

Preparation and Crystal Structure of $[\text{NEt}_4]_3[\text{Fe}_6\text{W}_2\text{S}_8(\text{SEt})_9]$; Structural and Electrochemical Comparisons with its Molybdenum Analogue

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ABSTRACT

$[\text{NEt}_4]_3[\text{Fe}_6\text{M}_2\text{S}_8(\text{SEt})_9]$ (M = Mo or W) compounds are isomorphous and contain molybdenum and tungsten atoms in an essentially identical environment. These complexes undergo an irreversible one-electron oxidation at -0.46 V (Mo) and -0.51 V (W) and two one-electron reductions at -1.56 and -1.76 V (Mo) and -1.52 and -1.84 V (W), in DMSO solution versus Ag/Ag^+ (0.1 M). The only distinction between the behavior of these molybdenum and tungsten complexes identified thus far is that, for the former the reductions are reversible whereas for the latter they are irreversible. This difference may be relevant to the low activity found for nitrogenases reconstituted with tungsten in place of molybdenum.

$[\text{Fe}_6\text{Mo}_2\text{S}_8(\text{SR})_9]^{3-}$ (R = Ph [1], $\text{CH}_2\text{CH}_2\text{OH}$ [2], Et [3] or *p*-Cl- C_6H_4 [3]) and $[\text{Fe}_6\text{Mo}_2\text{S}_9(\text{SEt})_8]^{3-}$ [4] complexes are of current interest as they involve molybdenum atoms in an environment which, on the basis of EXAFS data [5], correspond closely to that obtained for this element in the nitrogenase enzymes and their FeMo-cofactor. Tungsten, although capable of incorporation into the nitrogenase FeMo-protein in place of molybdenum [6], does not permit the efficient function of the enzyme; indeed there is doubt as to whether this substitution leads to any biological activity at all [7].

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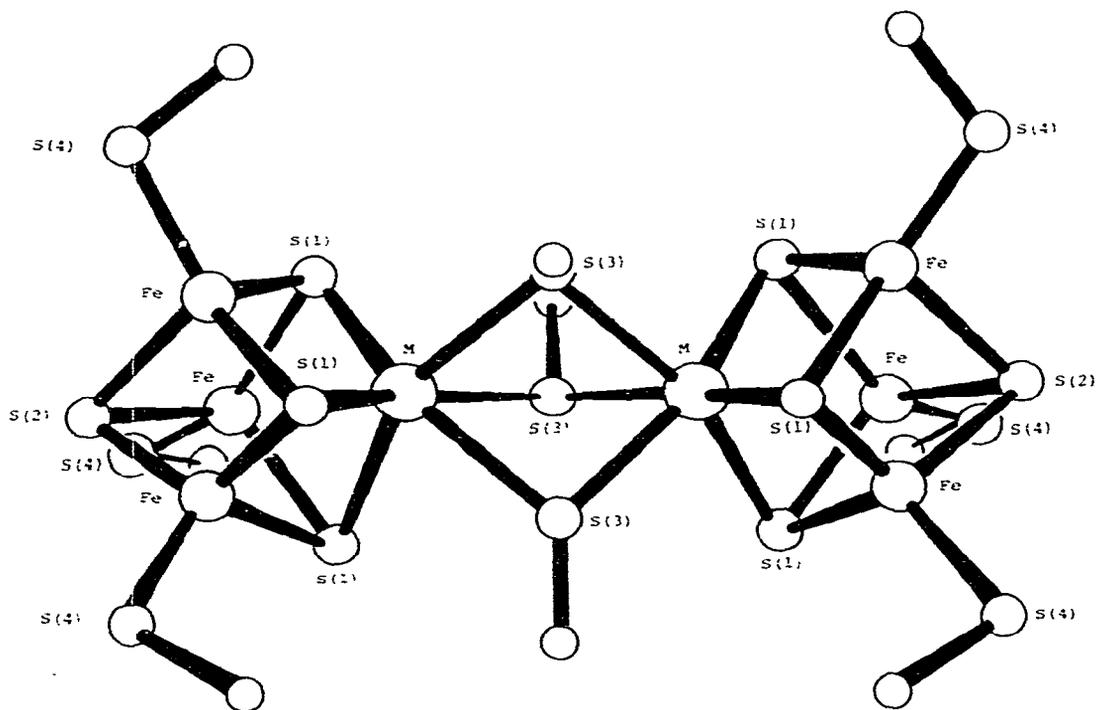
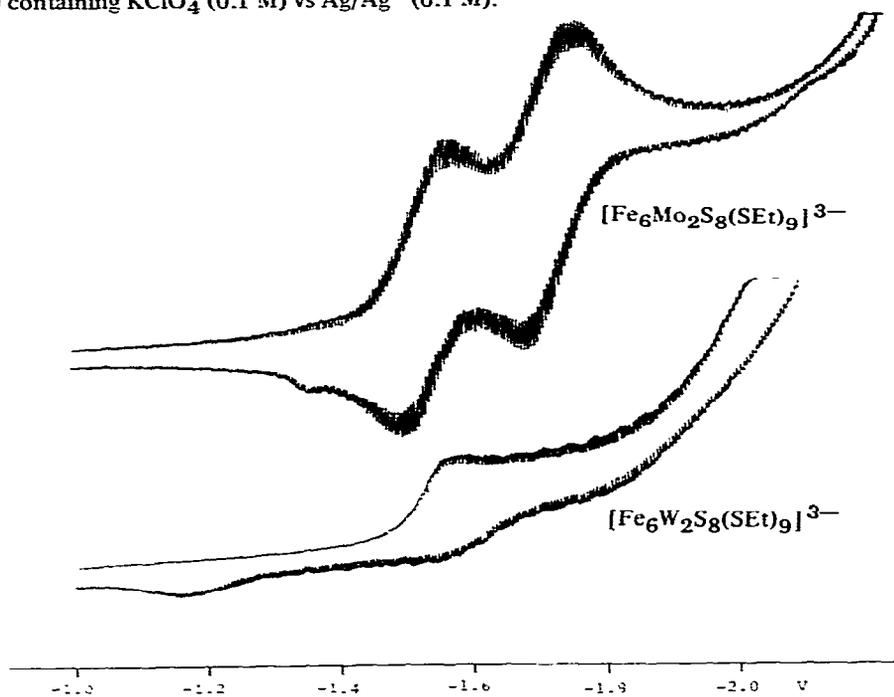


