amino-2-methylpropane (11.9) > 2,2′-dipyridyl (2.4) > *o*-phen (1.0) > 4,7-diphenyl-*o*-phen (0.5). This is also the expected order of increasing electrostatic and steric hindrance to a nucleophilic attack.

The basicity of the attacking ligand also plays an important role in the magnitude of k_2 as can be assessed from the data in Table VI. The exact effect of the ligand basicity on k_2 however is difficult to ascertain becase all too often steric hindrance caused by the geometry of the ligand greatly complicates the interpretation. In general, k_2 decreases with L in the order: $P(n\text{-}C_4H_9)_3 > PO_3C_6H_9 > P(OCH_2)_3CCH_3 > P(OC_2H_5)_3 > P(C_6H_5)_3 > P(OC_6H_5)_3$. This is the same trend in second-order rate constants as was found by Basolo, *et al.*,[13,14] in the reaction of some Rh and Co carbonyl complexes with a number of different nucleophilic reagents.

The size of the central metal atom is of considerable importance in determining the value of k_2. For the group VI metals, the smallest atom, Cr, shows no k_2 term in its rate law for complexes of the type $Cr(CO)_4(N\text{-}N)$. Although $Cr(CO)_6$ does follow a two-term rate law, dependence on [L] is very small. The relative importance of k_2 over k_1 for the group VI hexacarbonyls increases in going from Cr to Mo to W.[10] This is readily apparent if the ratios of k_2/k_1 for their reaction with $P(n\text{-}C_4H_9)_3$ at 112° are compared. Values of k_2/k_1 for the $Cr(CO)_6$, $Mo(CO)_6$, and $W(CO)_6$ reactions are 0.7, 9.6, and 34.8, respectively. A similar trend in k_2/k_1 is obtained for the Cr-, Mo-, and $W(CO)_4$(*o*-phen) reactions with $P(OCH_2)_3CCH_3$ at 47.9°. For these reactions values of k_2/k_1 are: Cr, 0.0; Mo, 1.0; and W, 9.5.

Acknowledgment.—Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for support of this research. We are also grateful to Professor H. Diehl for gifts of the substituted *o*-phenanthrolines.

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[14] E. M. Thorsteinson and F. Basolo, *ibid.*, **88**, 3929 (1966).

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Dialkyldithiocarbamate Complexes of Molybdenum(V) and Molybdenum(VI)

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Improved methods were developed for preparing dialkyldithiocarbamate complexes of Mo(VI) of the type $MoO_2[R_2NCS_2]_2$ (where R = methyl, ethyl, *n*-propyl, *n*-butyl) and of Mo(V) of the type $[(R_2NCS_2)_2Mo{=}O]_2O$ (where R = methyl, ethyl). A new compound whose analysis approximated $(C_4H_9)_2NCS_2MoOS$ was isolated by hydrogen sulfide treatment of a benzene solution of $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ or an aqueous solution of sodium molybdate and sodium di-*n*-butyldithiocarbamate. The Mo(V) complexes of dimethyl- and diethyldithiocarbamate and ethylxanthate were isolated in good yield by treating an aqueous solution of an alkali metal salt of the ligand with ammonium oxopentachloromolybdate(V). Infrared bands assignable to Mo–S absorption were found in the 460–515-cm^{-1} region, and the dimeric Mo(V) complexes showed a band at about 435 cm^{-1} due to a Mo–O–Mo stretching mode. It was concluded that the Mo(VI) complexes contain a *cis* O=Mo=O group since their infrared spectra contain two Mo=O bands at about 900 cm^{-1}. The Mo(V) dithiocarbamates contain a ligand field band at about 19,500 cm^{-1}.

Introduction

The dithiocarbamate group, $R_2NCS_2^-$ (R = H or alkyl), is a common univalent, bidentate ligand, and the preparation of some dialkyldithiocarbamate complexes of Mo(V) and Mo(VI) was briefly described by Malatesta.[1] The molybdenum(VI) dioxobis(dialkyldithiocarbamato) complexes, $MoO_2(R_2NCS_2)_2$ (where R = methyl, ethyl, and *n*-butyl), were prepared by dilute HCl acidification of solutions containing molybdate ions and the appropriate sodium dialkyldithiocarbamate. The diamagnetic Mo(V) complex, which we formulate as μ-oxo-dioxotetrakis(diethyldithiocarbamato)molybdenum(V), $\{[(C_2H_5)_2NCS_2]_2Mo{=}O\}_2O$, was prepared by the sulfur dioxide or sodium dithionite reduction of a solution containing molybdate and diethyldithiocarbamate ions. The related diamagnetic Mo(V) alkylxanthate complexes, $[(ROCS_2)_2Mo{=}O]_2O$ (R = alkyl), have also been prepared,[2,3] and recent determination of the molecular structure of the ethyl derivative[4] confirmed the dinuclear formulation with a bridging Mo–O–Mo group. The only other dithiocarbamate complex of molybdenum that appears to have been isolated is π-cyclopentadienyldicarbonyl(dimethyldithiocarbamato)molybdenum(II), $\pi\text{-}C_5H_5Mo(CO)_2S_2CN(CH_3)_2$, prepared by the reaction of tetramethylthiuram disulfide and π-cyclopentadienylmolybdenum tricarbonyl dimer.[5]

[1] L. Malatesta, *Gazz. Chim. Ital.*, **69**, 752 (1939).

[2] R. Montequi and M. Gallego, *Anales Real Soc. Espan. Fis. Quim.* (Madrid), **31**, 434 (1933).

