Intervalence Transfer in Outer-sphere Hexa-ammineruthenium(III) Pentacyanoferrate(II) Complexes

By **Henrique E. Toma**, Instituto de Química, Universidade de São Paulo, Caixa Postal 20780, São Paulo, Brasil

The ion $[Ru(NH_3)_6]^{3+}$ forms with substituted $[Fe(CN)_5]^{3-}$ complexes a series of typical outer-sphere mixed-valence complexes, suitable for systematic studies on intervalence-transfer phenomena. The complexes of general formula $[Ru(NH_3)_6][Fe(CN)_5L]\cdot nH_2O$ (L = CO, CN, dimethyl sulphoxide, pyrazine, pyridine, or imidazole) exhibit typical intervalence bands in the visible spectra, with energies strongly dependent on the nature of the ligand L. The i.r. spectra of the complexes are consistent with the trapped-valence Ru^{III},Fe^{II} formulation. A plot of optical electron-transfer energy against difference in the redox potential, $\Delta E^{\ominus}$, increases linearly with a slope of 1.39 ± 0.09 and an intercept of 108 ± 4 kJ mol^{-1}. The results are interpreted in terms of Hush's theory for intervalence transitions.

THE chemistry of outer-sphere complexes is usually described in terms of the individual properties of the associated ions. Although the degree of interaction should be much smaller in comparison with typical inner-sphere complexes, some outer-sphere complexes of oxidizing and reducing centres can exhibit properties characteristic of mixed-valence systems.[1-3] The colour of such complexes can become quite different from that expected for the simple association of the reactants; also, the conductivity in the solid may be enhanced by the presence of electron-donor and electron-acceptor centres. A number of outer-sphere complexes displaying mixed-valence properties has been reported in the literature;[4-6] however, except for a recent study,[7] no attempt at systematic investigation has been made.

The complexes between hexa-ammineruthenium(III) and substituted pentacyanoferrates here described form a set of typical outer-sphere mixed-valence complexes, suitable for systematic studies on the intervalence phenomena. By using a variety of ligands L [*e.g.* carbon monoxide, dimethyl sulphoxide (dmso), cyanide, pyrazine (pyz), pyridine (py), and imidazole (imH)] the properties of the outer-sphere $[Ru(NH_3)_6][Fe(CN)_5L]$ complexes can be changed gradually; this allows one to investigate systematically the behaviour of the optical electron-transfer energies within the series.

EXPERIMENTAL

The pentacyanoferrate(II) complexes were prepared from sodium amminepentacyanoferrate(II) trihydrate, as previously described.[8-11] The complex $[Ru(NH_3)_6]Cl_3$ from Johnson, Matthey and Co. was recrystallized twice by the Armor procedure.[12]

The outer-sphere mixed-valence complexes of general formula $[Ru(NH_3)_6][Fe(CN)_5L]\cdot nH_2O$ were prepared by the following procedure. The salt $[Ru(NH_3)_6]Cl_3$ (2 mmol) was dissolved in water (10 cm^3) containing an equimolar amount of $Na_3[Fe(CN)_5L]$. Except for $Na_3[Fe(CN)_5(CO)]$, an excess of the ligand L was maintained in the solution to prevent dissociation of the reactant. Precipitation was observed to take place rapidly, producing microcrystalline solids which were practically insoluble in water and in organic solvents. In the case of the dimethyl sulphoxide (dmso) complex, a supersaturated solution was initially formed, producing after 1 d, dark violet needles of the compound. The $[Ru(NH_3)_6]_4[Fe(CN)_6]_3$ and $[Ru(NH_3)_6][Fe(CN)_5(CO)]$ complexes were prepared in a similar way, starting from the potassium salts of the hexacyanides {Found: C, 17.9; H, 4.4; N, 36.4. Calc. for $[Ru(NH_3)_6][Fe(CN)_5(CO)]$: C, 17.25; H, 4.35; N, 36.95. Found: C, 13.4; H, 5.9; N, 36.2. Calc. for $[Ru(NH_3)_6]_4[Fe(CN)_6]_3\cdot 10H_2O$: C, 13.25; H, 5.70; N, 36.1. Found: C, 17.8; H, 5.4; N, 32.2. Calc. for $[Ru(NH_3)_6][Fe(CN)_5(dmso)]\cdot H_2O$: C, 17.3; H, 5.40; N, 31.75. Found: C, 24.7; H, 5.3; N, 35.4. Calc. for $[Ru(NH_3)_6][Fe(CN)_5(py)]\cdot H_2O$; C, 24.7; H, 5.20; N, 34.5. Found: C, 22.6; H, 5.1; N, 38.8. Calc. for $[Ru(NH_3)_6][Fe(CN)_5(pyz)]\cdot H_2O$: C, 22.2; H, 4.95; N, 37.35. Found: C, 17.8; H, 4.5; N, 42.1. Calc. for $[Ru(NH_3)_6][Fe(CN)_6]$: C, 17.35; H, 4.35; N, 40.5%}.

