Synthesis and Chemistry of Some Binuclear Oxomolybdenum(v) Xanthate (*O*-Alkyl Dithiocarbonate) Complexes

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A simple method for the preparation of pure μ-oxo-bis[bis(*O*-alkyl dithiocarbonato)oxomolybdenum(v)] complexes, $[Mo_2O_3(RO\cdot CS\cdot S)_4]$ (I; R = Me, Et, Pr^i, Bu^n, or Bu^i), and difficulties encountered with previous preparative methods are reported. Assignments of molybdenum–oxygen stretching frequencies in the i.r. spectra have been made and visible spectra have been reinvestigated. Reaction with dialkylamines, alcohols, or hydrogen sulphide results in loss of xanthate ligand and produces, in the last two cases, a series of new di-μ-sulphido-bis[(*O*-alkyl dithiocarbonato)oxomolybdenum(v)] complexes, $[Mo_2O_2S_2(RO\cdot CS\cdot S)_2]$ (II). Spectroscopic studies of these products indicate that those containing unbranched *O*-alkyl dithiocarbonate groups are polymers in the solid state, which dissociate in solution. Complexes (I) and (II) react with excess of xanthate ligand to produce the ion $[Mo_2O_2S_2(O\cdot CS\cdot S)_2]^{2-}$, (III).

THE preparation of some molybdenum(v) complexes of various *O*-alkyl dithiocarbonate ligands, $[Mo_2O_3(RO\cdot CS\cdot S)_4]$, has been briefly described by Malatesta.[1] Determination of the molecular structure of the ethyl derivative confirmed their binuclear formulation and established the presence of both a linear Mo–O–Mo bridge and *cis*-orientation of the two terminal oxo-ligands.[2] More recent investigations have been concerned primarily with i.r. and electronic spectroscopic properties of the complexes,[3-6] with little emphasis on their chemistry.[1,4,6-8]

Our continuing interest [9-11] in the chemistry of co-ordination compounds of molybdenum, particularly as an aid in understanding the behaviour of molybdenum as it participates in redox chemistry of various metallo-enzymes,[12] has led to closer examination of these oxo-molybdenum(v) xanthate (*O*-alkyl dithiocarbonate) complexes. This work constitutes an extension of our previous studies on analogous *NN*-dialkyldithiocarbamate complexes,[11] which form the basis of our tentative interpretation of the i.r. and visible spectra of the xanthate complexes. In this paper we demonstrate the drawbacks of previously reported [1,3,4] methods of preparation and describe a new simple method for synthesis of pure μ-oxo-bis[bis(*O*-alkyl dithiocarbonato)oxo-molybdenum(v)] complexes, $[Mo_2O_3(RO\cdot CS\cdot S)_4]$ (I; R = Me, Et, Pr^i, Bu^n, or Bu^i). Reactions of these complexes, some of which produce new molybdenum(v) dimers, are also reported.

EXPERIMENTAL

Potassium salts of the xanthate (*O*-alkyl dithiocarbonate) ligands were prepared by adding carbon disulphide to an alcoholic solution of the appropriate potassium alkoxide, followed by filtration, washing with diethyl ether, and drying *in vacuo*. Chloroform-soluble tetraethylammonium *O*-ethyl dithiocarbonate, apparently not reported in the literature, was prepared by mixing Et_4NCl–$CHCl_3$ with $K(EtO\cdot CS\cdot S)$–EtOH and removing precipitated KCl. The resulting crystalline solid gave appropriate n.m.r., titration (I_2), and C, H, N analytical data. Disodium tetraoxo-molybdate(vi) dihydrate and molybdenum pentachloride were supplied by the Climax Molybdenum Company.

I.r. spectra were recorded with a Beckman IR20A spectrophotometer (KBr discs), n.m.r. spectra with a Varian A60 spectrometer ($CDCl_3$ solutions), and visible spectra with a Cary model 14 recording spectrophotometer. Conductance measurements were made with a Radiometer CDM2 bridge and CDC114 electrode. Microanalyses were obtained with a Hewlett–Packard 185 C, H, N analyser. Sulphur analysis was carried out by Alfred Bernhardt, Mikroanalytisches Laboratorium, Elbach über Engelskirchen, West Germany. Gas–liquid chromatography (g.l.c.) was undertaken with a Hewlett–Packard 5750 Dual Flame instrument, using 72 × 1/8 in columns of either 10% methylvinyl silicone gum on Chromosorb W (at 140 °C for reaction products from excess of xanthate or aminolysis, and at 110 °C for alcoholysis products) or 10% Carbowax 20 M on Chromosorb W (used at 110 °C for detection of alcoholysis products only). All solvents were degassed and all reactions and physical measurements were carried out under an atmosphere of argon unless otherwise stated. Analytical data are collected in the Table.

