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Search for Intervalence Tunnelling in the Mixed-Valence Compound μ-(Pyrazine)-bis(pentaammineruthenium) Pentabromide

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Far-infrared Fourier transform spectra of the material $[(NH_3)_5Ru\text{-pyr-}Ru(NH_3)_5]Br_5$ taken at cryogenic temperatures do not show evidence of intervalence tunnelling transitions recently predicted by the theoretical analysis of the near-infrared absorption profile of its mixed-valence band by Piepho, Krausz, and Schatz. This absence clearly indicates that the complex is virtually delocalized in character and that the curious asymmetric absorption profile characteristic of the complex cannot be wholly vibronic in origin.

Introduction

There has been sustained interest and controversy concerning the valence delocalization character[2] of the pyrazine-bridged ruthenium mixed-valence dimer complex $[(NH_3)_5Ru^{II}\text{-pyr-}Ru^{III}(NH_3)_5]^{5+}$ since its first preparation by Creutz and Taube[3] (C&T). One of the most notable features of this C&T complex is an intense but relatively sharp and asymmetric intervalence band at $\sim 0.7 \times 10^3$ cm^{-1}.

The large width of intervalence bands in general is attributed to the considerable displacement of ligands in, e.g., going from a 2+ ion to a 3+ ion, giving rise to many quanta of the connecting vibrational mode ν^-. However $[Ru(NH_3)_6]^{2+}$ and $[Ru(NH_3)_6]^{3+}$ have very similar Ru–N distances of 2.144 Å and 2.104 Å,[4] and thus the relatively sharp intervalence band is easily rationalized.

Until recently no model existed that would predict the shape of an intervalence band. The PKS model[5] uses a vibronic coupling formalism that easily provides an absorption profile as a function of (exciton) coupling between the two centers ϵ and a displacement parameter λ corresponding directly to the difference in bond lengths in the hexaammine units from which (in the model) the mixed-valence complex is constructed. It was found that a closely defined and unique pair of parameters could be used to predict a band shape very similar to that observed in the C&T complex.[6] Further analysis of the eigenfunctions showed that several intense transitions were predicted in the far-infrared region, specifically at 131, 231, 250, and 275 cm^{-1}. The probability distribution of nuclear coordinates corresponded to a marginally *trapped* valence situation (i.e., there were two maxima, two most likely geometries rather than one).

The far-infrared transition is classified as a tunnelling transition. It corresponds to the rate at which the system *would* flip from a Ru(II)Ru(III) system to an equivalent Ru(III)Ru(II) configuration *if* in fact one could localize the system into one form initially. It is important to remember however that there is no classical analogue to tunnelling. The tunnelling mode cannot be thought of as a vibrational mode of the complex (such as ν^-) that has somehow been reduced in frequency. On the contrary, the tunnelling is a *consequence of electronic coupling* between the two centers. This splits the twofold degeneracy that would otherwise be present.

In the PKS model analysis, it is assumed that the frequency of the vibronically active mode is identical in the $Ru(NH_3)_6{}^{2+}$ and $Ru(NH_3)_6{}^{3+}$ monomer units and thus *unchanged* in going to the dimer ν^- mode. This approximation is well substantiated by infrared measurements on appropriate systems.[7]

Experimental Section

In order to distinguish clearly between any features in spectra not specifically due to the mixed-valence character of the C&T (II, III) complex, it was decided to prepare the analogous complexes $[(NH_3)_5Ru^{II}\text{-pyr-}Ru^{II}(NH_3)_5]^{4+}$ and $[(NH_3)_5Ru^{III}\text{-pyr-}Ru^{III}(NH_3)_5]^{6+}$ abbreviated as the (II, II) and (III, III) complexes. These were initially prepared as the *p*-toluenesulfonate salts according to the method of Creutz and Taube[3] but later converted to the bromide salts to improve the far-infrared background.