[3] L. Malatesta, *Gazz. Chim. Ital.*, **69**, 408 (1939).

[4] A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964).

[5] F. A. Cotton and J. A. McCleverty, *Inorg. Chem.*, **3**, 1398 (1964).

This paper describes improved methods for the preparation of dialkyldithiocarbamate complexes of Mo(V) and Mo(VI) and for the isolation of some new complexes. The infrared and visible spectra of these compounds were examined to elucidate further the structure of the molybdenyl groups and to determine the nature of the molybdenum to sulfur bonding.

Experimental Section

The sodium dithionite was 90% practical grade and the *t*-butyl hydroperoxide was a 70% solution (12.4% active oxygen) from the Lucidol Division of Wallace and Tiernan, Inc. Ammonium oxopentachloromolybdate(V), $(NH_4)_2MoOCl_5$, was prepared from $MoCl_5$ and isolated by drying over NaOH *in vacuo*.[6] Sodium di-*n*-propyldithiocarbamate and sodium di-*n*-butyldithiocarbamate were prepared from the amines[7] and isolated as hygroscopic solids for determination of their infrared spectra. The remaining materials were reagent grade chemicals used without further purification.

All melting points were obtained in sealed capillaries and were corrected. The elemental analyses of all organic molybdenum complexes and the molecular weight determinations were performed by Huffman Laboratories, Inc., Wheatridge, Colo. The molybdenum contents of ammonium tetrathiomolybdate, ammonium dithiomolybdate, and Mo(V) xanthates were determined by ignition to MoO_3 at 525°. The infrared spectra (4000–400 cm^{-1}) were determined using a Perkin-Elmer Corp. Model 21 instrument, and the visible–ultraviolet spectra were obtained using Beckman Instruments, Inc., Model DU and Model DB spectrophotometers.

$(NH_4)_2MoS_4$.—As described by Kruss,[8] treatment of a solution of ammonium paramolybdate in 11.5 *N* NH_4OH with H_2S resulted in the formation of the product in 90% yield. *Anal.* Calcd for $(NH_4)_2MoS_4$: Mo, 36.9. Found: Mo, 37.2.

$(NH_4)_2MoO_2S_2$.—A procedure given by Kruss[8] was also used to treat a solution of ammonium paramolybdate (10.0 g) in 60 ml of 3.3 *N* NH_4OH with H_2S at 4–5°. The product was isolated in 54% yield. *Anal.* Calcd for $(NH_4)_2MoO_2S_2$: Mo, 42.1. Found: Mo, 41.7.

Molybdenum(VI) Dithiocarbamates.—The dimethyl and diethyl derivatives were prepared by the method of Malatesta,[1] and the di-*n*-propyl and di-*n*-butyl complexes were prepared by improved methods.

$MoO_2[(CH_3)_2NCS_2]_2$.—A solution of $Na_2MoO_4·2H_2O$ (24.2 g, 0.10 mole) and $(CH_3)_2NCS_2Na·2H_2O$ (35.8 g, 0.20 mole) in 300 ml of water on slow acidification with 1.2 *N* hydrochloric acid formed a copious precipitate that was filtered off, washed, and vacuum dried to yield 36.4 g (99% yield) of yellow powder. *Anal.* Calcd for $MoO_2[(CH_3)_2NCS_2]_2$: C, 19.56; H, 3.28; N, 7.60; S, 34.82; Mo, 26.04. Found: C, 18.78; H, 3.28; N, 6.56; S, 36.67; Mo, 26.24. This material decomposed without melting over a broad range above 300°. It has very limited solubility in $CHCl_3$ (0.78 g/l. at 60°), CH_2Cl_2, C_6H_6, and acetone; it is insoluble in CCl_4, methanol, and aliphatic hydrocarbons.

$MoO_2[(C_2H_5)_2NCS_2]_2$.—The slow addition of 315 ml of 0.6 *N* hydrochloric acid to a solution of $Na_2MoO_4·2H_2O$ (14.5 g, 0.060 mole) and $(C_2H_5)_2NCS_2Na·3H_2O$ (16.0 g, 0.071 mole) in 300 ml of water resulted in the formation of the crude product (14.6 g, 97% yield) as an orange-brown precipitate. Double recrystallization from benzene–petroleum ether (bp 30–60°) yielded yellow crystals, mp 133.0–133.5°, that were slightly soluble in $CHCl_3$, CH_2Cl_2, acetone, and warm benzene (2.9% at 60°) and insoluble in CCl_4 and aliphatic hydrocarbons. *Anal.* Calcd for $MoO_2[(C_2H_5)_2NCS_2]_2$: C, 28.30; H, 4.75; N, 6.60; S, 30.22; Mo, 22.63. Found: C, 28.90; H, 4.86; N, 5.37; S, 31.02; Mo, 22.85.

$MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$.—A solution of $(n\text{-}C_3H_7)_2NCS_2Na$ was prepared by adding carbon disulfide (4 ml, 0.07 mole) to a stirred suspension of di-*n*-propylamine (6.07 g, 0.060 mole) and NaOH (2.40 g, 0.060 mole) in 250 ml of water and stirring for 1.5 hr. Sodium molybdate dihydrate (10.0 g, 0.041 mole) was dissolved in the filtered solution, and, on slow acidification with 210 ml of 0.43 *N* nitric acid at 5°, a brown tar separated. The product, 9.8 g (69% yield), was isolated as orange crystals, mp 108–109°, by precipitation from benzene solution with petroleum ether. The complex was further purified by crystallization from toluene–ligroin (bp 66–75°) to give crystals, mp 110.0–110.5° dec. *Anal.* Calcd for $MoO_2[(C_3H_7)_2NCS_2]_2$: C, 34.99; H, 5.87; N, 5.83; S, 26.69; Mo, 19.99; mol wt, 481. Found: C, 35.16; H, 5.89; N, 5.88; S, 28.62; Mo, 20.34; mol wt in C_6H_6, 491 (cryoscopic), 467 (ebullioscopic). This material was soluble in most common organic solvents, but insoluble in aliphatic hydrocarbons.

$MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$.—The cursorily described procedure of Malatesta[1] resulted in the formation of purple tar, believed to be the crude Mo(V) complex. A solution of sodium di-*n*-butyldithiocarbamate was prepared by adding carbon disulfide (27 ml, 0.45 mole) to a suspension of NaOH (17.0 g, 0.43 mole) and di-*n*-butylamine (51.7 g, 0.40 mole) in 1700 ml of water and stirring for 1.5 hr. A solution of $Na_2MoO_4·2H_2O$ (70.0 g, 0.29 mole) in 1 l. of water was added to the filtered dithiocarbamate solution, and, on slow acidification at 3–5° with 860 ml of 1.0 *N* nitric acid, a purple tar separated. This tar was washed by decantation and dissolved in 400 ml of toluene. The purple toluene solution was oxidized to dark orange by adding 6 ml of 70% *t*-butyl hydroperoxide (0.065 g-atom of oxygen) and stirring for 15 min. The product was isolated as yellow-orange crystals, 77.0 g (72% yield), mp 69.0–70.5° dec, by addition of 1200 ml of petroleum ether to the dried (Drierite) solution and cooling to 5°. Recrystallization from toluene–petroleum ether yielded crystals, mp 70.0–71.5° dec. *Anal.* Calcd for $MoO_2[(C_4H_9)_2NCS_2]_2$: C, 40.27; H, 6.76; N, 5.22; S, 23.90; Mo, 17.88. Found: C, 40.36; H, 6.90; N, 5.18; S, 23.66; Mo, 17.81. This compound is readily soluble in aromatic and chlorinated solvents and insoluble in petroleum ether.

An attempt was made to prepare molybdenum(VI) dialkyldithiocarbamates, with isopropyl, amyl, and 2-ethylhexyl as the alkyl groups, by using the method for preparing the di-*n*-butyl derivative. This method resulted in the formation of orange-brown tars that could not be purified and that did not have the correct stoichiometry on analysis.

Reaction of $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ with H_2S.—In an attempt to replace the molybdenyl oxygens of the Mo(VI) complexes with sulfur by treatment with H_2S, the diethyl and di-*n*-propyl derivatives yielded only indefinite brown tars, but the di-*n*-butyl derivative yielded a crystalline solid. Hydrogen sulfide was bubbled for 1 hr into a stirred solution of $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ (10.00 g) in 100 ml of benzene, and a solid settled after the solution had stood at 5° for 2 hr. Fine, bright orange crystals, 3.30 g (57.7% yield), were isolated by filtration, washing with benzene, and vacuum drying. Crystallization from benzene–petroleum ether yielded crystals, mp 248–250° dec. *Anal.* Calcd for $[(C_4H_9)_2NCS_2]MoOS$: C, 31.08; H, 5.21; N, 4.01; S, 27.61; Mo, 27.54; O, 4.59; mol wt, 348.4. Found: C, 31.19; H, 5.32; N, 3.80; S, 29.60; Mo, 27.53; O, 4.27 (Kapron and Brandt); mol wt, ebullioscopic in C_6H_6, 783 (7.05 mg/ml) and 797 (12.35 mg/ml). Determination of the electron spin resonance spectrum of a benzene solution indicated that the material is diamagnetic.[9] This compound was also isolated as orange crystals, mp 238–240° dec, in 7.1% yield by introducing H_2S into an aqueous solution of $(C_4H_9)_2NCS_2Na$ (0.036 mole) and $Na_2MoO_4·2H_2O$ (0.037 mole). This complex is soluble in warm aromatic hydrocarbons, slightly soluble in CH_2Cl_2 and $CHCl_3$, and insoluble in CCl_4, ethanol, and aliphatic hydrocarbons.

Molybdenum(V) Dialkyldithiocarbamates. $\{[(CH_3)_2NCS_2]_2$-

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

[7] H. L. Klopping and G. J. van der Kerk, *Rec. Trav. Chim.*, **70**, 936 (1951).

[8] G. Kruss, *Ann. Chem.*, **225**, 29 (1884).

[9] We are indebted to Professor J. T. Spence of Utah State University for determining the esr spectrum.

$\text{Mo}{=}\text{O}\}_2\text{O}$.—The pure complex could not be isolated using the SO_2 or sodium dithionite reduction methods.[1] The compound was prepared by adding a freshly prepared solution of $(NH_4)_2MoOCl_5$ (15.0 g, 0.046 mole) in 100 ml of water to a stirred solution of $(CH_3)_2NCS_2Na\cdot 2H_2O$ (16.5 g, 0.092 mole) in 100 ml of water. A violet precipitate formed immediately. After the solution was stirred for 1 hr, the product was filtered, washed with water, and vacum dried to yield 13.3 g (79% yield) of purple solid. *Anal.* Calcd for $Mo_2O_3[(CH_3)_2NCS_2]_4$: C, 20.00; H, 3.35; N, 7.77; S, 35.59; Mo, 26.62. Found: C, 18.88; H, 3.30; N, 6.77; S, 33.50; Mo, 28.72.

