Reactions of Bis(diethyldithiocarbamato)oxomolybdenum(IV)

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The title compound, $[\mathrm{MoO(S_2CNEt_2)_2}]$, abstracts an oxygen atom from the following compounds and is oxidised to the molybdenum(VI) compound $[\mathrm{MoO_2(S_2CNEt_2)_2}]$: oxygen; pyridine *N*-oxide; dimethyl sulphoxide, triphenylphosphine oxide; t-butyl nitrate; and tetraethylammonium nitrate. With dinitrogen mono-oxide and azoxybenzene the product is the molybdenum(V) compound $[\mathrm{Mo_2O_3(S_2CNEt_2)_4}]$. With benzohydrazide the product is a binuclear molybdenum(V) compound, $[\mathrm{Mo_2(NH_2NHCOPh)_2O_2S_2(S_2CNEt_2)_2}]$. The preceding reactions are oxidative additions. In the presence of triphenylphosphine or triphenylphosphine sulphide a valency disproportionation occurs to the molybdenum(III) compound $[\mathrm{Mo_2(S_2CNEt_2)_6}]$ and the molybdenum(V) compound $[\mathrm{Mo_2O_4(S_2CNEt_2)_2}]$. With the dithiocarbamato-compounds of molybdenum facile redox equilibria are established for the oxidation states III to VI involving both electron and oxygen-atom transfer.

BIS(DIETHYLDITHIOCARBAMATO)OXOMOLYBDENUM(IV), $[\mathrm{MoO(S_2CNEt_2)_2}]$, (I), is one of a series of diamagnetic five-co-ordinate molybdenum(IV) compounds which we first prepared in 1966.[1] Its chemistry is of particular interest because (*a*) $\mathrm{Mo^{IV}}$ is considered to be the catalytic species in various molybdoenzymes [2] and in the molybdenum-catalysed *in vitro* reduction of, for example, nitrate,[3] (*b*) molybdenum is bound to sulphur as in molybdoenzymes,[2] and (*c*) the co-ordination number of five suggests the possibility of a vacant site at which substrate binding and reaction could occur. In the present paper we report reactions of (I) with nitrogen and oxygen compounds including substrates of metalloenzymes. Previously Schneider *et al.*[4] showed that (I) undergoes oxidative addition with compounds containing N=N, C≡C, and C=C bonds.

EXPERIMENTAL

All preparations and manipulations were carried out under nitrogen or *in vacuo*. Solvents were deoxygenated before use.

Bis(*diethyldithiocarbamato*)*oxomolybdenum*(IV), $[\mathrm{MoO(S_2CNEt_2)_2}]$, (I).—An aqueous solution of sodium dithionite was added to an aqueous solution containing sodium molybdate and sodium diethyldithiocarbamate [1] (Found: C, 29.2; H, 4.7; N, 6.7; S, 31.3. Calc. for $\mathrm{C_{10}H_{20}MoN_2OS_4}$: C, 29.4; H, 4.9; N, 6.9; S, 31.4%).

Reactions of (I).—*With oxygen compounds.* Reactions of (I) (0.1 g, 0.25 mmol) with the following compounds (*ca.* 0.8 mmol) were carried out in chloroform solution (10 cm^3) at *ca.* 20 °C: azoxybenzene; t-butyl nitrate; dimethyl sulphoxide; pyridine *N*-oxide; tetraethylammonium nitrate; dinitrogen oxide; triphenylphosphine oxide; and oxygen. Chloroform solutions of (I) were saturated with the gaseous reactants ($\mathrm{N_2O}$ and $\mathrm{O_2}$) and kept in a closed vessel containing the gases in three-fold molar excess. Reactions were followed until there was no further change indicated by e.s.r., i.r., and visible spectroscopy. Products were identified spectrophotometrically (i.r. and visible), and in some cases, by g.l.c. (dimethyl sulphide and pyridine) by comparison of retention times with those of authentic samples, by product isolation and analysis (triphenylphosphine, azobenzene, and nitrite), and by mass spectrometry (nitrogen).