Infrared spectra were recorded in CsI and KBr disks prepared in the usual way. Near-infrared spectra were recorded on a Cary 17 spectrophotometer to establish the presence of the characteristic intervalence band in the (II, III) material and its absence in the other two materials.

Initial room-temperature far-infrared spectra were recorded by using Vaseline mulls on a Hitachi Model FIS3 spectrometer, but they showed no distinctive features peculiar to the C&T complex.

Further measurements were made by using a laboratory designed Fourier transform far-infrared apparatus[8] with the sample temperature held at 6 K and at room temperature. Here the samples were prepared by carefully dispersing the finely ground material in zone-refined docosane and pressing a thin disk of the conglomerate between sheets of polythene.

Results and Discussion

Figure 1 shows the low-temperature infrared spectra obtained from samples of the (II, II) and (II, III) bromide salts. Both traces show a very broad absorption around 120 cm^{-1} with a half-width of 50 cm^{-1}, but there is no significant difference in intensity or position of this band between the (II, II) and the (II, III) C&T complex. Furthermore there is no strong temperature dependence of the band up to room temperature, whereas the predicted tunnelling transition is expected to show a very marked effect. The dipole strength of the broad band is still considerable due to its width and is $(0.3 \pm 0.1)D^2$ for both materials. [Dipole strengths are a more significant measure of intensity rather than the dimensionless quantity oscillator strength when comparison of bands at significantly different frequencies must be made. The ratio of the oscillator strengths is related to the ratio of the dipole strengths by the ratio of the frequencies of the transitions f_1/f_2

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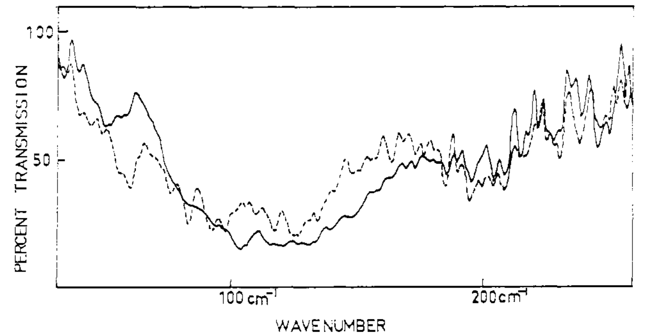

Figure 1. Far-infrared spectra of 10 mg of (II, II) bromide (dashed curve) and 10 mg of (II, III) bromide (solid curve) dispersed in 25 mg of docosane and pressed into disks 14 mm in diameter and ~0.25 mm thick. Spectra were ratioed against that of an equivalent disk of 25 mg of docosane and were accumulated at 6–10 K to give a resolution of 1.22 cm^{-1}. Most of the finer details on the traces are due to instrumental noise.

$= (D_1^2/D_2^2)(\nu_2/\nu_1)$.] Weaker bands in the spectrum are mostly masked by noise and would have a dipole strength at least 1 or 2 orders of magnitude smaller than the broad band. The predicted intensity of the tunnelling transition at 6 K is $3.1D^2$. Thus there is at least 2 or 3 orders of magnitude discrepancy between the observed and predicted intensities.

It is still very difficult on general grounds however to account for the lack of an observable tunnelling transition *if* in fact the C&T complex does correspond to a system with a "double welled" ground-state potential surface, i.e., with $\lambda^2 > |\epsilon|$, by using the parameters of the PKS model. Such a potential surface will always give rise to a splitting between the lower Φ_+ and Φ_- states and transitions between these states are dipole allowed.

The predicted tunnelling intensity of $3.1D^2$ has already been scaled to the observed intensity of the intervalence band of $9.9D^2$. The basic electric dipole intensity in a mixed-valence system of course derives from the change in the dipole moment in transferring an electron from one center to another resulting in eq 1 (eq 32 of ref 5), where R is the distance between the

$$\langle \psi_+|m_z|\psi_-\rangle = Re/2 \tag{1}$$

two centers and ψ_+ and ψ_- are the symmetric and antisymmetric combinations of the purely electronic wave functions of the hexaammine units.