The preparation was repeated by adding a solution of $(CH_3)_2NCS_2Na\cdot 2H_2O$ (9.50 g, 0.053 mole) in 50 ml of water to a fresh solution of $(NH_4)_2MoCl_5$ (8.00 g, 0.025 mole) in 100 ml of water; on filtration 7.61 g (86.2% yield) of purple solid was obtained. *Anal.* Calcd for $Mo_2O_3[(CH_3)_2NCS_2]_4$: Mo, 26.62. Found: Mo, 28.12. This material is not as pure as desired and appears to contain an inorganic molybdenum impurity; however, since it could not be purified, it was considered pure enough for determination of its infrared and visible spectra. The compound decomposed without melting above 200° and was insoluble in most common organic solvents.

$\{[(C_2H_5)_2NCS_2]_2\text{Mo}{=}\text{O}\}_2\text{O}$.—The SO_2 reduction method[1] was nonreproducible and yielded amorphous, purple solids that were impure.

Addition of a fresh solution of sodium dithionite (4.0 g, 0.023 mole) in 50 ml of water to a stirred solution of $(C_2H_5)_2NCS_2Na\cdot 3H_2O$ (20.0 g, 0.089 mole) and $Na_2MoO_4\cdot 2H_2O$ (9.70 g, 0.040 mole) in 200 ml of water resulted in the formation of a violet precipitate. On filtration, washing, and vacuum drying, the purple complex was isolated in 16% yield (2.71 g). It decomposed without melting at 188–190°. *Anal.* Calcd for $Mo_2O_3[(C_2H_5)_2NCS_2]_4$: C, 28.84; H, 4.84; N, 6.73; S, 30.79; Mo, 23.03. Found: C, 29.50; H, 4.82; N, 5.11; S, 30.98; Mo, 22.35. This material was initially soluble in C_6H_6 and $CHCl_3$, but after standing 1 week it was insoluble in C_6H_6 and only partially soluble in $CHCl_3$. These observations confirm those of Malatesta,[1] who reported that the initially soluble complex becomes insoluble on standing because of an intermolecular polymerization.

The complex was also prepared by adding a freshly prepared solution of $(NH_4)_2MoOCl_5$ (1.00 g, 0.0031 mole) in 25 ml of water to a solution of $(C_2H_5)_2NCS_2Na\cdot 3H_2O$ (1.35 g, 0.0062 mole) in 25 ml of water, which caused formation of a purple precipitate. On filtration and vacuum drying, 1.04 g (81% yield) of purple solid was isolated. *Anal.* Calcd for $Mo_2O_3[(C_2H_5)_2NCS_2]_4$: C, 28.84; H, 4.84; N, 6.73; S, 30.79; Mo, 23.03. Found: C, 28.86; H, 4.98; N, 6.59; S, 30.73; Mo, 23.29. This product decomposed without melting above 160°. It was initially soluble in $CHCl_3$ and only slightly soluble in C_6H_6. The differences between the solubility and thermal properties of this product and the dithionite-derived material are probably due to differences in crystallinity and degree of polymerization. Treatment of a $CHCl_3$ solution of the complex with 10% H_2O_2 resulted in isolation of the yellow Mo(VI) complex, $MoO_2[(C_2H_5)_2NCS_2]_2$, which was identified by its infrared spectrum and mixture melting point with the pure complex.

Attempts to prepare Mo(V) complexes with di-*n*-propyl- and di-*n*-butyldithiocarbamates resulted in the formation of impure purple tars.

Molybdenum(V) Alkylxanthates. $[(CH_3OCS_2)_2\text{Mo}{=}\text{O}]_2\text{O}$.—A solution of KS_2COCH_3 was prepared by adding CS_2 (16.0 ml, 0.26 mole) to a solution of KOH (13.1 g, 0.20 mole of 85.6% KOH) in methanol (50 ml, 1.23 mole). A slow stream of SO_2 was introduced for 1.5 hr at 0–5° into the combined solution of the KS_2COCH_3 and $Na_2MoO_4\cdot 2H_2O$ (24.2 g, 0.100 mole) in 300 ml of water. After standing overnight at 0–5°, the crude product (16.3 g, 48.2% yield) was isolated by filtration and vacuum drying. Dark green crystals were obtained on crystallization from benzene–petroleum ether. *Anal.* Calcd for $Mo_2O_3(S_2COCH_3)_4$: Mo, 28.70. Found: Mo, 28.07. This solid decomposed without melting at 112–117° (lit.[3] 100–120° dec).

$[(C_2H_5OCS_2)_2\text{Mo}{=}\text{O}]_2\text{O}$.—Sulfur dioxide was passed for 1.5 hr at 5° into a solution of $C_2H_5OCS_2K$ (9.60 g, 0.060 mole) and $Na_2MoO_4\cdot 2H_2O$ (6.10 g, 0.025 mole) in 30 g of water and 30 g of ice. After the solution stood overnight at 0–5°, dark green needlelike crystals, 7.65 g (85% yield), were obtained on filtration and vacuum drying. Double recrystallization from benzene–petroleum ether yielded crystals, mp 108–109° dec (lit.[3] 118.5°). After 4 months of storage, the complex decomposed to an orange, amorphous, organic-insoluble powder.