The *X*-ray powder diffractograms were obtained using a Philips diffractometer with Cu-K_α radiation. The i.r. spectra of the solids were recorded on a Perkin-Elmer model 180 spectrophotometer, with the samples dispersed in Nujol or Fluorolube. Near-i.r. red and visible spectra were obtained on a Cary 17 spectrophotometer. The solids were dispersed in Fluorolube and placed between two quartz windows. Commercial transparencies from 3M, previously cleaned with acetone, were also used successfully as windows, combined with the conventional spectrophotometric cells. A sample of $[Ru(NH_3)_6]Cl_3$ was used as a blank for most measurements in the visible–near-i.r. region (380—1 300 nm).

RESULTS AND DISCUSSION

Association of the hexa-ammineruthenium(III) complex with cyanoferrates is strongly favoured electrostatically. For the complexes reported, the solubility product is very small, preventing accurate spectral measurements in solution. The solids, obtained from the direct reaction (1), exhibit characteristic colours,

$$[Ru(NH_3)_6]^{3+} + [Fe(CN)_5L]^{3-} \longrightarrow [Ru(NH_3)_6][Fe(CN)_5L] \quad (1)$$

which cannot be explained in terms of the individual contributions of each species.

The visual and structural features of the complexes are listed in Table 1. Some selected i.r. bands of the solids are collected in Table 2 for comparison purposes.

Except for the isomorphic $[Ru(NH_3)_6][Fe(CN)_6]$ and $[Ru(NH_3)_6][Fe(CN)_5(CO)]$ complexes, the presence of water was confirmed by the absorption bands in the 3 400—3 650 cm^{-1} region of the i.r. spectra. The absorption bands associated with the $Ru(NH_3)_6$ moiety are practically identical with those reported for the $[Ru(NH_3)_6]Cl_3$ complex.[13,14] The observed bands associated with the CN stretching vibration are characteristic of $[Fe^{II}(CN)_5L]$ complexes[9,15] and agree, in number, with a C_{4v} symmetry, where a set of $2A_1 + E$ normal modes are i.r. active. Therefore, within the vibrational time scale, the results are consistent with a Ru^{III},Fe^{II} trapped-valence formulation for the outer-sphere complexes.

TABLE 1

Colours and *X*-ray powder diffractograms of $[Ru(NH_3)_6]$-$[Fe(CN)_5L]$ complexes

Compound [a]	Colour	*X*-Ray powder diffractogram [b]
$[RuA_6][Fe(CN)_5(CN)]$	Yellow	7.16 (5), 5.53 (100), 4.76 (10), 3.60 (5), 3.45 (10), 3.19 (15), 3.02 (30), 2.76 (5), 2.39 (5), 2.19 (5)
$[RuA_6][Fe(CN)_5(CO)]$	Brown	7.17 (20), 5.53 (100), 4.73 (80), 3.63 (70), 3.45 (5), 3.19 (5), 3.00 (80), 2.76 (5), 2.40 (30), 2.18 (40)
$[RuA_6][Fe(CN)_5(dmso)]\cdot H_2O$	Violet	5.70 (100), 5.39 (20), 4.33 (10), 3.83 (5), 3.81 (5), 3.37 (5), 3.34 (5)
$[RuA_6][Fe(CN)_5(pyz)]\cdot H_2O$	Green	7.82 (25), 7.02 (5), 6.19 (40), 5.78 (*t*), 5.57 (50), 5.06 (10), 4.48 (10), 3.91 (10), 3.81 (100), 3.50 (5), 3.03 (15)
$[RuA_6][Fe(CN)_5(py)]\cdot H_2O$	Green	7.56 (50), 7.37 (30), 6.86 (50), 6.83 (10), 6.32 (10), 5.47 (60), 4.98 (30), 4.77 (100), 3.90 (60), 3.83 (50), 3.78 (20), 3.46 (30), 3.42 (15), 3.14 (15), 3.07 (30)
$[RuA_6][Fe(CN)_5(imH)]\cdot H_2O$	Green	7.75 (20), 7.39 (30), 6.96 (5), 5.64 (40), 5.57 (20), 5.40 (20), 5.12 (100), 4.74 (10), 4.52 (5), 3.86 (10), 3.72 (5), 3.57 (10), 3.47 (30), 3.31 (5), 3.25 (5), 3.14 (10), 3.03 (10), 2.79 (20), 2.71 (5), 2.56 (10)
$[RuA_6]_4[Fe(CN)_6]_3\cdot 10H_2O$	Blue	7.12 (10), 5.86 (20), 5.64 (100), 5.21 (30), 5.00 (5), 4.92 (10), 4.82 (30), 4.69 (30), 4.50 (5), 4.41 (10), 4.15 (20), 3.93 (20), 3.73 (20), 3.40 (20), 2.59 (20), 2.52 (30)

