

Electron Transfer Rates in a Trinuclear Mixed-valence Iron(III,III,II) Molecule: A Variable-temperature Infrared Spectroscopic Study

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In IR spectra of the mixed-valence compound $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{OCCMe}_3)_6(\text{C}_5\text{D}_5\text{N})_3]$, the bands assigned to in-plane vibration of the central oxygen atom show exceptional temperature dependence, interpreted as being due to electron transfer within the trinuclear cluster, with a rate constant of ca. 10^{11} s^{-1} at 300 K.

Mixed-valence trinuclear complexes of the type $[\text{M}^{\text{III}}_2\text{M}^{\text{II}}\text{O}(\text{OOCR})_6\text{L}_3]$ offer the possibility of measuring rates of intramolecular electron transfer, and there have been numerous attempts to do this, using a variety of spectroscopic techniques.¹ In the solid state, the complex $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{OCCMe})_6(\text{py})_3](\text{py})$ was studied by Hendrickson *et al.* using NMR and Mössbauer line broadening.² Limiting values of rate constants k for the intramolecular electron transfer reaction (1) were estimated^{2c} as $k \leq 3 \times 10^4 \text{ s}^{-1}$ at $T \approx 173 \text{ K}$



and $k \geq 10^7 \text{ s}^{-1}$ at $T \approx 190 \text{ K}$. Over the range 100 to 200 K, however, discrete phase transitions occur with strong cooperative interactions, and simple Arrhenius behaviour was not observed. Motions of the non-coordinated pyridine molecules are involved in the transitions, as shown by NMR² and neutron scattering³ experiments. In solution at room temperature, using the closely related pivalate complex $[\text{Fe}^{\text{III}}_2\text{Fe}^{\text{II}}\text{O}(\text{OCCMe}_3)_6(\text{py})_3]$,¹ reaction (1) has been shown to be rapid on the NMR timescale, but slow on the IR timescale.⁴ This complex is a promising material for mixed-valence studies, since it crystallises with no non-coordinated solvent molecules, and the large alkyl groups are expected to shield the complex molecules from each other and so favour independent motions of the central metal clusters. Here we report a remarkable temperature-dependent effect in the IR spectrum of **1** which we attribute to electron transfer.

The two bands marked **A** and **B** (Fig. 1) are assigned⁴ to the two components of $\nu_{\text{as}}(\text{Fe}_3\text{O})$, the asymmetric in-plane vibration of the central oxygen atom. With increasing temperature in the range 80 to 410 K, they broaden substantially and the frequency separation between them decreases. To allow for the thermal broadening always seen in IR spectroscopy, we note that other bands in the same spectrum broaden to a much lesser extent, and that they hardly shift at all within the limits of instrument resolution. We have also measured the behaviour of the corresponding bands in the spectrum of the analogous mixed-metal complex $[\text{Fe}^{\text{III}}_2\text{Ni}^{\text{II}}\text{O}(\text{piv})_6(\text{C}_5\text{D}_5\text{N})_3]$. Although the two components of $\nu_{\text{as}}(\text{Fe}_2\text{NiO})$ do change with

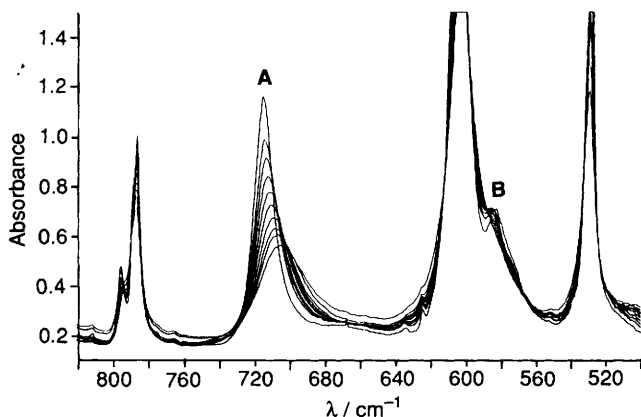


Fig. 1 The infrared spectra of $[\text{Fe}_3\text{O}(\text{OCCMe}_3)_6(\text{C}_5\text{D}_5\text{N})_3]$, at temperatures $T = 80, 170, 200, 230, 260, 290, 320, 350, 380$ and 410 K

temperature, the effect is much smaller than with the complex **1**. Evidently the mixed-valence complex remains valence-localised, on the IR timescale, through this temperature range, but in some sense the extent of localisation becomes less as the temperature is raised.

We suggest that this behaviour is a lifetime-broadening effect, resulting from the rapid electron transfer reaction (1). Infrared line broadening due to fast dynamic processes is a rare phenomenon, and has apparently not been seen before in connection with electron transfer. A few examples attributed to other mechanisms have been reported in the past, however,⁶⁻⁸ and the theory has been discussed.^{7b} In general, vibrational line broadening is not strictly analogous to NMR broadening, and the standard Bloch equations⁹ do not

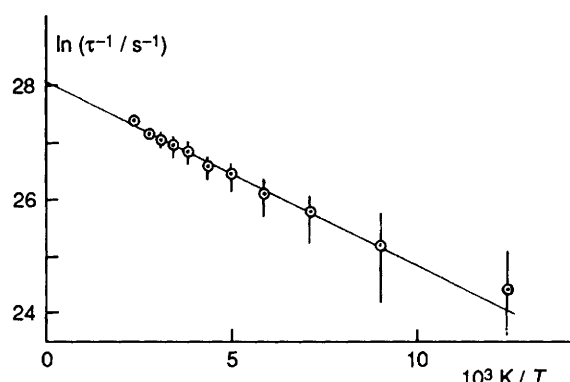


Fig. 2 Temperature dependence of width of Band A for $[\text{Fe}_3\text{O}(\text{OCCMe}_3)_6(\text{C}_5\text{D}_5\text{N})_3]$ —see text, eqns. (2) and (3)

