Near I.r. Transition of the μ-Quinoxaline-bis(penta-ammineruthenium)(5+) Ion

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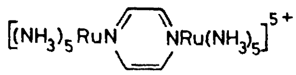
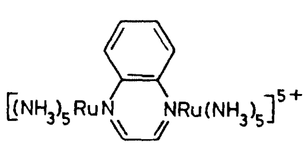
Summary Although the π^* system of the bridging ligand in the μ-quinoxaline-bis(penta-ammineruthenium) (5+) ion (**2**) is considerably lower in energy than the π^* system of the bridging ligand in the previously reported μ-pyrazine-bis(penta-ammineruthenium)(5+) ion (**1**), the near i.r. transition for (**2**) (ν_{max} 5900 cm^{-1}) occurs at essentially the same energy as that for (**1**) (ν_{max} 6300 cm^{-1}), a result suggestive of the mixed-valence $\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ representation of the ion as opposed to a delocalized $\mathrm{Ru^{II\frac{1}{2}}}$–$\mathrm{Ru^{II\frac{1}{2}}}$ description.

Originally prepared by Creutz and Taube,[1] the μ-pyrazine-bis(penta-ammineruthenium)(5+) ion (**1**) has generated considerable controversy concerning both its electronic structure and the nature of the near-i.r. transition (ν_{max} 6300 cm^{-1}) associated with the complex.[2] If a localized $\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ description is assumed,[1] the transition may be assigned to intervalence transfer (IT) [equation (1)]. If a

$$\mathrm{Ru^{II}\text{–}Ru^{III}} \xrightarrow{h\nu} \mathrm{Ru^{III}\text{–}Ru^{II*}} \qquad (1)$$

delocalized $\mathrm{Ru^{II\frac{1}{2}}}$–$\mathrm{Ru^{II\frac{1}{2}}}$ is assumed, the band may be associated with a transition between orbitals in a molecular orbital scheme which incorporates strong and equal interaction between the metal orbitals and the π system of the bridging ligand.[2a,d,f] To provide insight into the problem, we prepared (**2**) by solution oxidation of the corresponding 4+ ion which was isolated as a hexafluorophosphate salt. A comparison between the mixed-valence properties of (**1**) and (**2**) is revealing.


(1)


(2)

Firstly, the $\mathrm{Ru^{II}} \rightarrow \pi^*$ (quinoxaline) transition in (**2**) occurs at a considerably lower energy (15,500 cm^{-1}) than the analogous $\mathrm{Ru^{II}} \rightarrow \pi^*$ (pyrazine) transition in (**1**) (17,700 cm^{-1}).[1] Hence, the π^* system of the more delocalized quinoxaline ligand is considerably lower in energy than the π^* system of pyrazine, as expected,[3] and is of a suitable symmetry to interact with the appropriate d orbitals on ruthenium.

Secondly, (**2**) displays a near-i.r. band (ν_{max} 5900 cm^{-1}) in acetonitrile at nearly the *same* energy as that found for (**1**) (ν_{max} 6300 cm^{-1}; the band maximum was insensitive to

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solvent changes) This observation is more suggestive of a $\mathrm{Ru^{II}}$–$\mathrm{Ru^{III}}$ description of the complex than a delocalized $\mathrm{Ru^{II\frac{1}{2}}}$–$\mathrm{Ru^{II\frac{1}{2}}}$ description The energy of the IT transition is primarily dependent upon the vibronic barrier to thermal electron transfer [4] Since this barrier should be similar for both complexes, the IT transition for both complexes would be expected to be at similar energies Previous molecular orbital (M O) schemes developed for (**1**)[1b,2a,2d] (assuming a delocalized $\mathrm{Ru^{II\frac{1}{2}}}$–$\mathrm{Ru^{II\frac{1}{2}}}$ description) may be applied to (**2**) The ordering of the orbitals should be identical in both complexes, but energy differences between orbitals should be apparent because of the considerably different π and π^* energies of quinoxaline Consequently, if the near-i r transition is due to transitions between M O 's in the complexes, it would be expected to occur at different energies in (**2**) than in (**1**) The evidence, however, is not conclusive, since it is difficult to judge the magnitude of the energy differences expected in the M O schemes for (**1**) and (**2**)