With benzoylhydrazine. The product was a new compound, di-μ-sulphido-bis[(diethyldithiocarbamato-*SS′*)-(*N′*-benzohydrazide)oxomolybdenum(V)], $[\mathrm{O(PhCONHNH_2)(Et_2NCS_2)Mo(\mu\text{-}S)_2Mo(S_2CNEt_2)(NH_2NHCOPh)O}]$, (II).—Compound (I) (0.5 g) was added to a solution of benzohydrazide (0.5 g) in methanol (20 cm^3). The mixture was heated under reflux for 2 d. The solution was then evaporated to 10 cm^3 and the dark orange solid which separated was filtered off, washed with ice-cold methanol, and dried *in vacuo* (Found: C, 34.1; H, 4.2; Mo, 22.3; N, 9.9; S, 22.3. Calc. for $\mathrm{C_{24}H_{36}Mo_2N_6O_4S_6}$: C, 33.6; H, 4.2; Mo, 22.4; N, 9.8; S, 22.4%).

With triphenylphosphine sulphide and triphenylphosphine. The products from both reactions were di-μ-(diethyldithiocarbamato-*SS′*)-bis[bis(diethyldithiocarbamato-*SS′*) molybdenum(III)], $[\mathrm{(Et_2NCS_2)_2Mo(\mu\text{-}S_2CNEt_2)_2Mo(S_2CNEt_2)_2}]$, (III), and di-μ-oxo-bis[diethyldithiocarbamato-*SS′*)oxomolybdenum(V)], $[\mathrm{O(Et_2NCS_2)Mo(\mu\text{-}O)_2Mo(S_2CNEt_2)O}]$,

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

[2] R. C. Bray, *Proc. Climax 1st Internat. Conf. Chem. and Uses of Molybdenum*, ed. P. C. H. Mitchell, Climax Molybdenum Co. Ltd., London, 1973, p. 216; J. T. Spence, *Co-ordination Chem. Rev.*, 1969, **4**, 475.

[3] G. P. Haight, *Acta Chem. Scand.*, 1961, **15**, 2012. See also C. D. Garner, M. R. Hyde, F. E. Mabbs, and V. I. Routledge, *Nature*, 1974, **252**, 579.

[4] P. W. Schneider, D. C. Bravard, J. W. McDonald, and W. E. Newton, *J. Amer. Chem. Soc.*, 1972, **24**, 8640.

(IV). Compound (I) (0.35 g) was added to a solution of triphenylphosphine sulphide (0.26 g) in chloroform–ethanol (3 : 2, 25 cm^3). The solution was heated under reflux for 15 h whereupon a red-brown solution and a fine yellow precipitate were obtained. The components of the mixture were separated by chromatography on alumina. Elution with chloroform–ethanol (3 : 2) gave a red-brown solution which was evaporated to dryness. Triphenylphosphine sulphide was removed from the product by washing with toluene. The final product, compound (III), was a red-brown solid (Found: C, 33.4; H, 5.6; N, 7.4; S, 35.5. Calc. for $C_{30}H_{60}Mo_2N_6S_{12}$: C, 33.4; H, 5.5; N, 7.8; S, 35.6%). Subsequent elution with chloroform gave a yellow solid, compound (IV) (Found: C, 21.7; H, 3.7; Mo, 34.7; N, 5.0; S. 22.9. Calc. for $C_{10}H_{20}Mo_2N_2O_4S_4$: C, 21.7; H, 3.6; Mo, 34.6; N, 5.1; S, 23.2%). Compounds (III) and (IV) were similarly isolated when the reaction was carried out with triphenylphosphine.

Other Reactions.—Solutions of (I) in chloroform and suspensions in water did not react with hydrogen, carbon monoxide, nitrogen, azide ion, hydrazine, nitrogen monooxide, pyridine, and azobenzene. There were no spectroscopic changes and (I) was recovered unchanged from the reaction mixtures.

