Mössbauer and Electrochemical Studies on Fe_3MoS_4 and Fe_3WS_4 Cubane-like Cluster Dimers

By **George Christou**, **C. David Garner,*** and **Richard M. Miller**, The Chemistry Department, Manchester University, Manchester M13 9PL
Charles E. Johnson and **James D. Rush**, Oliver Lodge Laboratory, University of Liverpool, Liverpool L69 3BX

^{57}Fe Mössbauer parameters of several $[Fe_6M_2S_8(SR)_9]^{3-}$ (where M = Mo or W) complexes and $[Fe_6W_2S_8(OMe)_3(SPh)_6]^{3-}$ have been obtained at 4.2, 77, 195, and 293 K. These are seen to be very similar to those obtained for $[Fe_4S_4(SR)_4]^{2-}$ complexes and, on the basis of the isomer shift, each iron atom is considered to have a net oxidation state of *ca.* 2.5, thus implying that each molybdenum or tungsten atom has an oxidation state between 3 and 4. Electrochemical reduction of the trianions to the 4−, 5−, 6− and, in some instances, 7− species has been monitored. The first of these reductions occurs at a potential virtually identical to that of the corresponding $[Fe_4S_4(SR)_4]^{2-}$ complex, the second reduction occurs at a potential *ca.* 200 mV more negative. These two reductions generally appear to be reversible for most of the complexes in acetonitrile solution. However, rapid scan, staircase cyclic voltammetry showed that only $[Fe_6M_2S_8(SEt)_9]^{3-}$ (M = Mo or W) in acetonitrile solution approach good electrochemical reversibility.

ON the basis of the extended *X*-ray absorption fine structure (e.x.a.f.s.) associated with the molybdenum *K* edge of the molybdenum–iron proteins from the nitrogenases of *Azotobacter vinelandii* and *Clostridium pasteuranium*, and the molybdenum-containing cofactor of the former, molybdenum appears to be surrounded by three or four sulphur atoms *ca.* 2.35 Å away and two or three iron atoms, *ca.* 2.72 Å away (with perhaps one or two sulphur atoms 2.49 Å away). An attractive structural possibility for such an arrangement is an Fe_3MoS_4 cubane-like cluster (with perhaps one or two thiolato-groups bound to the molybdenum).[1]

Recently, we reported the preparation and crystallographic characterisation of $[NBu^n_4]_3[Fe_6Mo_2S_8(SPh)_9]$,[2] $[NEt_4]_3[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]$,[3] $[NEt_4]_3[Fe_6M_2S_8(SEt)_9]$ (where M = Mo or W),[4] and $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$.[5] Each of these anions comprises two Fe_3MS_4 cubane-like clusters, the M centres of which are linked by three μ_2-thiolato- or μ_2-methoxo-groups. Similar systems have been described by Wolff *et al.*[6-8] The environment about the molybdenum or tungsten atom in all of these compounds is very similar to that proposed [1] for molybdenum in nitrogenase on the basis of the e.x.a.f.s. studies.

^{57}Fe Mössbauer spectroscopy has proved to be a most useful probe of the electronic structure of the various iron–sulphur centres in proteins and their synthetic analogues.[9] Therefore, we have measured Mössbauer spectra for those Fe_3MS_4 (where M = Mo or W) cluster dimers which have been crystallographically characterised, for comparison with similar data obtained for $[Fe_4S_4(SR)_4]^{2-}$ clusters and the iron–molybdenum centre of nitrogenase which, at 90 K in its $S = \frac{3}{2}$ level, has an ^{57}Fe Mössbauer spectrum [10] corresponding to an average isomer shift of 0.37 mm s^{-1} and quadrupole splitting of 0.75 mm s^{-1}. The electrochemical reduction characteristics of the crystallographically characterised and some other Fe_3MS_4 (where M = Mo or W) cluster dimers have also been determined. Again comparisons with $[Fe_4S_4(SR)_4]^{2-}$ centres have been sought to provide information about the effects of the inclusion of molybdenum (or tungsten) into the cluster and having two such clusters in close proximity.

EXPERIMENTAL

Analytically pure samples of the compounds were prepared using the synthetic procedures described elsewhere.[2-5, 11]

Mössbauer Measurements.—Samples were prepared in a glove-box under an atmosphere of purified dinitrogen by grinding the appropriate crystalline solid and mixing it with silicone vacuum grease until a homogeneous paste was obtained. The paste was placed in a standard polytetrafluoroethylene cell and sealed with a clear adhesive.

Mössbauer spectra were recorded using sources of ^{57}Co in rhodium. An absorber of pure iron maintained at 293 K was used for calibration and the spectra were plotted with the centre of the iron spectrum as the zero of velocity. Computer-simulated spectra were obtained as described previously.[12]

Electrochemical Measurements.—Data were obtained for dimethyl sulphoxide (dmso) or acetonitrile (MeCN) solutions of each compound (*ca.* 5×10^{-3} mol l^{-1}) containing $K[ClO_4]$, $[NPr^n_4][ClO_4]$, or $[NBu^n_4][BF_4]$ (*ca* 0.1 mol l^{-1}) as the background electrolyte. The solvents were dried and thoroughly degassed prior to use; solvent and solution transfers were accomplished using syringe and septum cap techniques.