[a] A = NH_3. [b] Distances in Å, relative intensities in parentheses.

It is remarkable that the trends in the CN stretching frequencies follow the π-backbonding properties[16] of L in the $[Fe^{II}(CN)_5L]$ complexes, *i.e.* CO > CN^- ~ dmso > pyz > py > imH. This reflects basically the importance of intramolecular[17] electronic effects in the complexes, influencing the CN stretching frequencies. As the electron-acceptor properties of L increase, the tendency of the electronegativity equalization is expected to reduce the population of the π*-CN orbitals involved in backbonding interactions with the metal ion. Consequently, the CN stretching frequencies increase with the π-acceptor properties of the ligands L in the complexes.

The assignments of the metal–ligand frequencies are somewhat uncertain since the bands are usually weak and a number of combination bands of the ligands are allowed in this region.

The electronic spectra of the carbon monoxide, cyanide, dimethyl sulphoxide, and pyridine mixed-valence complexes are shown in Figure 1. The visible and near-i.r. spectra are dominated by a broad absorption band which is not observed in the spectra of the iron(II) and ruthenium(III) moieties, or in the spectrum of the $[Ru^{III}(NH_3)_6][Fe^{III}(CN)_6]$ complex. As in a number of mixed-valence complexes previously reported,[18-22] the observed absorption band can be assigned to an intervalence transition of the type (2).

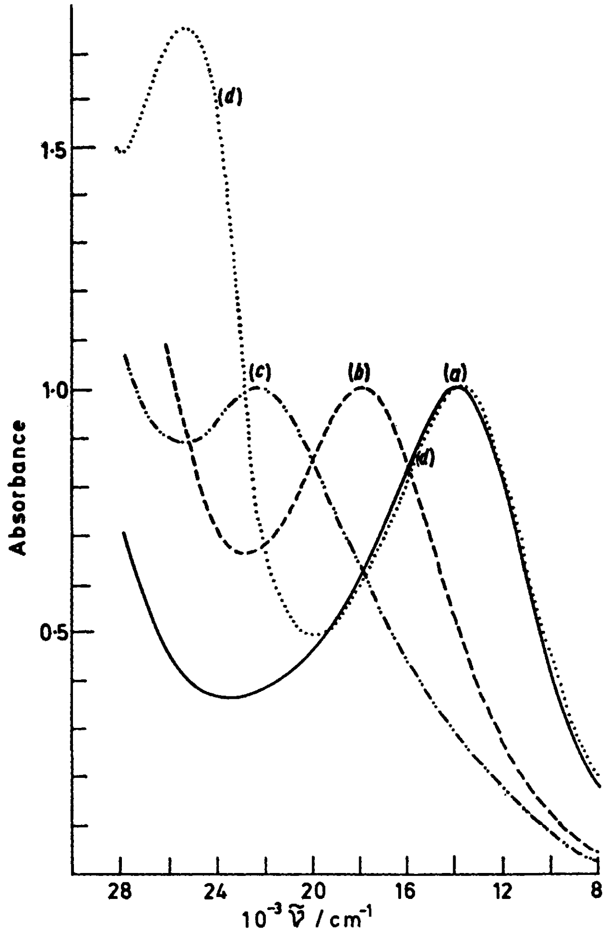


FIGURE 1 Intervalence-transfer spectra of outer-sphere complexes between $[Ru(NH_3)_6]^{3+}$ and (*a*) $[Fe(CN)_6]^{4-}$, (*b*) $[Fe(CN)_5(dmso)]^{3-}$, (*c*) $[Fe(CN)_5(CO)]^{3-}$, and (*d*) $[Fe(CN)_5(py)]^{3-}$

$$[Ru^{III}(NH_3)_6][Fe^{II}(CN)_5L] \xrightarrow{h\nu} [Ru^{II}(NH_3)_6][Fe^{III}(CN)_5L] \quad (2)$$

