$Fe_4S_4 \rightarrow Fe_3S_4$ Conversions: Spectroscopic Evidence for the Generation of Fe_3CoS_4 Clusters

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The controlled aerobic oxidation of $[Fe_4S_4(tibt)_4]^{2-}$ (tibt = $SC_6H_2Pr^i_3$-2,4,6) generates, in the presence of $CoCl_2$, the new $[Fe_3CoS_4]^{2+}$ cluster species, which can also be quantitatively obtained by reaction of the linear trimer $[Fe_3S_4(tibt)_4]^{3-}$ with $CoCl_2$; this new mixed valence $[Fe^{2+},2Fe^{3+},Co^{2+}]$ species, with an $S_{tot} = 1/2$ ground state, was characterised by EPR and Mössbauer spectroscopy, magnetic susceptibility and cyclic voltammetry.

Since 3Fe clusters were first shown to exist,[1] it has been demonstrated that some are intrinsic components of the functional enzymes,[2] while others are considered as artifacts being formed under physiological conditions, as intermediates of cluster formation, rearrangement or degradation.[3] Most of these 3Fe structures can be interconverted with 4Fe cubanes; treatment of 4Fe proteins with chemical oxidants produces 3Fe centres,[3] which can reincorporate a fourth Fe,[3d,4] or Co or Zn as in the case of *Desulfovibrio gigas* Fd II.[5] So far, synthetic efforts to create adequate 3Fe model systems have produced the ring structure $[Et_4N]_3[Fe_3(SPh)_3Cl_3]$[6a] and the capped structure $Fe_3S\{1,2\text{-}(SCH_2)_2\text{-}4,5\text{-}(Me)_2C_6H_2\}_3$.[6b] More recently, it has been reported[7] that $[Fe_4S_4(SBu^t)_4]^{2-}$ can be oxidised by $Fe(CN)_6^{3-}$ in dimethylformamide (DMF)–H_2O to yield a 3Fe species spectroscopically similar to the 3Fe centres in proteins. However, this species is unstable at temperatures above −40 °C and brief incubation at room temperature causes a total and irreversible disappearance of the 3Fe EPR

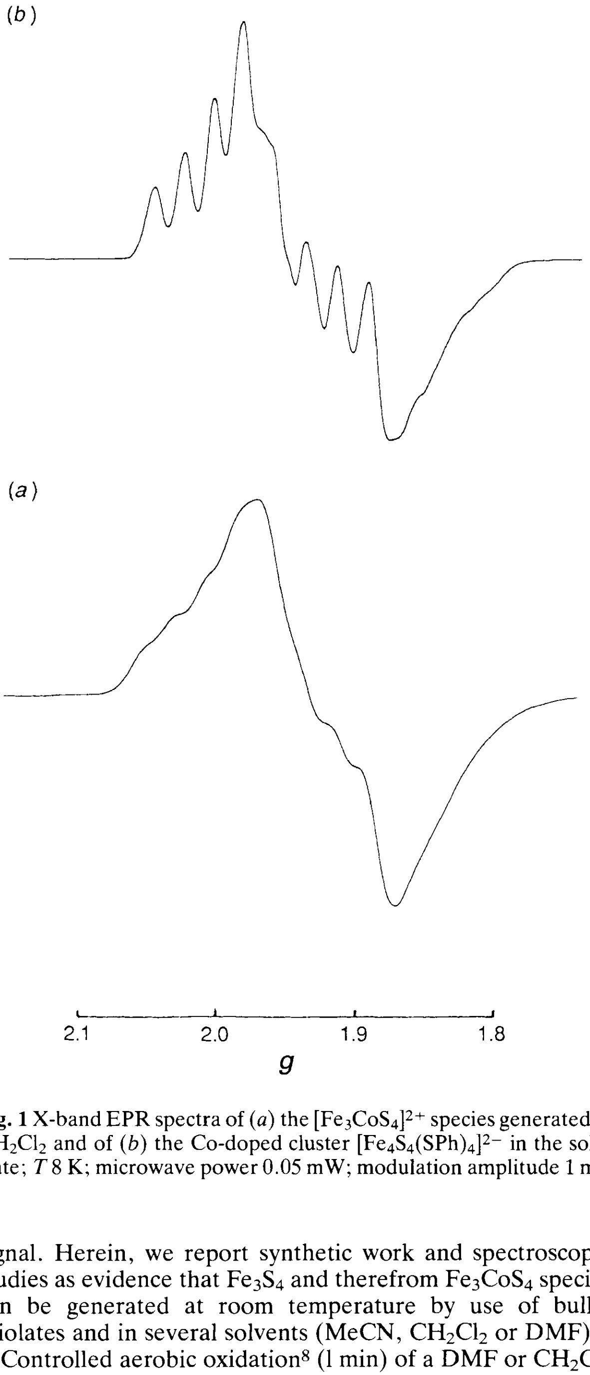
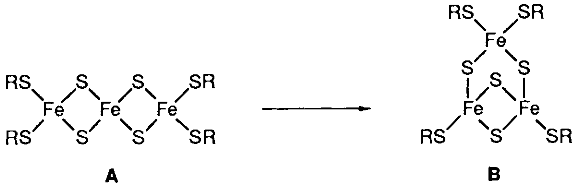


