Thiol Exchange for MO^{3+} (M = Mo or W) Centres; Synthesis and Structure of $[PPh_4][MO(SCH_2CH_2S)_2]$

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Stoicheiometric thiol exchange between $[MO(SPh)_4]^-$ (M = Mo or W) and $HSCH_2CH_2SH$ provides a convenient synthesis for the $[MO(SCH_2CH_2S)_2]^-$ complexes: the structures of the $[PPh_4]^+$ salts of these anions have been determined to provide a clear structural comparison between these homologues [the two anions have very similar dimensions Mo–O 1.678(5), W–O 1.641(10), Mo–S 2.372(3), W–S 2.363(6) Å]; on the basis of e.s.r. spectroscopic studies, it is concluded that $[MoO(SCH_2CH_2S)_2]^-$ is formed when $[MoO_4]^{2-}$ reacts with $HSCH_2CH_2SH$ *and* when this dithiol reacts with the oxidised molybdenum centre of xanthine oxidase.

The nature of the molybdenum centre in the oxomolybdoenzymes continues to attract much attention.[1] The ligation of molybdenum by sulphur in these enzymes has been generally accepted for some 20 years, especially since the studies of Meriwether *et al.*[2] who demonstrated the qualitative similarity in the e.s.r. parameters of the molybdenum signals observed for xanthine oxidase and those obtained by reacting $Na_2[MoO_4]$ with several thiols, including ethane-1,2-dithiol. This postulation of sulphur ligation was subsequently extended to other oxomolybdoenzymes, since they display similar molybdenum e.s.r. spectra[3] and possess a common molybdenum-containing cofactor (Moco),[4] then reinforced by molybdenum *K*-edge EXAFS studies,[5] and is consistent with the latest ideas concerning the nature of Moco.[6] Although the work of Meriwether *et al.*[2] was very influential and these workers obtained some indication of the thiol : molybdenum ratio of the reaction products, these complexes have remained uncharacterised.

As part of our systematic studies of the chemistry of molybdenum relevant to the nature and behaviour of this metal in enzymes, we have found that $[PPh_4][MoO(SPh)_4]$[7] reacts with 2 equivalents of ethane-1,2-dithiol, in CH_2Cl_2 under a dinitrogen atmosphere, to produce $[PPh_4][MoO(SCH_2CH_2S)_2]$ (**1**). This anion has been obtained previously, by reaction of an Mo^{VI} butanediolato-complex with $^-SCH_2CH_2S^-$ in MeOH, but not structurally characterised.[8] Thiol exchange provides an alternative and convenient synthesis; the process, as monitored by e.s.r. spectroscopy, is essentially quantitative. Black crystals of (**1**) were obtained by controlled diffusion of Et_2O into a CH_2Cl_2 solution. Black crystals of $[PPh_4][WO(SCH_2CH_2S)_2]$ (**2**) were obtained in an analogous manner from $[PPh_4][WO(SPh)_4]$. *X*-Ray crystallographic studies† have been accomplished for

† Crystals of (**1**) and (**2**) are isomorphous and isostructural: $C_{28}H_{28}MOPS_4$ (M = Mo or W), orthorhombic, space group *Pbca*, *Z* = 8: (**1**) *a* = 19.710(1), *b* = 18.881(1), *c* = 15.075(1) Å, *U* = 5610.1 Å^3, D_c = 1.505 g cm^{-3}, *F*(000) = 2600, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 0.82 mm^{-1}, crystal size 0.65 × 0.50 × 0.38 mm; (**2**) *a* = 19.690(1), *b* = 18.897(1), *c* = 15.164(1) Å, *U* = 5642.2 Å^3, D_c = 1.703 g cm^{-3}, *F*(000) = 2856, Mo-K_α radiation, λ = 0.71073 Å, μ(Mo-K_α) = 4.54 mm^{-1}, crystal size 0.75 × 0.23 × 0.08 mm. The structures were solved by normal heavy-atom methods and refined by weighted least-squares [$w^{-1} = \sigma^2(F) + gF^2$; (**1**) *g* = 0.00032, (**2**) *g* = 0.00003]. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included with all C–H = 0.96 Å; aromatic hydrogens were placed on the external bisectors of ring angles and aliphatic hydrogens included with H–C–H = 109.5°. The refinement for (**1**)[(**2**)] converged with *R* = 0.0687 [0.0674] and R_w = 0.0718 [0.0564] for 3607 [2654] unique empirical-absorption-corrected reflections with $F_o \geq 4\sigma(F_o)$. Data were collected on a Siemens AED2 diffractometer with a graphite monochromator. An ω/θ scan was employed, $2\theta_{max.}$ = 50°. Analysis and refinement was accomplished using the SHELXTL programs[16] and complex scattering factors were taken from ref. 17.

Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1, 1986.

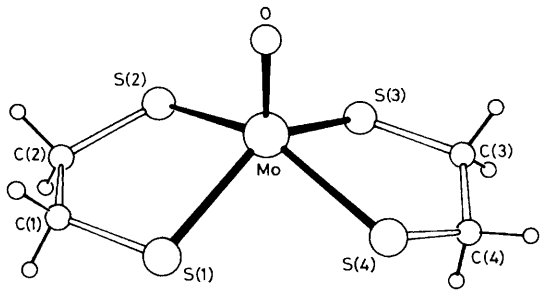

Figure 1. Structure of the $[MoO(SCH_2CH_2S)_2]^-$ anion.

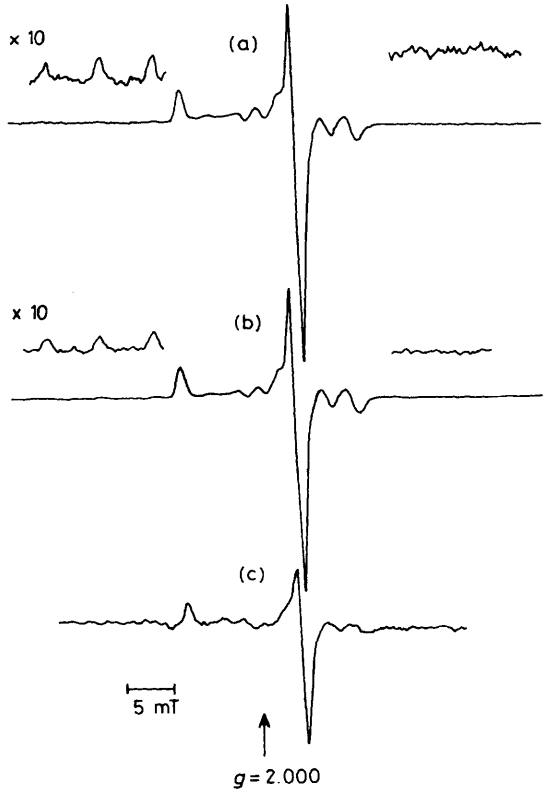

Figure 2. Comparison of *X*-band molybdenum(v) e.s.r. spectra recorded for solutions at 77 K: (a) $HSCH_2CH_2SH$ plus $Na_2[MoO_4]$ in H_2O/EtOH/MeCN (10:10:1); (b) $[PPh_4][MoO(SCH_2CH_2S)_2]$ in H_2O/EtOH/MeCN (10:10:1); (c) oxidised xanthine oxidase in 2.3 M $[NH_4]_2[SO_4]$ containing *ca.* 0.02% sodium salicylate plus $HSCH_2CH_2SH$/EtOH. Having regard to the amounts of molybdenum present, the three signals are of comparable intensity.

(**1**) and (**2**) to define the structure of these anions and to provide a clear comparison between these homologous Mo^V and W^V complexes.