Polarograms were recorded using a PAR 174 polarographic analyser and the PAR 172A drop timer. Sampled D.C. polarograms were recorded to determine the sense of the electron transfer and differential pulse polarograms were recorded to establish the reduction potentials; these measurements were obtained at scan rates of 1 mV s^{-1} with a drop lifetime of 0.5 s. The modulation amplitude for the differential pulse polarography was 25 mV. The sensitivity of the current follower was typically 50 or 100 µA full-scale deflection. All polarograms were recorded for dmso solutions and were referenced to an Ag/Ag$^+$ electrode, consisting of a silver-plated platinum wire partially immersed in a solution of $Ag[NO_3]$ (0.1 mol l^{-1}) and the appropriate background electrolyte (0.1 mol l^{-1}) in dmso. This reference cell was connected to the experimental cell *via* a salt bridge and a Luggin capillary containing a solution of the background electrolyte (0.1 mol l^{-1}) in dmso. This configuration ensured a small and reproducible liquid junction potential.

Cyclic staircase voltammograms [13,14] were recorded for dmso or MeCN solutions of the compounds of interest using equipment designed and constructed in these laboratories and which included a fast potentiostat and a PET microcomputer based data collection system.[15] The reference electrode was the same as in the differential pulse polarographic studies when dmso was used as the solvent; with MeCN as the solvent, this was used throughout the system. The working electrode was either a hanging mercury-drop electrode (Metrohm E410) or a dropping mercury electrode. The latter was used at smaller step widths, where the length of the scan was small with respect to the drop lifetime. In these cases, the scan was synchronised with the drop lifetime using the PAR 174/51 linear sweep module. Step widths ranged from 32 ms to 0.512 ms and each step was nominally 5 mV. A scan consisted of 512 steps, 256 in each direction. The current was usually measured at the mid-point of the step. Up to 100 separate scans were averaged using the data acquisition system to give a reasonable signal-to-noise ratio.

RESULTS AND DISCUSSION

The crystal structures of $[NEt_4]_3[Fe_6M_2S_8(SR)_9]$ (where M = Mo and R = CH_2CH_2OH [3] or Et [4]; M = W and R = Et [4]) and $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SPh)_9]$ [2] have been determined. These $[NEt_4]^+$ salts crystallise in the hexagonal space group *P*6$_3$/*m*, with the cubane-like cluster dimer located on a site of C_{3h} ($\bar{6}$) symmetry. Although $[NBu^n{}_3]_4[Fe_6Mo_2S_8(SPh)_9]$ crystallises in the monoclinic space group *Cc*, the central portion of this anion closely approximates to the C_{3h} symmetry established for the other anions and the atomic arrangement of this framework is illustrated in Figure 1. The molybdenum–molybdenum or tungsten–tungsten separation spanned by the three μ_2-thiolato-groups is *ca.* 3.66 Å. The compound $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$ also crystallises [5] in the *P*6$_3$/*m* space group; the anion comprises two $Fe_3WS_4(SPh)_3$ cubane-like clusters bridged by three μ_2-methoxo-groups over a tungsten–tungsten distance of 3.174(2) Å. Hydrogen-1 n.m.r. data have indicated that the $[Fe_6Mo_2S_8Cl_6(SR)_3]^{3-}$ (where R = Et or CH_2CH_2OH) anions contain three μ_2-thiolato-groups and therefore each chloride atom is presumed to occupy the terminal ligand site on an iron atom.

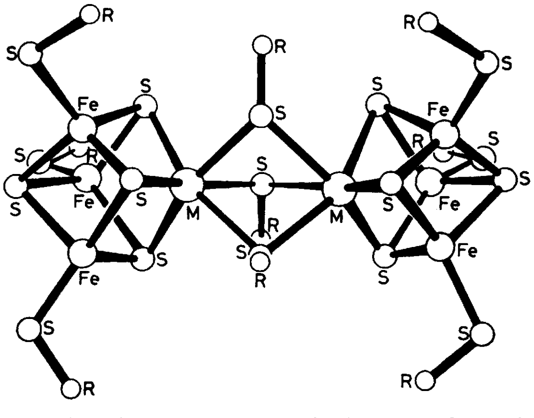

FIGURE 1 Atomic arrangement of the central portion of $[Fe_6M_2S_8(SR)_9]^{3-}$ (where M = Mo and R = Ph, Et, CH_2CH_2OH; M = W and R = Et) complexes, the alkyl or aryl groups have been omitted for clarity

The zero-field ^{57}Fe Mössbauer spectra of the tetra-alkylammonium salts of $[Fe_6M_2S_8(SR)_9]^{3-}$ (where M = Mo and R = Ph, CH_2CH_2OH, or Et; M = W and R = Et) and $[Fe_6W_2S_8(SPh)_6(OMe)_3]^{3-}$ anions consist (Figure 2) of an asymmetric quadrupole doublet, the line widths of which increase with decreasing temperature, as illustrated in Figure 3 for $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SPh)_9]$. In each case, the spectral profile indicates that the iron atoms are nearly, but not exactly, equivalent. Figure 2 shows that $[NBu^n{}_4]_2[Fe_4S_4(SPh)_4]$ has a sharper and smoother profile for the quadrupole doublet than do all of the Fe_3MS_4 systems. This Fe_4S_4 ^{57}Fe Mössbauer spectrum may be best fitted using a theoretical model [12] with four shifts having respective isomer shifts and quadrupole splittings of 0.43 and 0.62; 0.43 and 0.78; 0.44 and 0.95; 0.44 and 1.12 mm s^{-1}. The ^{57}Fe Mössbauer spectra of the Fe_3MS_4 cubane-like cluster dimers have been fitted using the same theoretical model,[12] assuming that the observed spectral envelope arises from three separate quadrupole doublets, the components of which have a Lorentzian line shape and are of equal area and line width. This approach gave a good interpretation of the experimental