Fig. 1 X-band EPR spectra of (*a*) the $[Fe_3CoS_4]^{2+}$ species generated in CH_2Cl_2 and of (*b*) the Co-doped cluster $[Fe_4S_4(SPh)_4]^{2-}$ in the solid state; *T* 8 K; microwave power 0.05 mW; modulation amplitude 1 mT

signal. Herein, we report synthetic work and spectroscopic studies as evidence that Fe_3S_4 and therefrom Fe_3CoS_4 species can be generated at room temperature by use of bulky thiolates and in several solvents (MeCN, CH_2Cl_2 or DMF).

Controlled aerobic oxidation[8] (1 min) of a DMF or CH_2Cl_2 solution of $[Et_4N]_2[Fe_4S_4(tibt)_4]$ **1** (tibt = $SC_6H_2Pr^i_3$-2,4,6, 5 mmol) at room temperature produces partial breakdown of the Fe_4S_4 cluster to give a Fe_3S_4 centre and a Fe^{3+} species. Indeed, when monitoring the reaction by EPR, a signal characteristic of high-spin monomeric Fe^{3+} species appears first at $g = 4.3$, followed (after 1–2 min) by another almost isotropic signal at $g = 2.022$ (it broadens on the high-field side) that we attribute to the $[Fe_3S_4]^+$ entity.[9] When anhydrous $CoCl_2$ is added in an equimolar ratio to the above solution, oxygen is admitted (1 min) and the solution stirred for 2 h at room temperature, a $[Fe_3CoS_4]^{2+}$ centre is generated. The EPR spectrum (Fig. 1*a*) shows the total disappearance of monomeric Co^{2+} ($S = 3/2$) and the appearance of an $S = 1/2$ signal with principal resonances centred at $g_z = 1.987$, $g_y = 1.938$ and $g_x = 1.810$. The spectrum also shows the presence of eight hyperfine lines with a coupling of $A = 4.4$ mT. These *g* values and the presence of Co ($I = 7/2$) hyperfine resonances are strikingly similar features to those associated with the Fe_3Co species present in *D.gigas* Fe II[5a] and in the cobalt-doped diamagnetic matrix $[Bu_4N]_2[Fe_4S_4(SPh)_4]$ (Fig. 1*b*).[10]



Scheme 1

They suggest that the Co^{2+} has indeed been incorporated into the vacant site of the Fe_3S_4 species in its reduced state. Double integration of the EPR signal relative to a Cu standard indicates 60–70% conversion of Fe_4S_4 into Fe_3CoS_4 cluster.