The remaining characteristics of the near-i r band of (**2**) are very similar to that of (**1**) The band width of (**2**) is 1300 $\mathrm{cm^{-1}}$ compared to 1500 $\mathrm{cm^{-1}}$ for (**1**), both of which are considerably narrower than that predicted from Hush theory [3700 and 3800 $\mathrm{cm^{-1}}$ for (**2**) and (**1**) respectively] [4] The extinction coefficients are also comparable [4000 and 5000 l $\mathrm{mol^{-1}}$ $\mathrm{cm^{-1}}$ for (**2**) and (**1**),[1] respectively] The Hush,[4] Hopfield,[5] and 'PKS'[6] models for mixed-valence compounds all relate increasing intensity of the IT transition to increasing ground-state electronic interaction Although the π-system of the bridging ligand, which presumably transmits these electronic effects is more energetically amenable in (**2**) than in (**1**), electronic interactions are apparently similar in both complexes The advantage gained by the more energetically appropriate π system in (**2**) may be offset by the more severe steric restraints between the bridging ligand and the $\mathrm{Ru(NH_3)_5}$ groups of (**2**) compared with (**1**)

Finally the free energy change (ΔG_{com}) for equation (**2**)

$$(\mathrm{Ru^{II}}\text{–}\mathrm{Ru^{II}}) + (\mathrm{Ru^{III}}\text{–}\mathrm{Ru^{III}}) \rightleftharpoons 2(\mathrm{Ru^{II}}\text{–}\mathrm{Ru^{III}}) \qquad (2)$$

is also nearly identical for both complexes [0 43 and 0 45 V for (**1**)[7] and (**2**), respectively, in acetonitrile at 25 ± 2 °C in 0·1 M supporting electrolyte, estimated error is ± 0 01 V] The result consistent with the intensity measurements, suggests similar electronic interactions in both complexes Presumably, differences in ΔG_{com} for the two complexes would arise if the stabilizing resonance delocalization energies for the two mixed-valence complexes were significantly different [8]

We thank the Research Corporation and the Foundation of the University of North Carolina at Charlotte for support of this research, and also Dr D Paul Rillema for the use of the electrochemical equipment

(*Received*, 1st *September* 1980, *Com* 954)

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[1] C Creutz and H Taube, *J Am Chem Soc* , (a) 1969, **91**, 3988, (b) 1973, **95**, 1086

[2] See, for example (a) J Elias and R S Drago, *Inorg Chem* , 1972, **11**, 415 (b) C Creutz M L Good and S Chandra, *Inorg Nucl Chem Lett* , 1973, **9**, 171 (c) P Citrin, *J Am Chem Soc* , 1973, **95**, 6472, (d) I Trietel, Ph D Thesis California Institute of Technology, 1971, (e) T Strekas and T Spiro, *Inorg Chem* , 1976, **15**, 974, (f) J Beattie, N Hush and P Taylor, *Inorg Chem* , 1976, **15**, 992, (g) B C Bunker, R S Drago, D N Hendrickson, R M Richman, and S L Kessell, *J Am Chem Soc* , 1978, **100**, 3805

[3] G W H Cheeseman and E S G Werstiuk, *Adv Heterocycl Chem* , 1972, **14**, 99

[4] (a) N S Hush, *Prog Inorg Chem* , 1967, **8**, 391, (b) N S Hush, *Electrochim Acta*, 1968, **13**, 1005

[5] J J Hopfield, *Biophys J* , 1977, **18**, 311

[6] (a) S B Piepho, E R Krausz, and P N Schatz, *J Am Chem Soc* , 1978, **100**, 2996, (b) K Y Wong, P N Schatz, and S B Piepho, *J Am Chem Soc* , 1979, **101**, 2793

[7] R W Callahan and T J Meyer, *Chem Phys Lett* , 1976, **39**, 82

[8] K K Cloninger and R W Callahan, *Inorg Chem* , submitted for publication