac voltammetry, and triangular-wave stationary-electrode cyclic voltammetry were performed on a Princeton Applied Research (PAR) Model 170 electroanalytical system using a three-electrode configuration in $CH_2Cl_2|0.1$ M [*n*-$Bu_4N$]$PF_6$ solution vs. an Ag|AgCl|0.1 M LiCl reference electrode or an isolated saturated calomel electrode. All potentials are reported with respect to the SCE. Normal-pulse polarograms were obtained at a scan rate of 10 mV $s^{-1}$ with a pulse frequency of 2.0 pulses/s. Normal-pulse and cyclic voltammetry was performed at a platinum wire electrode, pretreated by electrolysis at 0.0 V vs. SCE in 0.1 N $HClO_4$ solution. Cyclic voltammograms were also recorded at vitreous carbon and hanging mercury drop electrodes. Since the rate of polarization is limited by the XY recorder to approximately 1.0 V $s^{-1}$, cyclic voltammograms were also recorded on a Chemtrix Model SSP-2 polarograph equipped with a Tektronix Model 546B storage oscilloscope, allowing scan rates of up to 20 V $s^{-1}$. Phase-sensitive ac voltammograms were obtained at a scan rate of 10 mV $s^{-1}$ at 80 Hz with a phase angle of 90° with respect to the input alternating potential and with an ac perturbation of 5 mV peak–peak. Instrument stability and solvent purity were monitored by observing the reversible one-electron oxidations of $[NiS_4C_4(CN)_4]^{2-}$ [38] in methylene chloride. Values consistent with the literature were obtained throughout. Solutions were $10^{-3}$–$10^{-4}$ M in complex. The working range was +1.5 to −2.4 V in methylene chloride and +1.2 to −2.5 V in dimethylformamide.

**Crystal Preparation and Collection and Reduction of Diffraction Data.** Needle-shaped crystals of $MoO(S_2CS-i-C_3H_7)_2$ were grown from a concentrated carbon disulfide/pentane solution cooled to 4 °C overnight. A well-formed crystal was mounted along the needle axis for preliminary photographic investigation.

Approximate cell dimensions were obtained from Weissenberg and precession photographs of the crystals taken with Cu Kα (λ 1.5418

**Table II.** Summary of Crystal Data for $MoO(S_2CS-i-C_3H_7)_2$ [a]

| | |
|---|---|
| Fw 413.9 | Space group: $P\bar{1}$ |
| $a = 6.14$ (1) Å | $Z = 2$ |
| $b = 10.24$ (1) Å | $\rho_{calcd} = 1.76$ g cm$^{-3}$ |
| $c = 12.924$ (8) Å | $\rho_{found} = 1.74$ (2) g cm$^{-3}$ |
| $\alpha = 109.71$ (1)° | $F(000) = 416.00$ |
| $\beta = 93.25$ (1)° | λ(Mo Kα) 0.7107 Å |
| $\gamma = 99.80$ (1)° | Crystal dimensions: 0.12 × |
| $V = 780.98$ Å³ | 0.24 × 0.14 mm |
| Crystal system: triclinic | μ(Mo Kα) = 15.68 cm$^{-1}$ |
| Systematic absences: none | |

[a] 1450 Symmetry-independent reflections with $I > 2.50\sigma(I)$ in the range $2° < \theta < 45°$ (of a total of 1939 reflections scanned). Reflections with $2\theta < 2°$ were not collected due to significant scatter off the backstop.

Å) radiation and used to generate angle settings for reflections with $16 < 2\theta < 23°$. Twenty reflections within this range were accurately centered in the window of a Picker full-circle automated diffractometer. A least-squares procedure was used to obtain a best fit between the observed and calculated values of χ, φ, and $2\theta$ for these reflections. The cell parameters and relevant crystal data are presented in Table II.

Intensity data were collected using Mo Kα radiation filtered through zirconium foil. A scan speed of 1°/min was employed in measuring each reflection by the moving crystal–moving counter technique with a scan range in $2\theta$ of 2°, plus an allowance for the splitting of the $K\alpha_1$ and $K\alpha_2$ radiation. Backgrounds were determined by 10-s stationary counts at each end of the scan range. The net count $N$ was calculated as $N = T - (BG1 + BG2)(SCT)/20$, where $T$ is the total integrated peak intensity, BG1 and BG2 are the background counts, and SCT is the total measuring time for the peak in seconds. Four standard reflections were employed to monitor diffractometer and crystal stability. The fluctuation in the integrated intensities of the standards was no greater than that expected from Poisson statistics.

The observed intensities were corrected for background, Lorentz, and polarization effects. Only reflections with $I \geq 2.5\sigma(I)$ were included in the refinement.

**Solution and Refinement of the Structure.** The initial Patterson map revealed the positions of molybdenum and four sulfur atoms. The space group $P\bar{1}$ was chosen and successful structure refinement indicated that that choice was correct.

Full-matrix least-squares refinement was based on $F$, and the function was minimized as $\sum w(|F_o| - |F_c|)^2$. The weights $w$ were taken as $(2F_o/\sigma(F_o^2))^2$ where $|F_o|$ and $|F_c|$ are the observed and calculated structure factor amplitudes. Atomic scattering factors for nonhydrogen atoms were taken from Cromer and Waber.[39] The anomalous dispersion corrections for molybdenum and sulfur were included. The programs used in the refinement were those compiled in the 1972 version of the x-ray system of Stewart et al.[40] and operated on a Univac 1110 computer.

A difference-Fourier synthesis phased on the five heavy atoms revealed the remaining part of the structure. Refinement of positional and individual isotropic temperature factors for the atoms converged at a value of 0.115 for the conventional $R$ factor. At this stage, anisotropic temperature factors were introduced. Five cycles of full-matrix least-squares refinement converged to $R = 0.059$ and $R_w = 0.076$, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

A final difference-Fourier synthesis revealed no excursions in electron density greater than 0.8 e Å$^{-3}$ on a scale where the average value for a carbon atom was 6.5 e Å$^{-3}$.

At this stage attempts were made to refine the structure in the space group $P1$. This led invariably to difficulties with the individual temperature factors and to somewhat larger discrepancy factors. This seemed to confirm the original choice of space group.

A table of the observed and calculated structure factors is available as supplementary material.

## Results and Discussion

**Preparations.** The syntheses of the ligand salts proceed in a manner analogous to that previously described.[27] Addition of carbon disulfide to a solution of the sodium alkyl mercaptides produces a bright yellow precipitate, characteristic of the thioxanthates, according to eq 2. The resulting yellow

$$Na^+SR^- + CS_2 \underset{H_2O}{\rightleftarrows} Na^+(S_2CSR)^- \qquad (2)$$
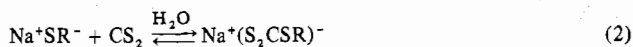
crystalline material is dissolved in a minimum amount of water and allowed to react with aqueous $MoOCl_5^{2-}$ in air to yield a reaction mixture containing a number of products. Although the reaction of Mo(V) with sodium thioxanthate salts under strictly anaerobic conditions yields the monomeric Mo-$(S_2CSR)_4$ complexes as major products, the main product in air appears to be the dimeric $Mo_2O_3(S_2CSR)_4$, a species readily purified by column chromatography. The analytical data characterizing the crystalline, dimeric complexes are presented in Table I. The properties of the $Mo_2O_3(S_2CSR)_4$ complexes are similar. All complexes decompose slowly in atmospheric oxygen over a period of 4–7 days. In solution, the complexes decompose in a period of several hours in air and more slowly, 24–48 h, under strictly anaerobic conditions. The decomposition is characterized by the discharge of the intense purple color of the solution and the formation of an unidentified blue residue. The complexes are readily soluble in nonpolar or weakly polar solvents such as benzene, carbon disulfide, chloroform, and methylene chloride.
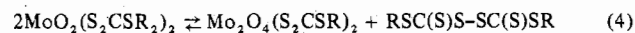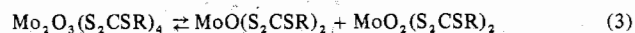
The dissociation of the dimeric molybdenum(V) dithiocarbamates to produce monomeric species according to eq 1 has been demonstrated.[5] A similar equilibrium is evident in the behavior of the thioxanthate dimers (vide infra) which may be exploited to synthesize monomeric species not readily isolable by more conventional methods. Column chromatography of a carbon disulfide solution of the dimeric Mo(V) complex on fine-mesh activated silica results in a rapid discharge of the characteristic purple color of the dimer and the isolation of a variety of products.

The initial red fraction yielded, after workup, a crystalline *air-stable* Mo(IV) monomer analyzing as $MoO(S_2CSR)_2$ (Table I). The monomeric species is unaffected by atmospheric oxygen in both the solid and solution states and is readily soluble in carbon disulfide, chloroform, methylene chloride, and benzene. The synthesis of this species from solutions of the Mo(V) dimer indicates the reducing nature of the thioxanthate ligand and the stabilization of the metal +4 oxidation state, as previously observed.[27] This is in strong contrast to the electron-rich dithiocarbamate ligand which stabilizes the higher oxidation states Mo(V) and Mo(VI). The instability of the molybdenum(IV) dithiocarbamates MoO-$(S_2CNR_2)_2$ toward oxidation supports this observation.

The second major product of the decomposition of the dimeric Mo(V) species on silica is a yellow oil which exhibits an elemental analysis, mass spectrometric data, and infrared properties consistent with isolation of the disulfide RSC-(S)SSC(S)SR.

A small amount of a tan product may also be collected. The infrared spectrum of this material exhibits a number of bands at 970 cm$^{-1}$ ($\nu(Mo=O)$) and 735 cm$^{-1}$ ($\nu(MoO_2Mo)$), suggesting the presence of dimeric Mo(V) species. These bands have been reported previously with the molybdenum(V) dithiocarbamates $Mo_2O_4(S_2CNR_2)_2$ and with the amino acid complexes of Mo(V). The complex may be isolated in good yield and in analytically pure form by refluxing a carefully degassed solution of the ligand and molybdenum pentachloride for 24 h, followed by chromatography on an alumina column to remove the monomeric side product $Mo(S_2CSR)_4$. Analytical (Table I) and infrared (Table VIII) data are consistent with the formulation $Mo_2O_4(S_2CSR)_2$.

These observations of the product mixture are consistent with the disproportionation of the Mo(V) dimers on activated silica according to the equilibria

$$Mo_2O_3(S_2CSR)_4 \rightleftarrows MoO(S_2CSR)_2 + MoO_2(S_2CSR)_2 \qquad (3)$$

$$2MoO_2(S_2CSR_2)_2 \rightleftarrows Mo_2O_4(S_2CSR)_2 + RSC(S)S-SC(S)SR \qquad (4)$$

All attempts to isolate the Mo(VI) monomer $MoO_2(S_2CSR)_2$ proved unsuccessful; nor was any evidence found in the spectroscopic or electrochemical investigation for the presence of the Mo(VI) species, suggesting that the second equilibrium is established rapidly. The instability of the Mo(VI) species toward decomposition to the Mo(V) dimer is consistent with the reducing nature of the thioxanthate ligand.

