Electronic *d–d* Spectra and Ligand-dissociation Rates of Pentacyanoruthenate(II) Ions

José A. Olabe *
Departamento de Química Inorgánica, Analítica y Química Física, Facultad de Ciencias Exactas y Naturales, Universidad de Buenos Aires, 1428 Capital Federal, República Argentina
Hugo O. Zerga and Luis A. Gentil
Departamentos de Química e Ingeniería Química, Universidad Nacional de Mar del Plata, República Argentina

The electronic spectra of a series of $[Ru(CN)_5L]^{n-}$ complexes (L = H_2O, NH_3, pyrazine, dimethyl sulphoxide, or CN^-) have been measured in aqueous solution. The *d–d* bands were assigned on the basis of a ligand-field model for tetragonally distorted octahedra and the energy of the transitions, which depends on the nature of L, were found to correlate with the rate constant for the dissociation of L from $[Ru(CN)_5L]^{n-}$, k_{-L}. Comparisons are made with the similar $[Fe(CN)_5L]^{n-}$ series. A new value of $10Dq$, 4.2 μm^{-1}, is proposed for $[Ru(CN)_6]^{4-}$, which is significantly higher than that corresponding to $[Fe(CN)_6]^{4-}$, as expected from ligand-field theory.

Routes to the synthesis of complexes of type $[Ru(CN)_5L]^{n-}$ have recently been developed where L is a π-acceptor ligand such as NO[1] or a *N*-heterocyclic species related to pyridine and pyrazine.[2,3] Electron-transfer spectra,[3] as well as ligand-substitution kinetic studies,[4,5] have shown that strong similarities exist with the chemistry of related complex ions, such as those from the $[Fe(CN)_5L]^{n-}$ [6] and $[Ru(NH_3)_5L]^{n+}$ series.[7]

It is likely that a larger variety of ligands are able to bind to the $Ru(CN)_5{}^{3-}$ moiety; the series with L = H_2O, NH_3, pyrazine (pyz), dimethyl sulphoxide (dmso), or CN^- is the subject of the present work. Electronic *d–d* spectra and rate constants for dissociation of L from the $[Ru(CN)_5L]^{n-}$ ions are measured and shown to provide useful information on the nature of the Ru–L bond interaction.

Experimental

The salt $K_4[Ru(CN)_6]\cdot3H_2O$ was from Ventron. The ligands L were reagent-grade chemicals. Aqueous solutions of the $[Ru(CN)_5(H_2O)]^{3-}$ ion were obtained through the reaction of bromine with $[Ru(CN)_6]^{4-}$;[2] solutions of $[Ru(CN)_5(NH_3)]^{3-}$ and $[Ru(CN)_5(dmso)]^{3-}$ [8] were obtained from $[Ru(CN)_5(NO)]^{2-}$ ion by reaction with hydrazine, in an excess of L.[5] Electronic spectra and kinetic runs were monitored in a Shimadzu UV-210A spectrophotometer; the dissociation rate constants, k_{-L} (25 °C), were measured under pseudo-first-order conditions, with pyz as a scavenger for the $Ru(CN)_5{}^{3-}$ intermediate, by measuring the increase in absorbance of the product, $[Ru(CN)_5(pyz)]^{3-}$.[5]

Results and Discussion

The $[Ru(CN)_5L]^{n-}$ complexes exhibit an intense (ε = *ca.* 10^4 dm^3 mol^{-1} cm^{-1}) asymmetric band at 200—210 nm, which as in the case of $[Ru(CN)_6]^{4-}$ [9] and $[Ru(CN)_5(NO)]^{2-}$,[1] we assign to the metal-to-ligand charge-transfer (m.l.c.t.) transitions from Ru^{II} to antibonding orbitals in cyanide ligands; their energies are nearly independent of the nature of ligand L.

Weak-to-medium intensity bands (ε = *ca.* 10^3 dm^3 mol^{-1} cm^{-1}) protrude from the low-energy tail of the m.l.c.t. bands in the case of L = H_2O (310 nm) and NH_3 (285 nm), as shown in Figure 1. A shoulder in the same region (280 nm) was measured for $[Ru(CN)_5(pyz)]^{3-}$,[2] and a very weak shoulder can also be detected in the spectrum of $[Ru(CN)_5(dmso)]^{3-}$, at *ca.* 260 nm.[8] In the case of $[Ru(CN)_6]^{4-}$, our measurements do in fact suggest that a band is also present at *ca.* 250 nm, according to a gaussian analysis on the tail of the m.l.c.t. band (Figure 1).

