Ligand and Induced Internal Electron Transfer Pathways to New Mo–S and W–S Dithiocarbamate Complexes

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Addition of tetra-alkylthiuram disulphides [$R_2NC(S)S–SC(S)NR_2$] to $Mo^{VI}S_4^{2-}$, $W^{VI}S_4^{2-}$ and $Mo^{VI}O_2S_2^{2-}$ yields the new complexes $Mo^{V}(S_2)(S_2CNR_2)_3$ and $W^{VI}S(S_2)(S_2CNR_2)_2$ and the known complex $Mo^{VI}O(S_2)(S_2CNR_2)_2$, respectively, revealing redox behaviour involving induced internal electron transfer and ligand electron transfer processes.

Molybdenum[1] and to a lesser extent tungsten[2] are capable of existing in several oxidation states when bound by sulphur ligands. Likewise, sulphur ligands can exist in several oxidation states.[3] The ability of sulphur ligands to undergo redox reaction while in the co-ordination sphere of Mo has been demonstrated in dinuclear and trinuclear systems.[4,5]

Recently, several examples have been reported in which the oxidation state of both the metal and the sulphur ligand changes during the course of the reaction.[6] One manifestation of this involves the reaction shown in equation (1) in which internal electron transfer from S to Mo is induced by the external oxidant RS–SR.[6b] The internal redox reaction explains what seems to be a paradox in that reagents acting as oxidants, RS–SR, can nevertheless lead to the reduction of molybdenum centres. An example in W–S chemistry involves reaction of WS_4^{2-} with elemental sulphur according to equation (2).[7] Clearly, oxidants with S–S bonds can lead, by reaction with hexavalent tetrathiometallates (MS_4^{2-} M=Mo,W), to new lower valent dinuclear M–S systems. In this communication we report that incorporation of the S–S

$$2Mo^{VI}S_4^{2-} + RS\text{–}SR \rightarrow Mo^{V}{}_2S_4(S_2)_2^{2-} + 2RS^- \qquad (1)$$

$$2W^{VI}S_4^{2-} + 5/8S_8 \rightarrow W^{V}{}_2S_4(S_4)_2^{2-} + S^{2-} \qquad (2)$$

group into a potentially chelating ligand leads to new mononuclear Mo–S and W–S systems. In the Mo–S case the new complex contains pentavalent Mo. In contrast, the W–S complex, through a fully ligand-based redox process, maintains hexavalent W, revealing an important difference between Mo and W in their redox ability.

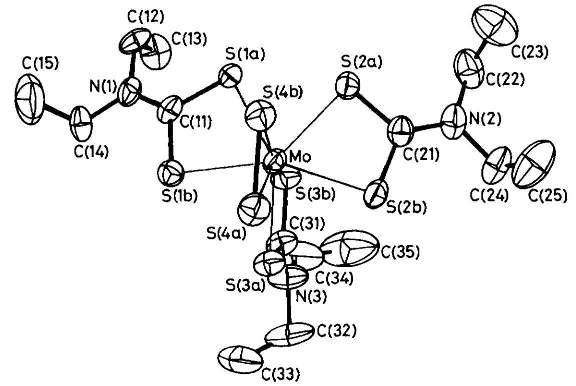


Figure 1. Structure of $Mo(S_2)[S_2CN(C_2H_5)_2]_3$. Key distances are Mo–S(1a) 2.534(2), Mo–S(1b) 2.523(2), Mo–S(2a) 2.553(2), Mo–S(2b) 2.516(2), Mo–S(3a) 2.496(2), Mo–S(3b) 2.507(2), Mo–S(4a) 2.445(2), Mo–S(4b) 2.418(2), and S(4a)–S(4b) 2.022(3) Å. *Crystal data: M* = 604.91, $T = 20 \pm 1$ °C, monoclinic, space group $C2/c$ (C_{2h}^6, No. 15), $a = 16.273(4)$, $b = 11.025(3)$, $c = 31.219(7)$ Å, $\beta = 94.57(2)°$, $U = 5584(2)$ Å^3, $Z = 8$, $D_c = 1.44$ g cm^{-3}. Of 6429 independent reflections, 3539 having $I > 3\sigma(I)$ were used in the final full matrix least squares refinement. Anisotropic thermal parameters were utilized for all non-hydrogen atoms. The structure was solved by direct methods and Fourier difference techniques. Anomalous dispersion corrections were applied to Mo and S atoms. Final $R = 0.049$, $R_w = 0.060$, G.O.F. = 1.39.