Preparation of μ-Oxo-bis[bis(O-alkyl dithiocarbonato)oxo-molybdenum(v)] *Complexes*, $[Mo_2O_3(RO\cdot CS\cdot S)_4]$ (I; R = Me, Et, Pr^i, Bu^n, *or* Bu^i).—To a clear yellow aqueous solution of disodium tetraoxomolybdate(vi) dihydrate (1·5 g, 6·2 mmol) and the potassium salt of a xanthate (*O*-alkyl dithiocarbonate) ligand [K(RO·CS·S), *ca.* 25 mmol] was added 6M-hydrochloric acid (10 cm^3) with stirring in air. A yellow precipitate formed, which quickly turned purple to yield an oily solid. This product was washed repeatedly with water, dried *in vacuo* for 6 h, then washed with hexane (3 × 15 cm^3), and dried *in vacuo* for a further 1—2 h to give the microcrystalline product.

Attempted Preparation of Di-μ-oxo-bis[(O-*alkyl dithiocarbonato*)*oxomolybdenum*(v)] *Complexes*, $[Mo_2O_4(RO\cdot CS\cdot S)_2]$.—An aqueous solution of molybdenum pentachloride (1·0 g, 3·67 mmol) and potassium *O*-ethyl dithiocarbonate (0·59 g,

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[8] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1969, 2632.

[9] W. E. Newton, J. L. Corbin, P. W. Schneider, and W. A. Bulen, *J. Amer. Chem. Soc.*, 1971, **93**, 268.

[10] P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Amer. Chem. Soc.*, 1972, **94**, 8640.

[11] W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, in the press.

[12] See, for example, J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475; E. I. Stiefel, *Proc. Nat. Acad. Sci. U.S.A.*, 1973, **70**, 988.

3·67 mmol) was heated under reflux for 0·5 h when the initially deposited purple oil changed to a green solid. This solid was collected by filtration, washed with water and diethyl ether, and dried *in vacuo*. I.r. spectroscopy indicated that this solid was $[Mo_2O_3(EtO\cdot CS\cdot S)_4]$. Extended periods of heating resulted in loss of ligand from the complex and precipitation of essentially inorganic molybdenum products, which were not identified.

Complex	Yield (%)	Analytical data (%) [a]			Selected i.r. data (cm^{-1}) [b]			Visible spectral data (700—345 nm) [c]	
		C	H	S	ν(Mo=O)	ν(Mo–O–Mo)	ν(MoS)	Max.	Min.
$[Mo_2O_3(MeO\cdot CS\cdot S)_4]$	87	14·4 (14·3)	1·9 (1·8)		950s, 948sh	767w, 430w	374w	507 (12 900) [d]	440 (1 590)
$[Mo_2O_3(EtO\cdot CS\cdot S)_4]$	93	20·4 (19·9)	3·0 (2·8)		947s	754w, 428w	340w	508 (12 800) [d]	442 (1 450)
$[Mo_2O_3(Pr^iO\cdot CS\cdot S)_4]$	79	24·1 (24·6)	3·7 (3·6)		943s	748w, 432w	320w	508 (11 800) [d]	442 (1 450)
$[Mo_2O_3(Bu^nO\cdot CS\cdot S)_4]$	63	28·9 (28·7)	4·6 (4·3)		953s, 945sh	750w, 432w	385w	508 (13 200) [d]	442 (1 310)
$[Mo_2O_3(Bu^iO\cdot CS\cdot S)_4]$	96	29·5 (28·7)	4·7 (4·3)		953s	747w, 428w	377w	507 (12 000) [d]	440 (1 680)
$[Mo_2O_2S_2(MeO\cdot CS\cdot S)_2]$	71	9·8 (9·6)	1·6 (1·2)	38·4 (38·3)	825vs				
$[Mo_2O_2S_2(EtO\cdot CS\cdot S)_2]$	77	13·3 (13·6)	1·6 (1·9)	36·3 (36·3)	830vs 985s, 975sh [e]			372 (1 360) [e]	
$[Mo_2O_2S_2(Pr^iO\cdot CS\cdot S)_2]$	68	17·0 (17·2)	2·4 (2·5)	34·3 (34·5)	970s, 960sh 980s, 970sh [e]			370 (1 560) [e]	
$[Mo_2O_2S_2(Bu^nO\cdot CS\cdot S)_2]$	86	20·1 (20·5)	3·3 (3·1)	32·8 (32·8)	832vs 976s, 968sh [e]			371 (730) [e]	
$[Mo_2O_2S_2(Bu^iO\cdot CS\cdot S)_2]$	51	20·3 (20·5)	3·1 (3·1)		968s, 960sh			372 (970) [e]	
$(Et_4N)_2[Mo_2O_2S_2(O\cdot CS\cdot S)_2]$	100	29·1 (29·5)	5·2 (5·5)	26·7 (26·2)	968s, 955sh			347 (4 250) [e]	

[a] Calculated values are given in parentheses. [b] As KBr discs. [c] Molar absorption coefficient ($l\ mol^{-1}\ cm^{-1}$) in parentheses (see text). [d] In benzene. [e] In dichloromethane.

