

A New Mode of Antiferromagnetic Interactions: Tris(pyrrolidylthiocarbamato)iron(III)

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Summary Spin delocalisation to a dithiocarbamate ligand, and consequent antiferromagnetic interaction, occurs in the d^5 ($t_{2g}^3 e_g^2$) complex but not in the isomorphous d^3 (t_{2g}^3) complex; when these interactions are removed by dilution, a sextet-quartet equilibrium is apparent in the d^5 complex.

Using a newly developed superconducting susceptometer,¹ we have observed unusual behaviour in the susceptibility of tris(pyrrolidylthiocarbamato)iron(III), FePDC, and in the analogous chromium complex at low temperatures for various dilutions and at widely different field strengths over a wide temperature range. The importance of low-temperature magnetic data on these compounds in the interpretation of Mössbauer observations has been stressed,² but it has not been possible to understand the behaviour of these compounds from previous magnetic work using conventional apparatus.³

Contrary to previous interpretations,⁴ FePDC exhibits significant, though indirect, antiferromagnetic interactions; the moment μ remains close to the high spin value (5.9 BM)† down to temperatures near that of liquid helium, but at very low temperatures, μ falls dramatically and the susceptibility χ passes through a maximum near 2 K. No significant difference is observed in χ at 1 T and 1.15×10^{-2} T; therefore magnetic saturation is not responsible. The region of greatest interest is near liquid helium temperature and below, and typical results are given in Figures 1 and 2. The numbers on the graphs indicate the proportion of FePDC in the sample. On increasing dilution in the isomorphous CoPDC, μ_{Fe} and χ_{Fe} increase and the χ maximum disappears (Figure 1), indicating removal of antiferromagnetic interactions. The accuracy of the data

† All measurements given using the c.g.s. system of units.

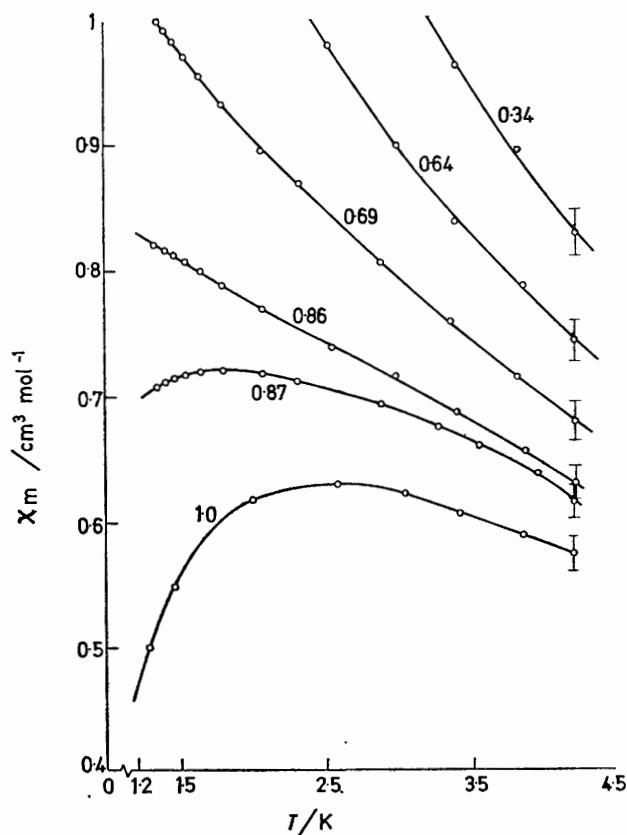


FIGURE 1

is much higher than the observed changes (error bars indicate the uncertainty in the absolute values due to sample preparation; the relative accuracy of the measurements is given by the size of the points).

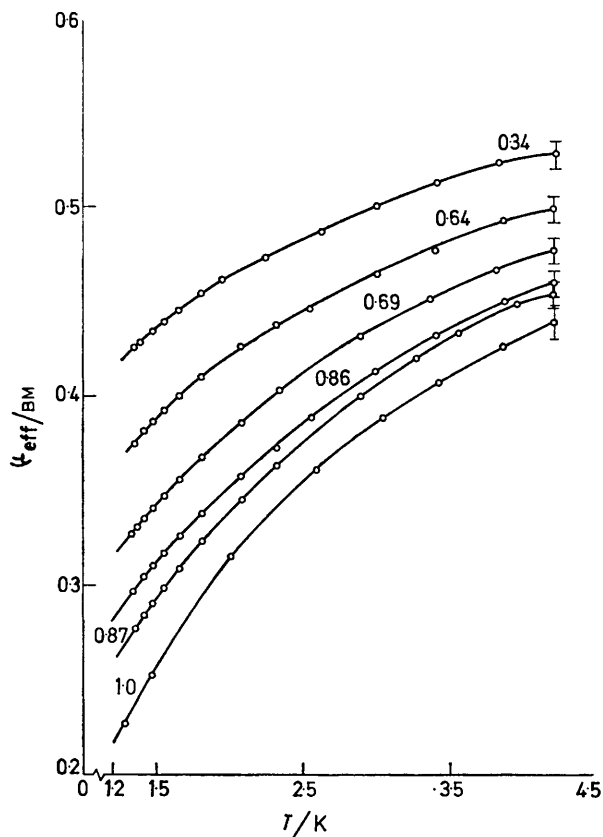


FIGURE 2

On approaching infinite dilution, μ_{Fe} falls again slightly, indicating removal of small ferromagnetic interactions, with a lower limit on μ_{Fe} of about 3.6 BM. This observation suggests an unprecedented $S = \frac{5}{2}(^6A_1) \rightleftharpoons S = \frac{3}{2}(^4T_1)$ electronic equilibrium. The high dilutions were made in both CoPDC and in frozen $CHCl_3$.

The Cr^{III} complex shows only very slight increase in μ on dilution, even though this compound has the same structure as FePDC [$\mu(100\%) = 3.72(4.2\text{ K}), 3.45(1.27\text{ K})$; $\mu(69\%) = 3.78(4.2\text{ K}), 3.54(1.27\text{ K})$; $\mu(41\%) \simeq 3.83(4.2, 1.27\text{ K})$]. The 1H n.m.r. of FePDC,⁵ confirmed by this work, indicates extensive delocalisation of unpaired electrons on to the ligands. However, from the 1H n.m.r. of CrPDC, we observe significant paramagnetic line broadening but negligible delocalisation. Consequently the e_g electrons, present only in the iron complex, must be primarily responsible for both the delocalisation and the antiferromagnetic interactions.

The metal atoms are separated by 9 Å,⁶ too far for the strong interactions observed in the iron complex, but not too far for the weaker interactions in the CrPDC. The bulk of the interactions in FePDC must occur between various ligand atoms which are separated by only van der Waals' distances. Although the system is obviously too complex for a detailed mathematical description, the mechanisms involved can be elegantly demonstrated by this method. The low temperature Mössbauer data on FePDC can now be interpreted in light of the present results.⁷

Although FePDC and CrPDC are isomorphous, very small bond length and angle differences between them may exist. The effect of the $CHCl_3$ molecule is significant but much smaller than the phenomena discussed above. The entire series MPDC- $CHCl_3$ and MPDC is under investigation with X-ray crystallography. The complexes MPDC- $CHCl_3$ (from solutions containing $CHCl_3$) and MPDC (obtained by removal of $CHCl_3$, or by crystallisation from benzene) form two isomorphous groups.

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