Physical Measurements.—U.v. and visible spectra were recorded for solutions with a Unicam SP 800 spectrophotometer. Diffuse-reflectance spectra of powdered solids were obtained against a magnesium oxide standard on a Unicam SP 700C spectrophotometer. I.r. spectra of solid compounds in Nujol mulls or KBr discs and of solutions in a cell with NaCl windows were recorded with Unicam SP 200 or Perkin-Elmer 457 spectrophotometers. E.s.r. spectra were obtained on a Varian E-3 spectrometer calibrated with 1,1-diphenyl-2-picrylhydrazyl (*g* 2.0037). ^{1}H N.m.r. spectra were recorded with Varian T-60 or Perkin-Elmer R-10 60 MHz spectrometers. Mass spectra were obtained on an A.E.I. MS12 spectrometer. G.l.c. was carried out on a Perkin-Elmer F11 gas chromatograph with a 2 m silicone gum-rubber column. Carbon, hydrogen, nitrogen, and sulphur were determined microanalytically. Molybdenum was analysed gravimetrically as $[MoO_2(ONC_9H_6)_2]$ after decomposing the complexes with concentrated nitric acid–concentrated sulphuric acid (1 : 1).

RESULTS AND DISCUSSION

Reactions with Oxygen and its Compounds.—The results are summarised in Table 1. Our object was to discover whether reaction occurred and, if so, to identify the products. We did not, at this stage, study the mechanisms of the reactions. Reactions were carried out under comparable conditions (*cf*. Table 1) and with an excess of the oxygen compound over the amount required to completely oxidise molybdenum(IV) to molybdenum(VI). The progress of reaction was followed visually and spectrophotometrically (i.r. and e.s.r.). Use of u.v. and visible spectroscopy to identify species in the solutions was not successful because of broad overlapping bands. In fact, the colour of the solutions was the best guide to the progress of the reactions. I.r. spectroscopy was used when ligand bands did not interfere.

TABLE 1

Reactions of oxygen compounds with $[MoO(S_2CNEt_2)_2]$,[a] $X^+ {-}O^- \longrightarrow X + O^{2-}$

Compound	Product (X) [b]	Reaction time [c] Max. e.s.r.	Completion	Observations [d]
C_5H_5NO	C_5H_5N		<1 min	pink → red → yellow; no e.s.r.
Bu^tONO_2	Bu^tONO		*ca.* 1 min	pink → yellow; no e.s.r.
Me_2SO	Me_2S	15 min	*ca.* 1 h	pink → purple → yellow; *g* 1.964, *a* 42 G
O_2	O^{2-}	3 h	24 h	pink → purple → yellow; *g* 1.964; i.r. 915 and 880 cm^{-1}
Ph_3PO	Ph_3P	5 h	3 d	pink → purple → yellow; *g* 1.964
N_2O	N_2 [e]	2 d		pink → purple; *g* 1.965; i.r. 935 and 915 cm^{-1}
PhNO:NPh	PhN:NPh	2 d		pink → purple; *g* 1.964
$[Et_4N][NO_3]$	$[Et_4N][NO_2]$ [f]		1 week	pink → yellow; no e.s.r.
$HCONMe_2$	No reaction			

[a] Compound (I) (0.1 g) was dissolved in chloroform (10 cm^3) and the oxygen compound added in a *ca*. three-fold stoicheiometric excess at *ca*. 20 °C. [b] Separated by evaporation to dryness and extraction with chloroform or by g.l.c. (pyridine and dimethyl sulphide) and characterised by analysis, i.r. spectroscopy, and chemical tests. Molybdenum-containing products were either $[MoO_2(S_2CNEt_2)_2]$ (yellow) or $[Mo_2O_3(S_2CNEt_2)_4]$ (purple) (see text). [c] Approximate times for the e.s.r. signal at *g* 1.964 to reach its maximum intensity (when observed) and for the reaction system to undergo no further change. [d] Colour changes, e.s.r. signals, and new i.r. bands observed during the reactions. [e] The mass spectrum of the gas above the solution was compared with that of N_2O. Values of *m*/*e* and, in parentheses, abundances relative to $[N_2O]^+$ were as follows: (product gas) 44 (100), $[N_2O]^+$; 30 (21), $[NO]^+$; 28 (134), $[N_2]^+$. (dinitrogen mono-oxide) 44 (100), $[N_2O]^+$; 30 (23), $[NO]^+$; and 28 (100), $[N_2]^+$.

Reduction products. From compounds $X^+{-}O^-$ the products were compounds X (Table 1), *i.e.* one oxygen atom was abstracted from each molecule of reactant. Covalent and ionic nitrate were reduced only to nitrite.