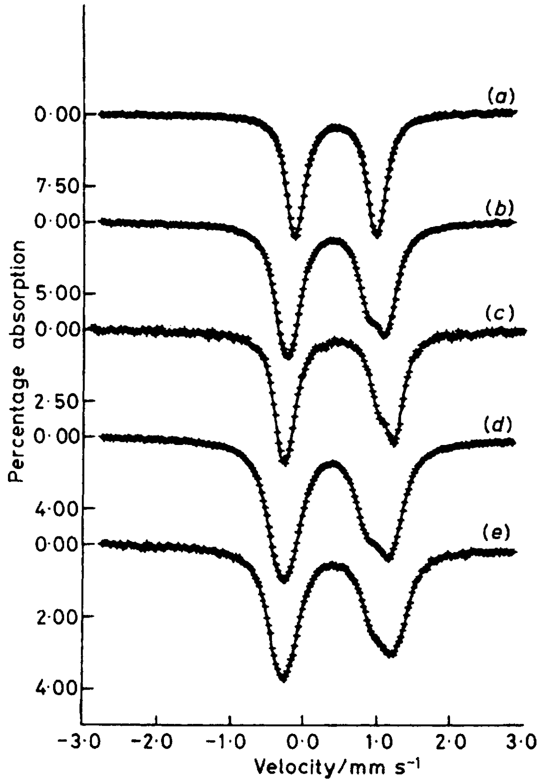

FIGURE 2 ^{57}Fe zero-field Mössbauer spectra of (*a*) $[NBu^n{}_4]_2[Fe_4S_4(SPh)_4]$, (*b*) $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SPh)_9]$, (*c*) $[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$, (*d*) $[NEt_4]_3[Fe_6Mo_2S_8(SEt)_9]$, (*e*) $[NEt_4]_3[Fe_6W_2S_8(SEt)_9]$ at 4.2 K referenced to pure iron metal at 293 K. The solid line shows the computer fit for a three-site model (see text)

TABLE 1

^{57}Fe Mössbauer data on some compounds containing Fe_3MS_4 (M = Mo or W) cubane-like clusters

Compound	T/K	Isomer shift/mm s^{-1} [a] individual [b]	Isomer shift/mm s^{-1} [a] average [c]	Quadrupole splitting/mm s^{-1} individual [b]	Quadrupole splitting/mm s^{-1} average [c]
$[NBu^n_4]_3[Fe_6Mo_2S_8(SPh)_9]$	77	0.41, 0.40, 0.44	0.42 (1)	0.94, 1.10, 1.37	1.14 (2)
	4.2	0.39, 0.43, 0.45	0.42 (1)	1.00, 1.27, 1.48	1.25 (2)
$[NEt_4]_3[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]$	77	0.39, 0.40, 0.44	0.41 (1)	0.91, 1.17, 1.42	1.17 (2)
	4.2	*d*	0.45 (2)	*d*	1.19 (5)
$[NEt_4]_3[Fe_6Mo_2S_8(SEt)_9]$	77	0.39, 0.41, 0.44	0.41 (1)	0.92, 1.20, 1.46	1.19 (2)
	4.2	0.38, 0.43, 0.45	0.42 (1)	0.99, 1.36, 1.63	1.33 (2)
$[NEt_4]_3[Fe_6W_2S_8(SEt)_9]$	77	0.41, 0.42, 0.47	0.43 (1)	1.07, 1.28, 1.53	1.33 (2)
	4.2	0.41, 0.45, 0.48	0.45 (1)	1.10, 1.44, 1.69	1.41 (2)
$[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$	77	0.45, 0.46, 0.50	0.47 (1)	1.15, 1.37, 1.53	1.35 (2)
	4.2	0.44, 0.48, 0.50	0.47 (1)	1.18, 1.47, 1.59	1.41 (2)

[a] Referenced to pure iron metal at 293 K. [b] Individual values represent numbers obtained from the optimal fit of the experimental data by a theoretical model (ref. 12) of three separate doublets having equal peak area and linewidth. [c] The average value represents the mean of the individual values and the estimated error is given in parentheses. [d] Peaks broadened by magnetic hyperfine effects.

data in every case, the quality of the agreement being typified by the examples shown in Figure 3. The values of the isomer shift and the quadrupole splitting parameters thus obtained are listed in Tables 1 and 2. These isomer-shift values do not agree with those reported by Wolff *et al.*[6-8] and, although there is only one complex in common, $[Fe_6Mo_2S_8(SEt)_9]^{3-}$, we presume this discrepancy to be systematic and arises because a different reference point has been chosen in the two studies.

