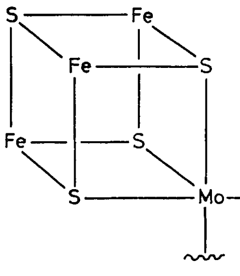
Synthesis and *X*-Ray Structural Characterization of $[Me_4N]_3\{[(SCH_2CH_2S)MoS_3]_2Fe\}$, the First Example of a Heteronuclear Trimer containing Molybdenum in a Square-pyramidal Geometry

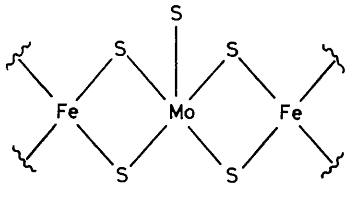
By PHILLIP L. DAHLSTROM, SURENDRA KUMAR, and JON ZUBIETA*
(*Department of Chemistry, State University of New York at Albany, Albany, New York,* 12222)

Summary Reaction of a mixture of $(NH_4)_2MoS_4$ and disodium ethane-1,2-dithiolate in dimethylformamide–MeCN with a methanolic solution of anhydrous $FeCl_3$, followed by the addition of Me_4NBr, gives the trinuclear complex $[Me_4N]_3\{[(SCH_2CH_2S)MoS_3]_2Fe\}$, an *X*-ray crystal structure of which shows the molybdenum atoms to have distorted square-pyramidal geometry and the iron atom to be tetrahedrally co-ordinated to four μ-sulphido-ligands.

MOLYBDENUM EXAFS† studies of both nitrogenase and the iron–molybdenum co-factor suggest that molybdenum is ligated by sulphur donors and is at close proximity to one or more adjacent iron atoms.[1] Two distinct models, (A) and (B), were proposed to account for the EXAFS data. Synthetic analogues of these models have been of two basic structural types: complexes containing the cubane $MoFe_3S_4$ core,[2,3] and complexes containing the $[MoS_4]^{2-}$ unit in heterodinuclear systems.[4,5] We here report a new structural type, a Mo–Fe–Mo trimer with square-pyramidal coordination of sulphur donors about the Mo atoms.



(A)



(B)

The title complex $[Me_4N]_3\{[(SCH_2CH_2S)MoS_3]_2Fe\}$ was prepared by the reaction of a mixture of $[MoS_4]^{2-}$ and an eight-fold excess of disodium ethane-1,2-dithiolate in dimethylformamide (DMF)–acetonitrile (1:1 v/v) with a methanolic solution of anhydrous $FeCl_3$ containing Me_4NBr. Upon addition of isopropyl alcohol, lustrous black crystals of the complex were isolated in small yield (10—25 %).

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† Abbreviation for molybdenum *K*-edge *X*-ray absorption fine structure.

$[Me_4N]_3\{[(SCH_2CH_2S)MoS_3]_2Fe\}$ is an air-stable, paramagnetic species, readily soluble in DMF. Its u.v.–visible spectrum in DMF is qualitatively similar to those observed for Mo–Fe dimers and trimer where the absorptions from the MoS_4 chromophore dominate, displaying bands at 572 (1100), 446 (2600), 382 (sh), and 318 (7700) nm (molar absorptivities in parentheses). The complex is electrochemically active, showing a quasi-reversible one-electron reduction at −0·67 V (*vs.* standard calomel electrode MeCN solution), and an irreversible multi-electron reduction at *ca.* −1·5 V. Suitable crystals for an *X*-ray study were obtained from DMF–methanol.