The pentacyanoferrate(II) ions containing N-heterocyclic ligands exhibit strong charge-transfer bands[8] in the visible–u.v. region, which are also observed in the spectra of the corresponding mixed-valence complexes. Based on a comparison of the intensity of the charge-transfer band at 25 500 cm^{-1} for the pyridine complex with that of the intervalence band at 13 800 cm^{-1}, one can estimate the absorption coefficient for the outer-sphere transition as *ca.* 10^3 dm^3 mol^{-1} cm^{-1}.

TABLE 2

Some i.r. bands (cm^{-1}) of $[Ru(NH_3)_6][Fe(CN)_5L]$ complexes[a]

CN[b]	CN[c]	CO	dmso	pyz	py	imH	Tentative assignment
	3 600w,		3 550m,	3 630m,	3 650m,	3 610m,	$\nu(H_2O)$
	3 480m		3 380m	3 480m	3 480w	3 460m	
3 270s,	3 270s,	3 250s,	3 200 (sh),	3 200 (sh),	3 220m,	3 250m,	$\nu(NH_3)$
3 140s	3 150s	3 070s	3 100s	3 100s	3 060s	3 100m	
	2 093w,	2 122w,	2 095w,	2 085w,	2 082w,	2 079m,	$\nu(CN)$
2 116s	2 065m,	2 105m,	2 065m,	2 048m,	2 040m,	2 036m,	
	2 027s	2 083s	2 050s	2 028s	2 016s	2 016s	
		1 930s					$\nu(CO)$
1 630m	1 620m	1 622m	1 630w	1 620w	1 610w	1 600m	$\delta(NH_3)$
	1 580 (sh)		1 580 (sh)	1 580m	1 580 (sh)	1 540w	$\delta(H_2O)$
1 350m	1 320m	1 345m	1 340m	1 320m	1 320m	1 310m	$\delta(NH_3)$
			1 045m				$\nu(SO)$
810s	820s	812m	820m	815m	810m	820s	$\rho(NH_3)$
		640m					$\delta(FeCO)$
520w	583m	597m	565m	568m	575m	570m	$\delta(FeCN)$
460w	460w	460w	460w	460w	465w	460w	$\nu(Ru{-}N)$
		427m	396m	390m	390w	390w	$\nu(Fe{-}L)$
396m	420w	400w	420w	415w	415w	420w	$\nu(Fe{-}C)$

w = Weak, m = medium, s = strong, sh = shoulder.

[a] In Nujol or Fluorolube. [b] Fe^{III}. [c] Fe^{II}.

The intervalence-transfer energies of several mixed-valence complexes are collected in Table 3 for comparison. For the $[Ru(NH_3)_6][Fe(CN)_5]$ complexes the energies increase with the acceptor properties of the ligand L, as expected from equation (3) where I is the

$$E_{IT} = I - A + C \qquad (3)$$

ionization potential of the donor, A the electron affinity of the acceptor, and C a coulombic term, nearly constant in the series. The acceptor properties of L stabilize the occupied orbitals of the donor, increasing its ionization potential and the energy of the intervalence transitions.

TABLE 3

Intervalence-transfer energies (kJ mol^{-1}) of outer-sphere mixed-valence complexes