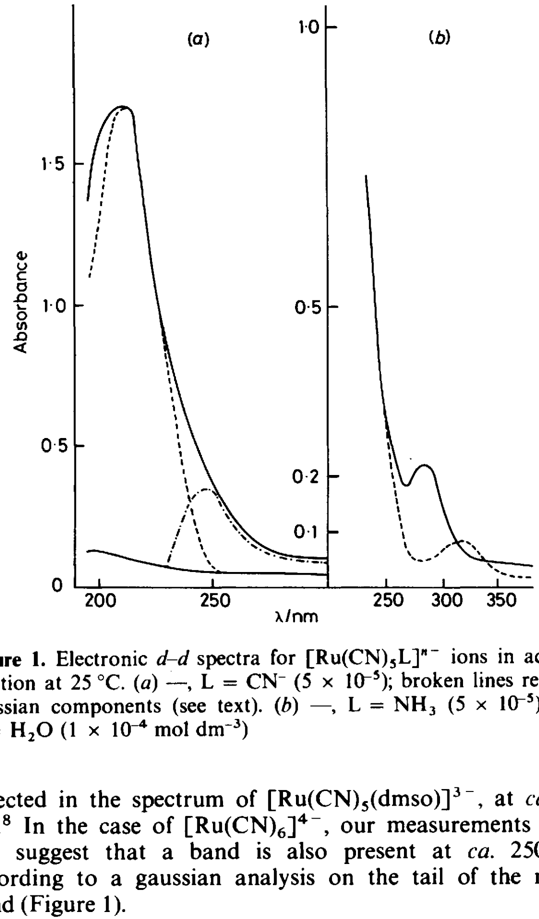

Figure 1. Electronic *d–d* spectra for $[Ru(CN)_5L]^{n-}$ ions in aqueous solution at 25 °C. (*a*) —, L = CN^- (5×10^{-5}); broken lines relate to gaussian components (see text). (*b*) —, L = NH_3 (5×10^{-5}); ----, L = H_2O (1×10^{-4} mol dm^{-3})

The assignment of *d–d* bands of $[Ru(CN)_6]^{4-}$ requires further consideration; the very weak absorption at 322 nm, previously assigned to the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition,[10] should preferentially be assigned to the spin-forbidden transition $^1A_{1g} \longrightarrow {}^3T_{1g}$.[11] The presently measured band at 250 nm is indeed a better candidate for the former spin-allowed transition. A perfect correlation is found if our value for $[Ru(CN)_6]^{4-}$ is included in a plot of the energy of the $^1A_{1g} \longrightarrow {}^1T_{1g}$ transition for a series of $Ru^{II}L_6$ ions against the energy of corresponding

Table. Electronic *d–d* transitions, ligand-field parameters, and dissociation rate constants for $[M(CN)_5L]^{n-}$ ions

$[Ru(CN)_5L]^{n-}$ [a]					$[Fe(CN)_5L]^{n-}$ [b]			
$\tilde{\nu}_{d-d}/\mu m^{-1}$	$Dq/\mu m^{-1}$	$Dt/\mu m^{-1}$	k_{-L}[c]$/s^{-1}$	L	$\tilde{\nu}_{d-d}/\mu m^{-1}$	$Dq/\mu m^{-1}$	$Dt/\mu m^{-1}$	k_{-L}[c]$/s^{-1}$
3.23[d]	0.29	0.043	0.5[e]	H_2O	2.26	0.15	0.048	2.2×10^{2}
3.51	0.34	0.029	3.7×10^{-4}	NH_3	2.51	0.20	0.034	1.7×10^{-2}
3.55[d]	0.35	0.026	2.4×10^{-5}[f]	pyz	2.59[g]	0.22	0.026	4.2×10^{-4}[h]
3.87[i]	0.39	0.014	3.3×10^{-6}[i]	dmso	2.85	0.27	0.014	7.5×10^{-5}
4.00	0.44	0.000	1.0×10^{-8}[j]	CN^-	3.10	0.32	0.000	4.0×10^{-7}[k]

[a] This work, unless stated otherwise. [b] Ref. 13, unless stated otherwise. [c] 25.0 °C. [d] Ref. 2. [e] Estimated value, *cf.* ref. 5. [f] Ref. 5. [g] Value corresponding to the related $[Fe(CN)_5(N_2C_4H_3CO_2)]^{4-}$ ion ($N_2C_4H_3CO_2$ = pyrazinecarboxylate). [h] Ref. 6. [i] Ref. 8. [j] Calculated value, obtained from data at 80 °C, with E_{act} = 125 kJ mol^{-1}. [k] Calculated from J. Legros, *J. Chim. Phys. Phys-Chim. Biol.*, 1964, **61**, 909.

