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Valence Delocalization Coefficients for $[(NH_3)_5Ru^{II}(pyr)Ru^{III}(NH_3)_5]^{5+}$

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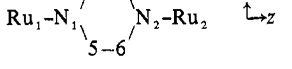
The electronic absorption[1] and Mossbauer spectra[2] of $[(NH_3)_5Ru(pyr)Ru(NH_3)_5]^{5+}$ (pyr = pyrazine) suggest very strongly that, despite the fact that the ligands surrounding them are identical, the environments of the two Ru atoms differ in such a way that one may be considered to a first approximation as Ru^{II} and the other as Ru^{III}; *i.e.*, the complex is a class II[3] mixed-valence system. We recently pointed out[4] that this apparently surprising observation is capable of rationalization if the resonance interaction between the two equivalent valence structures ($Ru_1{}^{II}Ru_2{}^{III}$) and ($Ru_1{}^{III}$-$Ru_2{}^{II}$), where 1 and 2 are the two sites, is smaller than the energy needed to transfer an electron adiabatically from one site to the other. It is thus a matter of some interest to calculate rough values for the resonance interaction and hence the valence delocalization coefficients for this important model compound.

It is reasonable to suppose that since 1 and 2 are usually separated by quite a large distance in class II mixed-valence compounds (6.9 Å in the Ru dimer), they do not interact directly but only through higher order perturbations involving nonorthogonal $\pi \rightarrow Ru^{III}$ and $Ru^{II} \rightarrow \pi^*$ charge-transfer states. This simple idea was recently set out within the general formalism of perturbation theory[5,6] and applied with some sucess to Fe^{II}-Fe^{III} interactions in cyanides and silicates. The purpose of the present note is to apply it to the Ru^{II}-Ru^{III}-pyr dimer.

Consider the system



and assume that valence delocalization between the low-spin metal ions occurs only *via* the π, π^* molecular orbitals of the bridging pyrazine. The component of the zeroth-order ground state in which the unpaired electron on Ru occupies d_{yz} may be written

$$\psi_0 = |yz_1\overline{yz}_1\pi y\overline{\pi y}yz_2|\psi_0' \tag{1}$$

where ψ_0' takes account of the remaining electrons in the d shells of Ru_1 and Ru_2 and the π MO's of the pyrazine. The $Ru_1{}^{II} \rightarrow Ru_2{}^{III}$, $Ru_1{}^{II} \rightarrow \pi^*$ and $\pi \rightarrow Ru_2{}^{III}$ configurations are then

$$\psi_1 = |yz_1\overline{yz}_2\pi y\overline{\pi y}yz_2|\psi_0' \tag{2}$$

$$\psi_2 = |yz_1\overline{\pi y}^*\pi y\overline{\pi y}yz_2|\psi_0' \tag{3}$$

$$\psi_3 = |yz_1\overline{yz}_1\pi y\overline{yz}_2yz_2|\psi_0' \tag{4}$$

The ground and $Ru^{II} \rightarrow Ru^{III}$ charge-transfer states are then formed as linear combinations of ψ_0 and ψ_1

$$\Psi_G = \psi_0 + \gamma_1\psi_1 \tag{5}$$

$$\Psi_{E1} = \psi_1 + \gamma_0'\psi_0 \tag{6}$$

Taking into account all the pyrazine π, π^* MO's, the valence delocalization coefficients are now given[5] by

$$\gamma_1 = \sum_{i=1,3}\frac{(yz_1|H|\pi i^*)(yz_2|H|\pi i^*)}{(E_{i+1} - E_0)(E_1 - E_0)} - \sum_{i=1,3}\frac{(yz_1|H|\pi i)(yz_2|H|\pi i)}{(E_{i+4} - E_0)(E_1 - E_0)} \tag{7}$$

$$\gamma_0' = -\sum_{i=1,3}\frac{(yz_1|H|\pi i^*)(yz_2|H|\pi i^*)}{(E_{i+1} - E_1)(E_1 - E_0)} + \sum_{i=1,3}\frac{(yz_1|H|\pi i)(yz_2|H|\pi i)}{(E_{i+4} - E_1)(E_1 - E_0)} \tag{8}$$

where the πi label occupied π MO's of pyrazine in order of decreasing energy and πi^* the vacant π MO's in order of increasing energy. $(E_1 - E_0)$ is the energy of the $Ru_1{}^{II} \rightarrow Ru_2{}^{III}$ configuration, $(E_{i+1} - E_0)$ that of $Ru_1{}^{II} \rightarrow \pi i^*$, and $(E_{i+4} - E_0)$ that of $\pi i \rightarrow Ru_2{}^{III}$. We express the integrals $(yz_1|H|\pi i^*)$, $(yz_2|H|\pi i^*)$, $(yz_1|H|\pi i)$, and $(yz_2|H|\pi i)$ in terms of MO coefficients C_{ia} and $C_{ia}{}^*$ for pyrazine and Ru^{II}-N, Ru^{III}-N resonance integrals and then estimate the coefficients from a Pariser-Parr-Pople[7] calculation[6] on the pyrazine molecule.