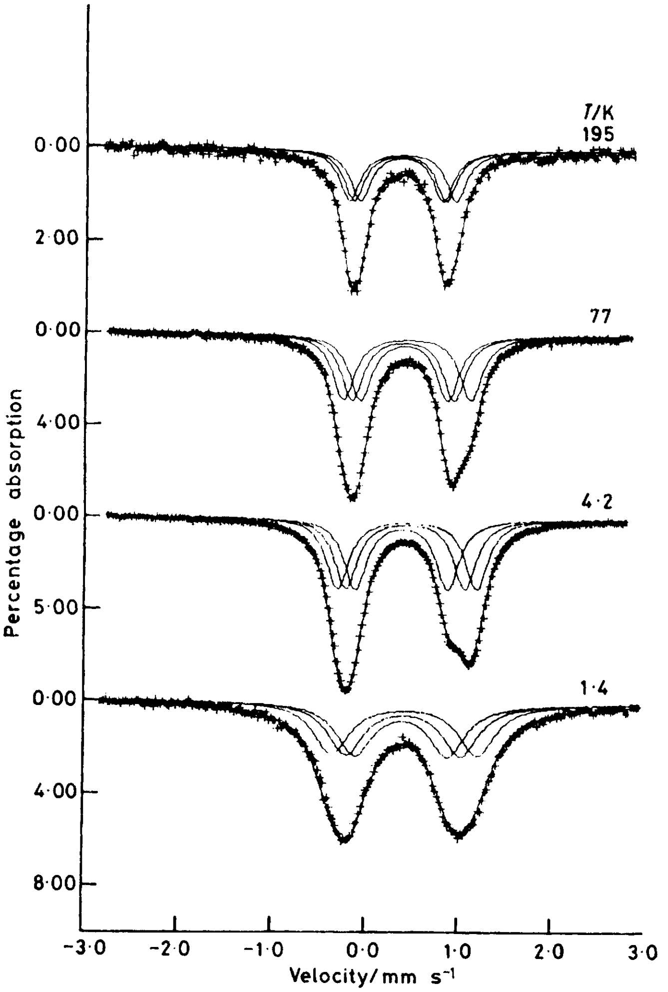

FIGURE 3 ^{57}Fe zero-field Mössbauer spectra of $[NBu^n_4]_3[Fe_6Mo_2S_8(SPh)_9]$ at various temperatures referenced to pure iron metal at 293 K; experimental data (+); optimal fit by a theoretical model (—) (ref. 12) of three doublets having equal area and line width

Other possible interpretations of the ^{57}Fe Mössbauer spectra of these Fe_3MS_4 cubane-like cluster dimers were also explored, including a model in which the iron atoms were assumed to occupy two different sites. However, these led to no improvement in the interpretation of the experimental data. Furthermore, since there are three iron atoms in each cubane-like cluster, the choice of a three-site model seems justifiable. The range of the different ^{57}Fe isomer shifts, obtained from the interpretation of the Mössbauer spectrum of each of the Fe_3MS_4 cubane-like cluster dimers, at each temperature (Tables 1 and 2) is slightly larger than that obtained for $[Fe_4S_4(SPh)_4]^{2-}$ at 77 K (see above). The simplest interpretation of these non-equivalences is that, within each cluster, each iron atom has an electronic environment which differs slightly from that of the other two such atoms. This is observed despite C_{3h} crystallographic symmetry having been characterised at room temperature, for the anions of the majority of the salts studied by Mössbauer spectroscopy. Possible ways in which these inequivalences could arise include: a distortion to an atomic arrangement which is lacking three-fold symmetry, the extent of which becomes more pronounced as the temperature is lowered, and/or the presence of a

TABLE 2

^{57}Fe Mössbauer data for $[NBu^n_4]_3[Fe_6Mo_2S_8(SPh)_9]$ at various temperatures

T/K	Isomer shift/mm s^{-1} [a] individual [b]	Isomer shift/mm s^{-1} [a] average [c]	Quadrupole splitting/mm s^{-1} individual [b]	Quadrupole splitting/mm s^{-1} average [c]
293	0.31, 0.32, 0.32	0.32 (3)	0.85, 0.97, 1.10	0.97 (5)
195	0.37, 0.35, 0.38	0.37 (2)	0.89, 0.99, 1.14	1.01 (5)
77	0.41, 0.40, 0.44	0.42 (1)	0.94, 1.10. 1.37	1.14 (2)
4.2	0.39, 0.43, 0.45	0.42 (1)	1.00, 1.27, 1.48	1.25 (2)
1.4	0.39, 0.42, 0.43	0.41 (1)	0.99, 1.22, 1.55	1.25 (2)

[a] Referenced to pure iron metal at 293 K; *cf.* average values for $[NBu^n_4]_2[Fe_4S_4(SPh)_4]$: 293 K 0.32 (3) and 0.55 (5) mm s^{-1}; 77 K 0.44 (1) and 0.87 (2) mm s^{-1}; 4.2 K 0.45 (1) and 1.10 (2) mm s^{-1}. [b] and [c] See corresponding footnotes to Table 1.

magnetic (or electronic spin) distribution within these anions which has less than three-fold symmetry. The ^{57}Fe Mössbauer spectra observed[16] for $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SPh)_9]$ in a magnetic field of various intensities provide partial support for such possibilities in that the iron spins within each cluster appear to be inequivalent.