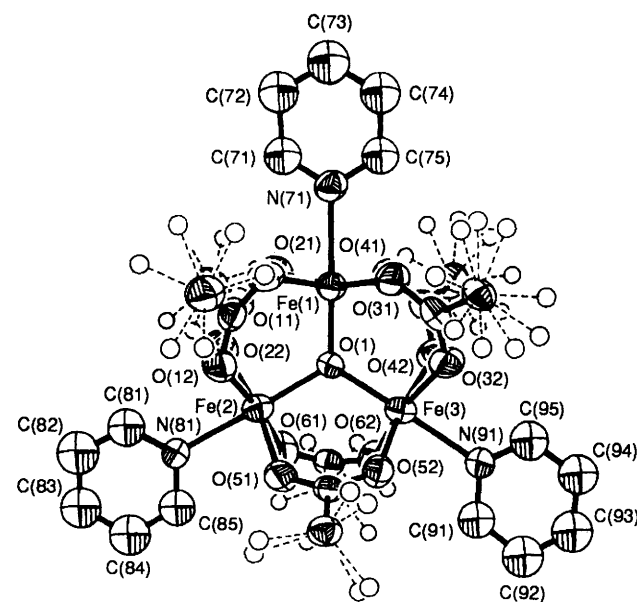


Fig. 3 Molecular structure of $[\text{Fe}_3\text{O}(\text{OCCMe}_3)_6(\text{C}_5\text{H}_5\text{N})_3]$, at room temperature

necessarily apply. This is particularly so when the coordinate of the vibration which is measured is also the reaction coordinate for the rate process of interest. In the present case electron transfer is coupled to metal–ligand vibrations, and the most important of these is $\nu_{\text{as}}(\text{Fe}_3\text{O})$, as is shown by the very large separation of the components, bands **A** and **B**. However, the shifts and broadenings we observe are small, hence we have provisionally used the theory as for NMR in the limit of slow-exchange, in which these problems do not apply.^{5,7b} The time constant τ of the rate process is given by eqn. (2), where $\nu_{1/2}$ is the full-width at half maximum

$$\tau^{-1} = 2\pi \{ \nu_{1/2} - \nu_{1/2}^0 \} \quad (2)$$

(FWHM) at a given temperature and $\nu_{1/2}^0$ is the FWHM at that temperature in the absence of exchange. We have chosen the better-resolved band **A** for analysis, and to allow for effects other than electron transfer we have taken the difference between the results for the mixed-valence and the mixed-metal complex *i.e.* eqn. (3), where in both cases $\Delta\nu_{1/2}$ is

$$\tau^{-1} = 2\pi \{ \Delta\nu_{1/2}(\text{Fe}_2\text{Fe}) - \Delta\nu_{1/2}(\text{Fe}_2\text{Ni}) \} \quad (3)$$

the increase in line-width over the (extrapolated) value at $T = 0$. A plot of τ^{-1} against $1/T$ gives $\tau^{-1} \cong 5 \times 10^{11} \text{ s}^{-1}$ at $T = 300 \text{ K}$ (Fig. 2).

The room-temperature crystal structure (Fig. 3) of **1** shows that the iron centre Fe(1) has metal–ligand distances consistent with fully oxidised iron(III). The other two have geometries intermediate between those expected for iron(III) and iron(II) but nevertheless crystallographically distinct.¹⁰ It seems likely that the dynamic electron transfer process involves the latter pair.

At the same time we note the possibility of an alternative mechanism which we call ‘static’ delocalisation in contrast to the ‘dynamic’ electron hopping. The IR data would be satisfied by any model in which two or more iron atoms of the cluster are structurally inequivalent. In a static model the electronic ground state would be expressed by a mixture of oxidation states (+2) and (+3) at each iron centre, subject to a mean value of (+8/3), with no time-dependent fluctuation. The actual values at each site would be smooth functions of the mean atomic coordinates, and the temperature effect would indicate that these coordinates in turn varied with temperature. The increase in geometric distortion with decrease in temperature would be attributed to the increase in crystal packing forces. We consider that this static model cannot completely explain the data. In solution there are no steric forces to lower the molecular symmetry, but as already noted,⁴ the solution-state IR spectrum shows the non-three-fold symmetry, and the comparison of NMR and IR data shows that the thermal barrier to rapid electron transfer is

present. Hence we propose a similar dynamic mechanism in the solid state.

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- O(1) to Fe(1), 1.807 ± 0.007 ; O(1) to Fe(2), 1.969 ± 0.006 ; O(1) to Fe(3), $1.938 \pm 0.006 \text{ \AA}$ (distances and e.s.d.). Fe(1) to O(11, 21, 31, 41), 2.03 ± 0.02 ; Fe(2) to O(12, 22, 51, 61), 2.07 ± 0.04 ; Fe(3) to O(32, 42, 52, 62), $2.06 \pm 0.05 \text{ \AA}$ (means and standard deviations). C. E. Anson, A. K. Powell, R. D. Cannon and U. A. Jayasooriya, to be published.