

X-Ray Crystal Structure of Bis(tetraethylammonium)Di- μ -thio-[bis(phenylthio)-ferrate(III)][dithiomolybdate(V)], $[\text{Et}_4\text{N}]_2[(\text{PhS})_2\text{FeMoS}_4]$: a Dinuclear Complex with the FeMoS_2 core

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Summary An X-ray crystallographic investigation shows that the dinuclear anion $[(\text{PhS})_2\text{FeMoS}_4]^{2-}$ consists of two edge-sharing MS_4 tetrahedra ($M = \text{Mo}$ and Fe) and the FeS_2Mo planar unit.

NITROGENASE, an enzyme that catalyses the reduction of N_2 to ammonia is composed of two proteins. An iron protein and a molybdenum-iron protein (MoFe). Recently, the isolation of an iron-molybdenum cofactor (Fe-Mo-co) from the MoFe component of nitrogenase has been described.¹ The Fe:Mo:S ratio in the cofactor has been determined to be *ca.* 8:1:6. The Fe-Mo-co in various nitrogen fixing organisms seem to be very similar² and extracts of the MoFe component from inactive mutant strains of nitrogen fixing bacteria are activated by the Fe-Mo-co.¹

Molybdenum *K*-edge X-ray absorption fine structure (EXAFS) analysis of the MoFe protein of nitrogenase³ and of the Fe-Mo-co⁴ have shown that the sites that contain molybdenum are very similar and consistent with a Mo-Fe-S aggregate. The data also rule out the presence of doubly-bound oxygen (Mo-O) (bond length 1.6–1.8 Å).

† Mössbauer spectra, magnetic properties, contact shifted n.m.r. spectra, and electrochemical characteristics of this compound will be reported in a forthcoming publication.

With the structure of the Mo-Fe-S aggregate subject to speculation at present, two independent reports have appeared concerning two similar Fe-Mo-S complexes: one having the stoichiometry $[\text{Mo}_2\text{Fe}_8\text{S}_9(\text{SEt})_8]^{3-}$,⁴ and the other, $[\text{Mo}_2\text{Fe}_8\text{S}_8(\text{SPh})_8]^{3-}$.⁵ For both, the crystal structures reveal two Fe_3MoS_4 cubanes bridged at the molybdenum sites *via* S^{2-} or RS^- groups. The EXAFS analysis of the Mo centre in the former of the two complexes is very similar to that obtained for the Fe-Mo-co and suggests that fragments of this complex may be identical to fragments in Fe-Mo-co and the nitrogenases.⁴

In this communication we report on the crystal structure of a new Fe-Mo-S complex of the stoichiometry $[\text{Et}_4\text{N}]_2[(\text{PhS})_2\text{FeMoS}_4]$ (**1**). The complex (**1**) was obtained by the reaction of $[\text{MoS}_4]^{2-}$ with $[\text{Fe}(\text{SPh})_4]^{2-}$ (1:1)⁶ in dimethylformamide. The visible spectrum of this paramagnetic compound $[\mu_{\text{eff}}^{\text{calc.}}] = 4.95 \text{ B.M.}$ at 294 K) is characterized by five absorptions at 620sh, 550sh, 487 ($\epsilon = 8645$), 425 ($\epsilon = 7773$), and 330 ($\epsilon = 14705$) nm.†

Crystal data: Dark red, single crystals of (**1**) are monoclinic, space group $\text{P}2_1/c$, $a = 10.940(6)$, $b = 10.839(6)$,

$c = 31.009(9)$ Å, $\beta = 97.23(8)$; $Z = 4$. Single crystal, X-ray diffraction data were collected on a Picker-FACS 1, four-circle diffractometer using Cu- K_{α} radiation. The solution, by heavy atom Patterson and Fourier techniques, and refinement by full-matrix least-squares methods was based on 1719 unique reflections. Anisotropic temperature factors for the Mo, Fe, and S atoms were used and at the current stage of refinement with all atoms present in the asymmetric unit, $R = 0.082$.[‡]

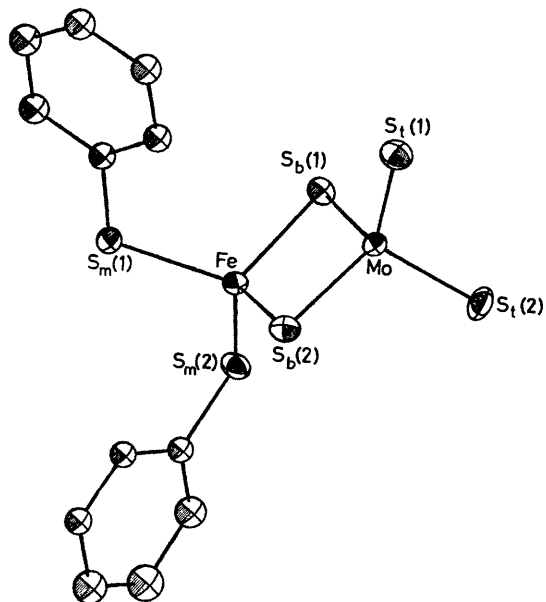


FIGURE. Structure of the $[(\text{PhS})_2\text{FeMoS}_4]^{2-}$ anion. Thermal ellipsoids as drawn by ORTEP (C. K. Johnson, ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tennessee, 1965) represent the 50% probability surfaces.