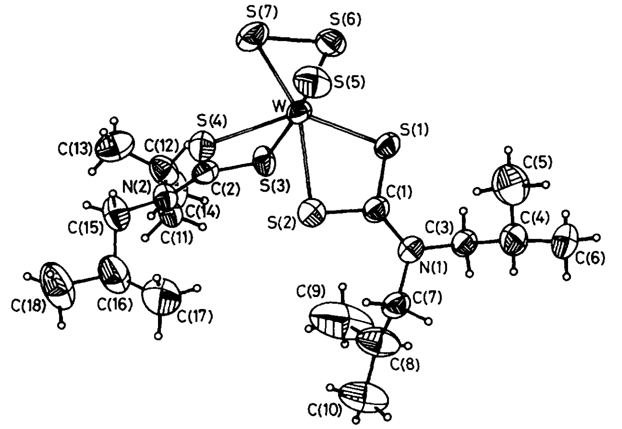
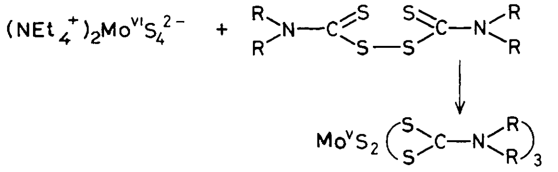


Figure 2. Structure of $WS(S_2)[(S_2CN(i\text{-}C_4H_9)_2]_2$. Key distances are W–S(1) 2.454(1), W–S(2) 2.528(2), W–S(3) 2.588(1), W–S(4) 2.506(1), W–S(5) 2.136(1), W–S(6) 2.366(3), W–S(7) 2.403(2), S(6)–S(7) 2.208(2) Å. *Crystal data: M* = 688.8, $T = 20 \pm 1$ °C, triclinic, space group $P\bar{1}(C_i^1$, No. 2), $a = 13.143(5)$, $b = 11.192(4)$, $c = 10.471(4)$ Å, $\alpha = 98.04(3)$, $\beta = 96.54(3)$, $\gamma = 111.04(3)+$, $U = 1400.9(9)$ Å^3, $Z = 2$, $D_c = 1.633$ g cm^{-3}. Of 7707 independent reflections ($3° \leq 2\theta \leq 58.7°$), 5817 having $I > 3\sigma(I)$ were used in the final cascade block diagonal matrix least squares refinement. Anisotropic thermal parameters were utilized for all non-hydrogen atoms. The structure was solved by Patterson and Fourier difference techniques. Methyl groups were refined as rigid rotors with CH bond length 0.96 Å. Other hydrogen atoms were included at fixed positions. Anomalous dispersion corrections were applied to W and S atoms. Final $R = 0.038$, $R_w = 0.037$, G.O.F. = 1.7.

Reaction of $Mo^{VI}S_4^{2-}$ with tetra-alkylthiuram disulphide, TMDS, leads to the brown Mo^V complex $Mo(S_2)(S_2CNR_2)_3$ (R=Et, Bu^i) in high yield. The reaction in equation (3)



(3)

proceeds smoothly at room temperature in anhydrous acetonitrile under argon using a ratio of five equiv. TMDS to two equiv. Mo. Although full mechanistic details are still not known, it is clear that the reaction involves reduction of both Mo (from VI to V) and TMDS (to the dithiocarbamate). Bound S^{2-} serves as the reductant, and is oxidized to S_2^{2-} in the process. The resultant air-sensitive pentavalent complex shows an e.s.r. signal [$\langle g \rangle = 1.980$, $\langle A \rangle (Mo^{95,97}) = 38$ G†], and has a characteristic i.r. mode [ν(S–S)]at 555 cm^{-1}. *X*-Ray diffraction reveals the eight-co-ordinate structure illustrated in Figure 1 (R=Et).‡§

Reaction of WS_4^{2-} under the same conditions with TMDS proceeds as shown in equation (4). The diamagnetic, air-

$$W^{VI}S_4^{2-} + TMDS \rightarrow W^{VI}S(S_2)(S_2CNR_2)_2 \qquad (4)$$

stable, green, mononuclear, seven-co-ordinate W^{VI} product shows ν(S–S) at 550 cm^{-1} and ν(W=S) at 500 cm^{-1}. The structure of the complex with R=Bu^i is shown in Figure 2.[8]‡§ Clearly, while internal redox reaction characterizes the formation of the Mo–S complex, the reaction of the W–S complex involves purely a ligand redox reaction. The distinction between MoS_4^{2-} and WS_4^{2-} in their reactions with TMDS illustrates the general tendency of Mo complexes to be more easily reduced than their W congeners.