The integral $\beta(Ru^{II}\text{-}N)$ is chosen so that the application of first-order perturbation theory and the dipole length operator to the $Ru^{II} \rightarrow \pi i^*$ charge-transfer excitation yields the observed transition moment as

$$\mu(\Psi_G \rightarrow \Psi_{E2}) = -\frac{2^{1/2}C_{11}{}^*\beta(Ru^{II}\text{-}N)R(Ru^{II}\text{-}pyr)}{E_2 - E_0} \tag{9}$$

From Creutz and Taube's work[1] we estimate that $\mu_{obsd}(\Psi_G \rightarrow \Psi_{E2})$ is about 1.12 e Å while $(E_2 - E_0)$ is set as the energy of the excitation $\Psi_G \rightarrow \Psi_{E2}$, again estimated from ref 1 as 17.7 kK. Finally, $R(Ru^{II}\text{-}pyr)$ is taken from structural data for related compounds[8] as 3.45 Å. Applying eq 9 then yields a value of $\beta(Ru^{II}\text{-}N) = 7.75$ kK, and for simplicity $\beta(Ru^{III}\text{-}N)$ is assigned the same value.

The configuration energy terms, $(E - E_0)$, are chosen by reference to both experimental and theoretical data. $(E_1 - E_0)$ and $(E_2 - E_0)$ are equated to the energies of the $Ru^{II} \rightarrow Ru^{III}$ and $Ru^{II} \rightarrow \pi 1^*$ charge-transfer bands in the spectrum of the mixed-valence ion, while $(E_3 - E_0)$ and $(E_4 - E_0)$ are calculated from $(E_2 - E_0)$ using the approximate formula

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$$(E_{i+1} - E_0)_{i=2,3} = (E_2 - E_0) + \epsilon(\pi i^*) - \epsilon(\pi 1^*) \qquad (10)$$

where $\epsilon(\pi i^*)$ is the energy of the πi^* MO of pyrazine, given by the Pariser-Parr-Pople calculation.

The $\pi 1 \rightarrow \mathrm{Ru^{III}}$ CT excitation is forbidden and is not observed in the mixed-valence ion; consequently, to estimate of the energy of $\pi i \rightarrow \mathrm{Ru^{III}}$ charge transfer we have to resort to an MO calculation on a hypothetical $\mathrm{Ru^{III}}$-pyr ion.[6] Combining all these sources of information yields the following estimates for the energies of the various excited configurations: $(E_1 - E_0) = 6.4$ kK, $(E_2 - E_0) = 17.7$ kK, $(E_3 - E_0) = {\sim}25$ kK, $(E_4 - E_0) = {\sim}45$ kK, $(E_5 - E_0) = {\sim}32.5$ kK, $(E_6 - E_0) = {\sim}60.0$ kK, $(E_7 - E_0) = {\sim}70.0$ kK. We now have all the information needed to evaluate eq 7 and 8 and thus obtain the valence delocalization parameters. The resulting values are $\gamma_1 - 0.145$ and $\gamma_0' + 0.22$.

A final point concerns the distribution of the hole in the d_{xy}, d_{xz}, and d_{yz} orbitals of $\mathrm{Ru^{III}}$, which depends on a balance between spin-orbit coupling and tetragonal distortion of the ligand field.

The hole distribution between d(0) and d(1,−1) is given by coefficients $c(0)$ and $c(1,-1)$ derived by solving a secular determinant containing the spin-orbit coupling constant of the metal and the energy difference δ between the configurations in which the hole occupies d(0) or d(1,−1) (d_{yz} and $d_{xy,xz}$ in the present case). Since NH_3 contains no π MO's, d_{xy} and d_{xz} are nonbonding, and the energy separation between d_{yz} and (d_{xy}, d_{xz}) depends only upon interactions involving the π, π^* MO's of pyrazine. The quantity δ then approximately equals the stabilization energy of the complex (when the hole is located entirely in the Ru-pyr π system) due to the $\mathrm{Ru^{II}}(d_{yz}) \rightarrow \mathrm{Ru^{III}}(d_{yz})$, $\pi \rightarrow \mathrm{Ru^{III}}(d_{yz})$ CT interaction and is given by

$$-\delta = \gamma_1^2(E_1 - E_0) + \sum_{i=1,3} \frac{C_{12}^2\beta^2(\mathrm{Ru^{III}\text{-}N})}{(E_{i+4} - E_0)} \qquad (11)$$