This complex was also prepared by adding a fresh solution of $(NH_4)_2MoOCl_5$ (8.98 g, 0.0276 mole) in 50 ml of water to a solution of $C_2H_5OCS_2K$ (10.00 g, 0.062 mole) in 50 ml of water at 0–5°. The product formed immediately, and, after the solution was stirred for 30 min, 9.18 g (92% yield) of dark green solid was isolated by filtration, washing with water, and vacuum drying. Dark green crystals, mp 114–115° dec (lit.[3] 118.5°), were formed on crystallization from benzene–petroleum ether. *Anal.* Calcd for $Mo_2O_3(C_2H_5OCS_2)_4$: Mo, 26.48. Found: Mo, 26.00. This product also decomposed on storage. Attempts were unsuccessful to oxidize the Mo(V) xanthates to Mo(VI) complexes with 10% H_2O_2 or *t*-butyl hydroperoxide.

Discussion

The preparation of the Mo(VI) complexes, $MoO_2(R_2NCS_2)_2$, by the acidification technique is similar to the method of Jones[10] for the preparation of molybdenyl bisacetylacetonate, $MoO_2(C_5H_7O_2)_2$. Since extensive studies[11,12] of the species formed on acidification of molybdate ion indicate that the concentration of cationic species is very low at pH greater than 1, the formation of MoO_2^{2+} complexes must result from shifting of the equilibrium by removal of the MoO_2^{2+} cation as an insoluble complex. Dilute hydrochloric acid acidification gave good results with the dimethyl and diethyl derivatives, but poor results were obtained with dithiocarbamates containing higher alkyl groups. The di-*n*-propyl derivative was prepared by using dilute nitric acid, and the di-*n*-butyl derivative was prepared by oxidizing the intermediate product with *t*-butyl hydroperoxide. The tendency to form a purple tar, believed to be the crude Mo(V) complex, increased with the size of the alkyl group, and pure Mo(VI) complexes with alkyl groups larger than *n*-butyl could not be isolated. This instability is probably related to the decreased electron-releasing ability of the higher alkyl groups that is necessary for formation of the stable $[\overset{-}{S_2}C{=}\overset{+}{N}R_2]^-$ group.[13] The higher dialkyldithiocarbamates, like the monoalkyldithiocarbamates[1] and alkylxanthates,[2,3] are probably incapable of forming stable Mo(VI) complexes because of oxidation of the ligand by Mo(VI).

The preparation of Mo(V) dialkyldithiocarbamates, $[(R_2NCS_2)_2\text{Mo}{=}\text{O}]_2\text{O}$, using sulfur dioxide was nonreproducible, and the use of sodium dithionite gave a low yield of the diethyl compound. Similar to the use of $(NH_4)_2MoOCl_5$ to prepare the dimeric Mo(V) acetylacetonate,[14] $[(C_5H_7O_2)_2\text{Mo}{=}\text{O}]_2\text{O}$, the Mo(V) complexes of $(CH_3)_2NCS_2^-$, $(C_2H_5)_2NCS_2^-$, and C_2H_5O-

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[12] C. Heitner-Wirguin and R. Cohen, *J. Inorg. Nucl. Chem.*, **27**, 1989 (1965).

[13] J. Chatt, L. A. Duncanson, and L. M. Venanzi, *Suomen Kemistilehti*, **B29**, 75 (1956).

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

CS_2^- could be prepared in high yield using $(NH_4)_2MoOCl_5$ as the source of Mo(V).

A diamagnetic, crystalline solid was isolated from the reaction of H_2S with $MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$ or an aqueous solution of Na_2MoO_4 and $(n\text{-}C_4H_9)_2NCS_2Na$. The analysis of this compound approximated $[(n\text{-}C_4H_9)_2NCS_2]MoOS$ and it appears to be dimeric in benzene solution. This material probably has a structure similar to that proposed[15] for $[\pi\text{-}C_5H_5MoOS]_2$ with a double sulfur bridge joining the molybdenum atoms.

Infrared Spectra.—The infrared spectra of metal dialkyldithiocarbamates contain a strong band in the 1480–1550-cm^{-1} region assigned[13] to the partial C═N bond of the canonical form $[S_2\overset{-}{C}{=}\overset{+}{N}R_2]^-$, which makes an important contribution to the over-all structure.[16,17] By using the data of Jensen[18] and Nakamoto and coworkers,[19] it is possible to make assignments for the C–S stretching modes. Table I summarizes the C═N and C—S stretching modes of the dithiocarbamate complexes.

TABLE I
DITHIOCARBAMATE C═N AND C—S STRETCHING FREQUENCIES[a]

R_2NCS_2M		Stretching frequency, cm^{-1}	
R	M	C═N	C—S
Methyl	Na	1485	960, 560–568
	Mo(VI)	1550	984, 575
	Mo(V)	1546	985
	Mo(II)[b]	1527	. . .
Ethyl	Na	1481	985, 568
	Mo(VI)	1522	1005, 606
	Mo(V)	1511	1000, 606
n-Propyl	Na	1464	966
	Mo(VI)	1522	971, 600
n-Butyl	Na	1466	975, 952
	Mo(VI)	1515	955, 610
$(C_4H_9)_2NCS_2MoOS$		1538	967, 613

[a] Nujol mulls. [b] $\pi\text{-}C_5H_5Mo(CO)_2S_2CN(CH_3)_2$.[5]

The C═N stretching frequencies of the Mo(VI) complexes decrease as the length of the alkyl group increases, like those of the Cu(II) complexes since the frequency of this absorption is a rough measure of the stability of complexes of the same stereochemistry.[13] Although the C–S stretching absorptions usually occur at lower frequency in the more stable complexes, the position of these bands cannot be used as a measure of stability because the position of the absorptions is influenced by other factors.[19]

The C–O–C bending and C–S stretching modes of the xanthate complexes are summarized in Table II. In contrast to the dithiocarbamates, the corresponding xanthate complexes from infrared spectral[20–22] and X-ray structural evidence[23] appear to contain the canonical group RO(C═S)S$^-$ rather than the $[R\overset{+}{O}{=}C\overset{-}{S}_2]^-$. Although there has been some disagreement[20–22] concerning the assignment of the C–O–C and C–S frequencies of xanthates, the studies of Jensen[18] with selenium analogs indicate that C–S frequencies should be expected in the 1020–1070-cm^{-1} region. The peak at 1046 cm^{-1} of molybdenum(V) ethylxanthate has previously been assigned to Mo═O absorption,[24] but we prefer to assign it to C–S absorption for reasons to be discussed later.