FIGURE 1. Representation of the structure of the central framework of the $[\text{Fe}_6\text{M}_2\text{S}_8(\text{SET})_9]^{3-}$ ($\text{M} = \text{Mo}$ or W) anions.

FIGURE 2. Staircase cyclic voltammograms of $[\text{NEt}_4]_3[\text{Fe}_6\text{M}_2\text{S}_8(\text{SET})_9]$ ($\text{M} = \text{Mo}$ or W) in DMSO containing KClO_4 (0.1 M) vs Ag/Ag^+ (0.1 M).



As part of our continuing investigations into the structure and reactivity of mixed-metal iron-sulphur complexes we have prepared and characterised $[\text{NEt}_4]_3\text{-}[\text{Fe}_6\text{W}_2\text{S}_8(\text{SPh})_6(\text{OMe})_3]$. This anion consists of two $\{\text{Fe}_3\text{WS}_4\}$ cubane-like clusters, linked across their tungsten centres by three μ_2 -methoxy-groups [8]. Although the incorporation of the latter groups is novel, it prevents a direct comparison between tungsten and molybdenum in this type of environment, as no such analogue has yet been isolated for molybdenum. The preparation of an $[\text{Fe}_6\text{W}_2\text{S}_8(\text{SR})_9]^{3-}$ complex was therefore attempted and herein we report that this has been achieved for $\text{R} = \text{Et}$.

$[\text{NEt}_4]_3[\text{Fe}_6\text{W}_2\text{S}_8(\text{SEt})_9]^{3-}$ was prepared according to the procedure described for its molybdenum analogue [3]. The crude material was recrystallised from methanol as well-formed black needles suitable for X-ray crystallographic studies. *Crystal Data*: $M = 1900.1$ hexagonal, $a = b = 17.268 \text{ \AA}$, $c = 16.291 \text{ \AA}$, $U = 4206.9 \text{ \AA}^3$: Space group $P6_3/m$, $Z = 2$. Single crystal X-ray diffraction data were collected on a Hilger and Watts four-circle diffractometer using $\text{Mo-K}\alpha$ radiation; 1353 unique reflections were considered observed ($I \geq 3\sigma$) 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 with anisotropic temper-

TABLE 1. Dimensions of $[\text{Fe}_6\text{M}_2\text{S}_8(\text{SEt})_9]^{3-}$
($\text{M} = \text{Mo}$ or W) Complexes