Unlike the dithiocarbamate dimers which exhibit disproportionation according to eq 3 but show no decomposition reactions, the solution chemistry of the thioxanthate complexes is further complicated by slow decomposition to unidentified "molybdenum blue" species. In addition to the products of the disproportionation reaction, silica chromatography of the molybdenum(V) thioxanthate dimer yields an acetone-soluble blue residue exhibiting a featureless infrared spectrum except for a broad band in the region assigned to the Mo–O stretch. The time-dependent visible spectra of the complex also indicate that slow decomposition of the Mo(V) solutions occurs.
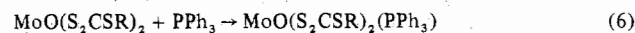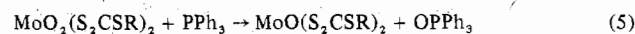
Attempts to synthesize $MoO(S_2CSR)_2$ from the dimer $Mo_2O_3(S_2CSR)_4$ using oxo abstraction by phosphines in a stoichiometric reaction yields impure preparations consisting of mixtures of $Mo_2O_3(S_2CSR)_4$, $PPh_3$, $OPPh_3$, and MoO-$(S_2CSR)_2$. The oxo-abstraction method, thus, seems to offer little advantage over the chromatographic preparation.

The addition of phosphine to a methylene chloride solution of the dimeric species $Mo_2O_3(S_2CSR)_4$ in threefold excess results in the preparation of a yellow crystalline material $MoO(S_2CSR)_2(Ph_3P)$ isolated in analytically pure form after repeated crystallizations and washings to remove $OPPh_3$. The complex is air stable and soluble in a variety of organic solvents: carbon disulfide, methylene chloride, and chloroform. The spectroscopic and physical data (vide infra) are consistent with the formulation as a monomeric 1:1 adduct of MoO-$(S_2CSR)_2$ and $PPh_3$. The complex may also be prepared directly by the reaction of $PPh_3$ and $MoO(S_2CSR)_2$ in methylene chloride.

Attempts to oxidize chemically the $MoO(S_2CSR)_2$ complexes were generally unsuccessful. Thus, it was found that reaction of $MoO(S_2CSR)_2$ with $Ph_3PO$ yielded no purple color over a 12-h period and no reaction over a 3-day period. An aerated solution of the Mo(IV) monomer was likewise unreactive, establishing the stability of the Mo(IV) species toward air and chemical oxidation and the absence of any evidence for oxo transfer between $MoO(S_2CSR)_2$ and $OPPh_3$.

In contrast to the above behavior, the complex MoO-$(S_2CSR)_2$ reacts rapidly with a stoichiometric quantity of the Mo(VI) species $MoO_2(S_2CNR_2)_2$ in methylene chloride to produce an intensely purple solution. Product analysis establishes the absence of the mixed-ligand dimer $Mo_2O_3$-$(S_2CNEt_2)_2(S_2CSC_3H_7)_2$. The major products under both aerobic and anaerobic conditions were found to be the dimeric Mo(V) species $Mo_2O_3(S_2CNEt_2)_4$ and $Mo_2O_3(S_2CSR)_4$. This result suggests rapid oxo transfer between the Mo(VI) species $MoO_2(S_2CNEt_2)_2$ and the Mo(IV) complex $MoO(S_2CSC_3$-$H_7)_2$, followed by the reaction of the $MoO_2(S_2CSC_3H_7)_2$ just formed with unreacted $MoO(S_2CSC_3H_7)_2$ to establish equilibrium 3.

These observations are consistent with the mechanism recently proposed for the reactions of oxomolybdenum complexes with reducing or oxo-abstracting reagents.[6] Where dissociation via the equilibrium in eq 3 occurs, as it does in the case of the thioxanthate complexes (vide infra), the first step of the reaction sequence involves abstraction of an oxo group from the Mo(VI) species $MoO_2(S_2CSR)_2$.

$$MoO_2(S_2CSR)_2 + PPh_3 \rightarrow MoO(S_2CSR)_2 + OPPh_3 \qquad (5)$$

$$MoO(S_2CSR)_2 + PPh_3 \rightarrow MoO(S_2CSR)_2(PPh_3) \qquad (6)$$

The equilibrium described by eq 3 ensures that there will

**Table III.** Final Positional and Thermal Parameters for $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2{}^a$

| Atom | $x$ | $y$ | $z$ | $U_{11}$ | $U_{22}$ | $U_{33}$ | $U_{12}$ | $U_{13}$ | $U_{23}$ |
|------|-----|-----|-----|----------|----------|----------|----------|----------|----------|
| Mo | 0.1051 (2) | 0.3631 (1) | 0.1315 (1) | 4.04 (9) | 3.95 (6) | 3.74 (6) | 0.91 (6) | 0.58 (6) | 1.37 (5) |
| S1 | −0.1375 (6) | 0.5153 (4) | 0.1345 (3) | 4.3 (3) | 5.5 (2) | 3.6 (2) | 1.6 (2) | 0.3 (2) | 1.2 (2) |
| S2 | 0.3371 (6) | 0.5861 (4) | 0.1799 (3) | 4.4 (3) | 4.5 (2) | 5.0 (2) | 0.5 (2) | 0.9 (2) | 1.5 (2) |
| S3 | −0.1069 (6) | 0.1854 (4) | −0.0342 (4) | 3.5 (3) | 5.3 (2) | 5.7 (2) | 0.8 (2) | 0.7 (2) | 0.3 (2) |
| S4 | 0.3521 (6) | 0.2491 (4) | 0.0097 (3) | 3.6 (3) | 4.9 (2) | 4.2 (2) | 1.3 (2) | 0.0 (2) | 0.6 (2) |
| S5 | 0.0965 (6) | 0.6643 (5) | 0.3729 (3) | 5.0 (3) | 5.9 (3) | 3.7 (2) | 1.0 (2) | 0.1 (2) | 0.5 (2) |
| S6 | 0.1275 (7) | 0.0582 (5) | −0.2185 (4) | 4.7 (3) | 6.3 (3) | 4.8 (2) | 2.0 (2) | −0.2 (2) | −0.7 (2) |
| O | 0.0904 (16) | 0.2969 (11) | 0.2323 (8) | 6.2 (8) | 5.4 (7) | 4.5 (6) | 1.6 (6) | 1.0 (6) | 2.1 (7) |
| C1 | 0.0913 (21) | 0.5896 (15) | 0.2285 (11) | 2.9 (10) | 4.8 (9) | 3.6 (7) | 0.4 (8) | 0.8 (8) | 2.4 (7) |
| C2 | −0.1837 (22) | 0.6434 (16) | 0.3974 (12) | 3.2 (11) | 5.2 (9) | 3.5 (8) | 2.2 (9) | 1.0 (8) | 1.2 (7) |
| C3 | −0.2830 (30) | 0.4965 (19) | 0.3905 (16) | 7.3 (16) | 7.9 (13) | 7.4 (13) | 1.2 (10) | 4.1 (12) | 4.7 (11) |
| C4 | −0.1893 (32) | 0.7566 (20) | 0.5114 (15) | 8.3 (18) | 10.9 (17) | 4.6 (11) | 5.7 (15) | 7.2 (11) | 0.4 (10) |
| C5 | 0.1301 (20) | 0.1576 (14) | −0.0819 (11) | 3.2 (11) | 2.6 (7) | 3.4 (8) | 0.6 (7) | −0.0 (8) | 0.6 (5) |
| C6 | 0.4016 (29) | 0.0394 (15) | −0.2353 (12) | 5.9 (12) | 3.2 (8) | 4.2 (9) | 2.6 (9) | 1.0 (9) | 0.2 (6) |
| C7 | 0.4369 (33) | 0.0232 (22) | −0.3550 (15) | 10.5 (20) | 7.7 (14) | 5.2 (11) | 2.4 (14) | 1.7 (12) | 0.8 (10) |
| C8 | 0.4452 (32) | −0.0858 (19) | −0.2035 (18) | 7.4 (16) | 4.5 (11) | 10.1 (15) | 3.2 (11) | 1.2 (13) | 1.6 (10) |

$^a$ Estimated standard deviations are given in parentheses. The $U_{ij}$ values are $\times 10^3$. The vibrational coefficients relate to the expression $T = \exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}h^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hla^*b^* + 2U_{13}hla^*c^* + 2U_{23}hlb^*c^*)]$.

always be $MoO_2(S_2CSR)_2$ present for reduction by $PPh_3$ until only $MoO(S_2CSR)_2$ remains; the instability of the molybdenum(VI) thioxanthate species relative to the Mo(IV) complex also suggests preferential reaction of the $PPh_3$ with $MoO_2(S_2CSR)_2$ until the species is entirely consumed. Only then is the Mo(IV) monomer attacked by $PPh_3$ in adduct formation. Thus, in the presence of a threefold excess of $PPh_3$, the only products of the reaction with $Mo_2O_3(S_2CSR)_4$ are $MoO(S_2CSR)_2(PPh_3)$ and $OPPh_3$, as illustrated by eq 5 and 6.

It appears, therefore, that the molybdenum(IV) thioxanthate complex is produced by reduction of a Mo(VI) complex without the "intermediate" Mo(V) dimer undergoing reduction. Although this mechanism is consistent with that proposed for the analogous dithiocarbamate complexes,[6] it cannot be established as unambiguously due to the reducing nature of the thioxanthate ligand and the resultant instability of the Mo(VI) species. The proposed rapid dissociation of this complex precluded isolation and direct investigation of the reaction mechanism. The indirect support for the proposed mechanism is convincing. It has been established that whereas oxomolybdenum complexes that dissociate according to eq 3 are reducible to isolable Mo(IV) species, complexes that do not ($MoO_2acac_2$, for example) are reducible to the Mo(V) stage only.[6] This equilibrium obviously exists for the thioxanthate complexes because the visible spectra of the $Mo_2O_3(S_2CSR)_4$ complexes do not obey Beer's law (Table X) and the anticipated product, $MoO(S_2CSR)_2$, is produced upon $PPh_3$ reduction. The electrochemical behavior (vide infra) of the solutions of the Mo(V) dimers also unambiguously establishes the equilibrium and the absence of any electrode process involving the reduction of the oxo-bridged dimer $Mo_2O_3(S_2CSR)_4$ to Mo(IV). We conclude, therefore, in full agreement with previous reports,[6] that the $Mo_2O_3(S_2CSR)_4$ complexes are not directly reducible to monomeric Mo(IV) species but that the Mo(IV) species are produced in the equilibrium interaction of $MoO(S_2CSR)_2$ and $MoO_2(S_2CSR)_2$. In this context, the inability of $OPPh_3$ to oxidize the Mo(IV) species is not surprising since a stoichiometric amount of $PPh_3$ will reduce the equilibrium mixture to $MoO(S_2CSR)_2$.