Reactions of Complexes (I).—*With hydrogen sulphide in chloroform solution.* In a given experiment, complex (I) (0·5 g, *ca.* 0·7 mmol) was dissolved in chloroform (*ca.* 50 cm^3) and hydrogen sulphide was bubbled through the solution for 2 h. The reaction mixture was stirred for 16 h, and the yellow precipitate of *di-μ-sulphido-bis*[(*O-alkyl dithiocarbonato*)*oxomolybdenum*(V)], $[Mo_2O_2S_2(RO\cdot CS\cdot S)_2]$ (II; R = Me, Et, Pr^i, Bu^n, *or* Bu^i) (*ca.* 0·25 g), was filtered off, washed with hexane (2 × 20 cm^3), and dried *in vacuo*.

With hydrogen sulphide in benzene–ethanol solution. After hydrogen sulphide had been bubbled through a 4 : 1 benzene–ethanol solution of complex (I; R = Et) (0·5 g, 0·7 mmol), a black precipitate of $[MoS_2(EtO\cdot CS\cdot S)]_n$ (yield 80%) (Found: C, 12·8; H, 2·0; S, 43·4. Calc. for $C_3H_5MoOS_4$: C, 12·8; H, 1·8; S, 45·6%) was filtered off, washed with hexane (3 × 30 cm^3), and dried *in vacuo*.

With alcohols. (*a*) After stirring for *ca.* 6 h, a solution of complex (I; R = Et) (0·68 g, 0·94 mmol) in dichloroethane (25 cm^3) and ethanol (5 cm^3) changed colour from purple to yellow-brown. G.l.c. analysis of the solution showed that *OO*-diethyl thiocarbonate (0·26 g, 1·9 mmol; identified by comparison with an authentic sample [13]) was present. Evaporation to dryness, followed by extraction with diethyl ether (2 × 40 cm^3) and drying *in vacuo*, gave *complex* (II; R = Et) (0·35 g, 0·66 mmol; identified by i.r. spectrum and elemental analysis). The n.m.r. spectrum of the oil obtained by evaporation of the ether extract confirmed the presence of *OO*-diethyl thiocarbonate.

(*b*) Similarly, complex (I; R = Me) (3·0 g, 4·5 mmol) in dichloroethane (70 cm^3) and methanol (20 cm^3) gave (II; R = Me) (1·90 g, 3·8 mmol; confirmed by i.r. spectrum and elemental analysis) and *OO*-dimethyl thiocarbonate (1·14 g, 10·8 mmol; identified by n.m.r. and g.l.c. comparison with an authentic sample [14]).

With dialkylamines. (*a*) On addition of gaseous dimethylamine (45 cm^3, 1·8 mmol) to a solution of complex (I; R = Et) (0·265 g, 0·37 mmol) in dichloromethane (10 cm^3), an instantaneous reaction occurred to produce a brown precipitate and a straw-coloured supernatant solution. G.l.c. analysis of the solution showed that *O*-ethyl dimethylthiocarbamate (0·18 g, 1·32 mmol; identified by comparison with an authentic sample [15]) was produced. I.r. spectroscopy showed the absence of both xanthate and *NN*-dialkyldithiocarbamate ligands in the precipitate.

(*b*) Similarly, complex (I; R = Me) (0·25 g, 0·39 mmol) and gaseous dimethylamine (45 cm^3, 1·8 mmol) gave *O*-methyl dimethylthiocarbamate (0·15 g, 1·26 mmol; identified by comparison with an authentic sample [15]).

With tetraethylammonium O-*ethyl dithiocarbonate.* A mixture of solid (I; R = Et) (0·50 g, 0·69 mmol) and $Et_4N(EtO\cdot CS\cdot S)$ (0·36 g, 1·38 mmol) was dissolved in chloroform. After 40 min the initial purple colour had changed to yellow-brown and a green precipitate was present. G.l.c. of the supernatant liquid showed the presence of *OS*-diethyl dithiocarbonate (0·30 g, 2·0 mmol). The reaction mixture was evaporated to dryness *in vacuo* and the residue was triturated with diethyl ether to yield a green solid (0·50 g). Extraction into acetone and evaporation to dryness gave yellow tetraethylammonium di-μ-sulphido-bis[(dithiocarbonato)oxomolybdate(V)], $(Et_4N)_2[Mo_2O_2S_2(O\cdot CS\cdot S)_2]$ (III) [0·43 g, 0·59 mmol; shown by i.r. spectroscopy and elemental analysis to be slightly impure (see Discussion section)].