Distance (\AA)	Mo	W
Fe-S(1)	2.259(4)	2.275(6)
Fe-S(2)	2.276(4)	2.272(6)
Fe-S(4)-R	2.228(4)	2.234(7)
M-S(1)	2.347(3)	2.343(5)
M-S(3)-R	2.568(3)	2.571(5)
Fe...Fe	2.699(3)	2.702(5)
M...Fe	2.726(2)	2.718(3)
S(1)...S(1)	3.668(5)	3.681(5)
S(1)...S(2)	3.577(5)	3.590(5)
M...M	3.662(2)	3.674(3)
Angle (degrees)		
S(1)-Fe-S(1)	108.5(1)	108.0(2)
S(1)-Fe-S(2)	104.1(1)	104.3(2)
S(1)-Fe-S(4)	116.0(4)	115.7(3)
S(2)-Fe-S(4)	107.0(2)	108.6(2)
S(1)-M-S(1)	102.7(1)	103.6(1)
S(1)-M-S(3)	88.3(1) 90.8(1)	88.3(2) 89.8(2)
S(3)-M-S(3)	74.8(1)	74.6(2)
M-S(1)-Fe	72.5(1)	72.1(2)
Fe-S(1)-Fe	73.4(1)	72.8(2)
Fe-S(2)-Fe	72.7(1)	73.0(2)

For specification of atoms see figure 1.

TABLE 2. Polarographic Data^a for [NEt₄]₃[Fe₆M₂S₈](SEt)₉ (M = Mo or W) Complexes^b

	Mo	W
oxidation	<i>-0.46</i>	<i>-0.51</i>
reduction	-1.56	-1.52
	-1.76	-1.84

^a In volts vs Ag/Ag⁺ (0.1 M); italicized values indicate irreversible processes.

^b For a 5 mM solution of the complex in DMSO containing KClO₄ (0.1 M).

ature factors for the iron, tungsten, sulphur and some of the carbon atoms. The terminal carbon atoms of the ethanethiolato- groups bonded to the iron atoms are disordered over three sites with equal occupancy; these positions were refined with isotropic temperature factors. The *R* value at convergence was 0.048. [NEt₄]₃[Fe₆W₂S₈(SEt)₉] is isomorphous with the corresponding molybdenum derivative; the anion (Figure 1) has crystallographic ($\bar{6}$) C_{3h} symmetry and the central framework comprises two {Fe₃WS₄} cubane-like clusters joined across their tungsten centres by three μ₂-ethanethiolato-groups. The dimensions of the two anions are compared in Table 1 and there are no significant differences observed between corresponding values for these two structures. This comparison confirms a conclusion of the [NEt₄]₃[Fe₆W₂S₈(SPh)₆(OMe)₃] study [8], that tungsten may be incorporated into an iron-sulphur cubane-like cluster as neatly as molybdenum. Therefore, if {Fe₃MoS₄} units are valid synthetic analogues for the immediate molybdenum environment of nitrogenase enzymes, there seems to be no *a priori* steric limitations which prevent the incorporation of tungsten into such a site.

The role of the molybdenum-iron-sulphur cofactor in the nitrogenases remains to be defined; however, it seems likely that this center will have (at least) an important part to play in the electron transport processes of the enzyme. Therefore, we have been particularly interested in defining the redox characteristics of these molybdenum- and tungsten- iron-sulphur clusters. Table 2 summarizes the observations made following preliminary staircase cyclic voltammetric and differential pulse polarographic studies of [NEt₄]₃[Fe₆M₂S₈(SEt)₉] (where M = Mo or W) complexes in DMSO containing KClO₄ (0.1 M). These clusters undergo a one-electron oxidation at a potential of -0.46 V (Mo) or -0.51 V (W) (vs Ag/Ag⁺ (0.1 M)) and two one-electron reductions at -1.56 and -1.76 V (Mo) and -1.52 and -1.82 V (W). (These reduction potentials can be compared to the two one-electron reductions of [NBu₄ⁿ]₂[Fe₄S₄(SEt)₄] which occur at -1.59 and -2.16 V under these conditions). It is interesting that the redox processes of the iron-molybdenum-sulphur cluster occur at such similar potentials to those of the corresponding tungsten derivative. Indeed the only difference we have observed thus far is that, whereas both of the reductions for the molybdenum complex are reversible, those for the tungsten are irreversible (Figure 2). If such a difference in behavior is representative of the behavior of molybdenum and tungsten in the nitrogenase enzymes, this could be an important reason for the catalytic activity occurring with molybdenum but not tungsten.

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