Although the $MoO(S_2CSR)_2$ complexes are remarkably stable to air or chemical oxidation, in contrast to $MoO(S_2CNEt_2)_2$ where the electron-rich sulfur donors of the dithiocarbamate stabilize the higher oxidation states of the metal, these species do undergo a number of reactions analogous to those of the dithiocarbamate complexes. Rapid oxidation occurs in the presence of $MoO_2(S_2CNR_2)_2$, presumably via oxo transfer to the Mo(IV) species and subsequent establishment of equilibrium 3. Likewise, reaction with molecular
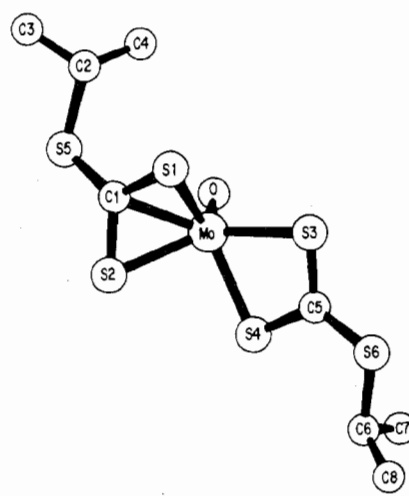


**Figure 1.** Perspective view of the molecule $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ giving the atom labeling scheme.

bromine occurs by oxidative addition to produce a yellow complex of stoichiometry $MoO(S_2CSR)_2Br_2$. The physical properties of the complex as described below are consistent with a seven-coordinate molybdenum(VI) complex.

**Solid-State Structure Determination and a Comparison of Oxomolybdenum Thioxanthate and Oxomolybdenum Dithiocarbamate Systems.** Atomic positional and thermal parameters with their standard deviations are collected in Table III. Figure 1 gives the atom labeling scheme and presents the molecular structure. The packing of the molecules in the unit cell is shown in a stereoscopic view in Figure 2. The intramolecular bond distances and angles are given in Table IV. The equations of relevant least-squares planes and the dihedral angles between planes are presented in Table V.

The structure consists of discrete monomers with two chemically distinct types of thioxanthate ligand coordination: the usual terminal bidentate coordination through the sulfur donor atoms with the Mo atom approximately in the $S_2CS$ plane and a unique coordination type in which the chelate ring is distinctly nonplanar with the ring carbon clearly within bonding distance to the Mo atom. The overall geometry about the molybdenum atom is severely distorted from the square-pyramidal coordination enjoyed by the analogous $MoO(S_2CNR_2)_2$ complex.[9] The coordination polyhedron is derived from the square pyramid with the molybdenum atom displaced 0.86 Å from the plane generated by the sulfur donor atoms S1–S2–S3–S4 toward the apical oxygen atom. A major stereochemical consequence of the ligation mode of the thi-
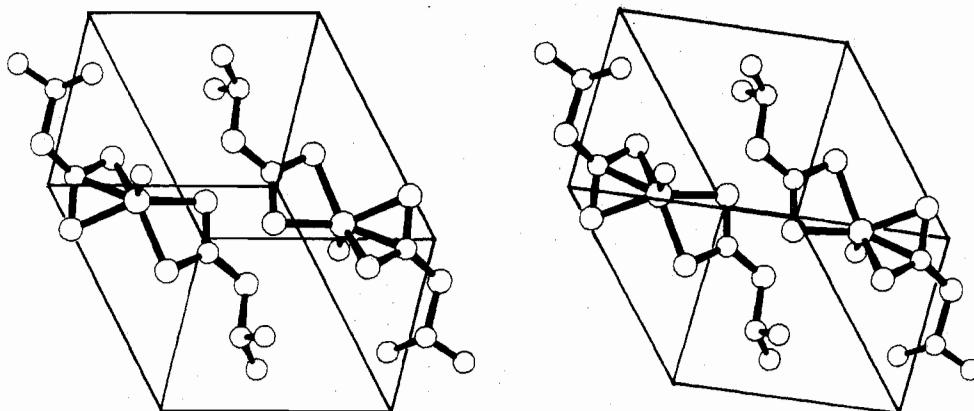
**Figure 2.** Stereoscopic view of the packing of the symmetry-related $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ molecules in the unit cell.

**Table IV.** Selected Bond Lengths, Angles, and Intramolecular Contacts for $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$

Distances, Å

| | | | |
|---|---|---|---|
| Mo–S1 | 2.375 (5) | S3–C5 | 1.70 (1) |
| Mo–S2 | 2.365 (4) | S4–C5 | 1.71 (1) |
| Mo–S3 | 2.438 (4) | S6–C5 | 1.71 (1) |
| Mo–S4 | 2.454 (5) | S5–C2 | 1.83 (2) |
| Mo–O | 1.66 (1) | S6–C6 | 1.82 (2) |
| Mo–C1 | 2.25 (1) | C2–C3 | 1.50 (3) |
| S1–C1 | 1.73 (1) | C2–C4 | 1.54 (2) |
| S2–C1 | 1.73 (2) | C6–C7 | 1.53 (3) |
| S5–C1 | 1.76 (1) | C6–C8 | 1.54 (2) |

Angles, Deg

| | | | |
|---|---|---|---|
| S1–Mo–S2 | 77.9 (2) | O–Mo–C1 | 99.6 (6) |
| S1–Mo–S3 | 89.2 (2) | S1–C1–S2 | 118.8 (8) |
| S1–Mo–S4 | 138.6 (2) | S2–C1–S5 | 125.1 (10) |
| S2–Mo–S3 | 137.7 (2) | S2–C1–S5 | 116.0 (8) |
| S2–Mo–S4 | 90.8 (2) | S3–C5–S4 | 115.4 (8) |
| S3–Mo–S4 | 72.2 (1) | S3–C5–S6 | 118.4 (9) |
| S1–Mo–O | 113.6 (4) | S4–C5–S6 | 125.8 (10) |
| S2–Mo–O | 114.6 (4) | S5–C2–C3 | 113.8 (13) |
| S3–Mo–O | 107.5 (4) | S5–C2–C4 | 105.8 (11) |
| S4–Mo–O | 107.4 (5) | S6–C6–C7 | 108.2 (14) |
| S1–Mo–C1 | 43.9 (4) | S6–C7–C8 | 109.6 (13) |
| S2–Mo–C1 | 43.9 (4) | C3–C2–C4 | 112.9 (15) |
| S3–Mo–C1 | 133.0 (4) | C7–C6–C8 | 113.2 (15) |
| S4–Mo–C1 | 134.3 (4) | | |

Intramolecular Contacts, Å

| | | | |
|---|---|---|---|
| S1···S2 (bite) | 2.981 (7) | S2···O | 3.41 (1) |
| S3···S4 (bite) | 2.882 (7) | S3···O | 3.34 (1) |
| S1···S3 | 3.393 (6) | S4···O | 3.35 (1) |
| S2···S4 | 3.432 (6) | O···C1 | 3.01 (2) |
| S1···O | 3.40 (1) | | |

**Table V**

Equations of Least-Squares Planes in $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$

| Atom | Dist from plane, Å | Atom | Dist from plane, Å |
|---|---|---|---|
| 1. $-0.2707X - 6.2557Y + 12.2748Z + 1.5425 = 0$ | | | |
| S1 | 0.007 (5) | S4 | 0.007 (5) |
| S2 | −0.007 (5) | Mo | 0.86 |
| S3 | −0.006 (5) | | |
| 2. $-1.0123X + 10.2019Y - 5.3917Z - 4.6730 = 0$ | | | |
| S1 | −0.003 (5) | S5 | −0.003 (5) |
| S2 | −0.003 (5) | C1 | 0.009 (6) |
| 3. $-0.6360X + 9.8194Y - 7.61087Z - 2.1354 = 0$ | | | |
| S3 | 0.014 (20) | S6 | 0.015 (20) |
| S4 | 0.014 (20) | C5 | −0.044 (20) |

Dihedral Angles between Least-Squares Planes

| Plane A | Plane B | Angle, deg |
|---|---|---|
| 1 | 2 | 132.6 |
| 1 | 3 | 144.1 |
| 2 | 3 | 168.4 |

as $\eta^2\text{-}CS_2$ and $\eta^3\text{-}CS_2$ thioxanthate.] The metal–sulfur distance for the conventionally ligated thioxanthate is similar to that observed for other molybdenum dithio acid complexes where Mo–S (dithio acid ligand) varies from 2.414 to 2.455 Å,[9–12,15,19,21] with the exception of those cases where crystallographic trans effects produce Mo–S distances in the range of 2.53 Å for a trans bridging oxo group and 2.65 Å for a trans terminal oxo group.[10–12]

The Mo–S1 and Mo–S2 distances, however, average to 2.370 (4) Å, a value significantly shorter than those previously observed for molybdenum–ligand sulfur bonds in dithio acid complexes of this type. It is also noteworthy that the angle between the line defined by the vector from the Mo atom to the centroid of the S1–S2–C1 plane and the normal to the S1–S2–C1 plane is 17°. These observations, together with the short molybdenum–ring carbon distance of 2.25 (1) Å, suggest interaction of the metal with the ligand $\pi$ system utilizing a molecular orbital bonding description similar to that proposed for $\pi$-allyl–metal interactions.[60] Also consistent with this model of the bonding is the retention of the planarity of the $CS_3$ atom grouping, indicating that C1 remains $sp^2$ hybridized and is not involved in a direct $\sigma$ interaction with the metal.

The effects of two distinct ligand coordination types are observed in the angular distortions at the Mo atom. The S3–Mo–S4 angle of 72.2 (1)° is consistent with the constraints imposed when a bidentate ligand participates in the formation of a four-membered ring. The angle may be compared to the values obtained in $MoO(S_2CNPr_2)_2$ (72.4 (1)°),[9] $Mo_2O$-

oxanthate-*S,S,C* ligand ($\eta^3\text{-}CS_2$) is the strong steric interaction between the oxo group and C1 (O···C1 = 3.01 (2) Å). As a result of this interaction, the Mo–O line is not perpendicular to the least-squares planes formed by the four basal sulfur atoms. The distortions in the coordination polyhedron arise in part from the geometrical constraints of the four-membered thioxanthate chelate ring and the more severe requirements of the puckered-ring geometry. Table VI presents a geometrical analysis of the coordination polyhedra of $MoO(S_2CNR_2)_2$[9] and $MoO(S_2CSC_3H_7)_2$ and compares the dihedral angles to those predicted for ideal tetragonal-pyramidal geometry.[41] In Table VII the geometry of the thioxanthate complex is compared to the structural parameters for square-pyramidal molybdenum complexes and fragments with apical oxo groups.