	Donor	Acceptor	$E_{IT}(\nu_{IT})$[a]	$E^{\ominus}$[b]	$-\Delta G_{12}$[c]	$(\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger})$	E_{th}
(1)	$[Fe(CN)_5(CO)]^{3-}$	$[Ru(NH_3)_6]^{3+}$	265 (22.2)	1.18	109	78	112
(2)	$[Ru(CN)_6]^{4-}$	$[Ru(NH_3)_6]^{3+}$	217 (18.2)	0.86[e]	78	69	84
(3)	$[Fe(CN)_5(dmso)]^{3-}$	$[Ru(NH_3)_6]^{3+}$	214 (17.9)	0.89	81	66	85
(4)	$[Fe(CN)_5(pyz)]^{3-}$	$[Ru(NH_3)_6]^{3+}$	179 (15.0)	0.55	48	65	60
(5)	$[Ru(CN)_6]^{4-}$	$[Ru(NH_3)_5(py)]^{3+}$	173 (14.5)[d]	0.86[e]	54	59	63
(6)	$[Fe(CN)_6]^{4-}$	$[Ru(NH_3)_6]^{3+}$	167 (14.0)	0.45	38	64	54
(7)	$[Fe(CN)_5(py)]^{3-}$	$[Ru(NH_3)_6]^{3+}$	165 (13.8)	0.48	41	62	55
(8)	$[Fe(CN)_5(imH)]^{3-}$	$[Ru(NH_3)_6]^{3+}$	161 (13.5)	0.35	29	62	47
(9)	$[Fe(CN)_6]^{4-}$	$[Ru(NH_3)_5(py)]^{3+}$	119 (10.0)[d]	0.45	14	53	35

[a] Wavenumbers in 10^3 cm^{-1}. [b] Formal reduction potentials of the donor, from ref. 10. [c] Calculated from equation (7), assuming $E^{\ominus}[Ru(NH_3)_6{}^{3+/2+}] = 0.05$ V and $E^{\ominus}[Ru(NH_3)_5(py)^{3+/2+}] = 0.30$ V (ref. 23). [d] Ref. 7. [e] Ref. 24.

Because of their similarities, it would be interesting to compare the intervalence-transfer and the thermal electron-transfer processes. The relationship between these two processes can be seen in the potential-energy diagrams in Figure 2.

The activation energies for outer-sphere electron-transfer reactions of type (4) have been expressed,

$$Ox_1 + Red_2 \longrightarrow Red_1 + Ox_2 \qquad (4)$$

according to Marcus,[25] Hush,[26] and Sutin,[27] as in (5). Here $\Delta G_{12}^{\ddagger}$ refers to the thermal activation barrier for electron transfer in the precursor complex, $\Delta G_{11}^{\ddagger}$ and $\Delta G_{22}^{\ddagger}$ are the intrinsic barriers associated with the self-

$$\Delta G_{12}^{\ddagger} = \frac{\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger}}{2} + \frac{\Delta G_r^{\ominus}}{2} + \frac{(\Delta G_r^{\ominus})^2}{8(\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger})} \qquad (5)$$

exchange reactions, and $\Delta G_r^{\ominus}$ is the net free-energy change for the process.

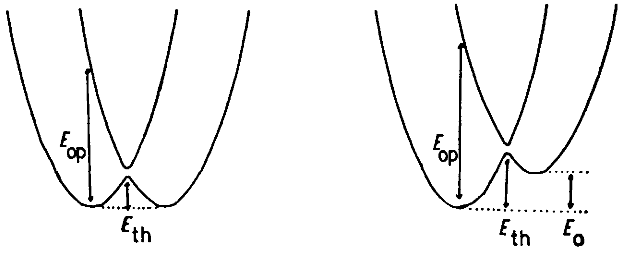
For the optical electron-transfer process, another equation has been proposed by Hush[28] in terms of harmonic potentials and E_0, the energy difference between the initial and final states. Substituting[27] $\Delta G_r^{\ominus}$ for E_0, Hush's equation can be formulated as in (6)

$$E_{op} = 2(\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger}) + \Delta G_r^{\ominus} \qquad (6)$$

$$E_{op} = 2(\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger}) - nF\Delta E_{12}^{\ominus} \qquad (7)$$

or (7). These equations predict that the energies of optical electron transfer in a series of complexes with similar intrinsic barriers should increase linearly with $\Delta G_r^{\ominus}$ of $-nF\Delta E_{12}^{\ominus}$, with a slope of unity.

The existence of a linear correlation between the intervalence transfer energies and $\Delta G_r^{\ominus} = -nF\Delta E_{12}^{\ominus}$ for the $[Ru(NH_3)_6][Fe(CN)_5L]$ complexes can be seen in Figure 3. It seems remarkable that the previously reported[7] $[Ru(NH_3)_5(py)][Fe(CN)_6]$ and $[Ru(NH_3)_6]_4[Ru(CN)_6]_3$ complexes are also correlated with the present series of complexes, allowing one to test for the changes in the donor and acceptor ions.



