Chemical Characterization and *X*-Ray Crystal Structure of a Trigonal Prismatic Mo^{IV} Complex with Mercapto- and Sulphide-sulphur Donors [Mo(SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$]

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Summary. Reaction of MoCl$_5$ with 2-mercaptoethyl sulphide, (HSCH$_2$CH$_2$)$_2$S, (mes), yields a Mo^{IV} complex [Mo(mes)$_2$], which possesses trigonal prismatic geometry through co-ordination to both mercapto- and sulphide-sulphur donors, the complex displays well behaved redox processes, which may be characteristic of certain Mo–thiolate systems.

THE chemistry of molybdenum with sulphur-containing ligands continues to receive a great deal of attention because of the possible relationship of these species to the redox-active molybdo-enzymes.[1,2] The suggestions of cysteinyl-sulphur co-ordination for a number of molybdo-enzymes, based on early e.s.r. studies,[3] have been substantiated by recent EXAFS investigations.[4–7] In sulphite oxidase[5,6] and xanthine oxidase,[7] the molybdenum is bound to a mixture of oxo and sulphur ligands whereas oxo-co-ordination is absent in nitrogenase, the molybdenum co-ordination sphere apparently being composed of sulphur donors and an iron–sulphur cluster.[4] In addition, there is some evidence that sulphide-sulphur co-ordination may be implicated in the stabilization of the Mo^{IV} state in the oxidases.[6]

We here report the preparation of [Mo(SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$], [Mo(mes)$_2$], a complex displaying trigonal prismatic geometry about Mo^{IV} co-ordinated to both thiolate and sulphide-sulphur donors.

Although reaction with Mo^{IV}–oxo species such as [MoO$_2$(acac)$_2$], yielded only the dimeric Mo^V species [Mo$_2$O$_3$(mes)$_2$],[8] reaction of (mes) in 2:1 molar ratio with MoCl$_5$ in CH$_2$Cl$_2$ yielded a mixture of products. Careful chromatography on alumina, using 3:1 CH$_2$Cl$_2$–MeOH as eluant, resulted in isolation of a dark green diamagnetic complex [Mo(mes)$_2$]. The i.r. spectrum of this complex showed bands at 930 and 838 cm^{-1} attributed to ν(C–S) and bands at 457 and 428 cm^{-1} characteristic of ν(Mo S). The electronic spectrum showed absorbances at 622, 444, 389, and 331 nm with extinction coefficients of 1·1 × 10^3, 4·8 × 10^3, 6·3 × 10^3, and 4·4 × 10^3, respectively. The low energy peak has been tentatively assigned to a *d–d* transition, while the three more intense absorption bands are probably S→Mo charge transfer bands. The spectrum is qualitatively similar to those previously reported for trigonal prismatic tris-dithiomaleonitrile complexes.[9]

Crystal data. [Mo(SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$], monoclinic, space group $P2_1$, with a = 8·284(4), b = 14·793(5), c = 12·184(4) Å, β = 103·72(2)°, U = 1450·2, D_c = 1·83 g cm^{-3}, D_{obs} = 1·83(2) g cm^{-3}, Z = 4 (two molecules per asymmetric unit), F(000) = 808·0. The structure analysis is based on 1579 independent reflections with $(I_{obs}) > 2·58\sigma(I_{obs})$ (Mo-K_α, μ = 16·76 cm^{-1}) and R is currently 0·067.†

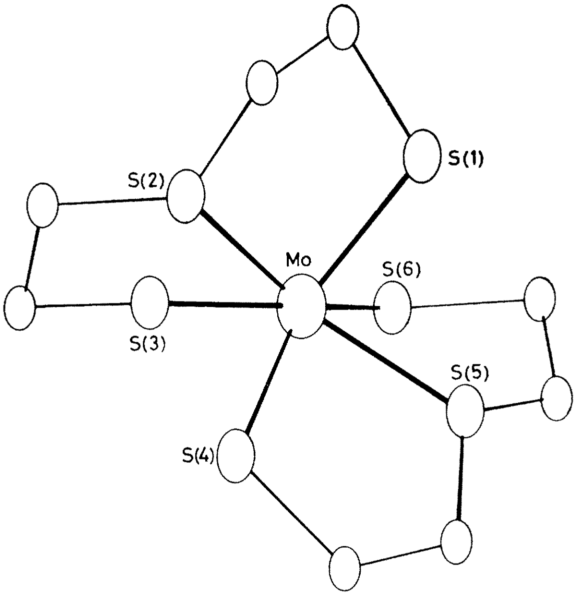

FIGURE 1. A perspective view of the conformation of one molecule of the asymmetric unit the stereochemistry of the second molecule is essentially identical. The relevant bond lengths and angles for the [Mo(mes)$_2$] complex are Mo–S (thio ether) 2·427(8) (av) Mo–S (mercapto) 2·361(9) Å (av) ∠S(1)–Mo–S(2) 87·0(4) ∠S(1)–Mo–S(6) 92·1(3) ∠S(2)–Mo–S(6) 83·8(4) ∠S(3)–Mo–S(4) 83·3(3) ∠S(3)–Mo–S(5) 81·3(3), ∠S(4)–Mo–S(5) 78·7(5) ∠S(1)–Mo–S(4) 78·1(4) ∠S(2)–Mo–S(3) 79·3(3) ∠S(5)–Mo–S(6) 78·1(3) ∠S(1)–Mo–S(3) 129·0(4) ∠S(1)–Mo–S(5) 138·6(4) ∠S(2)–Mo–S(4) 141·9(4) ∠S(2)–Mo–S(5) 130·7(3) ∠S(6)–Mo–S(4) 131·0(4) ∠S(6)–Mo–S(3) 133·9(4)°

The asymmetric unit contains two molecules [Mo(SCH$_2$CH$_2$SCH$_2$CH$_2$S)$_2$] of essentially identical stereochemistries. Figure 1 demonstrates the compressed trigonal prismatic geometry about one Mo^{IV} centre with pertinent bond lengths and angles displayed in the caption.