This simple expression however overestimates by a factor of 20 the intensity in the C&T complex. A reduction from the $eR/2$ based value is qualitatively attributable to a strong polarization of the bridging pyrazine ligand, substantially reducing the transition dipole moment involved. The polarizability of the bridging ligand will of course have some frequency dispersion with the value in the visible and near-infrared region necessarily being predominantly electronic in origin. An extra polarizability term may be present in the far-infrared region and beyond due to a nuclear displacement (ionic) polarization, but this is characteristically smaller than the electronic term.[7]

Thus it seems unlikely that the polarizability at the tunnelling frequency has increased so much that any change in dipole moment is reduced 10-fold (and thus D^2 is reduced 100-fold) beyond the reduction made by the electronic polarization to the intervalence band.

The detectability of any tunnelling transition will also depend on its line width. In the analysis of the C&T intervalence absorption profile, a very large line width of 700 cm^{-1} was used for each vibronic component in order to get a characteristically featureless absorption profile. The question then is what is a reasonable estimate of the line width of the far-infrared mode. It seems likely that the transition would be broader than a vibration or librational mode as its electronic charge-transfer character would allow it to interact more strongly with its environment. However a value of 700 cm^{-1} may be too high. Anharmonicity must be a strong contributing factor to this effective width in the intervalence band which involves 10 or more quanta of the ν^- mode. Tunnelling occurs between the lowest vibronic levels and may be less affected, giving a smaller line width. Yet even if the tunnelling intensity were distributed through or beyond the *entire* 0–300-cm^{-1} range, there would still be an easily noticeable increase in the background absorption which of course should be strongly temperature dependent. No such background was observed.

Calculations using the PKS model show that the position and intensity of the tunnelling transitions are sensitive to small amounts of asymmetry between the two centers quantified in the parameter W. There may be some slight difference between the two Ru centers crystallographically in our bromide salt although X-ray structural data on the mixed chloride–bromide material indicate an exact mirror symmetry in this case.[10] When a value of W is introduced into the calculations that reduce the tunnelling transition intensities even threefold, the intervalence absorption profile becomes much broader and more symmetric, completely at variance with the observed spectrum.

The only way to remove the tunnelling transition intensity to the level required by experiment is to let λ be very small. The model then predicts a single symmetric line at 2_ϵ and cannot account for the asymmetry on the high-energy side. In the PKS model λ is directly related to the change in bond lengths in the monomer units. It can be shown from the formulas of ref 4 that for an octahedral complex the change Δr is given by eq 2, where M_L is the mass of a ligand and ν^-

$$\Delta r = (\lambda/2\pi)(h/3M_L\nu^-)^{1/2} \tag{2}$$

is the frequency of the active mode (500 cm^{-1} in this case).

Using the crystallographically determined values of the Ru–N bond lengths for the hexaammine ions[3] gives a λ of 1.1, substantially lower than the value of 2.7 used in the published analysis. An even smaller value of λ could be attributed to the influence of the pyrazine ligand which by nature of its bonding character is considered to further decrease the Ru(II)–N bond length relative to the Ru(III)–N value.[10] The most recent analysis on the ESR spectrum of the C&T ion[2b] also indicates a completely delocalized situation.

Conclusion

The lack of an observable intervalence tunnelling transition in the C&T complex is consistent only with a small λ situation. The PKS model is then unable to account for the asymmetry on the high-energy side of the intervalence band. The origin of the asymmetry is at present being investigated.

Intervalence tunnelling may still be observable in systems of intermediate λ (i.e., $\lambda^2 > |\epsilon|$) when W is not too large. Experiments are in progress which look at a number of materials.

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Registry No. (II,II) bromide, 41557-48-6; (II,III) bromide, 41557-49-7.

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