

Intermolecular Magnetic Interactions in a Mixed-valence Compound: Inelastic Neutron Scattering Spectrum of $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$

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An inelastic neutron scattering spectrum of the mixed-valence compound $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$ shows 11 energy transfers in the frequency range 2–25 cm^{-1} , which disappear on dilution in a host lattice, indicating intermolecular origin; this is the first evidence of strong intermolecular electronic interactions in a mixed-valence system.

Trinuclear metal carboxylate complexes of the general formula $[\text{M}_3\text{O}(\text{RCO}_2)_6\text{L}_3]^{n+}$ (Fig. 1) are important models for the study of weak magnetic interactions between metal atoms in small clusters.¹ Magnetic exchange splittings of three complexes containing mixed trinuclear clusters, $[\text{Fe}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$, where M = Mn, Co and Fe, were observed using incoherent inelastic neutron scattering spectroscopy (IINS),² and further investigations at higher resolution showed that the lowest-energy band consisted of a number of well-defined but closely-spaced doublets.³ Here we present evidence that this multiplicity of bands is due to intermolecular exchange coupling.

The IINS spectrum of the mixed-valence compound $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$ ($\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$) at 1.5 K is shown in Fig. 2. At least 11 transitions can be seen in the energy transfer range 2 to 25 cm^{-1} . The variation of intensity with momentum transfer is consistent with their being of magnetic character. A spectrum of the analogous $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$ compound under the same conditions shows only a broad band—probably a doublet—at 22 to 24 cm^{-1} . The spectrum of a solid solution of the two compounds, of composition $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_{1-x}\text{Co}^{\text{II}}_x\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$, where $x = 0.79$, shows a weak and very broad feature centred at *ca.* 15 cm^{-1} and spreading over the range of the transitions of the $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ complex, together with the doublet already men-

tioned as characteristic of the $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$ complex [Fig. 3, curve 3(c)]. In contrast, a physical mixture of the two complexes, in the same ratio, shows all the features from the spectra of $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$, as also does a simulated spectrum calculated as the appropriately weighted mean of the spectra

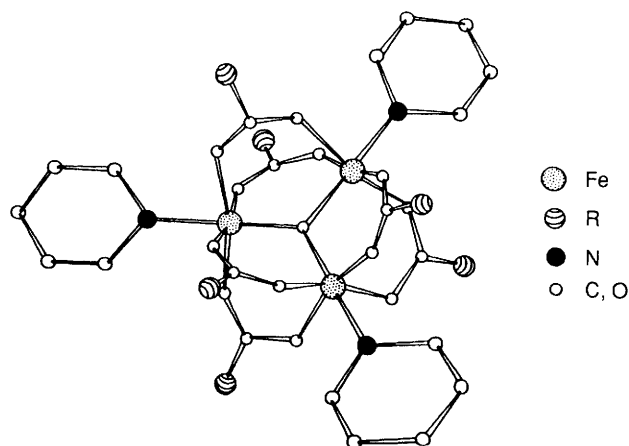


Fig. 1 Structural unit of the complex $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$

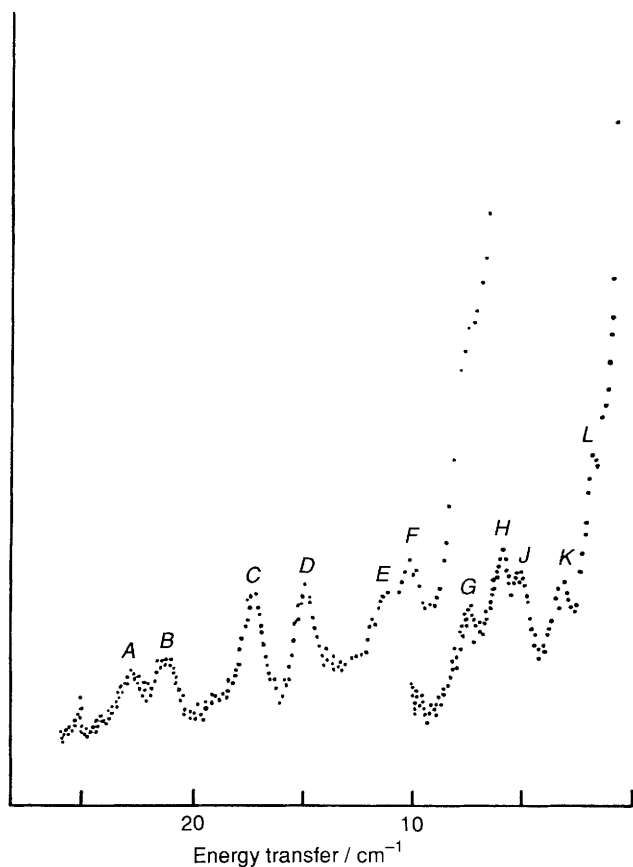


Fig. 2 Inelastic neutron scattering spectra of the mixed valent compound $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$. Vertical axis: neutron counts/arbitrary units. Left: $T = 1.5$ K, incident neutron beam wavelength $\lambda = 4.5$ Å. Right: $T = 1.5$ K, $\lambda = 6.0$ Å. Peak positions/ cm^{-1} : A 22.9, B 21.2, C 17.4, D 15.1, E 11.4, F 10.2, G 7.4, H 6.0, J 5.3, K 3.3, L 1.9. Recorded on instrument IN5, at the Institute Laue-Langevin, Grenoble.