Attempted Reactions of Complexes (II).—*With thiophenol.* After stirring a chloroform suspension of complex (II; R = Et, Pr^i, or Bu^n; 0·1—0·2 g, *ca.* 0·2 mmol) and thiophenol (2 cm^3) for 72 h, the starting material was recovered unchanged.

With diethylamine. Diethylamine (0·10 cm^3, 0·95 mmol) was added to a suspension of complex (II; R = Et) (0·11 g, 0·20 mmol) in chloroform (5·0 cm^3). After stirring for 24 h, g.l.c. showed that *O*-ethyl diethylthiocarbamate (0·046 g, 0·29 mmol; identified by comparison with an authentic sample [15]) was present.

With tetraethylammonium O-*ethyl dithiocarbonate.* Within 30 min, yellow crystals began to separate from a chloroform solution (5·0 cm^3) of complex (II; R = Et) (0·10 g, 0·19 mmol) and $Et_4N(EtO\cdot CS\cdot S)$ (0·11 g, 0·42 mmol). After 24 h, crystals of complex (III) (0·14 g, 0·19 mmol; identified by i.r. spectroscopy and elemental analysis) were isolated by filtration, washed with pentane, and dried *in vacuo*. The molar conductance of a 10^{-3}M-acetone solution of this product was 174 $\Omega^{-1}\ cm^2\ mol^{-1}$, which is consistent with its

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[13] G. Ingram and B. A. Toms, *J. Chem. Soc.*, 1961, 117.

[14] M. Delépine, *Bull. Soc. chim. France*, 1910, **7**, 404.

[15] O. Billeter, *Ber.*, 1910, **43**, 1853; J. F. Harris, jun., *J. Amer. Chem. Soc.*, 1960, **82**, 155.

formulation as a 2 : 1 electrolyte. G.l.c. of the original filtrate showed the presence of *OS*-diethyl dithiocarbonate (0·058 g, 0·39 mmol; identified by n.m.r. and g.l.c. comparison with an authentic sample [16]).

RESULTS AND DISCUSSION

Preparation of Complexes.—The usual method [1,3,4] of passing sulphur dioxide through an ice-cold aqueous solution of disodium tetraoxomolybdate(VI) and potassium *O*-alkyl dithiocarbonate in a 1 : 2 molar ratio gave complexes $[Mo_2O_3(RO{\cdot}CS{\cdot}S)_4]$, (I), for R = Me and Et, but with R = Pr^i or Bu contamination with a second species was always observed. The contaminant is thought to be the monomeric reduction product $[OMo(RO{\cdot}CS{\cdot}S)_2]$ and the evidence to support this formulation is based on comparative visible spectroscopy and on its oxidation to produce complex (I) (see Visible Spectra section).

The reaction, at 0 °C, between the anaerobic hydrolysis product of molybdenum pentachloride [' molybdenum(V) oxochloride '] and a 10-fold excess of ligand, which had resulted in pure products for the analogous *NN*-dialkyldithiocarbamate ligands,[11] was then attempted, but gave similar ' contaminated ' products. Variations in the order of addition, the molar ratio of the reactants (from 1 : 2·5 to 1 : 17), or the temperature (0 and 25 °C) made no difference to the products obtained. However, the length of time that the ' molybdenum(V) oxochloride ' solution was degassed with argon had a significant influence on product composition, as did the starting concentration of molybdenum pentachloride. Both factors would affect the acidity of the reaction mixture and apparently as the acidity increases, so does the amount of reduction. This observation is consistent with detection of molybdenum(IV) species from continuous bubbling of sulphur dioxide through reaction mixtures containing higher molecular weight, more reducing, xanthate ligands.

We then carried out careful acidification (6M-HCl) of aqueous solutions of disodium tetraoxomolybdate(VI) containing two equivalents of the potassium salt of the various xanthate ligands. Green (R = Me or Et) or purple (R = Pr^i, Bu^n, or Bu^i) microcrystalline complexes (I) were produced. No contamination with molybdenum(IV) products was spectrally discernible. However, very large excesses of acid did produce some molybdenum(IV).