The magnitude of the ^{57}Fe Mössbauer isomer shift for the pseudo-tetrahedral FeS_4 centres of the iron–sulphur proteins and their synthetic analogues has been shown[9] to exhibit a nearly linear correlation with the (average) oxidation state of the iron atom(s), between the limits of 2 and 3. It seems reasonable to expect that this correlation will be at least approximately applicable to the Fe_3MS_4 cluster dimers studied here since the immediate environment of the iron atoms closely resembles that[17] in $Fe_4S_4(SR)_4$ systems. On this basis, the average values of the ^{57}Fe isomer shifts given in Table 1 indicate that, in each case, the average oxidation state of the iron atoms is 2.5 ± 0.1. This value implies that the average oxidation state of the molybdenum or tungsten atoms is between 3 and 4 (arithmetically 3.5). We do not favour a precise interpretation of the oxidation state of the molybdenum or tungsten atoms in these systems, in contrast to the interpretations of Wolff *et al.*,[6-8] not only because of the uncertainty in the strict validity of the ^{57}Fe isomer shift–oxidation state correlation for these Fe_3MS_4 clusters but also because such precision seems to over-interpret the experimental data and ignore the inequivalence of the iron centres. The major conclusion to be drawn from the ^{57}Fe isomer shifts is that the iron atoms in these $[Fe_6Mo_2S_8(SR)_9]^{3-}$ anions are in a very similar formal oxidation state to those in $[Fe_4S_4(SR)_4]^{2-}$ clusters and this is similar to that observed[10] for the iron atoms for the $S = \frac{3}{2}$ state of the iron–molybdenum cofactor of nitrogenase (isomer shift 0.37 mm s^{-1}). This observation of a fractional value for the average oxidation state of the iron atoms in Fe_3MS_4 cluster dimers is consistent with extensive electron delocalisation occurring over the metal centres of these systems. An interesting feature to emerge is that there is only a small change in the ^{57}Fe isomer shifts when molybdenum is substituted by tungsten, as the data for $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ and $[Fe_6W_2S_8(SEt)_9]^{3-}$ (Table 1) demonstrate.

The quadrupole splittings observed for these Fe_3MS_4 clusters are somewhat larger than values typical of $[Fe_4S_4(SR)_4]^{2-}$ clusters[9] and the iron–molybdenum cofactor of nitrogenase,[10] at a comparable temperature. This difference may represent a lower-symmetry electric field about the iron atoms in the Fe_3MS_4 clusters, for which C_{3v} is the highest point symmetry, as compared to Fe_4S_4 clusters, for which T_d is the highest point symmetry. The values of the quadrupole splittings are larger for the tungsten–iron–sulphur clusters than for the analogous molybdenum systems.

The reduction potentials observed polarographically for tetra-alkylammonium salts of $[Fe_6M_2S_8(SR)_9]^{3-}$ (where M = Mo and R = Ph, C_6H_4Me-*p*, C_6H_4Cl-*p*, Et, or CH_2CH_2OH; M = W and R = Et), $[Fe_6Mo_2S_8Cl_6(SR)_3]^{3-}$ (where R = Et or CH_2CH_2OH), and $[Fe_6W_2S_8(SPh)_6(OMe)_3]^{3-}$ in dmso solution and referenced to an Ag/{Ag[NO$_3$] (0.1 mol l^{-1}) in dmso} electrode, together with comparable data for tetraethylammonium salts of $[Fe_4S_4(SR)_4]^{2-}$ (where R = Ph, Et, or CH_2CH_2OH), are presented in Table 3. A differential pulse polarogram recorded for $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]$ is shown in Figure 4; Figure 5 shows the staircase cyclic voltammogram recorded for $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]$.

TABLE 3

Reduction potentials[a] for some compounds containing Fe_3MS_4 (M = Fe, Mo, or W) cubane-like clusters

Compound	Reduction potential/V			
$[NBu^n{}_4]_2[Fe_4S_4(SPh)_4]$ [b]	−1.29		−1.99	
$[NBu^n{}_4]_3[Fe_6Mo_2S_8(SPh)_9]$ [c]	−1.24	−1.44	−2.54	
$[NEt_4]_3[Fe_6Mo_2S_8(SC_6H_4Me\text{-}p)_9]$ [d]	−1.30	−1.50	−2.40	
$[NBu^n{}_4]_3[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]$ [c]	−1.11	−1.29	−2.33	−2.59
$[NEt_4]_3[Fe_6Mo_2S_8(SPh)_6(OMe)_3]$ [d]	−1.31	−1.51	−2.44	
$[NEt_4]_3[Fe_6W_2S_8(SPh)_6(OMe)_3]$ [b]	−1.42	−1.59		
$[NEt_4]_2[Fe_4S_4(SEt)_4]$ [b]	−1.58		−2.15	
$[NEt_4]_3[Fe_6Mo_2S_8(SEt)_9]$ [b]	−1.56	−1.76		
$[NEt_4]_3[Fe_6W_2S_8(SEt)_9]$ [b]	−1.52	−1.83		
$[NEt_4]_2[Fe_4S_4(SCH_2CH_2OH)_4]$ [b]	−1.50		−2.01	
$[NEt_4]_3[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]$ [b]	−1.49	−1.69		
$[NEt_4]_3[Fe_6Mo_2Cl_6(SEt)_3]$ [d]	−1.11	−1.31	−2.04	−2.29
$[NEt_4]_3$-$[Fe_6Mo_2S_8Cl_6(SCH_2CH_2OH)_3]$ [d]	−1.11	−1.31	−2.01	−2.26
$[NEt_4]_3[Fe_6Mo_2S_8Br_6(SEt)_3]$ [d,e]	−1.13	−1.33	−2.03	−2.25