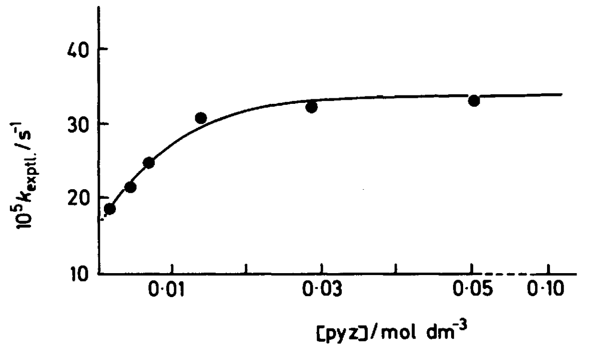

Figure 2. Plot of the experimental pseudo-first-order rate constant for the dissociation of L from $[Ru(CN)_5(NH_3)]^{3-}$ against the concentration of the entering ligand, pyrazine; pH 9, I = 1 mol dm^{-3} (NaCl), and 25.0 °C

transitions for $Co^{III}L_6$ complexes[9] (both with low-spin d^6 configurations and L = H_2O, NH_3, ethylenediamine, or CN^-).

From the previous assignment, a new value for 10*Dq*, 4.2 µm^{-1}, is calculated for $[Ru(CN)_6]^{4-}$;[9] this is reasonably higher than that found for $[Fe(CN)_6]^{4-}$ (3.28 µm^{-1}),[9] as expected from the increase in σ-bonding and π-back bonding interactions when going from the first to the second transition series.

When applying a ligand-field treatment[12] to tetragonal low-spin d^6 complexes, the $^1T_{1g}$ excited state in O_h symmetry splits into $^1A_2$ and $^1E(1)$ states (C_{4v} microsymmetry): the $^1A_1 \longrightarrow {}^1A_2$ transition is orbitally forbidden and should have a low intensity; on the other hand, the $^1A_1 \longrightarrow {}^1E(1)$ transition should be allowed and be highly sensitive to the nature of the ligand L. Our results do agree with this simplified model, assuming that the $^1A_1 \longrightarrow {}^1A_2$ transition is hidden by the more intense absorption of the m.l.c.t. band. A very similar pattern was found in the $[Fe(CN)_5L]^{n-}$ series,[13] the corresponding bands being shifted to lower energies, as seen in the Table. A unit slope is obtained when plotting the energies of the $^1A_1 \longrightarrow {}^1E(1)$ transitions for both iron(II) and ruthenium(II) complexes. The results for the $[Co(CN)_5L]^{n-}$ series have also been discussed on the basis of this model.[14]

If the energy splittings are analysed in terms of ligand-field parameters, *Dq* and *Dt*, where *Dq* is the octahedral field strength of the ligand L and *Dt* is its tetragonal distortion parameter, a reasonable trend is obtained when changing the ligand L, as shown in the Table. As expected, *Dq* increases and *Dt* decreases when L is more able to stabilize the appropriate metal orbitals of π symmetry (d_{xz}, d_{yz}) or to destabilize the σ orbital (d_{z^2}).

The interchange of L in the $[Ru(CN)_5L]^{n-}$ system occurs through a dissociative mechanism [equations (1)—(3)].[5] The

$$[Ru(CN)_5L]^{n-}\,(aq) \underset{k_1}{\overset{k_{-1}}{\rightleftharpoons}} [Ru(CN)_5]^{3-}\,(aq) + L(aq) \quad (1)$$

$$[Ru(CN)_3]^{3-}\,(aq) + H_2O \overset{K}{\rightleftharpoons} [Ru(CN)_5(H_2O)]^{3-}\,(aq) \quad (2)$$

$$[Ru(CN)_5]^{3-}\,(aq) + L'(aq) \overset{k_3}{\rightleftharpoons} [Ru(CN)_5L']^{3-}(aq) \quad (3)$$

experimental first-order rate constant, $k_{obs.}$, is dependent on the concentration of L′ (pyz); when a steady-state treatment is applied to $[Ru(CN)_5]^{3-}$, $k_{obs.}$ attains a saturation value at high concentrations of L′, and reduces to $k_{-1} = k_{-L}$, the rate constant for loss of ligand L. This is shown in Figure 2 for the case of L = NH_3.