TABLE II
INFRARED SPECTRA OF Mo(V) XANTHATES

Compound	C–O–C bend, cm^{-1}	C–S stretch, cm^{-1}
$Mo_2O_3(CH_3OCS_2)_4$	1242 s, 461 s	1056 s, 1036 s, 562 w, br
$Cr(CH_3OCS_2)_3$[a]	1250 vs, br, 459 s	1045 s, sh, 1038 s, 563 vw
$Mo_2O_3(C_2H_5OCS_2)_4$[b]	1227 s, 444 m	1046 s, 1031 s, 560 w
$Cr(C_2H_5OCS_2)_3$[a]	1250 vs, 1275 vs, 440 m	1032 s, 563 vw

[a] See ref 22. [b] Agrees with ref 24.

Assignments for probable Mo–S stretching absorptions were made by comparing spectra of compounds such as $(NH_4)_2MoS_4$ (Table III). During the course of this investigation, infrared spectra of tetrathiomolybdates[25,26] and dithiomolybdates[27] were reported that are in agreement with our results. An assignment cannot be made for Mo–S absorption in the dimethyldithiocarbamate complexes of Mo(V) and Mo(VI) because they show only a medium band at 444 cm^{-1}, which also appears in the sodium and zinc salts. In addition, a definite Mo–S assignment cannot be made for the methylxanthate complex because of strong C–O–C absorption at 461 cm^{-1}. Like the C–S frequencies, the frequency of the metal-to-sulfur bands is not a true measure of the stability of the complex because other factors influence its position.[19]

TABLE III
PROBABLE Mo–S ABSORPTIONS

Compound	Frequency, cm^{-1}
MoS_2	467 w
$(NH_4)_2MoS_4$[a]	480 s, 460 m
$(NH_4)_2MoO_2S_2$[b]	490–493 s, 476–481 w
$MoO_2[(C_2H_5)_2NCS_2]_2$	490–495 w
$Mo_2O_3[(C_2H_5)_2NCS_2]_4$	490–495 w
$MoO_2[(n\text{-}C_3H_7)_2NCS_2]_2$	513–515 m
$MoO_2[(n\text{-}C_4H_9)_2NCS_2]_2$	483 m
$MoOS[(n\text{-}C_4H_9)_2NCS_2]$	472–474 m
$[\pi\text{-}C_5H_5MoOS]_2$[c]	455 m, sh, 451 m
$Mo_2O_3(C_2H_5OCS_2)_4$	476–481 w

[a] See also ref 25 and 26. [b] See also ref 27. [c] We are grateful to Dr. P. M. Treichel, University of Wisconsin, for a sample of this compound.

Assignments for Mo–O absorptions were made by comparison with spectra of complexes of other metals (Table IV). The strong C–S absorptions may some-

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TABLE IV

PROBABLE Mo–O ABSORPTIONS[a]

Compound	Absorption, cm^{-1}
$\mathrm{(NH_4)_2MoO_2S_2}$	877 w, sh, 833 s, 794 s, br
$(n\text{-}\mathrm{C_4H_9})_2\mathrm{NCS_2MoOS}$	935 w, sh
$\mathrm{MoO_2[(CH_3)_2NCS_2]_2}$[b]	909 s, 875 s
$\mathrm{MoO_2[(C_2H_5)_2NCS_2]_2}$	905 s, 877 s, 784 w
$\mathrm{MoO_2[(}n\text{-}\mathrm{C_3H_7)_2NCS_2]_2}$[c]	909 s, 875 s
$\mathrm{MoO_2[(}n\text{-}\mathrm{C_4H_9)_2NCS_2]_2}$[d]	909 s, 877 s
$\mathrm{Mo_2O_3[(CH_3)_2NCS_2]_4}$	930 m, 433 m
$\mathrm{Mo_2O_3[(C_2H_5)_2NCS_2]_4}$	930 s, 877 m, 810 w, 431 s
$\mathrm{Mo_2O_3[CH_3OCS_2]_4}$	952 s, 945 s, sh, 766 w, 432 s, 420 w
$\mathrm{Mo_2O_3[C_2H_5OCS_2]_4}$	948 s, 766 w, 431 s

[a] Nujol mulls. [b] In agreement with ref 24. [c] Benzene solution (5%) absorbs at 915 (s) and 882 (s). [d] Benzene solution (5%) absorbs at 917 (s) and 882 (s).