In $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ there are two chemically different types of molybdenum–sulfur bonds, which may be recognized from their respective average bond lengths, 2.446 (5) Å for Mo–S (thioxanthate-*S,S*) and 2.370 (4) Å for Mo–S (thioxanthate-*S,S,C*). [The coordination types will be designated

**Table VI.** Ideal and Observed Angles (deg) for $ML_5$ and $MO(LL)_2$ Complexes

| Complex | Shape-determining angles, δ' | | S angles | | | | Axial deformation angle[e] |
|---|---|---|---|---|---|---|---|
| Ideal tetragonal pyramid, $ML_5$, $C_{4v}$[a] | 0.0 | | | 75.7 | 75.7 | | 0.0 |
| | 75.7 | 75.7 | 119.8 | 119.8 | 119.8 | 119.8 | |
| $Ni(CN)_5{}^{3-}$ [b] | 0.3 | | | 78.2 | 78.2 | | 0.2 |
| | 75.0 | 79.4 | 115.6 | 115.7 | 118.4 | 119.6 | |
| $MoO(S_2CN(C_3H_7)_2)_2$[c] | 0.0 | | | 74.0 | 72.8 | | 1.8 |
| | 73.2 | 73.3 | 119.5 | 120.0 | 124.7 | 125.9 | |
| $MoO(S_2CS\text{-}i\text{-}C_3H_7)_2$ | 0.5 | | | 74.2 | 74.1 | | 3.9 |
| | 73.6 | 72.4 | 120.2 | 120.3 | 123.5 | 124.8 | |
| Ideal $MO(LL)_2$, $C_{2v}$[d] | 0.0 | | | 73.4 | 73.4 | | 0.0 |
| | 73.4 | 73.4 | 119.7 | 119.7 | 125.1 | 125.1 | |

[a] E. L. Muetterties and L. J. Guggenberger, *J. Am. Chem. Soc.*, **96**, 1748 (1974). [b] K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 1367 (1968). [c] L. Ricard, J. Estienne, P. Karagiannidis, P. Toledano, J. Fischer, A. Mitschler, and R. Weiss, *J. Coord. Chem.*, **3**, 277 (1974). [d] Calculation based on the following idealized geometry: Mo–O, 1.66 Å; S···S bite, 2.85 Å; distance of Mo from the basal plane, 0.84 Å. [e] Angle between the line normal to the basal plane and the line generated through the metal and the axial ligand.

**Table VII.** Structural Parameters for Square-Pyramidal Molybdenum Complexes or Fragments with Apical Oxo Groups MoOL$_4$

| Complex | Mo–$O_t$, Å | Mo–L, Å | L | Mo displacement, Å | Ref |
|---|---|---|---|---|---|
| $Mo_2O(S_2CNEt_2)_2$-$(C_6H_5CON_2)_2$·$CH_2Cl_2$ | 1.66 (1) | 2.431 (6) | S | 0.72 | 26 |
| | | 1.971 (1) | N | | |
| $Mo_2O(S_2CNEt_2)_2$-$(ClC_6H_4CSN_2)_2$·$CHCl_3$ | 1.67 (1) | 2.437 (6) | S | 0.69 | 58 |
| | | 1.97 (1) | N | | |
| $Mo_2O_4(S_2CNEt_2)_2$ | 1.678 (2) | 2.455 (3) | S | 0.74 | 15 |
| | | 1.941 (1) | O | | |
| $[MoO_2S_2(S_2C$-$(CN)_2)_2]^{2-}$ | 1.664 (7)[a] | 2.434 (3) | $S_t$ | 0.72 | 20 |
| | | 2.206 (3) | $S_b$ | | |
| $MoO(S_2CNPr_2)_2$ | 1.664 (8) | 2.413 (5) | S | 0.82 | 9 |
| $MoO(S_2CS$-$i$-$Pr)_2$ | 1.66 (1) | 2.370 (4) | S | 0.86 | This work |
| | | 2.446 (5) | S | | |

[a] Average values.

$(S_2CNEt_2)_2(C_6H_5CON_2)_2$·$CH_2Cl_2$ (72.1 (1)°),[26] and $Mo_2O(S_2CNEt_2)_2(ClC_6H_4CSN_2)_2$·$CHCl_3$ (72.2 (1)°),[42] where similar or approximate square-pyramidal geometry about the Mo atom is observed. The S1–Mo–S2 angle is significantly less constrained, 77.9 (2)°, as a result of the unusual ligation mode. Reduction of metal valence angles from the usual value of 90° is required to relieve steric strain in the small rings. In general, a decrease of the metal valence angle results in poorer metal–ligand overlap and, for chelating ligands, a decrease in the "bite" distance. The geometrical consequences of the two distinct ligand coordination types are, thus, apparent in the ligand stereochemistries. As expected from these considerations, the S3–C5–S4 angle is considerably more constrained than the S1–C1–S2 angle (115.4 (8)° vs. 118.8 (8)°). Similarly, the ligand "bite" distance S3···S4 of 2.882 (7) Å is significantly smaller than that observed for the $\eta^3$-$CS_2$ ligand (S1···S2 = 2.981 (7) Å).

The intraligand geometry is similar to that observed for analogous thioxanthate and dithio acid complexes. The average of the four crystallographically independent C=S bond lengths is 1.72 (1) Å with a standard deviation from the mean of 0.01 Å. This value is similar to the average C=S bond distances obtained in $Fe_2(S_2CSC_2H_5)_4(SC_2H_5)_2$ (1.680 (2) Å),[43] $Co_2(S_2CSC_2H_5)_4(SC_2H_5)_2$ (1.688 (7) Å),[30] $Fe(S_2CS$-$C_4H_9)_3$ (1.694 (8) Å),[44] $Mo_2O_3(S_2CSC_3H_7)_4$ (1.67 (2) Å),[12] $MoO_2(S_2CN(C_3H_7)_2)_2$ (1.723 (6) Å),[9] $Mo_2O_3(S_2CN(C_3H_7)_2)_4$ (1.705 (12) Å),[9] and $MoO(S_2CN(C_3H_7)_2)_2$ (1.728 (2) Å).[9]

Examination of the C1–S5 and C5–S6 bond distances reveals them to be significantly shorter than the single-bond value of 1.81 Å calculated by correcting the average of the

C2–S5 and C6–S6 bond lengths for the difference between single-bond radii of sp$^3$- and sp$^2$-hybridized carbon atoms. As noted previously,[30] this is consistent with the participation of resonance form III, along with I and II, in the overall electronic
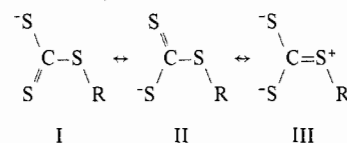


structure of the coordinated ligands. A calculation for $MoO(S_2CSC_3H_7)_2$, using the data of Table IV and the method of Merlino,[45] indicates that the normally chelated $\eta^2$-$CS_2$ ligand consists of 33% I, 33% II, and 33% III while the $\eta^3$-$CS_2$ ligand has a composition of 39% I, 39% II, and 22% III. Since the classically coordinated thioxanthate is involved in the formation of a constrained four-membered ring, it is reasonable that resonance form III would contribute to a greater extent to its structure than to that of the $\eta^3$-$CS_2$ ligand.

A final point of interest with regard to the ligand geometry is the nonequivalence of the S–C–S angles (for example, S1–C1–S2 = 118.8 (9)°, S1–C1–S5 = 125.1 (10)°, and S2–C1–S5 = 116.8 (8)°) within the thioxanthate ligands, although the CS$_3$ atom groupings are planar. The larger S–C–S angle always occurs on the same side as the isopropyl group, suggesting that intramolecular packing forces distort the angles at C1 and C5 in order to accommodate the bulky isopropyl group. Similar results have been observed for $Fe_2(S_2CSC_2H_5)_4(SC_2H_5)_2$ and $Fe(S_2CSC_4H_9)_3$[44] and for the S–C–O angles of ethyl xanthate ligands in the $Fe(S_2COC_2H_5)_3$[46] and $Co(S_2COC_2H_5)_3$[47] complexes.

It is noteworthy that there are no intermolecular contacts shorter than 3.6 Å and that the packing diagrams of the structure do not suggest any evident crystal-packing constraints as a rationale for the unusual coordination type.

**Infrared Spectra.** Although there has been some controversy surrounding the assignments of molybdenum–oxygen stretching frequencies in complexes of the type $Mo_2O_3$-$(S_2CR)_4$,[48–51] recent detailed investigations allow more definitive assignments.[5,52] In the case of the thioxanthate complexes (see Table VIII), the assignments are complicated by the presence of strong ligand absorptions in the 950–1000-cm$^{-1}$ range. Comparison of the spectra with those obtained for the $Mo(S_2CSR)_4$ complexes,[27] where the thioxanthate ligand is terminal and no oxo coordination is involved, allowed the assignment of the C–S bands at ~990 and ~970 cm$^{-1}$ and consequently the assignment of the strong band at ~940 cm$^{-1}$, which is unique to the $Mo_2O_3(S_2CR)_4$ complexes, to the terminal molybdenum–oxygen stretching vibration ($\nu(Mo=O)$). Our data agree with those recently published for the analogous $Mo_2O_3(S_2CNR_2)_4$ complexes.[52] Thus, the

**Table VIII.** Selected Mid-Infrared Spectral Frequencies of Dimeric and Monomeric Molybdenum Thioxanthate Complexes (cm$^{-1}$)[a]

| Mo$_2$O$_3$(S$_2$CSR)$_4$ | | | | Mo$_2$O$_4$(S$_2$CSR)$_2$ | | MoO(S$_2$CSR)$_2$ | | |
|---|---|---|---|---|---|---|---|---|
| R = C$_2$H$_5$ | R = i-C$_3$H$_7$ | R = t-C$_4$H$_9$ | R = CH$_2$C$_6$H$_5$ | R = i-C$_3$H$_7$ | R = t-C$_4$H$_9$ | R = i-C$_3$H$_7$ | R = t-C$_4$H$_9$ | Assignment |
| 1059 n | 1062 m | 1101 n | 1022 n | 1059 n | 1012 n | 1060 m | 1099 m | $\nu$(C$\dddot{\,}$S) |
| 986 s | 995 s | 995 s | 978 s | 982 s | 987 s | 982 s | 991 s | |
| 971 s | 964 s | 974 s | 964 s | | | | | |
| 939 s | 942 m | 931 s | 951 vs | 973 s | 965 s | 975 s | 971 s | $\nu$(Mo=O) |
| | | | | 962 m | 958 sh | | | |
| | | | | | | 938 s | 924 s | |
| | | | | | | 923 m | | $\nu$(C-S) |
| | | | | | | 884 m | 898 n | |
| | | | | | | 876 n | 863 m | |
| 758 w | 761 w | 745 w | 762 w | | | | | $\nu$(Mo-O-Mo) |
| | | | | 732 m | 728 m | | | $\nu$(Mo-O$_2$-Mo) |
| 439 m | 435 n | 441 n | 438 m | | | | | $\nu$(Mo-O-Mo) |
| | | | | 472 m | 476 m | | | $\nu$(Mo-O$_2$-Mo) |
| 358 m | 359 n | 360 n | 354 m | 379 m | 375 m | 380 m | 374 m | $\nu$(Mo-S) |
| | | | | | | 366 m | 368 m | |

**Table IX.** Electronic Spectral Bands of Molybdenum Thioxanthate Complexes in Chloroform

| Compd | Absorption maxima, cm$^{-1}$ $\times$ 10$^{-3}$ (log $\epsilon$) |
|---|---|
| Mo$_2$O$_3$(S$_2$CSC$_2$H$_5$)$_4$ | 18.2 (3.45)   25.3 (3.51)   31.6 (4.59)   33.8 (sh) |
| Mo$_2$O$_3$(S$_2$CS-i-C$_3$H$_7$)$_4$ | 18.2 (3.50)   25.3 (3.62)   31.2 (4.70)   33.9 (sh) |
| Mo$_2$O$_3$(S$_2$CS-t-C$_4$H$_9$)$_4$ | 18.1 (3.42)   25.5 (3.61)   31.0 (4.62)   33.9 (sh) |
| Mo$_2$O$_3$(S$_2$CSCH$_2$C$_6$H$_5$)$_4$ | 18.3 (3.54)   25.4 (3.62)   31.5 (4.74)   34.0 (sh) |
| MoO(S$_2$CS-i-C$_3$H$_7$)$_2$ | 19.3 (2.55)   25.3 (3.17)   31.2 (4.43)   34.5 (4.29) |
| MoO(S$_2$CS-t-C$_4$H$_9$)$_2$ | 19.4 (2.61)   25.3 (3.21)   31.1 (4.51)   34.4 (sh) |
| MoO(S$_2$CS-i-C$_3$H$_7$)$_2$·PPh$_3$ | 19.6 (2.79)                 31.0 (4.54)   35.0 (4.15) |
| Mo$_2$O$_4$(S$_2$CS-i-C$_3$H$_7$)$_2$ |               25.4 (3.78)   31.1 (4.55)   33.9 (sh) |

medium absorptions at ~750 and 400 cm$^{-1}$ are assigned to the antisymmetric and symmetric vibrations of the Mo–O–Mo bridge, respectively.