To illustrate further the varied redox nature in these and related systems we treated $MoO_2S_2^{2-}$ with TMDS. The major product, $MoO(S_2)(S_2CNR_2)_2$, is the known[9] heptaco-ordinate Mo^{VI} complex whose structure is analogous to that of $W^{VI}S(S_2)(S_2CNR_2)_2$ reported above. The substitution of sulphido by oxo ligands leads in general to greater difficulty in reduction of the Mo centre[10] and therefore, ligand → ligand rather than ligand → metal electron transfer is favoured.

This work shows that induced internal redox and ligand redox processes lead to new mononuclear Mo–S and W–S complexes. Further, the differing redox ability of Mo and W

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† $1\ G = 10^{-4}\ T$

‡ *X*-Ray crystallography was carried out by Dr. C. S. Day of Crystalytics Co., P.O. Box 82286, Lincoln, NB, 68501. Data was obtained on a Four-circle Nicolet Autodiffractometer, using Mo-K_α radiation. All reflections were corrected for absorption, Lorentz, and polarization factors. Calculations were carried out using versions of the Nicolet (Syntex) E-XTL and SHELXTL software package as modified at Crystalytics Company. $R_w = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; G.O.F. (goodness of fit) = $[\Sigma w(|F_o|-|F_c|)^2/(NO-NV)]^{1/2}$ where NO = number of observations, NV = number of variables.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

may allow one to predict whether an internal L → Mo or purely ligand redox process will be favoured in a given case.

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References

1 E. I. Stiefel, *Progr. Inorg. Chem.*, 1977, **22**, 1; J. T. Spence, *Coord. Chem. Rev.*, 1983, **98**, 59; M. T. Pope, E. R. Still, and R. J. P. Williams, in 'Molybdenum and Molybdenum-containing Enzymes,' ed. M. P. Coughlan, Pergamon Press, New York, 1980, p. 3.

2 Z. Dori, *Progr. Inorg. Chem.*, 1981, **28**, 239.

3 R. C. Elder, M. J. Heeg, M. D. Payne, M. Trkula, and E. Deutsch, *Inorg. Chem.*, 1978, **17**, 431; S. I. Zhdanov in 'Encyclopedia of Electrochemistry of the Elements,' ed. A. J. Bard, vol. IV, Marcel Dekker, New York, 1975, p. 273; F. A. Cotton and G. Wilkinson, 'Advanced Inorganic Chemistry,' Fourth Edition, Wiley, New York, 1980, pp. 177—189.

4 K. F. Miller, A. E. Bruce, J. L. Corbin, S. Wherland, and E. I. Stiefel, *J. Am. Chem. Soc.*, 1980, **102**, 5102; A. Müller, B. G. Bhattacharya, N. Mohan, and B. Pfefferhorn, *Z. Anorg. Allg. Chem.*, 1979, **454**, 118.

5 T. R. Halbert, K. McGauley, W.-H. Pan, R. S. Czernuszewicz, and E. I. Stiefel, *J. Am. Chem. Soc.*, 1984, **106**, 1849; A. Müller and U. Reinsch, *Angew. Chem., Int. Ed. Engl.*, 1980, **19**, 72.

6 (a) W. Clegg, N. Mohan, A. Müller, A. Neumann, W. Ritter, and G. M. Sheldrick, *Inorg. Chem.*, 1980, **19**, 2026; E. D. Simhon, N. C. Baenziger, M. Kanatzidis, M. Draganjac, and D. Coucouvanis, *J. Am. Chem. Soc.*, 1981, **103**, 128; (b) W.-H. Pan, M. A. Harmer, T. R. Halbert, and E. I. Stiefel, *ibid.*, 1984, **106**, 459.

7 S. A. Cohen and E. I. Stiefel, *Inorg. Chem.*, submitted for publication.

8 Tungsten dithiocarbamate complexes believed to adopt this structure have also have been prepared recently from the reaction of $W(CO)_3(dithiocarbamate)_2$ and SO_2; J. A. Broomhead, XXIII International Co-ordination Chemistry Conference, Boulder, CO, August, 1984, Poster Fp 62—3.

9 K. Leonard, K. Plute, R. C. Haltiwanger, and M. R. DuBois, *Inorg. Chem.*, 1979, **18**, 3246; J. Colin-Dirand, L. Ricard, R. Weiss, and M. Schappacher, *J. Less-Common. Met.*, 1977, **54**, 91.

10 F. A. Schultz, V. R. Ott, P. S. Rolison, D. C. Bravard, J. W. McDonald, and W. B. Newton, *Inorg. Chem.*, 1978, **17**, 1758.