times obscure $\mathrm{Mo{=}O}$ bands in the 940–1000-cm^{-1} region. Compounds containing the $\mathrm{MoO_2^{2+}}$ group absorb in the 900-cm^{-1} region in agreement with earlier findings.[28] It has been postulated that the oxygens of this group in octahedral complexes are *trans* (linear),[28] but Cotton and Wing proposed[24] that the oxygens of $\mathrm{MoO_2[(CH_3)_2NCS_2]_2}$ may be *cis* on the basis of the appearance of two $\mathrm{Mo{=}O}$ bands in the 900-cm^{-1} region. The appearance of two $\mathrm{Mo{=}O}$ bands in the benzene solution spectra of $\mathrm{MoO_2[(}n\text{-}\mathrm{C_3H_7)_2NCS_2]_2}$ and $\mathrm{MoO_2[(}n\text{-}\mathrm{C_4H_9)_2NCS_2]_2}$ confirms that the molybdenyl oxygens of these complexes are probably *cis* since solid-state effects are eliminated and the *n*-propyl derivative is monomeric in benzene solution. The spectrum of molybdenyl oxinate also contains two $\mathrm{Mo{=}O}$ bands in the 900-cm^{-1} region[29] and the second $\mathrm{Mo{=}O}$ band of molybdenyl acetylacetonate[28] is probably obscured by strong ligand absorption. It can be concluded from the infrared data that octahedral complexes containing the $\mathrm{MoO_2^{2+}}$ group have a bent rather than a linear $\mathrm{O{=}Mo{=}O}$ group.

Complexes of the type $\mathrm{(L_2Mo{=}O)_2O}$, where L is a univalent bidentate ligand, have a single $\mathrm{Mo{=}O}$ stretching mode in the 930–970-cm^{-1} region.[29] The present complexes and the acetylacetonate, $\mathrm{[(C_5H_7O_2)_2Mo{=}O]_2O}$, also possess a medium to strong band in the 430–435-cm^{-1} region that may be assigned to a symmetrical Mo–O–Mo stretching mode since this absorption appears at 465 cm^{-1} in sodium dimolybdate, $\mathrm{Na_2Mo_2O_7}$.[30] In addition, a weak band in the 766–810-cm^{-1} region can be assigned to an antisymmetrical Mo–O–Mo stretching mode in these complexes. Although the band at 1046 cm^{-1} of molybdenum(V) ethylxanthate has been assigned to an $\mathrm{Mo{=}O}$ mode,[24] we prefer to assign both of the peaks in the 1030–1056-cm^{-1} region of the xanthate spectra to C–S stretching absorption since this band is split in other metal xanthates[20,22] and similar complexes of the type $\mathrm{(L_2Mo{=}O)_2O}$ do not absorb in this region. It is proposed that the strong band at about 950 cm^{-1} be assigned to $\mathrm{Mo{=}O}$ absorption and that the band at 766 cm^{-1} be assigned to the antisymmetrical Mo–O–Mo mode since this band usually occurs as a weak peak in this region.

Visible Spectra.—The visible spectra of the complexes under discussion and related compounds are summarized in Table V. The spectra of the dimeric Mo(V) complexes can be assigned by using the assignments given for $\mathrm{[(C_5H_7O_2)_2Mo{=}O]_2O}$,[14] which are based on the spectrum of the diamagnetic dimer formed from $\mathrm{(NH_4)_2MoOCl_5}$ in dilute HCl.[31,32] Like the thioether complexes of $\mathrm{MoOCl_3}$,[33] the ligand field band, $^2B_2 \rightarrow {}^2B_1$, of the Mo(V) dithiocarbamates is found at a lower energy than for the related oxygen-coordinated complexes in agreement with the expected ligand field order.[34] The intense absorption at 19,700 cm^{-1} of the Mo(V) xanthate complexes is assigned to S-to-Mo charge transfer rather than to $^2B_2 \rightarrow {}^2B_1$ because of its intensity, but an unambiguous assignment cannot be made since no corresponding Mo(VI) xanthates exist for comparison. The band at 26,000 cm^{-1} in the dithiocarbamate complexes is apparently a true S-to-Mo charge-transfer band rather than an internal ligand transition,[34] and this assignment is supported by the fact that $\mathrm{MoS_4^{2-}}$ has S-to-Mo charge-transfer bands in this region (21,500 and 30,800 cm^{-1}).[25] The S-to-Mo charge-transfer band of the xanthate complexes appears at 6000 cm^{-1} below that of the corresponding dithiocarbamate complexes indicating that xanthates are better reducing agents

TABLE V

VISIBLE SPECTRA[a]

Compound	Media	Charge transfer	$^2B_2 \rightarrow {}^2B_1$	Charge transfer
$\mathrm{(NH_4)_2MoOCl_5}$[b]	1 *N* HCl		25,970 (88)	33,780 (1850)
$\mathrm{Mo_2O_3(C_5H_7O_2)_4}$	$\mathrm{CH_2Cl_2}$	20,620 (6240)	25,000 (2070)	30,580 (9670)
$\mathrm{MoO_2[(CH_3)_2NCS_2]_2}$	$\mathrm{CH_2Cl_2}$			26,460 (3770)
$\mathrm{MoO_2[(C_2H_5)_2NCS_2]_2}$	$\mathrm{CH_2Cl_2}$			26,320 (3700)
$\mathrm{MoOS[(}n\text{-}\mathrm{C_4H_9)_2NCS_2]}$[c]	$\mathrm{C_6H_6}$			25,320 (1020)
$\mathrm{Mo_2O_3[(CH_3)_2NCS_2]_4}$	$\mathrm{CH_2Cl_2}$		19,610 (1325)	26,670 (4000) (sh)
$\mathrm{Mo_2O_3[(C_2H_5)_2NCS_2]_4}$	$\mathrm{CH_2Cl_2}$		19,420 (1950)	26,320 (5600)
$\mathrm{Mo_2O_3[CH_3OCS_2]_4}$	$\mathrm{C_6H_6}$	19,700 (5020)		
$\mathrm{Mo_2O_3[C_2H_5OCS_2]_4}$	$\mathrm{CH_2Cl_2}$	19,760 (6150)		

[a] Peak maxima in cm^{-1} and molar extinction coefficients in parentheses. [b] E. Wendling, *Bull. Soc. Chim. France*, 437 (1965). [c] Mo-ecular weight of 348.4 used to calculate ϵ.