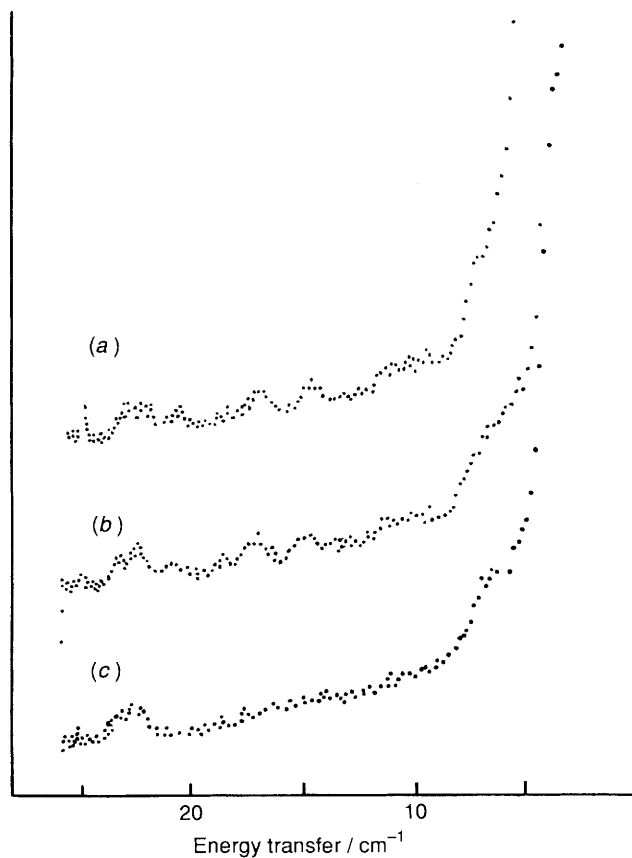


Fig. 3 Inelastic neutron scattering spectra. Vertical axis: neutron counts/arbitrary units (spectra linearly displaced for clarity). (c) The solid solution $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}_{(1-x)}\text{Co}^{\text{II}}\text{O}(\text{O}_2\text{CCD}_3)_6(\text{C}_5\text{D}_5\text{N})_3](\text{C}_5\text{D}_5\text{N})$, $x = 0.8$; (b) the physical mixture, $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}} + \text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$, ratio $[\text{Fe}^{\text{II}}]/[\text{Co}^{\text{II}}] = 0.25$; (a) calculated spectrum, the mean of $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$, in the same ratio.

of the pure compounds [Fig. 3, curves (a) and (b)]. These comparisons clearly demonstrate that the fine structure of the spectrum of $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ is due to intermolecular interactions. Three independent preparations of the mixed-valence material have given the same spectrum.

The pure mixed-valence and mixed-metal compounds are isomorphous at room temperature, with space group $R32$, implying that the Fe^{III} and Fe^{II} sites in $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$, and likewise the Fe^{III} and Co^{II} sites in $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$, are indistinguishable due to rotational disorder.⁴ In the case of $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$ the disorder must be static, and must persist down to low temperatures. In the case of $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$, however, the disorder is dynamic at sufficiently high temperatures,^{5,6} as a result of intramolecular electron transfer $\text{Fe}^{2+} \rightarrow \text{Fe}^{3+}$. Thus, at low enough temperatures, the molecules can 'freeze' into localised electronic configurations, in an ordered manner. Hendrickson and co-workers have in fact proposed that one of the low-temperature phases consists of domains ordered in this way.⁶ Such ordering will create local field anisotropies which can split the ground states of the individual molecules. We propose that this is the cause of the complications in the spectrum. In the crystal the three terminal pyridines of each molecule are coplanar, and the molecules are stacked with the pyridines interleaved; this could provide an exchange pathway *via* the electrons of the aromatic rings.⁷

Intermolecular coupling has been postulated before⁸ to explain magnetic properties of fully oxidised iron(III,III,III) and chromium(III,III,III) trimetallic clusters, but Tsukerblat

*et al.*⁹ showed that in those cases intercluster interaction is extremely weak. In particular, for the complex $[\text{Cr}_3\text{O}(\text{O}_2\text{CCH}_3)_6(\text{H}_2\text{O})_3]\text{Cl}\cdot 5\text{H}_2\text{O}$, low-temperature specific heat and magnetic data implied that the coupling constant could not exceed *ca.* 0.1 cm^{-1} . The chromium compound of course has no mixed valences, nor—perhaps more significantly—does its crystal structure show any obvious exchange pathway.

Adachi *et al.*¹⁰ have developed theoretical models to understand the effects of the quenched disorder in solid solutions of $\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}$ and $\text{Fe}^{\text{III}}_2\text{Co}^{\text{II}}$, and they have calculated a phase diagram which shows that at zero temperature, as x is progressively decreased, magnetic order is destroyed at a critical concentration of $x = 0.69$. We chose our value of x in order that our sample would be well within their ordered phase III. However Jang *et al.* have indicated the need for further development of such models by showing experimentally the presence of three phase transition temperatures in the $x = 0.5$ solid solution, in disagreement with the single transition from phase II to III predicted by the above model.⁷ The results we report here show that inelastic neutron scattering spectroscopy can be of use in mapping out these phase diagrams and, more importantly, in understanding the specific interactions present in separate phases. Further experiments to determine the nature of the magnetic ordering at the low temperatures used in this work will be of interest: for examples these could include thermodynamic data and spin-density mapping in single crystals by polarised diffraction.

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