[a] Estimated error ±5 mV; data obtained in dmso solution at *ca.* 293 K, referenced to an Ag/{Ag[NO$_3$] (0.1 mol l^{-1}) dmso} electrode apart from *e*. [b] Supporting electrolyte K[ClO$_4$]. [c] Supporting electrolyte $[NBu^n{}_4][BF_4]$. [d] Supporting electrolyte $[NPr^n{}_4][ClO_4]$. [e] Data obtained in MeCN solution at *ca.* 293 K, referenced to an Ag/{Ag[NO$_3$] (0.1 mol l^{-1}) in MeCN} electrode.

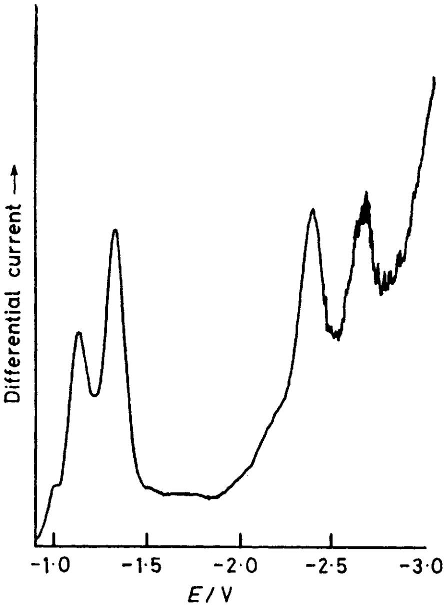

FIGURE 4 Differential pulse polarogram of $[NBu^n{}_4]_3[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]$ in dmso containing $[NPr^n{}_4][ClO_4]$ (0.1 mol l^{-1}), referenced to an Ag/{Ag[NO$_3$] (0.1 mol l^{-1}) in dmso} electrode

Polarographic studies have established that all of the Fe_3MS_4 cluster dimers studied thus far undergo several distinct reductions. In all cases two reductions were clearly identified, for the majority of the complexes a third process was observed; only $[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]^{3-}$ and $[Fe_6Mo_2S_8X_6(SR)_3]^{3-}$ (where X = Cl and R = Et or CH_2CH_2OH; X = Br and R = Et) showed clear evidence for a fourth reduction. The pattern of these reductions is similar for each compound; the second reduction occurs at a potential some 200 mV more negative than the first, the third is 1.0 ± 0.1 V more negative than the second for the complexes with thiolato-ligands exclusively or *ca.* 0.7 V more negative for those complexes with three thiolato- and six halo-ligands, and the fourth reduction occurs at a potential *ca.* 250 mV more negative than the third. The chloro- and bromo-substituted clusters also showed evidence of a fifth reduction process at *ca.* −2.45 V for the chloro-derivatives in dmso solution; $[Fe_6Mo_2S_8Br_6(SEt)_3]^{3-}$ appeared to be unstable in dmso and was therefore studied in MeCN where it underwent a fifth reduction at *ca.* −2.58 V. These latter reductions occurred very close to the limit imposed by the background electrolyte and may not be genuine features of these systems and will not be discussed further.

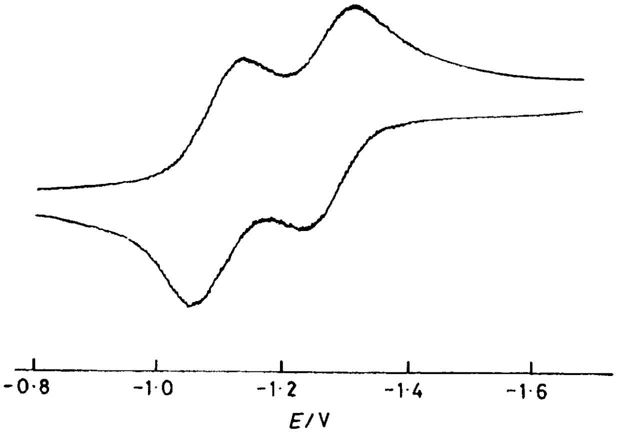

FIGURE 5 Staircase cyclic voltammogram of $[NBu^n_4]_3$-$[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]$ in dmso containing $[NPr^n_4][ClO_4]$ (0.1 mol l^{-1}) (step-width 128 × 10^{-3} s)

We consider that each of the electrochemical reductions of the trianions corresponds to a one-electron change for two reasons. Firstly, in the differential polarographic studies the peak width at half height was typically *ca.* 110 mV for each of the peaks. Parry and Osteryoung [18] have shown that the theoretical peak widths at half height for one-, two-, and three-electron processes in differential pulse polarography are 90.4, 45.2, and 30.1 mV, respectively. Therefore, the observed values are each taken to correspond to a one-electron reduction process, perhaps broadened by the close approach of another such peak. Secondly, Ryan [13] has indicated that in cyclic staircase voltammetry, the separation of forward and reverse peaks should be $68/n$ to $100/n$ (where n represents the number of electrons transferred), for reversible processes. The corresponding peak separation observed in all of the staircase cyclic voltammetric studies reported here was >80 mV and thus it seems most probable that $n = 1$. Furthermore, we note that the characteristics observed in both differential pulse polarography and cyclic staircase voltammetry for the individual redox changes of the Fe_3MS_4 cubane-like cluster dimers correspond very closely to those observed by us for the Fe_4S_4 cubane-like cluster for which the one—electron nature of the processes has been established.[19]