Molybdenum complexes formed. During the reactions the initial pink solution of (I) changed colour to purple and/or yellow (Table 1). The reactions with oxygen and N_2O were followed by i.r. spectroscopy. During the reactions a band at 960 cm^{-1}, assigned to the Mo–O stretching vibration of (I),[1] decreased in intensity. The yellow solution ultimately formed in the reaction with oxygen had new bands at 915 and 880 cm^{-1} which we assign to Mo–O stretching vibrations of the molybdenum(VI) compound $[MoO_2(S_2CNEt_2)_2]$.[5] The purple solutions had new bands at 935 and 915 cm^{-1} which increased in intensity as the 960 cm^{-1} band decreased. We assign these bands as Mo–O vibrations of the binuclear molybdenum(V) compound $[Mo_2O_3(S_2CNEt_2)_4]$.[5] In the reactions with oxygen the band at 935 cm^{-1} decreased in intensity as those at 915 and 880 cm^{-1} increased showing oxidation of the molybdenum(V)

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[5] R. N. Jowitt and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 1702.

compound to molybdenum(VI). The purple solutions also had a new band at 945 cm^{-1} which is absent in the spectra of known oxomolybdenum dithiocarbamato-compounds and so apparently arises from a new species. The band was absent from the spectrum of the purple solid obtained on evaporating to dryness the solution in the reaction with N_2O. The spectrum of this solid was identical with that of $[Mo_2O_3(S_2CNEt_2)_4]$. This compound was also isolated from the reaction with azoxybenzene which also did not proceed beyond the purple stage.

E.s.r. signals. The e.s.r. signals of reaction mixtures were recorded in e.s.r. tubes. As expected, the initial pink solution and the final yellow solutions did not give any signals. For reactions in which purple solutions were formed, e.s.r. signals were observed at *g* 1.964 and *a* 42 G which, as the reaction proceeded, increased in intensity to a maximum value and then decreased.*

Course of the reactions. Except with N_2O and azoxybenzene, the ultimate oxidation product of (I) was the molybdenum(VI) compound $[MoO_2(S_2CNEt_2)_2]$. Thus the overall reaction was oxygen-atom transfer to and two-electron oxidation of molybdenum(IV). In the

$$[MoO(S_2CNEt_2)_2] + X\text{–}O \longrightarrow [MoO_2(S_2CNEt_2)_2] + X \quad (1)$$

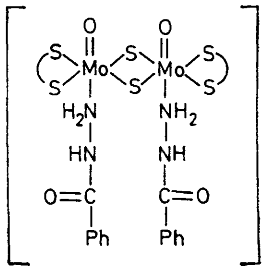
reactions with N_2O and azoxybenzene the product was the purple molybdenum(V) compound $[Mo_2O_3(S_2CNEt_2)_4]$. Formation of this compound was also observed during all but the fastest reactions (those with pyridine *N*-oxide and t-butyl nitrate) and could occur directly [equation (2)] or indirectly from $[MoO_2(S_2CNEt_2)_2]$ and unchanged (I) [equation (3)]. Reaction

$$2[MoO(S_2CNEt_2)_2] + X\text{–}O \longrightarrow [Mo_2O_3(S_2CNEt_2)_4] + X \quad (2)$$

$$[MoO(S_2CNEt_2)_2] + [MoO_2(S_2CNEt_2)_2] \longrightarrow [Mo_2O_3(S_2CNEt_2)_4] \quad (3)$$

(3) is known and is instantaneous compared with those reactions listed in Table 1.[6] We suggest that the purple molybdenum(V) compound is not, in fact, an intermediate [equation (2)] but is formed subsequent to the oxidation of part of the Mo^{IV} to Mo^{VI} [equation (3)]. Consistent with this suggestion is our observation(Table 1) that the purple compound is not formed when the overall reaction [equation (1)] is fast. Subsequently the molybdenum(V) compound could be slowly oxidised by changed oxygen compound. There remains the problem of the nature of the species responsible for the e.s.r. signal at *g* 1.964 and the new i.r. band at 945 cm^{-1}. The e.s.r. signal, which exhibits molybdenum hyperfine splitting, is presumably due to Mo^V but the observation of the signal does not necessarily imply that the species giving rise to the signal has any significance in the reactions. Indeed, there is no reason why oxygen-atom transfer to Mo^{IV} [equation (1)] should involve an intermediate molybdenum(V) species. We are currently carrying out detailed mechanistic studies of these reactions.