The structure of the anion of $[PPh_4][MoO(SCH_2CH_2S)_2]$ is shown in Figure 1 and the corresponding tungsten complex has an essentially identical geometry. Selected dimensions of the two anions are compared in Table 1. These anions have a structure which closely resembles that of $[VO(SCH_2CH_2S)_2]^{2-}$.[9] Dimensions of the anion of (**1**) closely resemble the corresponding values of $[MoO(SPh)_4]^-$ [7] and $[MoO(SCH_2CH_2CH_2S)_2]^-$.[10] $[WO(SCH_2CH_2S)_2]^-$ is the first $W^VO(thiolate)_4$ complex to be structurally characterised.

Table 1. Comparison of selected dimensions[a] (Å,°) of $[MO(SCH_2CH_2S)_2]^-$ (M = Mo or W) complexes.

	Mo	W
M–O	1.678(5)	1.641(10)
M–S	2.372(3)	2.363(6)
S–C	1.76(1)	1.75(2)
Bite distance S · · · · S[b]	3.181(5)	3.177(8)
Displacement of M from S_4 plane	0.760(1)	0.739(2)
O–M–S	108.8(2)	108.3(4)
S–M–S_{cis}[c]	84.6(1)	84.5(2)
M–S–C	104.6(4)	105.2(8)

[a] E.s.d.s given in parentheses represent the precision of individual values rather than their concordance. [b] The two chelate rings in each complex have a different conformation, the S(1)–S(2) ligand is an envelope with an MoS_2 flap and the S(3)–S(4) ligand has a twist conformation. [c] There is no significant difference between the intra- and inter-ligand S–M–S_{cis} angles.

As expected, in view of the similar size of Mo^V and W^V,[11] the two anions have very similar dimensions, the Mo–O and Mo–S bond lengths being slightly but not significantly longer than their tungsten counterparts. The closest comparative structure data available are those for $[AsPh_4][MoOCl_4]$[12] and $[PPh_4][WOCl_4]$,[13] the anions of which involve Mo–O and W–O bonds of length 1.610(10) and 1.676(7) Å, respectively; the Mo–Cl and W–Cl bonds are of length 2.333(3) and 2.379(1) Å, respectively.

Both (**1**) and (**2**) show the expected e.s.r. activity. The *Q*-band e.s.r. spectrum of a powdered sample of (**1**) at *ca.* 293 K is indicative of rhombic symmetry with *g*-values of 2.025, 1.989, 1.983 ($\bar{g}$ = 1.999). The *X*-band e.s.r. spectrum of (**1**) in MeCN at *ca.* 293 K is typical of that of a mobile Mo^V species with $\bar{g}$ = 1.999 and $\bar{A}$ = 30.3 × 10^{-4} cm^{-1}; at 77 K in this solvent a rhombic signal was observed with *g*-values of 2.012, 1.997, and 1.975 ($\bar{g}$ = 1.995). The room temperature data are in excellent agreement with those reported previously[14] for the species obtained by aerial oxidation of $[MoO(SCH_2CH_2S)_2]^{2-}$ but the concordance of the frozen solution data is poorer. The e.s.r. spectrum of (**2**) in MeCN at 77 K manifests *g*-values of 2.105, 1.919, and 1.894 ($\bar{g}$ = 1.974).

Repetition of an experiment performed by Meriwether *et al.*, in which $HSCH_2CH_2SH$ was added to a solution of $Na_2[MoO_4]$ in H_2O/EtOH (1:1) produced an e.s.r. active species, the spectrum of which, recorded at *X*-band for a sample at 77 K, was in agreement with the previous[2] results; *g* = 2.047, 1.978, 1.974 ($\bar{g}$ = 2.000). This spectrum remained unchanged for a solvent of composition H_2O/EtOH/MeCN (10:10:1) and (Figure 2) is indistinguishable from that obtained for (**1**) in this medium at 77 K. Therefore, we conclude that the e.s.r. active species generated by Meriwether *et al.*[2] with $HSCH_2CH_2SH$ was $[MoO(SCH_2CH_2S)_2]^-$, an interpretation consistent with the 2:1 thiol:molybdenum ratio and the 'symmetrical square-planar arrangement of the four sulphur atoms about the molybdenum' predicted by these workers. This conclusion extends to the observations of Hawkes and Bray,[15] who showed that $HSCH_2CH_2SH$ binds molybdenum from inactivated (air-oxidised) Moco and converts it in high yield into a free Mo^V complex. Also, we have demonstrated that oxidised xanthine oxidase (Sigma, activity 0.5 units/mg protein) in 2.3 M aqueous $[NH_4]_2[SO_4]$ containing *ca.* 0.02% sodium salicylate reacts with $HSCH_2CH_2SH$ to produce an e.s.r. active species, the spectrum of which (Figure 2) is virtually

