Isolation and Characterisation by *X*-Ray Crystallography and Mössbauer Measurements of $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$, an Iron–Tungsten–Sulphur Cubic Cluster Dimer

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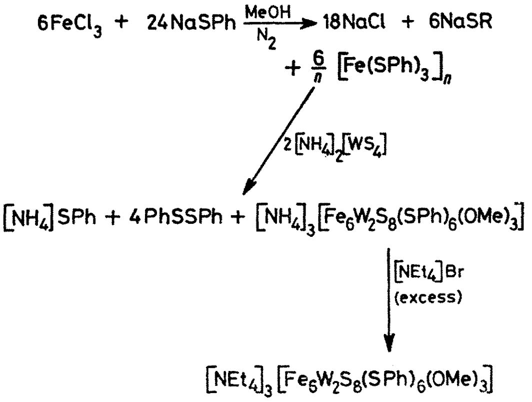
Summary $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$ is the major product of the anaerobic reaction between $[NH_4]_2[WS_4]$, $FeCl_3$, and NaSPh (1 : 3 : 12) in methanol followed by addition of excess of $[NEt_4]Br$, and a crystal structure determination has confirmed that the anion in this complex contains two $\{Fe_3WS_4\}$ cubane-like clusters, with terminal benzenethiolato-ligands co-ordinated to the iron atoms, and three μ_2-methoxo-groups bridging the tungsten atoms; ^{57}Fe Mössbauer measurements indicate that the iron atoms are nearly electronically equivalent.

WE have recently reported the synthesis of the complexes $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (where R = Ph,[1] CH_2CH_2OH,[2] Et,[3] or p-ClC_6H_4[3]) and crystallographic studies have confirmed that the first three of these complexes involve two $\{Fe_3MoS_4\}$ cubane-like clusters, bridged by three μ_2-thiolato-ligands over an Mo $\cdots$ Mo separation of *ca.* 3·66 Å. $[Fe_6Mo_2S_9(SEt)_8]^{3-}$ has a similar structure, involving two μ_2-ethanethiolato- and one μ_2-sulphido- ligands spanning an Mo $\cdots$ Mo distance of 3·306(3) Å.[4] These systems are currently the best structural analogues for the molybdenum centre of the nitrogenase enzymes. The similarities which often occur between the chemistries of molybdenum and tungsten do not extend to these enzymes. *Azotobacter vinelandii*, grown under nitrogen-fixing conditions on a medium containing tungsten in place of molybdenum, incorporates only 1·3 atoms of the former, in contrast to 2 atoms of the latter, per mol of the Mo(W)Fe protein.[5] The capacity of this tungsten system for acetylene reduction is very poor compared to that of its molybdenum counterpart and it is possible that even this low activity is due to traces of molybdenum being present.[6] Therefore, we investigated the possibility of preparing $\{Fe_3WS_4\}$ cubane-like clusters for comparison with their molybdenum counterparts and herein report the preparation, structure, and ^{57}Fe Mössbauer characteristics of $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$, the first compound of this type.

Treatment of $FeCl_3$ with NaSPh and $[NH_4]_2[WS_4]$ (Scheme), with overnight stirring at room temperature, produced an intense red-brown solution from which a fine black solid was obtained upon the addition of $[NEt_4]Br$.



SCHEME

Recrystallisation from MeCN–MeOH gave the analytically pure title compound in 51% overall yield as black, well formed, needle-like crystals suitable for *X*-ray diffraction studies.

Crystal data: $M = 2098{\cdot}1$, hexagonal, $a = 17{\cdot}725(3)$, $c = 15{\cdot}826(3)$ Å, $U = 4306$ Å^3, $Z = 2$, $D_m = 1{\cdot}65$, $D_c = 1{\cdot}62$ g cm^{-3}, space group $P6_{3/m}$. Single crystal *X*-ray diffraction data were collected on a Hilger and Watts four-circle diffractometer using Mo-K_α radiation; 1360 unique reflections were considered observed ($I > 3\sigma$) 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 temperature factors for all but the hydrogen atoms. The R value at final convergence was 0·052.†

The anions of the title compound have crystallographic C_{3h} symmetry and have a basic structure which is analogous to that of $[Fe_6Mo_2S_8(SR)_9]^{3-}$ (where R = Ph,[1] CH_2CH_2OH,[2] or Et[3]). The central framework (Figure 1) comprises two $\{Fe_3WS_4\}$ cubane-like clusters linked by three μ_2-methoxo-groups and it is of interest to observe that these groups are incorporated under conditions analogous to those employed

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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.