The trends in k_{-L} when going down the Table can be understood in terms of the influence of σ–π interactions, *i.e.* the same factors which determine $\tilde{\nu}_{d-d}$, the energy of the *d–d* transition. Thus, a good correlation may be obtained when plotting log k_{-L} against $\tilde{\nu}_{d-d}$; again, a very similar slope is found for both series of $[M(CN)_5L]^{n-}$ complexes.[14,15]

The higher value for $\tilde{\nu}_{d-d}$ for $[Ru(CN)_5(NH_3)]^{3-}$ compared to $[Ru(CN)_5(H_2O)]^{3-}$ can be explained by the higher basicity of ammonia and therefore a higher energy of the excited state (d_{z^2}), assuming that the ground state (d_{xz}, d_{yz}) is equally influenced by cyanide interactions in both complexes; thus, the Ru–N bond is more stabilized by the σ interaction than is the Ru–O bond and consequently a lower k_{-L} is expected. For the other complexes, the trends (Table), both for $\tilde{\nu}_{d-d}$ and for k_{-L}, show the increasing influence of the Ru^{II}–L π bond interaction, which stabilizes the d_{xz}, d_{yz} metal orbitals (note that the dmso ligand binds through the sulphur atom).[8]

From the Table, it can also be seen that the energy of the $^1A_1 \longrightarrow {}^1E(1)$ transition for any member of the $[Ru(CN)_5L]^{n-}$ series is about 0.9—1.0 µm^{-1} higher than for the corresponding member of the $[Fe(CN)_5L]^{n-}$ series. This difference should be related to changes in both the energy of the ground and excited states for each of the metal centres. On the other hand, a difference of *ca.* 0.4 µm^{-1} is observed between the energies of the m.l.c.t. band for any member of the $[Fe(CN)_5L]^{n-}$ and $[Ru(CN)_5L]^{n-}$ series when L is a *N*-heterocyclic ligand.[5] This value is equal to the difference in electrode potential for the M^{II}–M^{III} hexacyanide complexes (ΔE°_{Ru-Fe} = 0.51 V, *i.e.* 0.41 µm^{-1}).[16] These results are however not unexpected. The cyanide ligands make a dominant contribution to the overall bonding scheme in $[M(CN)_5L]^{n-}$ ions; in the case of π interactions, the competitive effect from cyanides makes the backbonding to L relatively poor (for L = pyz, about 7—9% in complexes of Fe^{II} and Ru^{II}, outside the accuracy).[2] According to this model, the energy of the excited state (antibonding pyz orbitals) is nearly the same for both series of complexes, while the ground state is significantly more stabilized for Ru^{II}.[3] Thus, energy changes in the m.l.c.t. bands of complexes of Ru^{II} and Fe^{II} reflect only the ground-state stabilization of π orbitals (mainly by cyanide interactions), while the changes in *d–d* bands also reflect the changes in the energy of the excited state, *i.e.* the $\sigma(d_{z^2})$ level. Then, it is reasonable that $\Delta[{}^1A_1 \longrightarrow \pi(\mathrm{L}^*)] =$ *ca.* $\frac{2}{5}\Delta[{}^1A_1 \longrightarrow {}^1E(1)]$, in agreement with a simplified formulation of ligand-field theory.

Acknowledgements

We thank Professor R. Mews (Göttingen) for a generous gift of ruthenium chemicals, and Consejo Nacional de Investigaciones Cientificas y Técnicas and Comisión de Investigaciones Cientificas de la Provincia de Buenos Aires for partial financial support.

References

1 J. A. Olabe, L. A. Gentil, G. Rigotti, and A. Navaza, *Inorg. Chem.*, 1984, **23**, 4297.
2 C. R. Johnson and R. E. Shepherd, *Inorg. Chem.*, 1983, **22**, 1117.
3 C. R. Johnson and R. E. Shepherd, *Inorg. Chem.*, 1983, **22**, 2439.
4 J. Mark A. Hoddenbagh, and D. H. Macartney, *Inorg. Chem.*, 1986, **25**, 380.
5 L. A. Gentil, H. O. Zerga, and J. A. Olabe, *J. Chem. Soc., Dalton Trans.*, 1986, 2731.
6 H. E. Toma and J. M. Malin, *Inorg. Chem.*, 1973, **12**, 1039, 2080.
7 P. C. Ford, *Coord. Chem. Rev.*, 1970, **5**, 75.
8 A. M. Rabino, L. A. Gentil, and J. A. Olabe, unpublished work.
9 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984.
10 H. B. Gray and N. A. Beach, *J. Am. Chem. Soc.*, 1963, **85**, 2922.
11 M. Mingardi and G. B. Porter, *Spectrosc. Lett.*, 1968, **1**, 293.
12 R. A. D. Wentworth and T. S. Piper, *Inorg. Chem.*, 1965, **4**, 709.
13 H. E. Toma, E. Giesbrecht, J. M. Malin, and E. Fluck, *Inorg. Chim. Acta*, 1975, **14**, 11.
14 V. M. Miskowski and H. B. Gray, *Inorg. Chem.*, 1975, **14**, 401.
15 H. E. Toma, J. M. Martins, and E. Giesbrecht, *J. Chem. Soc., Dalton Trans.*, 1978, 1610.
16 D. D. De Ford and A. W. Davidson, *J. Am. Chem. Soc.*, 1951, **73**, 1469.

Received 11*th June* 1986; *Paper* 6/1182