In the Mo$_2$O$_4$(S$_2$CSR)$_2$ series, complications arise due to the number of bands in the 970–1000-cm$^{-1}$ region. However, two $\nu$(Mo=O) absorptions are present at higher frequency than that observed for the Mo$_2$O$_3$(S$_2$CSR)$_4$ complexes, again consistent with the analogous dithiocarbamates Mo$_2$O$_4$-(S$_2$CNR$_2$)$_2$. The Mo–O$_2$–Mo bridge vibrations appear at ~740 and ~470 cm$^{-1}$ for the antisymmetric and symmetric modes, respectively.

The Mo(IV) monomers display a very strong absorption at ~980 cm$^{-1}$ which we assign as terminal Mo=O stretching frequencies. This shift to higher frequency is consistent with the strong Mo–O interaction as suggested by the short Mo–O distance.

Examination of the infrared spectra of the molybdenum thioxanthate complexes of the types Mo$_2$O$_3$(S$_2$CSR)$_4$, Mo$_2$O$_4$(S$_2$CSR)$_2$, and Mo(S$_2$CSR)$_4$ in the region 800–1000 cm$^{-1}$ reveals a close similarity in the frequencies and relative intensities of the C–S stretching bands. Assignments for these and other selected mid-infrared absorptions are suggested in Table VIII. Most of the bands have contributions from several individual oscillators.[53]

The Nujol and KBr spectra of the Mo(IV) monomers, however, exhibit two medium-intensity absorptions in the 870–890-cm$^{-1}$ region, which may be characteristic of the unusual $\eta^3$-CS$_2$ thioxanthate ligand. Intense absorptions have been observed between 880 and 900 cm$^{-1}$ in the infrared spectra of complexes having bridging thioxanthate groups. The ligand geometry of the bridging thioxanthate group is analogous to that of the $\eta^2$-CS$_2$ thioxanthate ligand in that the internal angles are considerably less constrained than those of the terminal thioxanthate ligand. The solution spectrum of the complex MoO(S$_2$CSC$_3$H$_7$)$_2$ in methylene chloride, however, shows absorptions attributable to $\nu$(Mo=O) at 970 cm$^{-1}$ and to $\nu$(C–S) at 990 and 940 cm$^{-1}$ but a complete absence of bands in the 850–900-cm$^{-1}$ region. This observation, together with the NMR and electrochemical data, indicates that in solution the complex adopts a different

structure from that discussed for the crystal state, most probably one in which both thioxanthate groups function in the usual manner as terminal bidentate ligands.

In the solid-state infrared spectrum of the adduct MoO-(S$_2$CSC$_3$H$_7$)$_2$·PPh$_3$, medium-intensity bands are observed at 871 and 882 cm$^{-1}$ and intense absorptions appear at 942 and 999 cm$^{-1}$. On the basis of previous assignments, the data support a structural model in which the two distinct thioxanthate coordination types $\eta^2$-CS$_2$ and $\eta^3$-CS$_2$ are preserved in the adduct. A very strong band at 952 cm$^{-1}$ is assigned to terminal $\nu$(Mo=O). The shift to lower frequency is consistent with the increase in the Mo coordination number and the presence of a ligand trans to the oxo group.[54] The magnitude of the shift, only some 20 cm$^{-1}$, suggests that the PPh$_3$ group occupies a cis coordination site. A more pronounced shift might be expected with the PPh$_3$ in the trans geometry competing directly with the oxo group for the metal electron density through d$\pi$–d$\pi$ back-acceptance.

The solid-state infrared spectrum of MoO(S$_2$CSC$_3$H$_7$)$_2$Br$_2$ exhibits a similar decrease in the $\nu$(Mo=O) band from 975 cm$^{-1}$ in the parent complex to 951 cm$^{-1}$ suggesting an increase in the found oxidation state and coordination number of the molybdenum. The complex is analogous to the dithiocarbonate species MoO(S$_2$CNEt$_2$)$_2$X$_2$, X = Br or Cl, prepared by the oxidation addition of X$_2$ to Mo(IV).[54]

**Electronic Spectra.** Summarized in Table IX are the electronic spectral bands of the various complexes. The visible spectra of the Mo$_2$O$_4$(S$_2$CSR)$_2$ complexes are characterized by a poorly resolved shoulder at 25 300 cm$^{-1}$, an intense absorption at ~31 000 cm$^{-1}$, and a shoulder at ~34 000 cm$^{-1}$. From their intensity and the fact that they are common to all the oxomolybdenum thioxanthate complexes, the latter two bands, 3 and 4, appear to be either charge-transfer or ligand internal absorptions.

The spectra of the Mo$_2$O$_3$(S$_2$CSR)$_4$ complexes contain an intense band at ~18 200 cm$^{-1}$. This band did not obey Beer's law and its molar absorptivity decreased as the concentration was lowered. This behavior appears to be common to the 1,1-dithio acid oxomolybdenum complexes of the type Mo$_2$O$_3$(S$_2$X)$_4$, X = PR$_2$,[6] P(OR)$_2$,[6] CNR$_2$,[5] COR,[55] and CSR.

**Table X.** Molar Absorptivities and Peak Positions for Molybdenum Thioxanthate Complexes as a Function of Concentration and Time[a]

| Complex | Time, h | Concn, M × 10⁴ | log $\epsilon_1$ | log $\epsilon_2$ | $\nu_1$ | $\nu_2$ |
|---|---|---|---|---|---|---|
| Mo₂O₃(S₂CS-*i*-C₃H₇)₄ | 0 | 2.41 | 3.50 | 3.62 | 18.2 | 25.3 |
| | 0 | 1.00 | 3.19 | 3.62 | 18.3 | 25.3 |
| | 0 | 0.48 | 3.06 | 3.62 | 18.6 | 25.3 |
| | 0 | 0.25 | 2.99 | 3.61 | 18.8 | 25.3 |
| | 1 | 2.41 | 3.50 | 3.61 | 18.2 | 25.3 |
| | 2 | 2.41 | 3.50 | 3.61 | 18.2 | 25.3 |
| | 10 | 2.41 | 3.47 | 3.61 | 18.2 | 25.3 |
| | 48 | 2.41 | 3.01 | 3.59 | 18.7 | 25.3 |
| Mo₂O₃(S₂CS-*t*-C₄H₉)₄ | 0 | 2.54 | 3.42 | 3.61 | 18.1 | 25.3 |
| | 0 | 0.99 | 3.14 | 3.61 | 18.3 | 25.3 |
| | 0 | 0.51 | 3.08 | 3.61 | 18.4 | 25.3 |
| | 0 | 0.29 | 2.98 | 3.60 | 18.2 | 25.3 |
| | 2 | 2.54 | 3.42 | 3.60 | 18.1 | 25.3 |
| | 10 | 2.54 | 3.40 | 3.60 | 18.1 | 25.3 |
| MoO(S₂CS-*i*-C₃H₇)₄ | 0 | 9.56 | 2.55 | 3.17 | 19.3 | 25.3 |
| | 0 | 7.38 | 2.54 | 3.16 | 19.3 | 25.3 |
| | 0 | 5.42 | 2.54 | 3.16 | 19.3 | 25.3 |
| | 0 | 3.10 | 2.54 | 3.16 | 19.3 | 25.3 |
| | 0 | 1.00 | 2.54 | 3.16 | 19.3 | 25.3 |
| | 4 | 3.10 | 2.54 | 3.16 | 19.3 | 25.3 |
| | 24 | 3.10 | 2.54 | 3.16 | 19.3 | 25.3 |

[a] Spectra recorded in degassed $CH_2Cl_2$.

Molar absorptivities as a function of concentration in methylene chloride solution for $Mo_2O_3(S_2CSR)_4$ are presented in Table X. The deviation from Beer's law behavior was shown to be reversible by diluting a solution of $Mo_2O_3(S_2CSC_3H_7)_4$, followed by reconcentration by evaporation in a stream of nitrogen to give an original and final solution of the same molar absorptivity. This establishes that the observed deviation from Beer's law behavior is due to an equilibrium and not a decomposition process. The dissociation described by eq 3 will rationalize the behavior. Independent observations of this behavior have been reported, and similar conclusions have been made regarding the equilibrium reaction.

Attempts to establish unambiguously the nature of the species produced by the dissociation of thioxanthate dimers proved somewhat difficult. Although the Mo(IV) monomer was easily prepared, all attempts to isolate $MoO_2(S_2CSR)_2$ species failed, presumably due to the reducing nature of the thioxanthate ligand, in contrast to the electron-rich dithiocarbamate species. In the chromatographic preparation of $MoO(S_2CSR)_2$ it was found, however, that the other products of the decomposition of the Mo(V) dimer were the disulfide RSC(S)S–SC(S)SR and $Mo_2O_4(S_2CSR)_2$. This observation suggested that, although dissociation according to eq 3 did occur, the unstable $MoO_2(S_2CSR)_2$ complex participates in a second equilibrium reaction described by eq 4 for which the equilibrium lies to the right. To test this hypothesis, equimolar solutions of the appropriate concentration of the Mo(IV) monomer, the dioxo-bridged Mo(V) dimer, and the disulfide $(RSCS_2)_2$ were mixed and found to produce spectra identical with those for solutions prepared directly from the oxo-bridged dimer $Mo_2O_3(S_2CSR)_4$. In addition, analysis of the product ratio of the chromatographic isolation showed that the products were obtained in approximately equimolar quantities. Finally, conductance measurements on solutions of the $Mo_2O_3$-$(S_2CSR)_4$ dimers revealed that no ions were produced in the dissociation. Taken together with the results of the reactions of $PPh_3$ with the dimer species $Mo_2O_3(S_2CSR)_4$, discussed previously, and the electrochemical investigations of the solutions of the various species produced in the dissociation reactions, the observations provide compelling support for the proposed dissociation scheme.