The first reduction potential of each of the $[Fe_6M_2S_8(SR)_9]^{3-}$ (M = Mo and R = Ph, Et, or CH_2CH_2OH; M = W and R = Et) complexes shows a striking resemblance to that of the corresponding $[Fe_4S_4(SR)_4]^{2-}$ system (Table 3). Furthermore, the variation in the values of this potential for the $[Fe_6Mo_2S_8(SR)_9]^{3-}$ complexes firstly, from R = Ph to R = C_6H_4Me-*p* and C_6H_4Cl-*p* and secondly, for R = Et upon substitution of the terminal thiolato-groups by halide ions, parallel the corresponding changes observed [19-23] in the first reduction potential of $[Fe_4S_4(SR)_4]^{2-}$ complexes. This similarity in behaviour between the Fe_3MS_4 cluster dimer trianions and the Fe_4S_4 cluster dianions, together with the similar first reduction potentials of $[Fe_6Mo_2S_8(SEt)_9]^{3-}$ and $[Fe_6W_2S_8(SEt)_9]^{3-}$, suggests that this first reduction of the Fe_3MS_4 cubane-like cluster dimer trianions adds an electron to an orbital which predominantly involves the iron and sulphido-atoms of the core. {We do note that the nature of the bridging ligands does appear to affect the first reduction potential to some slight extent; thus $[Fe_6Mo_2S_8(SPh)_9]^{3-}$ and $[Fe_6Mo_2S_8(SPh)_6(OMe)_3]^{3-}$ have their first reduction potentials at −1.26 and −1.31 V respectively, and the shift to a less negative potential upon chloride substitution of the terminal thiolato-groups is less (by 50 mV) than anticipated from the behaviour [22,23] of the corresponding Fe_4S_4 systems.}

Given the above information and the 500—700 mV separation of the first and second reduction potentials of $[Fe_4S_4(SR)_4]^{2-}$ complexes,[19-23] it is possible to offer a simple rationalisation of the pattern of the four reductions of these $[Fe_6M_2S_8L_9]^{3-}$ complexes, taking the view that electron addition occurs separately to each of the constituent Fe_3MS_4 cubane-like clusters. The first electron, when added to one Fe_3MS_4 centre, increases the negative potential required to add the second electron since this will be accommodated in the other half of the same anion, the third electron corresponds to the second reduction of one of the clusters and thus would be expected to be at a potential 500—700 mV more negative than the second reduction, plus *ca.* 200 mV because of the close proximity of the other reduced cluster; the fourth electron corresponds to the second reduction of the other cluster and thus will be *ca.* 200 mV more negative than the third reduction potential.

The extent of the electrochemical reversibility of the reduction of the Fe_3MS_4 dimer trianions has been explored using cyclic staircase voltammetry with varying scan widths. Two limitations on reversible behaviour were observed. The first was the stability of the reduced species, in particular towards reaction with the solvent. The second was the rate constant for electron transfer, as indicated by the profile of the cyclic staircase voltammogram, in particular the separation of the peaks for forward and reverse scans, ideally 68 to 100 mV (depending upon experimental conditions)[18] for a one-electron reversible process, and the reproducibility of this from scan rates of *ca.* 150 to 10 000 mV s^{-1}. For all the trianions studied, no behaviour which could be considered as reversible was observed for reductions to the 6– and 7– anions. The reductions of the 4– and 5– anions exhibited a solvent dependence, with MeCN allowing reversibility to be manifest to a significantly greater extent than dmso; this was particularly marked for $[Fe_6W_2S_8(SEt)_9]^{3-}$ which showed[4] no reduction that could be classified as reversible in dmso but (see below) showed clear evidence for reversibility in MeCN solution. The compound $[Fe_6Mo_2S_8X_6(SEt)_3]^{3-}$ (where X = Cl or Br) showed no good evidence for reversibility and, since the appearance of the peaks in the reverse scan became even less pronounced at slower scan rates, we attribute the lack of reversibility to decomposition of the products. At scan rates of 150 mV s^{-1} in MeCN solution, all of the other complexes studied showed good evidence for reversibility in respect of the 3– to 4– and 4– to 5– reductions; peak to peak separations were <100 mV and the ratios of peak currents for reverse scans were 1.0 ±0.1. However, at higher scan rates only $[Fe_6M_2S_8(SEt)_9]^{3-}$ (where M = Mo or W) showed behaviour for these reductions which could be classified as reversible. Thus for example, the peak to peak separations for $[Fe_6Mo_2S_8(SC_6H_4Cl\text{-}p)_9]^{3-}$ showed a general increase with scan rate, from *ca.* 100 mV at a scan rate of 150 mV s^{-1} to 270 mV for the first reduction, and 320 mV, for the second reduction, at 5 000 mV s^{-1}; in contrast the reductions for $[Fe_6M_2S_8(SEt)_9]^{3-}$ (where M = Mo or W) showed virtually no increase up to 5 000 mV s^{-1} and only near 10 000 mV s^{-1} did they increase to *ca.* 200 mV. Furthermore, at this 5 000 mV s^{-1}, the ratio of the peak current for forward and reverse scans was still close to 1.0 for the 3– to 4– reduction.

