Electron Spin Resonance Spectra of an Iron(III) Trisdicyano-1,2-dithiolene Complex

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WE report observations on the complex[1] $[Ph_4P]_3$-$[FeS_6C_6(CN)_6]^{3-}$, whose e.s.r. spectrum is similar to those obtained from certain reduced nonhaem iron compounds,[2] and certain proposed model compounds.[3]

At room temperature, a weak spectrum is observed. Intensity measurement by double integration suggests that this signal accounts for only 2% of the total iron in the sample and can thus be ascribed to impurity; the g values are 2·14, 2·10, and 2·01. As the temperature is lowered a strong spectrum appears (see Figure 1); the g values are 2·225, 2·114, and 1·986 ($\pm$0·002). No other absorption was observed.

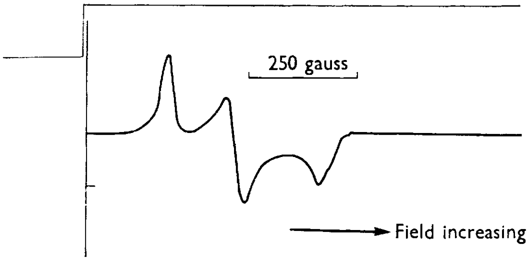

FIGURE 1. *The e.s.r. spectrum of* $[FeS_6C_6(CN)_6]^{3-}$ *at* 4·2° K.

The plot of signal intensity (allowing for the impurity) against $1/T$ is shown in Figure 2. This demonstrates that normal behaviour for a paramagnetic substance is followed only below 140° K, resembling the behaviour of reduced xanthine oxidase or spinach ferredoxin.[4] Double integrations carried out on the spectra at 113° and 29° K, and on the spectra of a 2 mmolar Cu^{2+} : 20 mmolar EDTA solution at the same temperatures indicate that, assuming a 1 : 1 relationship between the transition probabilities of the copper(II) and iron(III) signals, all the iron atoms in the sample contribute to the signal. Measurements at several power levels and temperatures showed that the sample was not being saturated with microwave power. The shoulder (g, 1·974) on the high-field side of the g, 1·986 peak at 4·2° K (Figure 1), is not seen at 20° K and above.

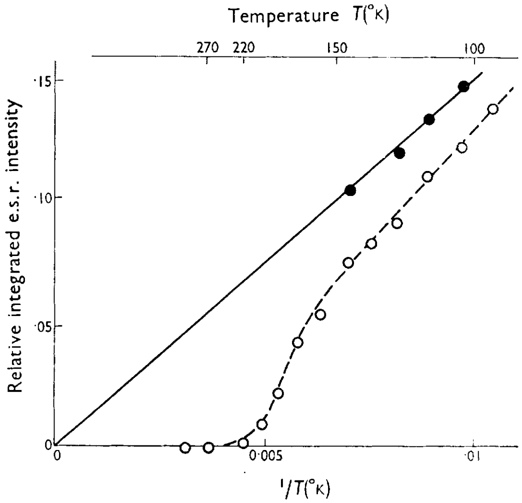

FIGURE 2. *Variation of e.s.r. signal intensity as a function of temperature for* $[FeS_6C_6(CN)_6]^{3-}$ (○) *and the copper*(II) *EDTA standard* (●).

Anaerobic solution studies (dichloromethane) show the same e.s.r. spectrum at low temperatures. If oxygen is admitted, this spectrum disappears and is replaced by a more complex one consistent with the presence of $[FeS_6C_6(CN)_6]^{2-}$. Subsequent sulphite or borohydride reduction causes a partial reappearance of the spectrum of the reduced form, $[FeS_6C_6(CN)_6]^{3-}$.

With the Griffith's method[5] [applicable to low-spin iron(III) complexes with an environment of lower than tetragonal symmetry] and taking the observed values of g_x, 2·225, g_y, 2·140, g_z, 1·986, it is found that the separation of the t_{2g} levels in this complex is $d_{xz} < d_{xy} < d_{yz}$ with $\Delta E(xz - xy) =$ 282 cm.$^{-1}$ and $\Delta E(xy - yz) = 338$ cm.$^{-1}$. In this calculation, the spin-orbit coupling constant ζ was taken to be -450 cm.$^{-1}$ and the orbital reduction factor, k, as unity. More realistic values of these parameters would require the t_{2g} orbitals to be closer in energy. This calculation shows: (i) the energy levels are about equally spaced, indicating symmetry considerably lower than tetragonal, (ii) the energy separations are much smaller than in certain haemoglobin derivatives,[5] consistent with the observation that spin pairing does not take place in the oxidised form, and (iii) the strong delocalisation implied requires an oxidation state considerably lower than (III) as formally required.

Mössbauer studies[6] on the di- and tri-anionic species also indicate marked distortion from O_h symmetry, as do X-ray powder diffraction patterns.[1]

We thank Dr. J. Locke for a sample of the complex and for stimulating discussions.

(*Received, May 20th,* 1968; *Com.* 639.)

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