Isolation and Crystal Structure of [Et4N]3[Fe6Mo2-S8(SEt)9]

STEPHEN R. ACOTT, GEORGE CHRISTOU, C. DAVID GARNER,* TREVOR J. KING,** FRANK E. MABBS and RICHARD M. MILLER

The Chemistry Department, Manchester University, Manchester M13 9PL, U.K.

EXAFS studies [1] of the molybdenum centre(s) in the nitrogenase enzymes and their molybdenum cofactors have indicated that this metal is possibly present in a cluster of iron and sulphur atoms. Attention has therefore been directed towards the synthesis and characterisation of such units. Studies in these laboratories have led to the preparation, under anaerobic conditions, of $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (*e.g.* R = Ph [2, 3] or p-Cl-C_6H_4) complexes by the reaction sequence (1)–(3).

$$6FeCl_3 + 24NaSR \xrightarrow{\text{MeOH}}$$
$$^6/_n[Fe(SR)_3]_n + 18NaCl + 6NaSR \quad (1)$$

$$^6/_n[Fe(SR)_3]_n + 2[NH_4]_2[MoS_4] \rightarrow$$
$$[NH_4]_3[Fe_6Mo_2S_8(SR)_9] + 4RSSR + [NH_4]SR \quad (2)$$

$$[NH_4]_3[Fe_6Mo_2S_8(SR)_9] + (\text{excess}) \ R'_4NBr \rightarrow$$
$$[R'_4N]_3[Fe_6Mo_2S_8(SR)_9] + 3[NH_4]Br \quad (3)$$
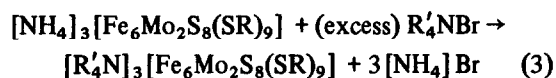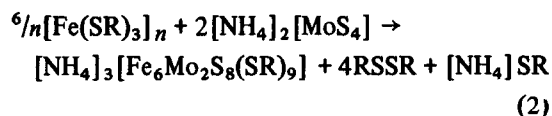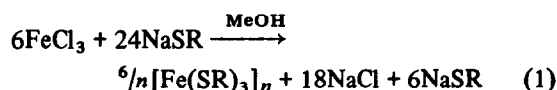
$[Et_4N]_3[Fe_6Mo_2S_9(SEt)_8]$ (I) has been prepared [4] in a similar manner.

We now report $[Et_4N]_3[Fe_6Mo_2S_8(SEt)_9]$(II) has been prepared in good yield (*ca.* 60%) by the route (1)–(3) (R = R' = Et). The crude material can be recrystallised from hot MeOH. The compound crystallises as black needles in the space group $P6_3/m$ with $a = b = 17.261(4)$, $c = 16.346(4)$ Å. Single crystal X-ray diffraction data were collected on a Hilger and Watts four-circle diffractometer using $Mo\text{-}K_\alpha$ radiation; 1317 reflections were considered observed and used in the solution and refinement of the crystal structure. The structure was solved by normal heavy atom Patterson and Fourier procedures and refined by full-matrix least squares methods. The refinement included anisotropic temperature factors for all non-

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*Author to whom correspondence should be addressed.
**The Chemistry Dept., Nottingham University, Nottingham, NG7 2RD, U.K.

hydrogen atoms and isotropic temperature factors for all of the hydrogen atoms. The current R value is 0.065. A representation of the Fe–Mo–S arrangement of the anion is shown in Fig. 1 and selected intramolecular dimensions are listed in Table I. The
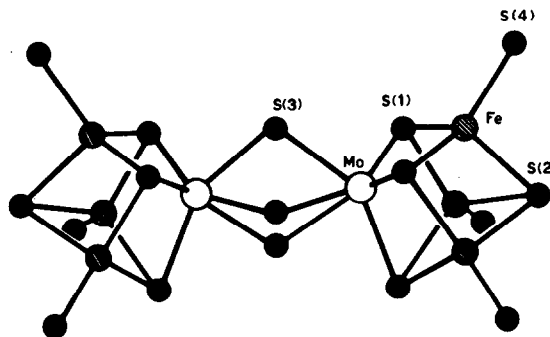

Fig. 1. Arrangement of central atoms of the $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ anion.

TABLE I. Selected Interatomic Dimensions[a] (Å) and Angles (degrees) and Their e.s.d. s of $[Et_4N]_3[Fe_6Mo_2S_8(SEt)_9]$.