However, we consider that the strict compliance with electrochemical reversibility should not be seen as necessarily limiting the chemical utility of these Fe_3MS_4 dimers. Thus we have already demonstrated[24] that $[Fe_6Mo_2S_8(SCH_2CH_2OH)_9]^{3-}$, in buffered aqueous media containing excess of 2-hydroxyethanethiol, serves as an electron-transfer agent between dithionite, or spinach Chloroplast, and the hydrogenase of *Clostridium pasteurianum.* Given the electrochemical information presented above, we feel that the Fe_3MoS_4 cubane-like dimer complexes may be useful two-electron transfer mediators for chemical (and biochemical) systems.

[0/312 *Received, 25th February,* 1980]

We thank the S.R.C. for financial support, and Climax Molybdenum Company Ltd. for their donation of chemicals.

REFERENCES

[1] S. P. Cramer, K. O. Hodgson, W. O. Gillum, and L. E. Mortenson, *J. Amer. Chem. Soc.*, 1978, **100**, 3398; 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, *ibid.*, p. 3814.

[2] G. Christou, C. D. Garner, F. E. Mabbs, and T. J. King, *J.C.S. Chem. Comm.*, 1978, 740.

[3] G. Christou, C. D. Garner, F. E. Mabbs, and M. G. B. Drew, *J.C.S. Chem. Comm.*, 1979, 91.

[4] S. R. Acott, G. Christou, F. E. Mabbs, R. M. Miller, T. J. King, and C. D. Garner, *Inorg. Chim. Acta*, 1979, **35**, L337; G. Christou, C. D. Garner, R. M. Miller, and T. J. King, *J. Inorg. Biochem.*, 1979, **11**, 349.

[5] G. Christou, C. D. Garner, T. J. King, C. E. Johnson, and J. D. Rush, *J.C.S. Chem. Comm.*, 1979, 503.

[6] 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.

[7] T. E. Wolff, J. M. Berg, K. O. Hodgson, R. B. Frankel, and R. H. Holm, *J. Amer. Chem. Soc.*, 1979, **101**, 4140.

[8] T. E. Wolff, J. M. Berg, P.P. Power, K. O. Hodgson, R. H. Holm, and R. B. Frankel, *J. Amer. Chem. Soc.*, 1979, **101**, 5454.

[9] R. Cammack, D. P. E. Dickson, and C. E. Johnson in, 'Iron-Sulfur Proteins,' ed. W. Lovenberg, Academic Press, New York, 1977, vol. III, pp. 283—330 and refs. therein.

[10] B. E. Smith and G. Lang, *Biochem. J.*, 1974, **137**, 169; J. Rawlings, V. K. Shah, J. R. Chisnell, W. J. Brill, R. Zimmerman, E. Münck, and W. H. Orme-Johnson, *J. Biol. Chem.*, 1978, **253**, 1001.

[11] G. Christou and C. D. Garner, preceding paper.

[12] D. P. E. Dickson, C. E. Johnson, P. Middleton, J. D. Rush, R. Cammack, D. O. Hall, R. N. Mullinger, and K. K. Rao, *J. Phys. (Paris), Colloq.*, 1976, **37**, C6.

[13] M. D. Ryan, *J. Electroanalyt. Chem. Interfacial Electrochem.*, 1977, **79**, 105.

[14] L. L. Miaw, P. A. Bondreau, M. A. Pichler, and S. P. Perone, *Analyt. Chem.*, 1978, **50**, 1988.

[15] R. M. Miller, Ph.D. Thesis, University of Manchester; unpublished work.

[16] C. E. Johnson, J. D. Rush, G. Christou, and C. D. Garner, unpublished work.

[17] R. H. Holm and J. A. Ibers in, 'Iron-Sulfur Proteins,' ed. W. Lovenberg, Academic Press, New York, 1977, vol. III, pp. 205—281 and refs. therein.

[18] E. P. Parry and R. A. Osteryoung, *Analyt. Chem.*, 1965, **37**, 1634.

[19] J. J. Mayerle, S. E. Denmark, B. V. DePamphilis, J. A. Ibers, and R. H. Holm, *J. Amer. Chem. Soc.*, 1975, **97**, 1032.

[20] B. V. DePamphilis, B. A. Averill, T. Herskovitz, L. Que, jun., and R. H. Holm, *J. Amer. Chem. Soc.*, 1974, **96**, 4159.

[21] C. L. Hill, J. Renaud, R. H. Holm, and L. E. Mortenson, *J. Amer. Chem. Soc.*, 1977, **99**, 2549.

[22] G. B. Wong, M. A. Bobrik, and R. H. Holm, *Inorg. Chem.*, 1978, **17**, 578.

[23] J. Cambray, R. W. Lane, A. G. Wedd, R. W. Johnson, and R. H. Holm, *Inorg. Chem.*, 1979, **16**, 2565.

[24] M. W. W. Adams, K. K. Rao, D. O. Hall, G. Christou, and C. D. Garner, *Biophys. Acta*, 1980, **589**, 1.