**Table XI.** Proton NMR Data for $Mo_2O_3(S_2CSR)_4$ and $MoO(S_2CSR)_2$ Complexes[a]

| Compd | Chemical shifts, ppm;[b] $J$, Hz | Rel intens |
|---|---|---|
| Mo₂O₃(S₂CSC₂H₅)₄ | 8.63 (t), 6.81 (q); $J$ = 7.1 | 3:2 |
| Mo₂O₃(S₂CS-*i*-C₃H₇)₄ | 8.52 (d), 5.87 (h); $J$ ≈ 7.0 | 6:1 |
| Mo₂O₃(S₂CS-*t*-C₄H₉)₄ | 8.24 (s) | |
| Mo₂O₃(S₂CSCH₂C₆H₅)₄ | 7.70 (s), 4.01 (c) | 2:5 |
| MoO(S₂CS-*i*-C₃H₇)₂ | 8.52 (d), 5.89 (h); $J$ = 6.9 | 3:2 |
| MoO(S₂CS-*t*-C₄H₉)₂ | 8.15 (s) | |
| MoO(S₂CS-*i*-C₃H₇)₂·PPh₃ | 8.39 (d), 5.82 (h), 2.55 (c); $J$ = 6.9 | 6:1:7.5 |

[a] Spectra recorded in $CS_2$ with internal $Me_4Si$ standard at 60 MHz. [b] Abbreviations: d, doublet; c, complex multiplet; h, heptet; s, singlet; t, triplet; q, quartet.

Comparison of the spectral results with those obtained for the dithiocarbamate dimers $Mo_2O_3(S_2CNR_2)_4$[5] and the analogous xanthate complexes $Mo_2O_3(S_2COR)_4$[10] suggests that the 18 200-cm⁻¹ band is due to a transition involving the Mo–O–Mo bridge. Similarly, the oxomolybdenum thioxanthate complexes display a shoulder at ~25 400 cm⁻¹ which obeys Beer's law in all cases (Table X) and which has been assigned to a molybdenum–oxygen transition[5] on the basis of the variation in the extinction coefficient as a function of the number of oxo ligands.

The five-coordinate Mo(IV) complexes $MoO(S_2CX)_2$ display a well-defined medium-intensity (log $\epsilon \approx 2.6$) absorption band in the ranges 19 400 cm⁻¹ for the thioxanthate complexes and 19 600 cm⁻¹ for the dithiocarbamate analogues.[5] From its intensity and unique appearance in the square-pyramidal monomers of approximate $C_{2v}$ symmetry, this band may be assigned to a spin-allowed transition of the low-symmetry species, $^2A_2-^2B_1$ or $^2A_2-^2B_2$.

**Magnetic Properties: Susceptibility and ¹H NMR Studies.** The oxomolybdenum complexes, whether dimeric Mo(V) or monomeric Mo(IV) species, were found to be diamagnetic (NMR to 300 K, Gouy method at room temperature). The diamagnetism of the oxo-bridged Mo(V) dimers has been rationalized in terms of spin pairing through the oxo-bridge system and of the angle of twist at the bridge for the xanthate analogue $Mo_2O_3(S_2COC_2H_5)_4$. As the structural identity of the xanthate,[10] dithiocarbamate,[9] and thioxanthate dimers[12] has been established, the observed diamagnetism was anticipated. The dioxo-bridged Mo(V) species $Mo_2O_4(S_2CSR)_2$, which are structurally analogous to the dithiocarbamate dimers $Mo_2O_4(S_2CNR_2)_2$,[15] achieve spin pairing through a direct Mo–Mo interaction (Mo–Mo = 2.580 (1) Å). The diamagnetism of the d²-Mo(IV) complex is consistent with square-pyramidal, $C_{2v}$ symmetry, where the electron pair populates the approximately nonbonding $d_{xy}$ ($A_2$) orbital. In this respect, it is suggested that the electronic transitions observed in these complexes at ~19 500 cm⁻¹ are most likely assigned to a transition from the nonbonding $d_{xy}$ orbital to the $\pi^*$ metal $d_{xz}$ or $d_{yz}$ orbital.

The complexes displayed proton nuclear magnetic resonance spectra with chemical shifts and line widths which were unexceptional (Table XI). The Mo(IV) complex Mo-O(S₂CSC₃H₇)₂ displayed a spectrum consistent with equivalent magnetic environments for the isopropyl protons, indicating either that the environments are averaged by a stereochemically nonrigid behavior of the molecule or that in solution the molecule exhibits a structure with two identical $\eta^2$-$CS_2$ thioxanthate ligands rather than the mixed-coordination types evident in the solid-state structure. In order to evaluate the possibility that the complexes $MoO(S_2CSR)_2$ might be stereochemically nonrigid, the proton NMR spectrum of
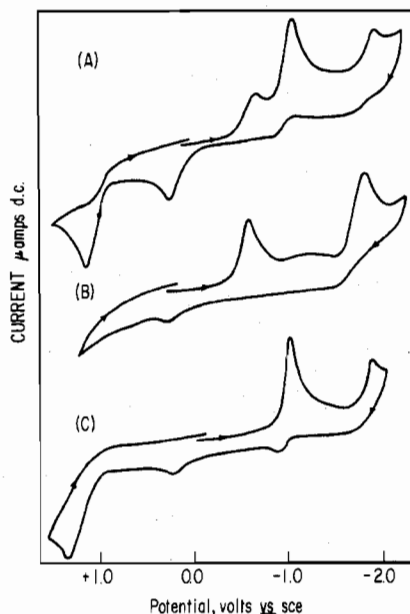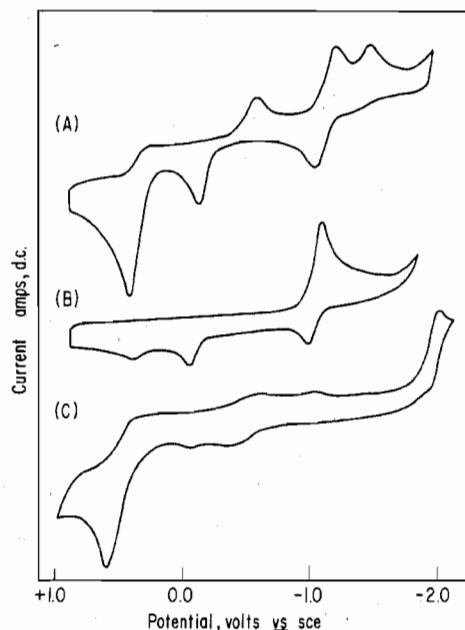
**Figure 3.** Cyclic voltammograms of (A) $10^{-3}$ M $Mo_2O_3(S_2CS$-$i$-$C_3H_7)_4$, (B) $10^{-3}$ M $Mo_2O_4(S_2CS$-$i$-$C_3H_7)_2$, and (C) $10^{-3}$ M $MoO(S_2CS$-$i$-$C_3H_7)_2$. Voltammograms were recorded at a platinum electrode in 0.1 M $[(C_4H_9)_4N]PF_6$ in $CH_2Cl_2$ at scan rates of 200 mV s$^{-1}$.



**Figure 4.** Cyclic voltammograms of (A) $10^{-3}$ M $Mo_2O_3(S_2C$-$N(C_3H_7)_2)_4$, (B) $10^{-3}$ M $MoO_2(S_2CN(C_3H_7)_2)_2$, and (C) $10^{-3}$ M $MoO(S_2CN(C_3H_3H_7)_2)_2$ in 0.1 M TBAHFP in $CH_2Cl_2$ at a scan rate of 200 mV s$^{-1}$.

$MoO(S_2CS$-$i$-$C_3H_7)_2$ was examined to −60 °C in carbon disulfide, where the complex crystallized from solution. No signal broadening or new resonance lines were observed at this limit of solubility. Three interpretations are possible: (1) only the symmetrically ligated isomer exists in solution; (2) the solution and solid-state structures are identical but the ligand environments are in rapid equilibrium at −60 °C; and (3) the proton chemical shifts of the $\eta^2$-$CS_2$ and $\eta^3$-$CS_2$ thioxanthate ligands are identical. Although none of these possibilities can be eliminated on the basis of NMR, the infrared evidence is consistent with the first interpretation.

**Electrochemical Studies.** The electrochemical data for the various oxomolybdenum complexes are summarized in Table XII. Figure 3 illustrates the cyclic voltammograms for the thioxanthate complexes $Mo_2O_3(S_2CS$-$i$-$C_3H_7)_4$ and $MoO$-$(S_2CS$-$i$-$C_3H_7)_2$ in methylene chloride solution. The voltammograms of the dithiocarbamate series are presented for comparison in Figure 4. The rate-dependent voltammograms for the reduction of $MoO(S_2CS$-$i$-$C_3H_7)_2$ are presented in Figure 5.

The cyclic voltammogram for $MoO(S_2CS$-$i$-$C_3H_7)_2$ is shown in Figure 3c. Controlled-potential electrolysis at a point just cathodic of the first reduction (−0.98 V vs. SCE) indicates a one-electron-per-molybdenum reduction. Subsequent cyclic voltammetry on the electrolyzed solution shows an appreciable peak at −1.92 V and a quasi-reversible process centered at −0.94 V. The process at −0.98 V was investigated in some detail by both coventional and cyclic voltammetric techniques. Normal-pulse voltammetry at a platinum electrode gave a value of $E_{1/2}$ of −0.94 V and values of the slopes of $E$ vs. $\log(i_l - i)/i$ that reached a limiting value of 60 ± 1 mV at sweep rates of 2 mV s$^{-1}$. Cyclic voltammetry confirmed the presence of the quasi-reversible reduction and showed that the product lifetime in methylene chloride was short. For potential sweep rates between 10 and 1000 mV s$^{-1}$, the value of $i_f/i_r$ varied from 0 to 1, respectively, as illustrated in Figure 5. The variation of $i_f/i_r$ is ascribed to rapid and irreversible decomposition of the reduced species. The rate constant for the reaction may be estimated from the variation of $i_f/i_r$ as a function of the time required to scan from $E_{1/2}$ to the switching
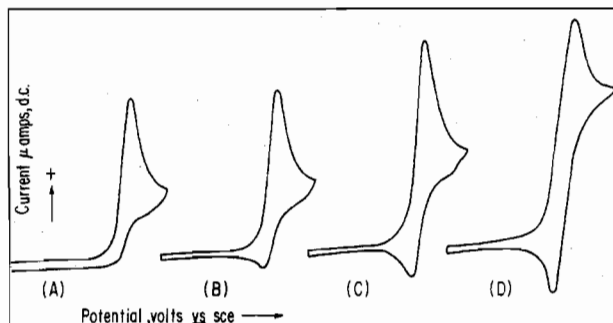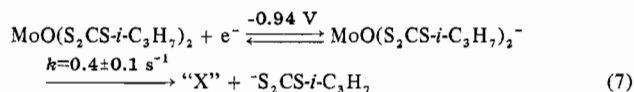


**Figure 5.** Cyclic voltammograms of $MoO(S_2CS$-$i$-$C_3H_7)_2$ in 0.1 M TBAHFP in $CH_2Cl_2$ recorded at scan rates of 10, 50, 200, and 1000 mV s$^{-1}$.

potential.[56] The value of $k$ is approximately 0.35 ± 0.1 s$^{-1}$.