(a) $E_{op} = 4E_{th}$ (b) $E_{op} \cong 4E_{th} - E_0$

FIGURE 2 Reaction co-ordinates for electron transfer: (a) $E_0 = 0$; (b) $E_0 > 0$

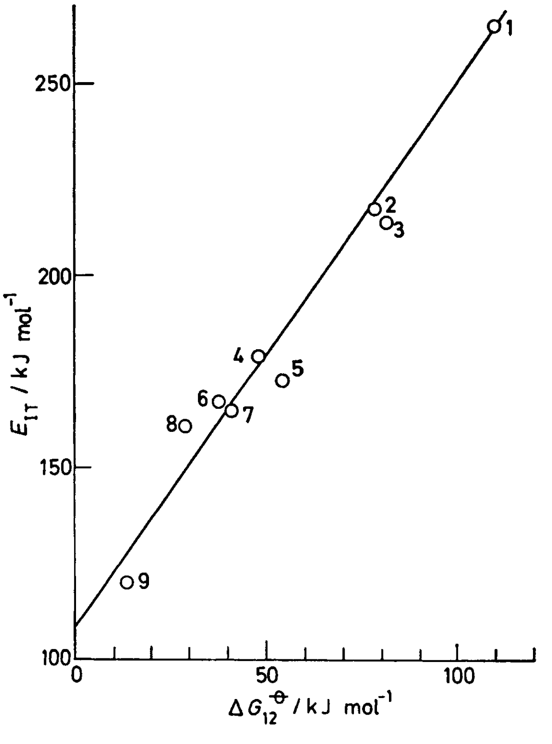


FIGURE 3 Correlation of intervalence-transfer energies with $E_{12}^{\ominus}$, for the outer-sphere mixed-valence complexes numbered as in Table 3

Although the trends in the optical electron-transfer energies are consistent with equation (7), the agreement is expected to be limited by the approximations involved in the use of harmonic potential models and of the free-energy changes in aqueous solution instead of the internal energy changes for the solids.

The experimental slope of 1.39 ± 0.09 suggests that the intrinsic barriers are not constant, but proportional to $\Delta G_r^{\ominus}$. In this case, based on equation (7), one can try to estimate the contributions of $\Delta G_{11}^{\ddagger} + \Delta G_{22}^{\ddagger}$ for each system, as shown in Table 3.

According to Hush,[28] for the symmetrical system of Figure 3(a), $E_0 = 0$, and the energy of the optical transfer [equation (6)] becomes four times the activation energy for the thermal electron-transfer process [equation (5)]. For a non-symmetrical system with small $\Delta G_r^{\ominus}$, the relationship between E_{op} and E_{th}, the optical and thermal electron-transfer energies, respectively, becomes (8).

$$E_{op} = 4E_{th} - E_0 \qquad (8)$$

For the present systems, because of their large $\Delta G_r^{\ominus}$, a more reasonable evaluation of E_{th} is obtained using equation (5) and the values estimated for the intrinsic barriers. The E_{th} values calculated in this way are shown in Table 3. For the $[Ru(NH_3)_5(py)]^{3+}$–$[Fe(CN)_6]^{4-}$ system, E_{th} was recently obtained by Haim and co-workers.[29] The reported value of $\Delta G_{12}^{\ddagger} = 42$ kJ mol^{-1} compares reasonably well with that estimated in this work.

The resonance energy (β) for the $[Ru(NH_3)_5(py)]_4[Fe(CN)_6]_3$ complex has been previously[7] evaluated using equations (9)[28] and (10),[30] where d is the internuclear separation between the metal ions.

$$\alpha^2 = (4.24 \times 10^{-4})\varepsilon_{\mathrm{max.}}\Delta\nu_{1/2}/\nu_{\mathrm{max.}}d^2 \qquad (9)$$

The reported value of $\beta \leqslant 0.37$ kcal mol^{-1} (1.55 kJ mol^{-1}) indicates that the perturbation of the vibrational barrier to electron transfer is small enough to justify the use of the present model for the correlation between E_{op} and E_{th}.

$$\beta \leqslant \alpha\nu_{\mathrm{max.}} \qquad (10)$$

The band half-width, $\Delta\nu_{1/2}$, estimated from the intervalence spectra using Hush's definition $(I\nu_{\mathrm{max.}}/I_{\mathrm{max.}}\nu = 0.5)$, showed an apparent increase from 5 400 cm^{-1} for the imidazole complex to *ca.* 8 000 and 9 000 cm^{-1} for the dimethyl sulphoxide and carbon monoxide analogues. Although these values approach, in magnitude, those predicted from equation (11), the agreement with the theory was not satisfactory.

$$\nu_{\mathrm{max.}} = E_0 + (16\,.\,\ln 2\,.\,kT)^{-1}(\Delta\nu_{1/2})^2 \qquad (11)$$

Besides the approximation assumed in the gaussian treatment,[28] it is possible that non-systematic changes in the Fe–Ru distances, due to the presence of water and of ligands of different sizes in the complexes, are also responsible for the observed deviation from the theoretical behaviour.