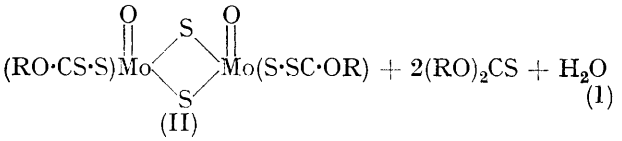
Attempts to produce di-μ-oxo-bis[(*O*-ethyl dithiocarbonato)oxomolybdenum(V)], $[Mo_2O_4(EtO{\cdot}CS{\cdot}S)_2]$, by the method used for *NN*-dialkyldithiocarbamates [11] of heating under reflux 1 : 1 molar mixtures of $MoCl_5$ and ligand in water, were unsuccessful. Initially, complex (I; R = Et) is formed, which, on further heating, decomposes with loss of ligands.

Reactions.—*With hydrogen sulphide.* A previous report [7] described the reaction of complex (I; R = Et) with hydrogen sulphide in benzene–ethanol solution as producing a black intractable solid of composition $[MoS_2(EtO{\cdot}CS{\cdot}S)]_n$. We have confirmed this reaction, but find that in chloroform solution a yellow crystalline solid is produced, which has the empirical formula MoOS(RO·CS·S). I.r. spectral comparison with similar complexes synthesised for other ligand systems [11,17–24] suggests that these products should be formulated as the dimer $[Mo_2O_2S_2(RO{\cdot}CS{\cdot}S)_2]$, (II), with two μ-sulphido-bridges between the two molybdenum(V) atoms. They were not sufficiently soluble to obtain meaningful molecular-weight data. These complexes did not react with thiophenol in 72 h, indicating (*i*) that the di-μ-sulphido-bridge is inert to protonation to give hydrogen sulphide and a μ-sulphido-bridged complex in contrast to ready reaction of a di-μ-oxo-bridge,[11] and (*ii*) that they are inert to reduction [8,17] to molybdenum(IV) under these conditions.

With alcohols and dialkylamines. Complexes (I) reacted with alcohols, both in the solid state (slowly) and in solution, at the xanthate ligand. In dichloroethane solution, 60% of all four xanthate ligands of complex (I; R = Me) reacted with methanol within 5 h to produce *OO*-dimethyl thiocarbonate, MeO·CS·OMe, while ethanol and (I; R = Et) produce *OO*-diethyl thiocarbonate (51%). As only *ca.* 50% of the ligands were lost, we isolated the molybdenum-containing product and found it to be the same as that produced with hydrogen sulphide, (II; R = Me or Et) [equation (1)].

$$[Mo_2O_3(RO{\cdot}CS{\cdot}S)_4] + 2ROH \longrightarrow$$

(I)



$$(RO{\cdot}CS{\cdot}S)\overset{O}{\overset{\|}{Mo}}(\mu\text{-}S)_2\overset{O}{\overset{\|}{Mo}}(S{\cdot}SC{\cdot}OR) + 2(RO)_2CS + H_2O \quad (1)$$

(II)

Dimethylamine reacted instantaneously with complexes (I; R = Me and Et) to produce *O*-alkyl dimethylthiocarbamate, $RO{\cdot}CS{\cdot}NMe_2$ (*ca.* 85% of all four xanthate ligands). I.r. spectra of the resulting brown precipitates contained no bands assignable to xanthate or *NN*-dimethyldithiocarbamate ligands. Therefore, C–S bond cleavage is occurring exclusively [equation (2)]. The formulation of the products, and the fact that the more basic reagent (dimethylamine) reacted more quickly, indicates that the reaction involves attack on the positively charged α-carbon atom of the xanthate ligands.

$$(I) + 4Me_2NH \longrightarrow RO{\cdot}CS{\cdot}NMe_2 + \text{' }Mo_2O_2S_4H_2\text{ '} + H_2O \quad (2)$$

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[16] G. Bulmer and F. G. Mann, *J. Chem. Soc.*, 1945, 666.

[17] W. E. Newton, J. L. Corbin, and J. W. McDonald, unpublished work.

[18] L. R. Melby, *Inorg. Chem.*, 1969, **8**, 349.

[19] A. Kay and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 2421.

[20] B. Spivack and Z. Dori, *Chem. Comm.*, 1970, 1716.

[21] J. R. Knox and C. K. Prout, *Chem. Comm.*, 1968, 1227.

[22] L. T. J. Delbaere and C. K. Prout, *Chem. Comm.*, 1971, 162.

[23] B. Spivack, A. P. Gaughan, and Z. Dori, *J. Amer. Chem. Soc.*, 1971, **93**, 5265.

[24] M. G. B. Drew and A. Kay, *J. Chem. Soc.* (*A*), 1971, 1846, 1851.