These results are interpreted in terms of eq 7. Although

$$MoO(S_2CS\text{-}i\text{-}C_3H_7)_2 + e^- \underset{k=0.4\pm0.1\ s^{-1}}{\overset{-0.94\ V}{\rightleftharpoons}} MoO(S_2CS\text{-}i\text{-}C_3H_7)_2^-$$

$$\xrightarrow{} \text{``X''} + {}^-S_2CS\text{-}i\text{-}C_3H_7 \qquad (7)$$

attempts to unambiguously identify all of the decomposition products proved unsuccessful, it was readily concluded that decomposition occurred with the loss of ligand anion. Cyclic voltammograms of a solution of the salt of the ligand $[(Ph_3PhCH_2)P]S_2CS$-$i$-$C_3H_7$ displayed a one-electron reduction at −1.92 V and an anodic process at +0.34 V. Analysis

$$^-S_2CS\text{-}i\text{-}C_3H_7 + e^- \xrightarrow{-1.92\ V} (S_2CS\text{-}i\text{-}C_3H_7)^{2-} \qquad (8)$$

$$2(^-S_2CS\text{-}i\text{-}C_3H_7) \xrightarrow{+0.34\ V} (S_2CS\text{-}i\text{-}C_3H_7)_2 + 2e^- \qquad (9)$$

$$(S_2CS\text{-}i\text{-}C_3H_7)_2 + 2e^- \xrightarrow{-1.51\ V} 2(^-S_2CS\text{-}i\text{-}C_3H_7) \qquad (10)$$
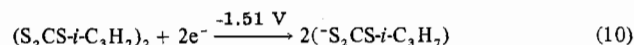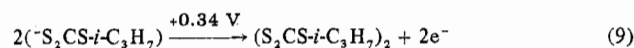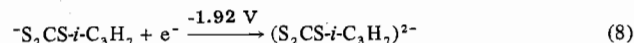
of a solution subjected to controlled-potential electrolysis at +0.40 V confirmed that the product of the oxidation is the disulfide compound $(RSCS_2)_2$. The coincidence of the potentials at which these ligand processes occur with those observed subsequent to the initial reduction in the voltammograms of the $MoO(S_2CSR)_2$ complex indicates that the
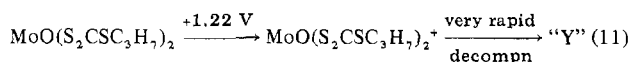
**Table XII.** Summary of Cyclic Voltammetric Data for Molybdenum Thioxanthate Complexes and Analogous Molybdenum Dithiocarbamate Complexes in $CH_2Cl_2$[a,b]

| R | $E'$, V | $E_{pc}$, V | $E_{pa}$, V | e/Mo[c] |
|---|---|---|---|---|
| (a) $Mo_2O_3(S_2CSR)_4$ | | | | |
| $C_2H_5$ | | | +1.18 | 1.10 |
| | | | +0.28 | |
| | | −0.44 | | 1.0 |
| | −0.87 | −0.90 | −0.83 | 1.0 |
| | | −1.88 | | |
| $i$-$C_3H_7$ | | | +1.16 | 1.0 |
| | | | +0.30 | |
| | | −0.45 | | 1.0 |
| | −0.93 | −0.97 | −0.89 | 1.0 |
| | | −1.92 | | |
| $t$-$C_4H_9$ | | | +1.20 | 1.0 |
| | | | +0.24 | |
| | | −0.62 | | 1.0 |
| | −0.88 | −0.92 | −0.84 | 1.0 |
| | | −1.84 | | |
| $CH_2C_6H_5$ | | | +1.12 | 1.0 |
| | | | +0.41 | |
| | | −0.59 | | 1.0 |
| | −0.91 | −0.95 | −0.86 | 1.0 |
| | | −1.82 | | |
| (b) $MoO(S_2CSR)_2$ | | | | |
| $i$-$C_3H_7$ | | | +1.24 | 1.0 |
| | | | +0.34 | |
| | −0.94 | −0.98 | −0.92 | 1.0 |
| | | −1.92 | | |
| $t$-$C_4H_9$ | | | +1.22 | 1.0 |
| | | | +0.24 | |
| | −0.90 | −0.93 | −0.87 | 1.0 |
| | | −1.85 | | |

| R | $E'$, V | $E_{pc}$, V | $E_{pa}$, V | e/Mo[c] |
|---|---|---|---|---|
| (c) $Mo_2O_4(S_2CSR)_2$ | | | | |
| $i$-$C_3H_7$ | | | +0.31 | |
| | | −0.44 | | 1.0 |
| | | −1.88 | | |
| $t$-$C_4H_9$ | | | +0.22 | |
| | | −0.63 | | 1.0 |
| | | −1.85 | | |
| (d) $Mo_2O_3(S_2CNR_2)_4$ | | | | |
| $C_2H_5$ | | | +0.55 | 2.0 |
| | | | −0.01 | |
| | | −0.50 | | 1.0 |
| | −1.11 | −1.14 | −1.07 | 1.0 |
| | | −1.39 | | 1.0 |
| $C_3H_7$ | | | +0.47 | 2.0 |
| | | | −0.10 | |
| | | −0.47 | | 1.0 |
| | −1.00 | −1.04 | −0.96 | 1.0 |
| | | −1.32 | | 1.0 |
| (e) $MoO_2(S_2CNR_2)_2$ | | | | |
| $C_2H_5$ | | | −0.02 | |
| | −1.09 | −1.12 | −1.06 | 1.0 |
| $C_3H_7$ | | | −0.09 | |
| | −1.02 | −1.04 | −0.98 | 1.0 |
| (f) $MoO(S_2CNR_2)_2$ | | | | |
| $C_2H_5$ | | | +0.58 | 2.0 |
| | | | | 1.0 |
| | | −1.94 | | |
| $C_3H_7$ | | | +0.49 | 2.0 |
| | | −1.96 | | 1.0 |
| (g) $Mo_2O_4(S_2CNR_2)_2$ | | | | |
| $C_3H_7$ | | −1.32 | | 1.0 |

[a] Using 0.1 M tetra-*n*-butylammonium hexafluorophosphate as supporting electrolyte. All potentials are referred to the saturated calomel electrode (SCE), KCl. [b] Cyclic voltammograms were obtained at sweep rate of 200 mV s⁻¹. The general electrochemical behavior was checked at vitreous carbon and hanging mercury drop electrodes. Concentrations have been calculated on the basis of the formulas given in the first column. [c] The value of $n$ (e/Mo) was determined by controlled-potential electrolysis at a potential 0.2 V from the process of interest. Normal-pulse voltammetry and ac voltammetry were also used as qualitative measures of the value of $n$. The voltammograms were run at a sweep rate of 5 mV s⁻¹ at a platinum electrode. Ac voltammograms were obtained at polarization rates of 10 mV s⁻¹ at 80 Hz with a phase angle of 90° with respect to the input alternating potential and with an ac perturbation of 5 mV peak–peak.

electroactive decomposition product is the ligand anion. Cathodic sweeps of solutions of the complex in $CH_2Cl_2$ subsequent to electrolysis at +0.40 V also display a peak at −1.51 V which coincides with the potential for the electrode process given in eq 10 for the solution of the disulfide complex RSC(S)S–SC(S)SR.

The anodic process observed in solutions of the Mo(IV) monomers at +1.20 to +1.25 V is completely irreversible by the usual voltammetric criteria. Controlled-potential electrolysis at +1.30 V of solutions containing the monomer species resulted in extensive decomposition and the discharge of the characteristic red color of the solution. Although no products of the oxidation were identified, the electrochemical behavior is consistent with eq 11, where "Y" is an unidentified de-

$$MoO(S_2CSC_3H_7)_2 \xrightarrow{+1.22\text{ V}} MoO(S_2CSC_3H_7)_2{}^+ \xrightarrow[\text{decompn}]{\text{very rapid}} \text{"Y" (11)}$$

composition mixture.

In a series of experiments at a mercury working electrode (HMDE) in acetonitrile solution, it was established that the reduction of $MoO(S_2CSR)_2$ at −0.94 V approached reversible behavior. The ratio of $i_f/i_r$ was equal to 1.0 and independent of the sweep rate from 5 to 200 mV s⁻¹. The value of $\Delta E_p$ was equal to 60 mV for sweep rates less than 20 mV s⁻¹. Using the analytical expressions derived by Nicholson and Shain,[56] the rate constant for the decomposition of $MoO(S_2CSC_3H_7)_2{}^-$
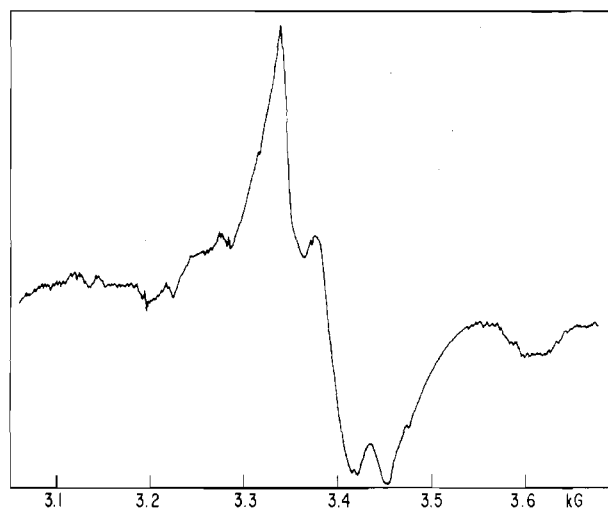


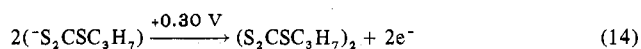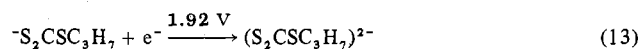**Figure 6.** ESR spectrum of a frozen solution of $MoO(S_2CS$-$i$-$C_3H_7)_2{}^-$ in acetonitrile at 9.018 GHz and ~77 K.

in these solutions was estimated as $k < 10^{-2}$ s⁻¹.

Controlled-potential electrolysis was performed on this solution. A mercury pool at −1.00 V served as the working electrode. After a decrease in the original current of 50%, an aliquot was removed and immediately transferred to an EPR

tube for frozen-solution ESR spectra. The orange sample gave an intense EPR signal shown in Figure 6. The three-line spectrum ($g_1$ = 1.99, $g_2$ = 1.91, $g_3$ = 1.84) is consistent with the low-symmetry square-pyramidal environment. Attempts to isolate the EPR-active species as the $(Ph_3PhCH_2)P^+$ salt were unsuccessful.