[9/169 *Received, 2nd February,* 1979]

REFERENCES

[1] G. C. Allen and N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 357.
[2] M. B. Robin and P. Day, *Adv. Inorg. Chem. Radiochem.*, 1967, **10**, 247.
[3] R. D. Cannon, *Adv. Inorg. Chem. Radiochem.*, 1978, **21**, 179.
[4] D. Waysbort, M. Evenor, and G. Navon, *Inorg. Chem.*, 1975, **14**, 514.
[5] A. J. Macfarlane and R. J. P. Williams, *J. Chem. Soc.* (*A*), 1969, 1517.
[6] I. G. Dance and P. S. Solstad, *J. Amer. Chem. Soc.*, 1969, **95**, 7256.
[7] J. C. Curtis and T. J. Meyer, *J. Amer. Chem. Soc.*, 1978, **100**, 6284.
[8] H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039.
[9] H. E. Toma, J. M. Malin, and E. Giesbrecht, *Inorg. Chem.*, 1973, **12**, 2084.
[10] H. E. Toma and C. Creutz, *Inorg. Chem.*, 1977, **16**, 545.
[11] H. E. Toma, J. M. Martins, and E. Giesbrecht, *J.C.S. Dalton*, 1979, 1610.
[12] J. N. Armor, Ph.D. Thesis, Stanford University, 1970; J. R. Pladziewicz, T. J. Meyer, J. A. Broomhead, and H. Taube, *Inorg. Chem.*, 1973, **12**, 639.
[13] A. D. Allen and C. V. Senoff, *Canad. J. Chem.*, 1967, **45**, 1337.
[14] P. C. Ford, *Co-ordination Chem. Rev.*, 1970, **5**, 75.
[15] K. Nakamoto, 'Infrared Spectra of Inorganic and Co-ordination Compounds,' 2nd edn., Wiley-Interscience, New York, London, Sydney, Toronto, 1970.
[16] H. E. Toma, E. Giesbrecht, J. M. Malin, and E. Fluck, *Inorg. Chim. Acta*, 1975, **14**, 11.
[17] R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, 1972, **11**, 437.
[18] G. Emschwiller and C. K. Jørgensen, *Chem. Phys. Letters*, 1970, **5**, 561.
[19] C. Creutz and H. Tabe, *J. Amer. Chem. Soc.*, 1973, **95**, 1086.
[20] R. W. Callahan, F. Richard Keene, T. J. Meyer, and D. J. Salmon, *J. Amer. Chem. Soc.*, 1977, **99**, 1064.
[21] F. Felix and A. Ludi, *Inorg. Chem.*, 1978, **17**, 1782.
[22] H. E. Toma, *J. Co-ordination Chem.*, 1978, **7**, 231.
[23] H. S. Lim, D. J. Barclay, and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460.
[24] D. A. Buckingham and A. M. Sargeson, in 'Chelating Agents and Metal Chelates,' eds. F. P. Dwyer and D. P. Mellor, Academic Press, New York, 1964, ch. 6.
[25] R. A. Marcus, *Ann. Rev. Phys. Chem.*, 1964, **15**, 155; *J. Chem. Phys.*, 1964, **43**, 679.
[26] N. S. Hush, *Trans. Faraday Soc.*, 1961, **57**, 557.
[27] N. Sutin, in 'Inorganic Biochemistry,' ed. G. L. Eichhorn, Elsevier, Amsterdam, London, New York, 1973, vol. 2, ch. 9.
[28] N. S. Hush, *Progr. Inorg. Chem.*, 1967, **8**, 391.
[29] A. J. Miralles, R. E. Armstrong, and A. Haim, *J. Amer. Chem. Soc.*, 1977, **99**, 1416.
[30] B. Mayoh and P. Day, *J. Amer. Chem. Soc.*, 1972, **94**, 2885.