Bond		Angle	
Fe–S(1)	2.259(4)	S(1)–Fe–S(1)	108.5(1)
Fe–S(2)	2.276(4)	S(1)–Fe–S(2)	104.1(1)
Fe–S(4)	2.228(4)	S(1)–Fe–S(4)	116.0(4)
Mo–S(1)	2.347(3)	S(2)–Fe–S(4)	107.0(2)
Mo–S(3)	2.568(3)	S(1)–Mo–S(1)	102.7(1)
		S(1)–Mo–S(3)	88.3(1); 90.8(1)
		S(3)–Mo–S(3)	74.8(1)
Fe---Fe	2.699(3)		
Mo---Fe	2.726(2)		
Mo---Mo	3.662(2)		

[a]See Fig. 1 For the specification of the sulphur atoms.

anions have the crystallographically imposed $\bar{3}/m(= \bar{6})$ symmetry characterised for the tris-$[Et_4N]^+$ salts of $[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]^{3-}$ [5] and $[Fe_6Mo_2S_9(SEt)_8]^{3-}$ [4]. This symmetry is also closely approximated by the Fe–Mo–S framework of the anion in $[Bu^n_4N]_3[Fe_6Mo_2S_8(SPh)_9]$ [3]. The temperature factors of the α- and β-carbon atoms of the ethanethiolato-ligands attached to the iron atoms of (II) are significantly higher than those of the other carbons of the compound, which appear to be normal. Thus there is probably some disorder in the position of these α- and β-carbon atoms.

The interatomic dimensions (Table I) do not differ significantly from the corresponding values obtained [3–5] for the three other anions of this type except that the Mo---Mo intramolecular distance of 3.662(2) Å resembles that of the other complexes with three bridging μ-thiolato-groups (3.685(3) Å for R = Ph

[3]; 3.64(1) Å for R = CH_2CH_2OH [5]) rather than that (3.306(3) Å [4]) of $[Fe_6Mo_2S_9(SEt)_8]^{3-}$, which contains one sulphido- and two thiolato-groups bridging the molybdenum centres. The Mo---Fe, Mo–S_{cube}, and Mo–SR distances in these complexes are in the ranges 2.71–2.75, 2.34–2.39, and 2.55–2.58 Å, respectively. These distances compare favourably with the structural deductions of the EXAFS data [1], that molybdenum in nitrogenase is in an environment of two or three iron atoms at 2.72 Å, three or four sulphur atoms at 2.35 Å, and one or two sulphur atoms at 2.49 Å (these latter probably being cysteinyl sulphurs which do not bridge across two molybdenums).

The compound (II) is isomorphous with (I), the c axis of the former being 0.35 Å longer due to the increased Mo---Mo separation; the sum of the oxidation levels of the metals in the anion of (II) is one below that of the anion of (I). The formation of the different species is probably a consequence of the excess of the ethanethiolate used in our procedure (1), since RS⁻ functions as a reducing agent in the synthesis (2). The electronic spectra of the anions of (I) and (II) are quite similar; the latter has λ_{max} of 280 (ϵ_M 56,000) and 390 nm (35,500) in DMSO. The ^{1}H n.m.r. spectrum of (II) in CD_3CN at room temperature exhibits signals at 53 and 17 ppm downfield of Me_4Si in an intensity ratio of *ca.* 2:1, which compare with the signals, at 54.2 ppm downfield and 3.1 ppm upfield of Me_4Si in *ca.* 3:1 intensity ratio, observed for (I). The data are consistent with the assignment of the former signal of each pair to the Fe–SCH_2 (or CH_3) and the latter signal to the Mo–SCH_2 (or CH_3) protons. Therefore, it would appear that it is the electronic structure of the Mo---Mo bridging region, rather than that about the Fe atoms, which experiences the greatest change from (I) to (II).

Electrochemical studies have shown that $[Fe_6Mo_2S_8(SR)_9]^{3-}$ complexes undergo an irreversible one-electron oxidation and two reversible one-electron reductions. Oxidation of $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ occurs at −0.46 V and reduction at −1.56 and −1.76 V (in DMSO *vs.* Ag/Ag⁺ (0.1 mol l⁻¹)). Oxidation of $[Fe_6Mo_2S_8(SPh)_9]^{3-}$ occurs at *ca.* −0.26 V and reductions [2] at −1.26 and −1.45 V under these conditions. This shift in reduction potentials from R = Et to R = Ph is comparable to that observed between $[Fe_4S_4(SR)_4]^{2-}$ (R = Et or Ph) clusters which undergo two one-electron reductions at −1.59, −2.16 and −1.29, −1.99 V, respectively. Further studies are necessary to establish unequivocally whether or not the redox processes of $[Fe_6Mo_2S_8(SR)_9]^{3-}$ complexes involve a change in the electronic structure of the whole dimeric assembly, or whether each cubane-like cluster is oxidised and reduced independently of the other. Our preference is for the former. However, on either view, the electrochemical data suggest that, in these systems each {Fe_3MoS_4} cluster may attain a maximum of three different oxidation levels.

Acknowledgments

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