The dioxo-bridged Mo(V) dimer $Mo_2O_4(S_2CSC_3H_7)_2$ is also electrochemically active as illustrated by Figure 3B. The major cathodic process in methylene chloride is an irreversible two-electron transfer occurring at −0.45 V. The subsequent appearance of a cathodic peak at −1.92 V, coincident with the potential for the reduction of the free ligand, and of an anodic process at +0.30 V, previously identified as the ligand oxidative couple, confirm that reduction occurs with complex dissociation. The observations are consistent with the reaction scheme in eq 12–14. The reduction potential of the dimeric species
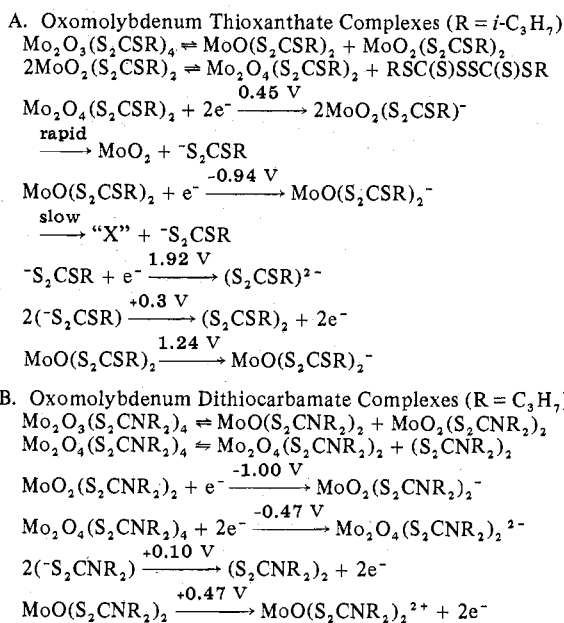
$$Mo_2O_4(S_2CSC_3H_7)_2 + 2e^- \xrightarrow{-0.45\ V} 2MoO_2(S_2CSC_3H_7)^-$$
$$\xrightarrow[\text{rapid decompn}]{} MoO_2\ (\text{insol}) + {}^-S_2CSC_3H_7 \qquad (12)$$

$$^-S_2CSC_3H_7 + e^- \xrightarrow{1.92\ V} (S_2CSC_3H_7)^{2-} \qquad (13)$$

$$2(^-S_2CSC_3H_7) \xrightarrow{+0.30\ V} (S_2CSC_3H_7)_2 + 2e^- \qquad (14)$$
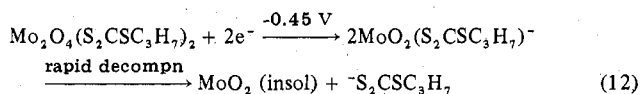
$Mo_2O_4(S_2CSC_3H_7)_2$ is considerably less negative than that of the monomer. The relative ease of reduction is consistent with the formal metal oxidation states (Mo(V) vs. Mo(IV)) and the dimeric, dioxo-bridged arrangement of the Mo(V) species. Similar behavior was observed for the dithiocarbamate species in $Me_2SO$ solution.[8]

Methylene chloride solutions of $Mo_2O_3(S_2CSC_3H_7)_4$ retain the characteristic purple color throughout the cyclic voltammetric investigation. Comparison of the cyclic voltammograms of these solutions, as illustrated by Figure 3C, with those for $MoO(S_2CSC_3H_7)_2$ and $Mo_2O_4(S_2CSC_3H_7)_2$ confirms that the $\mu$-oxo-dimolybdenum(V) complex disproportionates according to the scheme presented previously in eq 3 and 4. The overall electrochemical behavior of the oxomolybdenum thioxanthates is summarized and compared to the redox reactions of the oxomolybdenum dithiocarbamates in Table XIII. Since the electrochemistry of the dithiocarbamate complexes in acetonitrile, dimethyl sulfoxide, and dimethylformamide solutions have been discussed in detail[8] and the behavior in methylene chloride solution is consistent with the interpretations of previous authors, no detailed discussion of the results will be presented.

Although there are a number of similarities in the overall solution and redox characteristics of the two series of complexes, the most striking feature of the solution studies is the contrast in the abilities of the ligands to stabilize various oxidation states. Whereas the electron-rich dithiocarbamate ligand stabilizes the +6 oxidation state, as evidenced by the difficulty of reducing the monomeric $MoO_2(S_2CNR_2)_2$ complex ($E'$ = −1.00 V) and the ease of oxidation of the Mo(IV) species $MoO(S_2CNR_2)_2$ ($E_p$ = +0.47 V), the thioxanthate group serves as a reducing ligand. This accounts in part for the unusual stability of the Mo(IV) complex $MoO(S_2CSR)_2$ which exhibits an oxidation potential of +1.24 V. This contrast in complex behavior as a result of ligand character is likewise demonstrated by the potential of the Mo(IV)/Mo(III) redox couple: −0.94 V for $MoO(S_2CS-i-C_3H_7)_2$ vs. −1.93 V for $MoO(S_2CN(C_3H_7)_2)_2$. The trend is consistent with that observed in a number of electrochemical investigations of the complexes of the dithio acid ligands.[28,57]

**Conclusions.** The detailed investigation of the oxomolybdenum thioxanthate complexes establishes a number of homologies with the extensively studied dithiocarbamate analogues. The dissociation in solution of the Mo(V) oxo-bridged dimer to give monomeric Mo(IV) and Mo(VI) species

**Table XIII.** Summary of the Electrochemical Reactions for Molybdenum Thioxanthate and Dithiocarbamate Complexes in Methylene Chloride

A. Oxomolybdenum Thioxanthate Complexes ($R = i-C_3H_7$)

$$Mo_2O_3(S_2CSR)_4 \rightleftharpoons MoO(S_2CSR)_2 + MoO_2(S_2CSR)_2$$
$$2MoO_2(S_2CSR)_2 \rightleftharpoons Mo_2O_4(S_2CSR)_2 + RSC(S)SSC(S)SR$$
$$Mo_2O_4(S_2CSR)_2 + 2e^- \xrightarrow{0.45\ V} 2MoO_2(S_2CSR)^-$$
$$\xrightarrow[\text{rapid}]{} MoO_2 + {}^-S_2CSR$$
$$MoO(S_2CSR)_2 + e^- \xrightarrow{-0.94\ V} MoO(S_2CSR)_2^-$$
$$\xrightarrow[\text{slow}]{} \text{``X''} + {}^-S_2CSR$$
$$^-S_2CSR + e^- \xrightarrow{1.92\ V} (S_2CSR)^{2-}$$
$$2({}^-S_2CSR) \xrightarrow{+0.3\ V} (S_2CSR)_2 + 2e^-$$
$$MoO(S_2CSR)_2 \xrightarrow{1.24\ V} MoO(S_2CSR)_2^-$$

B. Oxomolybdenum Dithiocarbamate Complexes ($R = C_3H_7$)

$$Mo_2O_3(S_2CNR_2)_4 \rightleftharpoons MoO(S_2CNR_2)_2 + MoO_2(S_2CNR_2)_2$$
$$Mo_2O_4(S_2CNR_2)_4 \rightleftharpoons Mo_2O_4(S_2CNR_2)_2 + (S_2CNR_2)_2$$
$$MoO_2(S_2CNR_2)_2 + e^- \xrightarrow{-1.00\ V} MoO_2(S_2CNR_2)_2^-$$
$$Mo_2O_4(S_2CNR_2)_4 + 2e^- \xrightarrow{-0.47\ V} Mo_2O_4(S_2CNR_2)_2{}^{2-}$$
$$2({}^-S_2CNR_2) \xrightarrow{+0.10\ V} (S_2CNR_2)_2 + 2e^-$$
$$MoO(S_2CNR_2)_2 \xrightarrow{+0.47\ V} MoO(S_2CNR_2)_2{}^{2+} + 2e^-$$

is common to both series of complexes. The possible relevance of this equilibrium to the redox-active molybdenum-containing enzymes has been discussed.[5]

The facility of preparation and the stability of the Mo(IV) complex $MoO(S_2CSC_3H_7)_2$ illustrate the dramatic changes in complex characteristics that may be brought about by small modifications in the ligand structure. Although the $MoO(S_2CSC_3H_7)_2$ complex undergoes a number of reactions analogous to those of the dithiocarbamate species $MoO(S_2CNR_2)_2$, the complex is thermodynamically stable and also stable to air oxidation to the Mo(VI) state.

The solution and solid-state structures of the monomer $MoO(S_2CSR)_2$ are different as evidenced by the infrared spectra. The crystal structure confirms the presence of two distinct ligation modes for the thioxanthate ligand: as a classical terminal bidentate group ($\eta^2$-$CS_2$) and in an unusual $\pi$ overlap with the metal to give $\eta^3$-$CS_2$ ligation. The infrared and NMR evidence is consistent with a solution structure in which both thioxanthate ligands assume the usual $\eta^2$-$CS_2$ coordination mode.

The structural results demonstrate the versatility of the oxomolybdate(IV) fragment in binding common dithio acid ligands; the solution chemistry of the complex $MoO(S_2CS-i-C_3H_7)_2$ is consistent with coordinative unsaturation and a relatively low formal oxidation state of the metal. Since it has been suggested that the reactivity pattern of the substrate-reducing site of nitrogenase is consistent with the known chemistry of Mo(IV),[59] our structural and electrochemical investigations are being extended to the oxomolybdenum xanthate complexes and will be the subject of a future communication. The detailed reaction chemistry of the Mo(IV) complexes $MoO(S_2CX)_2$, X = SR and OR, is presently under investigation.

43-3; Mo$_2$O$_3$(S$_2$CSCH$_2$C$_6$H$_5$)$_4$, 64957-42-2; MoO(S$_2$CS-$t$-C$_4$H$_9$)$_2$, 64957-41-1; Mo$_2$O$_4$(S$_2$CS-$t$-C$_4$H$_9$)$_2$, 64957-40-0; Mo$_2$O$_3$(S$_2$C-N(C$_2$H$_5$)$_2$)$_4$, 20023-86-3; Mo$_2$O$_3$(S$_2$CN(C$_3$H$_7$)$_2$)$_4$, 53426-41-8; MoO$_2$(S$_2$CN(C$_2$H$_5$)$_2$)$_2$, 18078-69-8; MoO$_2$(S$_2$CN(C$_3$H$_7$)$_2$)$_2$, 17476-41-4; MoO(S$_2$CN(C$_2$H$_5$)$_2$)$_2$, 25395-92-0; MoO(S$_2$CN(C$_3$-H$_7$)$_2$)$_2$, 54515-55-8; Mo$_2$O$_4$(S$_2$CN(C$_3$H$_7$)$_2$)$_2$, 64957-39-7.

**Supplementary Material Available:** Listing of observed and calculated structure factors for MoO(S$_2$C-$i$-C$_3$H$_7$)$_2$ (13 pages). Ordering information is given on any current masthead page.

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