The $[Fe_3CoS_4]^{2+}$ species can also be generated under anaerobic conditions and in quantitative yield by addition of Co^{2+} to the oxidised state of the linear trimer $[Et_4N]_3[Fe_3S_4(tibt)_4]$ **2** in Me_3CN. Filtration and evaporation of the solvent *in vacuo* yields $[Et_4N]_2[Fe_3CoS_4(tibt)_4]$ **3** as a black microcrystalline solid.† The cyclic voltammogram‡ of **3** in MeCN shows a new one-electron quasi-reversible wave at $E_{1/2} = -1.09$ V *vs.* SCE ($E_p = 90$ mV) associated with the $[Fe_3CoS_4]^{2+/1+}$ couple, and an identical EPR signal to that in Fig. 1*a* is observed. Magnetisation measurements on a solid sample of **3** were made at 5 K in fields up to 30 kOe (1 Oe = 10^3 A m^{-1}). Variable temperature magnetic susceptibility data were collected at 3 kOe, in a region where the magnetisation varied linearly with the applied field. The temperature behaviour of the data strongly suggests the presence of an $S = 1/2$ ground state ($\mu_{eff} = 1.82$–1.83 μ_B at 18–80 K) and of both inter- and intra-cluster antiferromagnetism. The paramagnetic Mössbauer spectrum of **3** at 77 K[12] is composed of two broad lines exhibiting asymmetry; this suggests the existence of inequivalent iron sites. The best fit requires the superimposition of three quadrupole components with respective isomer shift (IS)§ (and quadrupole splitting) values of 0.46(1) [0.932(2) mm s^{-1}], 0.43(1) [1.32(2) mm s^{-1}] and 0.33(1) mm s^{-1} [0.78(2) mm s^{-1}]. Comparison of these data with those of the oxidised Fe_3Co cluster in the protein[5a,11] shows that the Mössbauer results are very similar. The IS values, which can be used as a primary oxidation state indicator, suggest that one iron site is Fe^{3+}, whereas the other two sites are similar to the mixed-valence irons of $[Fe_4S_4]^{2+}$ clusters. The system can therefore be described as being formed of an Fe^{3+} and of a delocalised Fe^{2+}/Fe^{3+} pair.

The structural rearrangement of the trinuclear cluster **2** from a linear to a pseudocubic geometry, observed here in the presence of Co^{2+}, has recently been found to take place with the analogous $[Fe_3S_4(SEt)_4]^{3-}$ in the presence of $Mo(CO)_3(MeCN)_3$ and to give a distorted Fe_3MoS_4 structural unit.[12] These rearrangements are accompanied by a change in oxidation state of the Fe atoms, as the starting Fe linear cluster is made of 3 Fe^{3+}, whereas the final Fe_3MS_4 cubanes contain formally 2 Fe^{3+} and 1 Fe^{2+}. This reduction is possibly due to the presence of reducing thiolate in the solution liberated from the linear species. It may well be that the [3 Fe^{3+}] to [2 Fe^{3+}, 1 Fe^{2+}] reduction enhances the following structural rearrangement in Scheme 1, where the **B** species can easily accommodate a fourth metal to form a pseudocubane Fe_3MS_4 structure.

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† Analytical data for $[(C_2H_5)_4N]_2$ $[Fe_3CoS_4(S\text{-}C_{15}H_{23})_4]$: Found: C, 58.9; H, 8.7; Co, 3.4; Fe, 10.3; N, 1.9; S, 16.1. $C_{76}H_{136}Co_1Fe_3N_2S_8$ requires C, 58.6; H, 8.55; Co, 3.79; Fe, 10.8; N, 1.8; S, 16.5%

‡ Electrochemical data were obtained for a cluster concentration of 2 mmol dm^{-3} in 0.1 mmol dm^{-3} solutions of Bu_4NPF_6 with platinum as the working electrode and a saturated calomel electrode (SCE) as the reference.

§ The isomer shift values are relative to the metallic Fe at 300 K.

Indeed, 3 Fe centres in proteins are always in the reduced state when the conversions 3 Fe → 3 Fe, 1 M (M = Fe, Co, Zn) occurs.[3d,4,5] We are pursuing at present applied field Mössbauer studies to characterise further these new entities. Experiments are also under way to try and incorporate metals other than Co (Zn, Mn, Cu).

Received, 23rd July 1990; Com. 0/03315D

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