Neither potassium *O*-alkyl dithiocarbonates nor bis(*O*-alkyl dithiocarbonato)nickel(II) complexes produce *OO*-dialkyl thiocarbonate with alcohols alone, but both are reported to react with dialkylamines to produce *O*-alkyl dialkylthiocarbamate (85% yield) [25] and bis(dithiocarbamato)nickel(II) [26] respectively. We find that potassium *O*-methyl dithiocarbonate gives both *O*-methyl dimethylthiocarbamate (48%) and *NN*-dimethyldithiocarbamate (15%) with dimethylamine. Similarly both C–S and C–O bond cleavage occurs in bis(*O*-ethyl dithiocarbonato)nickel(II). Dimethylamine produces *O*-ethyl dimethylthiocarbamate (61%) and bis(*NN*-dimethyldithiocarbamato)nickel(II) (6%), while diethylamine produces *O*-ethyl diethylthiocarbamate (66%) and bis(*NN*-diethyldithiocarbamato)nickel(II) (18%).

These data indicate that xanthate ligands on molybdenum react differently to both fully co-ordinated xanthate on nickel and ionic xanthate in the form of the potassium salt. Previous reports [4,8] have stated, without experimental details, that complex (I; R = Et) is somewhat unstable toward ligand dissociation. However, attack by these reagents on free xanthate ligands (analogous to reaction of potassium *O*-alkyl dithiocarbonate) would not explain the observed products from the molybdenum complexes. Possibly, partially co-ordinated, *i.e.* unidentate, ligands occur in solution and it is these that undergo the observed reactions. However, secondary amines also attack complexes (II) at the α-carbon atom of both xanthate ligands producing *O*-alkyl dialkylthiocarbamate in *ca.* 75% yield and essentially inorganic molybdenum products containing no xanthate or dithiocarbamate ligands.

With tetraethylammonium O-ethyl dithiocarbonate. While investigating the origin of the slight deviation from Beer's law exhibited by complexes (I) (see Visible Spectra section), chloroform solutions of tetraethylammonium *O*-ethyl dithiocarbonate and complex (I; R = Et) were mixed. A purple colour was immediately discharged. The supernatant liquid was shown (by g.l.c.) to contain *OS*-diethyl dithiocarbonate (73% of all four xanthate ligands) and from the green precipitate, a somewhat impure sample of yellow $(Et_4N)_2[Mo_2O_2S_2(O{\cdot}CS{\cdot}S)_2]$ (III) (85% yield) was obtained. This latter complex was more easily and cleanly prepared from complexes (II) and excess of xanthate ligand, where yellow crystals of the pure material separated from chloroform reaction mixtures in 100% yield. This product has an i.r. spectrum appropriately similar to that [27] of (dithiocarbonato)bis(triphenylphosphine)platinum(II) and behaves as a 2 : 1 electrolyte in acetone solution. Its formation [equation (3)] was confirmed

$$\begin{aligned}(\mathrm{II};\ R = Et) + 2Et_4N(EtO{\cdot}CS{\cdot}S) &\longrightarrow 2EtO{\cdot}CS{\cdot}SEt \\ &+ \underset{\text{(III)}}{(Et_4N)_2[Mo_2O_2S_2(O{\cdot}CS{\cdot}S)_2]} \qquad (3)\end{aligned}$$

by detection (g.l.c. and n.m.r.) of *OS*-diethyl dithiocarbonate (100%) in the supernatant liquid. No other products could be detected. This reaction, in contrast to those with alcohols and amines, cleaves the R–O bond of the xanthate ligand producing a dithiocarbonate complex. This type of cleavage was observed previously in reactions of bis(*O*-alkyl dithiocarbonato)platinum(II) complexes with phosphines.[27]

Visible Spectra.—Spectra of the complexes (I; R = Me and Et) have been reported previously,[3,4] but with large discrepancies in molar absorption coefficient values. This fact, together with our discovery that analogous dimeric *NN*-dialkyldithiocarbamate complexes dissociate into molybdenum(IV) and molybdenum(VI) monomers in solution,[11] prompted us to re-examine the visible spectra of the xanthate complexes. The spectra, in benzene or dichloroethane, all contained an intense band at *ca.* 510 nm, a shoulder at *ca.* 340 nm, and a well defined minimum at *ca.* 440 nm. The previously reported [4] band at 555 nm (ε 1 000 l mol^{-1} cm^{-1}) for complex (I; R = Et) was not obvious in our spectrum. Visible spectral data are listed in the Table. The *ca.* 510 nm band deviated slightly from Beer's law (from an ε *ca.* 13 000 at *ca.* $1{\cdot}2 \times 10^{-4}$ to *ca.* 10 500 l mol^{-1} cm^{-1} at $0{\cdot}4 \times 10^{-4}$M in benzene), but not nearly as significantly as that observed for analogous *NN*-dialkyldithiocarbamate complexes.[11]