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than dialkyldithiocarbamates, which agrees with the fact that no Mo(VI) xanthate complexes are known.

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Isotopic Exchange of Bromide Ligands in Platinum(II) Complexes. The Bromo(diethylenetriamine)platinum(II)–Tetrabromoplatinate(II)–Bromide Systems[1]

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The exchange rate of Pt(dien)Br$^+$ with Br$^-$ has been found to follow the rate law: $R_{ex} = \{k_1 + k_2[Br^-]\}[Pt(dien)Br^+]$. The addition of $PtBr_4^{2-}$ to the Pt(dien)Br$^+$–Br$^-$ solution has been shown to result in an increase in the exchange rate of both Pt(dien)Br$^+$ and $PtBr_4^{2-}$ by equal amounts. This mutually catalyzed exchange process is described by the expression: $R_{excess} = k_a[Pt(dien)Br^+][PtBr_4^{2-}]$.

Introduction

We have recently[2] reported a study of bromide exchange in aqueous solutions of the $PtBr_4^{2-}$ ion. The exchange rate between ligand bromide and bromide ion was described by a three-term expression. Two of the terms, first order, respectively, in $PtBr_4^{2-}$ and $PtBr_3(H_2O)^-$, probably describe the aquation of these species. A third term, which was predominant under some conditions, was second order, containing the product of concentrations, $[PtBr_4^{2-}][PtBr_3(H_2O)^-]$. The experimental evidence implied that this second-order rate term more likely described the formation of binuclear species or dimer containing a single bromide bridge rather than the doubly bridged $Pt_2Br_6^{2-}$, characterized by Harris, *et al.*[3]

It was decided to investigate exchange in a system in which only a single bromide bridge would be expected. The Pt(dien)Br$^+$–$PtBr_4^{2-}$ system (where dien = diethylenetriamine) was an obvious choice because it appeared unlikely that Pt–N bonds would be broken in the course of any exchange reaction. To the best of our knowledge, the kinetics of bromide exchange between Pt(dien)Br$^+$ and Br$^-$ have not been previously reported; therefore, it was necessary first to investigate this reaction.

Experimental Section

Materials.—The [Pt(dien)Br]Br was prepared by allowing $K_2[PtBr_4]$ to react with dien·2HBr in aqueous solution. $Rb_2[PtBr_4]\cdot H_2O$ was prepared and analyzed as described previously.[2] The platinum content of [Pt(dien)Br]Br was determined gravimetrically after hydrazine reduction, and bromide was estimated by a modified Volhard titration. *Anal.* Calcd for [Pt(dien)Br]Br: Pt, 42.6; Br, 34.9. Found: Pt, 42.1; Br, 34.5. Aqueous solutions of the dien complex exhibited an absorption maximum at 275 mμ in agreement with the prior observations of Gray on the material.[4] Bromine-82 was obtained by irradiating solid NH_4Br in the Ames Laboratory 5-Mw research reactor.

Water for exchange experiments was redistilled from alkaline $KMnO_4$ solution. All other materials were of Analytical reagent grade.

Procedures. A. Pt(dien)Br$^+$–Br$^-$ Exchange.—Solutions were prepared by dissolving weighed amounts of [Pt(dien)Br]Br and KBr in standardized $NaNO_3$ solutions in order to provide an over-all ionic strength of 0.318 *M*. The solutions were placed in flasks wrapped with opaque tape and permitted to stand for several hours in a thermostated water bath. Isotopic exchange was initiated by the addition of small volumes of solutions prepared from irradiated NH_4Br. Changes in volume were less than 1%. Except for solutions containing the lowest free bromide concentration (*i.e.*, 1.8×10^{-3} *M*), changes in bromide concentration were equally small. Known volumes of the reaction mixtures were withdrawn after measured time intervals; then all anions, including the free bromide ion, were replaced by the passage of these aliquots through columns containing large excesses of Amberlite IRA-400 anion-exchange resin in the nitrate form. Each effluent solution was diluted to 100 ml, and the 0.5–0.9-Mev γ activity was counted for a 25-ml aliquot in a plastic container placed over a 3-in. NaI crystal which formed the detector of a γ-ray scintillation spectrometer. After the application of a decay correction the fraction of exchange, F_i, at the separation time, t_i, was taken as

$$F_i = C_i/C_\infty \qquad (1)$$

where C_i is the counting rate of sample collected at t_i and C_∞ is the average counting rate of at least two samples which were collected after isotopic equilibrium had been established.

Figure 1 is a typical plot of log $(1 - F_i)$ *vs.* time. The excellent straight-line plot and the consistency of the experimental points indicated that the separation and counting procedures were most satisfactory. Half-lives of the reactions were determined from the plots of log $(1 - F_i)$. Exchange rates (R_{ex}) were calculated by use of the usual McKay equation[5]

$$R_{ex} = \frac{\ln 2[Pt(dien)Br^+][Br^-]}{([Pt(dien)Br^+] + [Br^-])t_{1/2}} \qquad (2)$$

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(1) Work performed at the Ames Laboratory of the U. S. Atomic Energy Commission. Contribution No. 1964.

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