Reaction with Benzohydrazide.—The product of heating (I) with benzohydrazide, $PhCONHNH_2$, in methanol was the new compound (II). We were unable to obtain crystals suitable for *X*-ray crystallography and the proposed structure is based on analysis and physical measurements (Table 2). The apparent magnetic moment (0.7 B.M. at 20 °C) is consistent with interacting molybdenum(V) units in a bi- or poly-nuclear structure. The solid compound and solutions in methanol and chloroform gave no e.s.r. signals. Exposure of the solutions to air caused the appearance of an e.s.r. signal (*g* 1.980, *a* 36 G). The presence of a terminal oxide ligand was shown by a strong i.r. band at 965 cm^{-1}, which was not present in the spectra of the organic ligands, and is assigned to the Mo–O stretching vibration. The presence of diethyldithiocarbamate and benzohydrazide in a 1 : 1 ratio is shown by the intensity ratios of the ethyl and phenyl resonances in the n.m.r. spectrum (Table 1). The i.r. spectrum of the dithiocarbamate ligand was the same as in the starting compound (I). The benzohydrazide is apparently coordinated only through the NH_2 group and not through the C=O group since the carbonyl-stretching frequency in the complex (at 1 655 cm^{-1}) was virtually unchanged from the free ligand (1 660 cm^{-1}) (*cf.* a decrease of *ca.* 30 cm^{-1} when the CO group becomes bound to a metal ion).[7] Bonding *via* the NH_2 group is indicated by deshielding of the H(N) protons according to the n.m.r. spectra. The proposed structure is the simplest which is consistent with the evidence. The $Mo_2O_2S_2$ unit, which has been characterised by *X*-ray crystallography in other molybdenum(V) compounds,[8] is presumably formed *via* decomposition of dithiocarbamate ligands.



(II)

Reactions with Triphenylphosphine Sulphide and Triphenylphosphine.—With triphenylphosphine sulphide we hoped to effect oxidation of (I) accompanied by transfer of sulphur (analogous to the reaction with triphenylphosphine oxide). However, disproportionation occurred to a molybdenum(III) compound, [Mo$_2$-

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* 1 G = 10^{-4} T, 1 B.M. ≈ 9.27×10^{-24} A m^2.

[6] W. E. Newton, J. L. Corbin, D. C. Bravard, J. E. Searles, and J. W. McDonald, *Inorg. Chem.*, 1974, **13**, 1100; P. C. H. Mitchell and C. F. Pygall, unpublished work.

[7] M. F. Iskander, S. E. Zayan, M. A. Khalifa, and L. El-Sayed, *J. Inorg. Nuclear Chem.*, 1974, **36**, 551.

[8] A. Kay and P. C. H. Mitchell, *J. Chem. Soc.* (*A*), 1970, 2421; M. G. B. Drew and A. Kay, *ibid.*, 1971, 1846, 1850.

$(S_2CNEt_2)_6]$, (III), and a molybdenum(V) compound, $[Mo_2O_4(S_2CNEt_2)_2]$, (IV). Compound (III) has been

$$4[\mathrm{MoO(S_2CNEt_2)_2}] \longrightarrow [\mathrm{Mo_2O_4(S_2CNEt_2)_2}] + [\mathrm{Mo_2(S_2CNEt_2)_6}] \quad (4)$$

prepared before and was identical in every respect with previous preparations.[9] While our work was in progress Newton *et al.*[6] reported the preparation of compound (IV) from molybdenum pentachloride and sodium diethyldithiocarbamate. The compound gave no e.s.r. signals. Its i.r. spectrum is given in Table 3 and is consistent with the structure shown below which is analogous to the five-co-ordinate binuclear compounds of Mo^{V} with cysteine esters.[8] An analogous disproportionation occurred in the presence of triphenylphosphine. Although the phosphine compounds did not appear in the molybdenum-containing products and were recovered unchanged at the end of the reaction, the disproportionation did not occur in their absence.