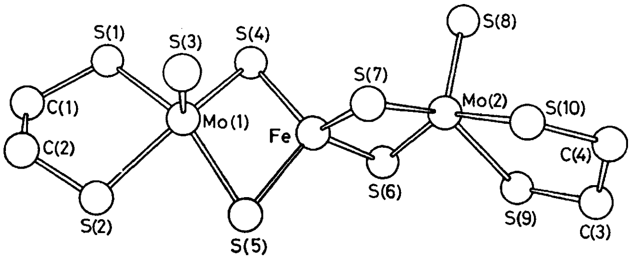

FIGURE. ORTEP representation of the molecular geometry of the anion $\{[(SCH_2CH_2S)MoS_3]_2Fe\}^{3-}$. Some relevant bond lengths (Å) and angles (°) are: Mo(1)–Fe 2·718(5); Mo(2)–Fe 2·774(5); Mo(1)–S(1) 2·410(9); Mo(1)–S(2) 2·389(9); Mo(1)–S(3) 2·118(8); Mo(1)–S(4) 2·317(8); Mo(1)–S(5) 2·339(8); Mo(2)–S(6) 2·349(8); Mo(2)–S(7) 2·284(8); Mo(2)–S(8) 2·160(9); Mo(2)–S(9) 2·407(8); Mo(2)–S(10) 2·403(2); Fe–S(4) 2·237(9); Fe–S(5) 2·225(9); Fe–S(6) 2·208(8); Fe–S(7) 2·214(8); ∠S(4)–Fe–S(5) 103·1(3); S(4)–Fe–S(6) 112·2(3); S(4)–Fe–S(7) 116·4(3); S(5)–Fe–S(6) 110·7(3); S(5)–Fe–S(7) 108·0(3); S(6)–Fe–S(7) 106·3(3); S(1)–Mo(1)–S(2) 81·1(3); S(1)–Mo(1)–S(3) 105·9(3); S(1)–Mo(1)–S(4) 81·0(3); S(1)–Mo(1)–S(5) 143·9(3); S(2)–Mo(1)–S(3) 106·2(3); S(2)–Mo(1)–S(4) 144·0(3); S(2)–Mo(1)–S(5) 79·8(3); S(3)–Mo(1)–S(4) 108·6(3); S(3)–Mo(1)–S(5) 108·6(3); S(4)–Mo(1)–S(5) 97·3(3); S(6)–Mo(2)–S(7) 99·6(3); S(6)–Mo(2)–S(8) 106·5(3); S(6)–Mo(2)–S(9) 78·7(3); S(6)–Mo(2)–S(10) 147·6(2); S(7)–Mo(2)–S(8) 109·5(3); S(7)–Mo(2)–S(9) 139·0(3); S(7)–Mo(2)–S(10) 80·1(2); S(8)–Mo(2)–S(9) 110·2(3); S(8)–Mo(2)–S(10) 104·0(2); S(9)–Mo(2)–S(10) 80·7(2); Mo(1)–Fe–Mo(2) 155·7(2). Dihedral angles (°): Mo(1)–S(4)–S(5), Fe–S(4)–S(5) 43·7; Mo(2)–S(6)–S(7), Fe–S(6)–S(7) 21·5.

Crystal data: $C_{16}H_{44}FeMo_2N_3S_{10}$, monoclinic, space group $P2_1/n$, $a = 9{\cdot}163(3)$, $b = 24{\cdot}392(5)$, $c = 15{\cdot}835(4)$ Å, $\beta = 93{\cdot}06(2)$ °, $U = 3534{\cdot}2$ Å³, $Z = 4$. The structure solution was based on 1682 reflections with $I_{obs} > 3{\cdot}0\,\sigma\,(I_{obs})$. The Fe and Mo atom positions were determined from an electron density map generated by conventional direct-method techniques and non-hydrogen atoms were located on subsequent difference Fourier maps. The current value for *R* is 0·069.‡

The structure of the anion (Figure) shows the tetrahedrally co-ordinated Fe atom bound by two $[(SCH_2CH_2S)MoS_3]^{3-}$ units which serve as bidentate chelates through the bridging sulphido-groups. The geometry about the Mo atoms is basically pseudotetragonal-pyramidal, with three distinct types of Mo–S bonds: Mo–terminal sulphido-, Mo–bridging sulphido-, and Mo–mercapto-sulphur, with average Mo–S bond distances of 2·139(9), 2·322(9), and 2·402(9) Å, respectively. The Mo co-ordination geometry is qualitatively identical to that found in the binuclear Mo^V anion, $[Mo_2S_4(SCH_2CH_2S)_2]^{2-}$.[6] The Mo–Fe–Mo array is distinctly non-linear with an Mo(1)–Fe–Mo(2) angle of 155·7 °, in contrast with the structure of $[(Cl_2Fe)_2MoS_4]^{2-}$ where the metal array is nearly linear.[4] Likewise, the non-planarity of the $MoFeS_2$ bridge units contrasts with the planar bridging moieties in $[S_2MoS_2FeCl_2]^{2-}$ and $[S_2MoS_2Fe(SPh)_2]^{2-}$.[4,5] The mean value for the two independent crystallographically non-identical Mo–Fe distances [2·746(5) Å] approaches a covalent-bond value and may indicate significant interaction between the metal atoms. However, the detailed electronic structure of the trianion has yet to be elucidated.

The magnetic properties of the complex are consistent with two Mo^V (d^1) systems antiferromagnetically coupled with a high spin Fe^{III} (d^5) atom, as suggested by a room-temperature magnetic moment of 4·4 B.M. Detailed magnetic susceptibility and Mössbauer studies are currently in progress.

Analogous products may be prepared with *o*-xylene-αα′-dithiol or benzenethiol as the mercapto-sulphur group. In the latter case, the ability of the phenylthiolato-group to act as a bridging ligand may provide a route to higher oligomers of mixed-metal species of this type.

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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.

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