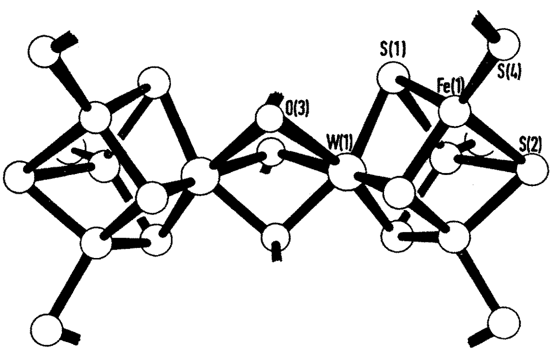

Figure 1. Structure of the central unit of the $[Fe_6W_2S_8(SPh)_6(OMe)_3]^{3-}$ complex. W(1)···W(1′), 3·174(2); W(1)–O(3), 2·123(9); W(1)–S(1), 2·335(4); W(1)···Fe(1), 2·710(2); Fe(1)···Fe(1′), 2·693(4); Fe(1)–S(1), 2·275(4); Fe(1)–S(2), 2·278(4); Fe(1)–S(4), 2·245(5); S(1)···S(1′), 3·678(5); S(1)···S(4), 3·815(5) and 3·874(5) Å; ∠O(3)–W–O(3′), 70·3(4); W(1)–O(3)–W(1′), 96·7(5); O(3)–W–S(1), 91·6(3); S(1)–W–S(1′), 103·9(1); Fe(1)–W–Fe(1′), 59·6(1); Fe(1)–Fe(1′)–Fe(1″), 60·0; S(1)–Fe–S(1′), 107·8(2); S(1)–Fe–S(2), 104·5(1) and 104·7(1); S(1)–Fe–S(4), 115·1(2) and 118·0(2); S(4)–Fe–S(2), 105·3(2); W(1)–S(1)–Fe(1), 71·9(1) and 72·0(1); Fe(1)–S(1)–Fe(1′), 72·6(2); Fe(1)–S(4)–Fe(1′), 72·8(2)°.

for the preparation of $[Fe_6Mo_2S_8(SPh)_9]^{3-}$.[1,3] The change from the three μ_2-thiolato groups, in the case of molybdenum, to the three μ_2-methoxo-groups, in the case of tungsten, leads to an appreciable shortening of the metal-metal separation which these ligands bridge, from 3·66(2) to 3·174(2) Å. This latter separation is within the range of a direct bonding interaction between two tungsten atoms {*cf.* the W–W single bond in $[(\eta^5\text{-}C_5H_5)W(CO)_3]_2$ of 3·222(1) Å[7]}. The dimensions of the $\{Fe_3WS_4\}$ cubane-like frameworks are virtually identical to the corresponding values for the $\{Fe_3MoS_4\}$ units[1–4] and clearly tungsten is capable of the isomorphous substitution of molybdenum in these systems. Therefore, we conclude that there are no structural constraints which would restrict the incorporation of tungsten into the type of site suggested for molybdenum in nitrogenase on the basis of EXAFS data.[8]

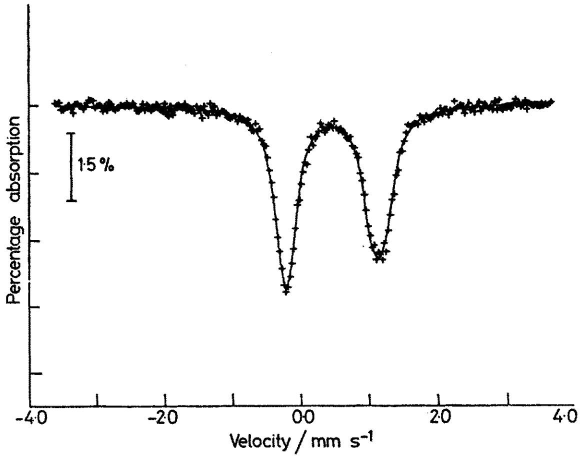

Figure 2. ^{57}Fe Mössbauer spectrum of $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$ at 77 K. The solid line represents the computer fit as described in the text.

The ^{57}Fe Mössbauer spectrum of the title compound at 77 K is shown in Figure 2. This spectrum indicates that the iron atoms are nearly, but not precisely, electronically equivalent. Although the spectrum of each site cannot be resolved the average values of the isomer shift and quadrupole splitting can be determined and are 0·47 ± 0·02 mm s^{-1} (relative to iron metal at room temperature) and 1·35 ± 0·02 mm s^{-1}, respectively. It is not possible to determine uniquely the number of iron sites, but good computer fits may be obtained assuming three distinct iron components with equal areas and linewidths. An example of such a fit is shown by the solid line in Figure 2. A comparison of the isomer shift with those obtained for iron in the redox active centres of the iron–sulphur proteins[9] and their synthetic analogues implies that the iron atoms of the title compound have an average oxidation state of approximately +2·5, thus suggesting that the compound involves tungsten(III)—(IV).

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