The structure of the anion of (1) is shown in the Figure. It can be described as a tetrahedral complex of iron of the type $[\text{Fe}(\text{SPh})_2\text{L}]^{2-}$ where $\text{L} = \text{tetrahedral MoS}_4^{2-}$ unit. The SMoS angles are in the range $104.5(3)$ – $116.6(3)^\circ$ with a mean value of 109.2° and a standard deviation from the mean of 2.4° . In the FeS_4 tetrahedron, the SFeS angles are in the range $102.0(3)$ – $116.9(3)^\circ$ with a mean value of 109.4° and a standard deviation of 6.2° . The FeS_2Mo rhombus is essentially planar with dimensions (Table)

TABLE. Comparison of some interatomic distances* (Å) and angles ($^\circ$) in the $[(\text{PhS})_2\text{FeMoS}_4]^{2-}$ and $[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}p\text{-tolyl})_4]^{2-}$ anions.

$[(\text{PhS})_2\text{FeMoS}_4]^{2-}$		$[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}p\text{-tolyl})_4]^{2-}$	
Mo–Fe	2.750(4)	Fe–Fe	2.691(1)
Mo–S _t (1)	2.148(6)		
Mo–S _t (2)	2.159(6)		
Mo–S _b (1)	2.247(6)		
MoS _b (2)	2.245(6)		
Fe–S _b (1)	2.242(7)	Fe–S _b	2.201(1)
Fe–S _b (2)	2.258(7)		
Fe–S _m (1)	2.303(7)	Fe–S _t	2.312(1)
Fe–S _m (2)	2.320(7)		
S _b (1)–Mo–S _b (2)	104.3(3)	$\angle \text{S}_b\text{–Fe–S}_b$	104.61(4)
$\angle \text{S}_b(1)\text{–Fe–S}_b(2)$	104.5(3)	$\angle \text{Fe–S}_b\text{–Fe}$	75.39(4)
$\angle \text{Mo–S}_b(1)\text{–Fe}$	75.6(2)		
$\angle \text{Mo–S}_b(2)\text{–Fe}$	75.3(2)		

* See the Figure for the labelling scheme. ^b Cf. ref. 7.

similar to those found in the Fe_2S_2 cores in $[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}p\text{-tolyl})_4]^{2-}$ ⁷ and $[\text{Fe}_2\text{S}_{12}]^{2-}$.⁸ Slightly longer Fe–S_b bond lengths and M–M distance are found in the FeMoS_4 core.

The terminal Mo–S_t bond lengths are significantly shorter than the Mo–S_b bond lengths, however they still are the longest Mo–S_t bonds reported to date. These bonds (2.085–2.129 Å) are formally described as Mo=S.⁹

Formally, two different combinations of oxidation states can be assigned to the metal ions: Fe^{II} and Mo^{VI} , or Fe^{III} and Mo^{V} . Preliminary Mössbauer results¹⁰ however show a room temperature and liquid N₂ quadrupole splitting of ca. 2.0 mm s⁻¹ and an isomer shift of 0.45 mm s⁻¹ which would favour the $\text{Fe}^{\text{III}}\text{–Mo}^{\text{V}}$ description albeit marginally. In the contact shifted n.m.r. spectra, the observed decrease in the separation of the phenyl proton resonances as the temperature is raised is not expected for a weakly or moderately antiferromagnetically coupled $d^1\text{–}d^5$ system. The mean Fe–S_m bond length in (1), 2.311(10) Å, however, is appreciably shorter than the mean Fe–S bond length in $[\text{Fe}(\text{PhS})_4]^{2-}$, 2.355(14) Å,¹¹ and quite similar to the Fe–S_t bond length in $[\text{Fe}_2\text{S}_2(\text{S}_2\text{-}p\text{-tolyl})_4]^{2-}$ (Table) which formally contains Fe^{III} .⁷

As in the previous Fe–Mo–S complexes, the overall environment of the molybdenum atom in (1) resembles one of the molybdenum atoms in nitrogenase (suggested by the EXAFS studies). An attractive feature of (1), not present in the other two Fe–Mo–S complexes, is the apparent co-ordination unsaturation of the molybdenum atom.

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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 Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ V. K. Shah and W. J. Brill, *Proc. Nat. Acad. Sci. U.S.A.*, 1977, **74**, 3249.

² J. Raulings, V. K. Shah, J. R. Chisnell, W. J. Brill, R. Zimmermann, E. Münck, and W. H. Orme-Johnson, *J. Biol. Chem.*, 1978, **253**, 1001.

³ 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.

⁴ T. E. Wolff, J. M. Berg, C. Warrick, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Amer. Chem. Soc.*, 1978, **100**, 4630.

⁵ G. Christou, C. D. Garner, and F. E. Mabbs, *Inorg. Chim. Acta*, 1978, **28**, L189; *J.C.S. Chem. Comm.*, 1978, 740.

⁶ D. G. Holah and D. Coucouvanis, *J. Amer. Chem. Soc.*, 1975, **97**, 6917.

⁷ J. J. Mayerle, S. E. Denmark, B. V. De Pamphilis, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, 1975, **97**, 1032.

⁸ D. Coucouvanis, D. Swenson, P. Stremple, and N. C. Baenziger, *J. Amer. Chem. Soc.*, submitted for publication.

⁹ J. T. Huneke and J. H. Enemark, *Inorg. Chem.*, 1978, **17**, 3698.

¹⁰ V. Petrouleas, communication.

¹¹ D. Coucouvanis, D. Swenson, N. C. Baenziger, D. G. Holah, A. Kostikas, A. Simopoulos, and V. Petrouleas, *J. Amer. Chem. Soc.*, 1976, **98**, 5721.