TABLE 2

Properties of compound (II)

(*a*) ^{1}H N.m.r. spectra [a]

	δ/p.p.m.	Relative intensity	*J*/Hz	Assignment
$PhCONHNH_2$				
	4.13	(1.6)	broad [b]	$NH{\cdot}NH_2$
	7.45	1	2	C_6H_5 (*p*)
	7.65	2	2	C_6H_5 (*m*)
	7.80	2	4	C_6H_5 (*o*)
$[O(PhCONHNH_2)(Et_2NCS_2)Mo(\mu\text{-}S)_2Mo(S_2CNEt_2)(NH_2NHCOPh)O]$, (II)				
	1.30	6	7	CH_3
	3.82	4	7	CH_2
	2.93, 3.07	(0.5)	N.r.	$NH{\cdot}NH_2$
	7.40	3	N.r.	C_6H_5 (*m*, *p*)
	7.80	2	N.r.	C_6H_5 (*o*)

(*b*) I.r. spectrum [c]

1 655m [ν(C=O)]	1 600m	1 540m	1 502vs [ν($N=CS_2$)]
1 458m	1 435s	1 380m	1 385m
1 305m	1 275m	1 233s	1 208m
1 210m [ν(C–CN)]	1 170m	1 150m	1 095m
1 065m	1 000w [ν(C–S)]	965s [ν(Mo=O)]	845m
780m	700s		

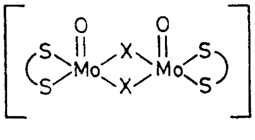
[a] Chemical shifts relative to tetramethylsilane (δ = 0) and proton coupling constants for solutions in $CDCl_3$ at *ca.* 20 °C; n.r. = not resolved. [b] Half width = 16 Hz. [c] Peak positions ($\bar{\nu}$/cm^{-1}), relative intensities (vs = very strong, s = strong, m = medium, and w = weak), and principal assignments.

TABLE 3

I.r. spectrum of the compound $[Mo_2O_4(S_2CNEt_2)_2]$, (IV) *

1 545vs[ν($N=CS_2$)]	1 460m	1 360m	1 295m	1 275s
1 200s[ν(C–CN)]	1 150m	1 095m	1 075m	1 065 (sh)
1 000m [ν(C–S)]	970vs and 955s [ν(MoO)]			845m
780m	710m[ν(MoO_2Mo)]			

* Peak positions ($\bar{\nu}$/cm^{-1}), relative intensities (sh = shoulder), and assignments of principal bands.



(IX) X = O or S

Conclusions.—The object of our work was to survey reactions of $[MoO(S_2CNEt_2)_2]$.

Addition reactions. Molybdenum in the compound has little tendency to expand its co-ordination number to six by undergoing addition reactions. We were unable to isolate adducts with pyridine, azobenzene, and PPh_3. The compound also did not react with carbon monoxide, nitrogen, and NO.

Oxidative-addition reactions. Compound (I) is oxidised to the molybdenum(VI) compound $[MoO_2(S_2CNEt_2)_2]$ by oxygen and oxygen compounds (Table 1). The reactions, in which one oxygen atom is transferred to molybdenum, presumably involve formation of a **1 : 1** adduct as the first step {*cf.* formation of a 1 : 1 adduct with, for example, diethyl azodicarboxylate which hydrolyses to $[MoO_2(S_2CNEt_2)_2]^4$}. Whether the reactions proceed directly from Mo^{IV} to Mo^{VI} or *via* a molybdenum(V) intermediate is not certain. Molybdenum(V) species observed in the reaction system could be produced by a secondary reaction (*cf.* p. 2554). Detailed mechanistic studies of these reactions are desirable.

Valency disproportionations. In the presence of PPh_3 or Ph_3PS, (I) disproportionates into dithiocarbamato-compounds of molybdenum(III), $[Mo_2(S_2CNEt_2)_2]$, and molybdenum(V), $[Mo_2O_4(S_2CNEt_2)]$. The type of compound formed, in particular the full co-ordination of Mo^{III} by sulphur, is in accordance with a general trend towards greater affinity for sulphur donors in lower oxidation states.[9] In this context we recall a redox equilibrium involving the dithiocarbamato-compounds of molybdenum-(IV), -(V), and -(VI) (see above). We now have facile equilibria between dithiocarbamato-compounds of molybdenum in oxidation states from III to VI involving both electron and oxygen-atom transfer.

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[5/997 *Received*, 28*th May*, 1975]

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[9] P. C. H. Mitchell and R. D. Scarle, *J.C.S. Dalton*, **1975**, 110.