If we take the spin-orbit coupling constant of $\mathrm{Ru^{III}}$ as 1180 $\mathrm{cm^{-1}}$ [9] and use eq 11 to estimate δ, the coefficient of the hole in d_{yz}, $c(0)$ is 0.693. Including this correction, the true valence delocalization coefficients[5] α_1 and α_0' are then −0.10 and +0.15. Our conclusion is therefore that the hole in $\mathrm{Ru^{III}}$ is delocalized onto the $\mathrm{Ru^{II}}$ in the ground state by approximately 1%.

It is worth noting that our estimate of α_1 by the perturbation method gives a value well within the range $\alpha < {}^1/_4$ required by our criterion[4] for valence trapping and class II behavior in a mixed-valence dimer with identical ligands around each site. Unfortunately, a direct test of the estimated value for α_1 is not easy. Such properties as transferred hyperfine interactions would be relevant, but the Ru Mossbauer spectrum[2] is not sufficiently resolved to yield the necessary data. There remains the intensity of the mixed-valence charge-transfer transition. The transition moment of the $\mathrm{Ru^{II}} \rightarrow \mathrm{Ru^{III}}$ excitation is given by

$$\mu(\Psi_G \rightarrow \Psi_{E1}) = (1/2)(\alpha_1 - \alpha_0')R(\mathrm{Ru^{II}\text{-}Ru^{III}})$$

Taking the $\mathrm{Ru^{II}\text{-}Ru^{III}}$ distance R as about 6.9 Å yields $\mu = 0.81$ e Å, which agrees very nicely with our estimate from the experimental data of ref 1 of about 0.9-1.0 e Å.

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Registry No. $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$, 35599-57-6.

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Resonance Raman Spectra of a Complex Containing the Rhenium-Iron Bond

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Bennet, *et al.*,[2] have synthesized a novel complex, shown in Figure 1A, of the formula $(CO)_2Rh{\cdot}C_7H_7{\cdot}Fe(CO)_3$. The Rh-Fe distance of 2.76 Å indicates the presence of a metal-metal bond.[2,3] This note reports the resonance Raman spectrum of this complex. The compound is dark brown and it is difficult to obtain its conventional Raman spectrum.[4] The absorption spectrum of this compound is shown in Figure 1. There is a strong maximum at about 4400 Å which has a tail covering the whole visible region.

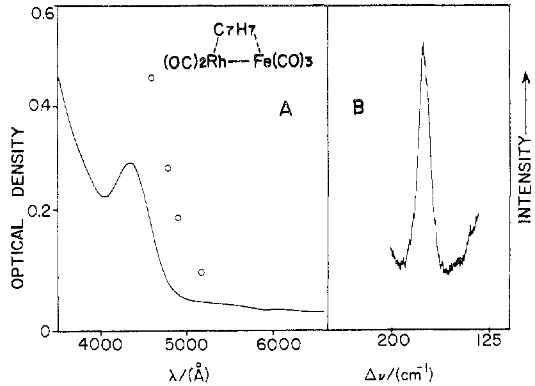

Figure 1. (A) Absorption spectra of a 4.3×10^{-4} *M* solution of $(CO)_2Rh{\cdot}C_7H_7{\cdot}Fe(CO)_3$ (path length 0.2 cm); relative intensity of the Raman band with different exciting radiations is indicated by circles. (B) Raman band observed using the 4880-Å laser line (resolution 4 $\mathrm{cm^{-1}}$).

The absorption spectrum was recorded with a Cary 14 spectrophotometer. Raman spectra were recorded using a Spex 1400 monochromator and an Ar^+ ion laser. The solutions of the complex were prepared in $CHCl_3$ under an atmosphere of dry N_2. The Raman spectra were recorded using a spinning-sample cell.[5] The ν_4 band of chloroform[6] was used as an internal reference to study the intensity of the band due to the complex as a function of the frequency of the exciting radiation.

The Raman spectrum of the solution of the complex showed a band at 172 ± 2 $\mathrm{cm^{-1}}$ in addition to the bands due to the solvent. The band is strongly polarized and is shown in Figure 1 as obtained from a 10^{-3} *M* solution of the complex with the 4880-Å line of the Ar^+ laser. Three other lines in the Ar^+ laser at 4579, 4765, and 5145 Å were also used and the dependence of the intensity of the band on the exciting frequency is also shown in Figure 1.

The band is polarized ($\rho \approx 0.1$ with 4880 Å) and can be assigned to the Rh-Fe stretching vibration giving a value of

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