The *ca.* 510 nm band arises from a transition involving the Mo–O–Mo bridge [2] and therefore any non-Beer's law behaviour by this band might be expected to arise from perturbations of this bridge. One possible explanation is that an equilibrium such as that demonstrated [11] for the dithiocarbamates (dtc) is occurring [equation (4)].

$$[Mo_2O_3(dtc)_4] \rightleftharpoons [MoO_2(dtc)_2] + [OMo(dtc)_2] \qquad (4)$$

But as there is only very sparse evidence for the existence of the complexes *cis*-bis(*O*-alkyl dithiocarbonato)dioxomolybdenum(VI), $[MoO_2(RO{\cdot}CS{\cdot}S)_2]$, and bis(*O*-alkyl(dithiocarbonato)oxomolybdenum(IV), $[OMo(RO{\cdot}CS{\cdot}S)_2]$, their formation *via* this equilibrium may not be favoured. However, a modest dissociation could explain the small deviation observed. The partial (or complete) dissociation of the xanthate ligands from complexes (I) (as discussed above), rather than Mo–O–Mo bridge rupture, could also contribute to the non-Beer's law behaviour observed. It was not possible, however, to determine the possible effect of ligand dissociation because of the reaction with tetraethylammonium *O*-alkyl dithiocarbonate ligands to give the dithiocarbonate complex.

Spectra of ' contaminated ' products from the sulphur dioxide or molybdenum pentachloride reactions contained, in addition to the band at *ca.* 500 nm, a sharp absorption at *ca.* 390 nm, which obscured the *ca.* 440 nm minimum. These spectra closely resembled those of the oxomolybdenum(IV) dithiocarbamate complexes [8,11,17] and lead us to believe that oxomolybdenum(IV) xanthate complexes are present in solution. This belief is supported by the oxidation of these species in solution.

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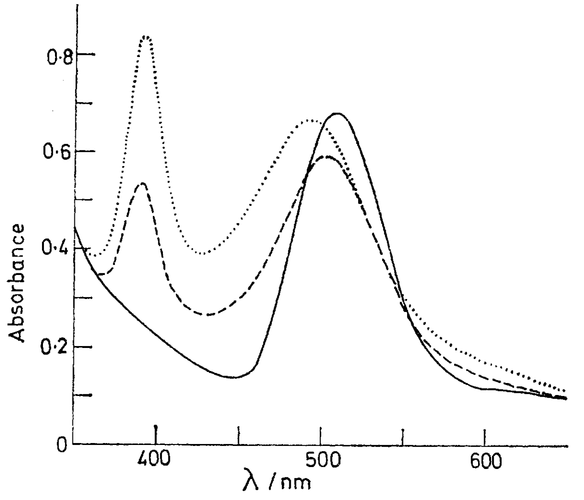
When an aliquot portion was exposed to air overnight complexes (I) resulted, while an aliquot portion stored under an atmosphere of argon retained the *ca.* 390 nm band. Loss of the *ca.* 390 nm band by oxidation was accompanied by shift of the *ca.* 500 nm band to *ca.* 510 nm (see the Figure).

Visible spectra of the complexes (II; R = Et, Pr^i, Bu^n, and Bu^i) in dichloromethane contained only a shoulder at *ca.* 370 nm, which obeyed Beer's law on dilution (see the Table). The spectra were all similar to one another and to those of analogous *NN*-dialkyldithiocarbamate complexes,[17] indicating that the complexes all have similar structures in solution.

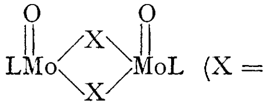


Visible spectral changes of solutions of the product of reaction of $MoCl_5$ with $K(Bu^nO{\cdot}CS{\cdot}S)$: (· · · ·) immediately after isolation; (— — —), after standing under an atmosphere of argon for 17 h; and(——), after exposure to oxygen for 17 h

I.R. Spectra.—The small number of complexes reported previously {only (I) and $[OMo(EtO{\cdot}CS{\cdot}S)_2(py)]$ (py = pyridine)} has made assignment of the various molybdenum–oxygen stretching vibrations using comparative methods very difficult. Several attempts at correlating various frequencies with certain molecular vibrations have been reported [3-5,28] for complex (I; R = Et), but those ascribed to the molybdenum–terminal oxygen stretching vibration [ν(Mo=O)] have varied by *ca.* 100 cm^{-1}. The two series of oxomolybdenum(V) xanthate dimers that we have prepared, together with a comparison of assignments made in related compounds,[6,11,13,29-31] has helped us to resolve these conflicting data.