The polyhedron for this bis(tridentate ligand) complex conforms closely to the criteria establishing trigonal prismatic geometry, the average torsion angle between the triangular faces S(1)S(2)S(6) and S(4)S(4)S(5) is *ca.* 5°, significantly closer to the trigonal prismatic limit of 0° than to the ideal octahedral value of 60°,[10] the ratio of the average triangular face edge length to the distance between the triangular faces is 1·06 suggesting a trigonal prism compressed along the pseudo C_3 axis,[11] the shape-determining dihedral angles associated with the edges labelled *e* in Figure 2, average 7·8°, is consistent with the rectangular faces of the trigonal prism.[12]

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

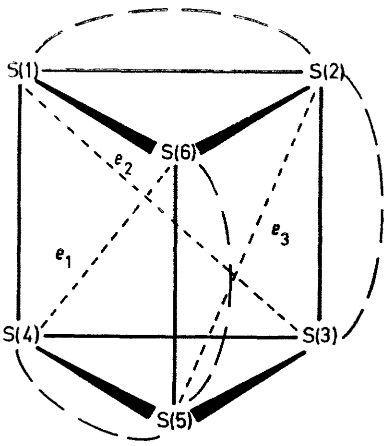

FIGURE 2 Schematic representation of the co-ordination polyhedron, showing the crossover pattern of tridentate ligand co-ordination The labelled edges define the shape-determining dihedral angles ∠S(1)S(2)S(3)–S(1)S(3)S(4), 12·5, ∠S(2)S(3)-S(5)–S(2)S(5)S(6), 3·0, ∠S(1)S(6)S(4)–S(4)S(5)S(6), 7·9° The dihedral angle between the triangular faces S(1)S(2)S(6) and S(3)S(4)S(5) is 2·4° Intramolecular distances defining the polyhedral edge lengths are S(1) ··· S(2), 3·24, S(1) ··· S(6), 3·39, S(2) ··· S(6), 3·19, S(4) ··· S(5), 3·02, S(4) ··· S(3), 3·18, S(3) ··· S(5), 3·14, S(1) ··· S(4), 2·95, S(2) ··· S(3), 3·07, S(5) ··· S(6), 3·02 Å

As illustrated in Figure 2, the tridentate ligands do not occupy opposite triangular faces of the trigonal prism, but rather cross over to span the triangular faces The compression of the trigonal prism along its pseudo-C_3 axis is, in part, a result of the steric constraints imposed by this mode of ligand folding

[Mo(mes)$_2$] is the first example, to our knowledge, of an Mo^{IV} complex with ligands possessing no extensive delocalization, i e, 'innocent' or non-dithiolene types,[13] exhibiting trigonal prismatic geometry

An unusual feature of the complex is the reversible nature of the electronic processes, demonstrating yet again that complexes of Mo in its higher oxidation states with saturated linear thiolate ligands are capable of sustaining well-behaved redox activity [14] The complex undergoes a reversible one-electron oxidation at +0·53 V and a reversible one-electron reduction at −1·07 V

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[1] J T Spence, *Co-ord Chem Rev*, 1969, **4**, 475

[2] E I Stiefel, *Progr Inorg Chem*, 1977, **22**, 1

[3] S P Vincent and R C Bray, *Biochem J*, 1978 **171**, 639

[4] S P Cramer K O Hodgson W O Gillum and L E Mortenson, *J Amer Chem Soc*, 1978, **100** 3398 S P Cramer, W O Gillum, K O Hodgson, L E Mortenson, E I Stiefel, J R Chisnell, W J Brill, and V K Shah *J Amer Chem Soc*, 1978, **100**, 3814

[5] S P Cramer H B Gray and K V Rajagopalan *J Amer Chem Soc* 1979, **101**, 2772

[6] J M Berg K O Hodgson S P Cramer, J L Corbin, A Elsberry, N Pariyadath, and E I Stiefel, *J Amer Chem Soc*, 1979, **101**, 2774

[7] T D Tullius, D M Kurta, Jr, S D Conradson, and K O Hodgson, *J Amer Chem Soc*, 1979, **101**, 2776

[8] J Hyde L Magin, and J Zubieta 'Stereodynamics of Molecular Systems, ed R Sarma, Pergamon, New York, 1979, pp 227—248

[9] G F Brown and E I Stiefel, *Inorg Chem*, 1973, **12**, 2140 and references therein

[10] R Eisenberg, *Progr Inorg Chem*, 1970, **12**, 295, and references therein

[11] E I Stiefel and G F Brown, *Inorg Chem*, 1972, **11**, 434

[12] E L Muetterties and L J Guggenberger, *J Amer Chem Soc*, 1974, **96**, 1748

[13] C K Jorgensen, *Inorg Chem Acta Rev*, 1968, **2**, 65

[14] N Kim, S Kim, P Vella, and J Zubieta, *Inorg Nuclear Chem Letters*, 1978, **14**, 457