indistinguishable from that of $[MoO(SCH_2CH_2S)_2]^-$. Thus, ethane-1,2-dithiol, in addition to acting as a reductant, appears to be capable of displacing the ligands from the oxidised molybdenum centre of xanthine oxidase to form $[MoO(SCH_2CH_2S)_2]^-$, presumably by thiol exchange.

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References

1 'Molybdenum Enzymes,' ed. T. G. Spiro, John Wiley, New York, 1985.
2 L. S. Meriwether, W. F. Marzluff, and W. G. Hodgson, *Nature*, 1966, **212**, 465.
3 R. C. Bray, 'Biological Magnetic Resonance,' eds. L. J. Berliner and J. Reuben, Vol. 2, Plenum, New York, 1980, pp. 45—84 and references therein.
4 P. T. Pienkos, V. K. Shah, and W. J. Brill, *Proc. Natl. Acad. Sci. USA*, 1977, **74**, 5468.
5 S. P. Cramer, 'Advances in Inorganic and Bioinorganic Mechanisms,' ed. A. G. Sykes, Vol. 2, Academic, London, 1983, pp. 259—316 and references therein.
6 J. L. Johnson and K. V. Rajagopalan, *Proc. Natl. Acad. Sci. USA*, 1982, **79**, 6856.
7 I. W. Boyd, I. G. Dance, K. S. Murray, and A. G. Wedd, *Aust. J. Chem.*, 1978, **31**, 279; J. R. Bradbury, M. F. Mackay, and A. G. Wedd, *ibid.*, p. 2423.
8 R. J. Burt, J. R. Dilworth, G. J. Leigh, and J. A. Zubieta, *J. Chem. Soc., Dalton Trans.*, 1982, 2295.
9 D. Szeymies, B. Krebs, and G. Henkel, *Angew. Chem., Int. Ed. Engl.*, 1984, **23**, 804; R. W. Wiggins, J. C. Huffman, and G. Christou, *J. Chem. Soc., Chem. Commun.*, 1983, 1313; J. K. Money, J. C. Huffman, and G. Christou, *Inorg. Chem.*, 1985, **24**, 3297.
10 P. T. Bishop, J. R. Dilworth, J. Hutchinson, and J. A. Zubieta, *J. Chem. Soc., Chem. Commun.*, 1982, 1052.
11 R. D. Shannon, *Acta Crystallogr., Sect. A*, 1976, **32**, 751.
12 C. D. Garner, L. H. Hill, F. E. Mabbs, D. L. McFadden, and A. T. McPhail, *J. Chem. Soc., Dalton Trans.*, 1977, 853.
13 D. Fenske, K. Stahl, E. Hey, and K. Dehnicke, *Z. Naturforsch, Teil B*, 1984, **39**, 850.
14 P. C. H. Mitchell and C. F. Pygall, *Inorg. Chim. Acta*, 1979, **33**, L109.
15 T. R. Hawkes and R. C. Bray, *Biochem. J.*, 1984, **222**, 587.
16 G. M. Sheldrick, SHELXTL: an integrated system for solving, refining, and displaying crystal structures from diffraction data, University of Göttingen, 1978.
17 'International Tables for X-Ray Crystallography,' Kynoch Press, Birmingham 1974, Vol. 4, pp. 99, 149.