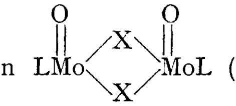
The only difference in solid-state spectra of complexes (I; R = Me) and (II; R = Me), between 1 400 and 1 000 cm^{-1}, was that all the absorptions were doubled for the former. This observation is consistent with the varying environments of the xanthate ligands [2] in complex (I; R = Me) and suggests an equivalence in (II; R = Me). From 1 000 to 400 cm^{-1}, complex (II; R = Me) has only two absorptions, a very strong, broad, band at 825 cm^{-1} and a weak band at 465 cm^{-1}. This latter band also appeared in the spectrum of complex (I; R = Me) and is attributed to a xanthate vibration. The band at 825 cm^{-1}, which is unique to the spectrum of complex (II; R = Me), is therefore due to ν(Mo=O) (see later). Similarly, unique bands in the spectrum of complex (I; R = Me) at 950, 767, and 430 cm^{-1} are attributed to ν(Mo=O) and to antisymmetric and symmetric Mo–O–Mo bridge vibrations respectively. The frequencies and intensities of these tentatively assigned bands correlate very well with those proposed previously by us [11] for analogous *NN*-dialkyldithiocarbamate complexes. Using similar comparisons, assignments were made for the other complexes in both series of compounds. Selected i.r. data are collected in the Table. The assignments of ν(Mo=O) made previously [2,4] at 1 046 cm^{-1} are thought to be erroneous and we suggest that this absorption is due to a ν(CS) vibration of the xanthate ligand. All the spectra contained very strong bands at 1 200—1 300 cm^{-1}, typical of xanthate ligands.

The i.r. spectrum of the dithiocarbonate complex (III) is strikingly similar over the range 2 000—1 000 cm^{-1} to that [27] of $[(Ph_3P)_2Pt(O{\cdot}CS{\cdot}S)]$. The vibration ν(C=O) is split into two bands at 1 710 and 1 620 cm^{-1}, with ν(CS) at 1 175 cm^{-1}; ν(Mo=O) has the typical double arrangement, with absorptions at 968 and 955 cm^{-1}, of the grouping

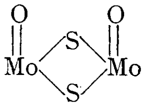

$\mathrm{L}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}\langle{}^{\mathrm{X}}_{\mathrm{X}}\rangle\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}\mathrm{L}$

(X = O or S; L = dithiocarbamate,[11,17] dithiophosphinate,[17] or amino-acids [14-20,32]), so supporting the proposed structure of this ion.

Solid-state spectra of the complexes (II; R = Me, Et, and Bu^n) had similar very strong, broad, absorptions at *ca.* 830 cm^{-1}, while the isopropyl and isobutyl analogues had a strong sharp absorption at 975 cm^{-1} with a shoulder at 960 cm^{-1}. This latter spectral arrangement is typical of complexes of the formulation


$\mathrm{L}\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}\langle{}^{\mathrm{X}}_{\mathrm{X}}\rangle\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}\mathrm{L}$

(see above). Therefore, two different solid-state structures exist, although visible spectra had indicated similar structures in solution. This discrepancy was clarified by solution i.r. spectroscopy when typical


$\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}\langle{}^{\mathrm{S}}_{\mathrm{S}}\rangle\overset{\mathrm{O}}{\overset{\|}{\mathrm{Mo}}}$

spectra were obtained for all the complexes. Spectra of solids isolated from these solutions again showed the solid-state anomaly where appropriate. A similar broadening and shift to lower frequency of ν(Mo=O) in the solid-state spectrum has been observed in five-co-ordinate $[OMo(S_2CNMe_2)_2]$,[17] $[OMo(S_2PF_2)_2]$,[33] and $[OMoCl_4]^-$

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(ref. 34) and may be attributed to ' polymerisation ' *via* an Mo=O $\longrightarrow$ Mo interaction to form a –Mo–O–Mo–O chain. The xanthate complexes (II; R = Me, Et, and Bu^n) are the first examples of such an interaction occurring for a dimer. Steric restriction towards polymerisation by the branched bulky isopropyl and isobutyl xanthate could account for the absence of spectral differences for the complexes containing these ligands. This suggestion is supported by the observation that *no* such ' polymerisation ' exists in the *NN*-dialkyldithiocarbamate analogues,[11,17] where the ligands, of necessity, contain branched groups.

We thank Drs. W. A. Bulen, G. D. Watt, and S. J. Pace for useful discussion, D. Bravard, J. Searles, and D. Work for skilled experimental assistance, and the Climax Molybdenum Company for generous gifts of molybdenum compounds.

[3/2313 *Received*, 12*th November*, 1973]

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