Kinetics of Formation, Dissociation, and Isomerization Reactions in Complexes of Cyanopyridines and Benzonitrile with Pentacyanoruthenate(II)

Alejandra E. Almaraz and Luis A. Gentil
Departamento de Química (Facultad de Ciencias Exactas y Naturales) and Departamento de Ingeniería Química (Facultad de Ingeniería), Universidad Nacional de Mar del Plata, República Argentina
Jose 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

The complexes of pentacyanoruthenate(II) with 3- and 4-cyanopyridines and benzonitrile have been prepared in aqueous solution by mixing $[Ru(CN)_5(H_2O)]^{3-}$ with the appropriate ligand. With the cyanopyridines, the reaction proceeds in two stages: the first corresponds to the formation of a mixture of pyridine- and nitrile-bonded isomers, and the second to the linkage isomerization of the unstable (nitrile-bonded) isomer to the stable one (pyridine-bonded). The complexes exhibit metal-to-ligand and intra-ligand charge-transfer absorptions. The rate constants for the formation, k_f, and dissociation, k_d, of all the complexes have been determined (25 °C), as well as the isomerization rate constant, k_{iso}, for the cyanopyridine complexes. Activation parameters were obtained for the formation reaction of the mixture of isomers, as well as for the dissociation reactions of the stable, pyridine-bonded complexes. The results for the formation and dissociation reactions are analysed in terms of dissociative mechanisms. From k_f and k_d, values of K_{st}, the stability constants of the different complexes, have been calculated. The discussion is supported by previous data obtained for related pentacyanoferrate(II) and penta-ammineruthenium(II) complexes. Thus, the influence of the metal centre, M, as well as that of the auxiliary ligands, X, on the spectral and substitution reactivity properties of MX_5L systems is described.

The ligand properties of cyanopyridines (CN-py) are of interest in relation to their bifunctional character. Linkage isomers binding either through the nitrile nitrogen or the pyridine nitrogen have been found in $[MX_5(CN\text{-}py)]$ systems, where $MX_5 = [Ru(NH_3)_5]^{2+}$ [1,2] or $[Fe(CN)_5]^{3-}$.[3] The nature and relative stability of the different co-ordinated species are dependent on the type of metal centre and auxiliary ligands, X, mainly through the influence of electronic and/or steric interactions. The rates of formation, dissociation, and interconversion of pentacyanoferrate(II) complexes with 2-, 3-, and 4-CN-py have also been measured.[3]

Elucidation of the structural and kinetic features in the latter complexes was crucial in understanding intramolecular electron-transfer reactions with $[Fe(CN)_5]^{3-}$ and $[Co(NH_3)_5]^{3+}$ as the electron donor and acceptor, respectively, in systems containing bridging cyanopyridines.[4] Other closely related bridging bimetallic systems proved useful in studying energy-transfer processes occurring after photochemical activation.[5] Bridging cyanopyridines have also been employed in investigations of metal–metal interactions in bi- and tri-nuclear complexes containing either $[Ru(NH_3)_5]^{2+}$, $[Fe(CN)_5]^{3-}$, or $[Ru(bipy)_2]^{2+}$ (bipy = 2,2′-bipyridine) as co-ordinating moieties.[6–8]

The preparation of $[Ru(CN)_5L]^{n-}$ complexes has been achieved in recent years,[9,10] and several spectroscopic[11,12] and substitution-kinetic[12–14] properties studied. A rich chemistry remains to be developed, as for the $[Fe(CN)_5L]^{n-}$ analogues. New families of bridging bimetallic systems containing $[Ru(CN)_5]^{3-}$ may be constructed when properly combined with other MX_5 moieties; an interesting precursor is the recently prepared $[(NC)_5Ru^{II}(pyz)Ru^{III}(NH_3)_5]$ mixed-valence species (pyz = pyrazine).[15] Outer-sphere complexes derived from $[Ru(CN)_6]^{4-}$ have also proved useful in promoting light-induced electron-transfer reactions with several electron acceptors.[16] Given this framework, our purpose is to explore the properties of cyanopyridines as bridging ligands in systems containing the $[Ru(CN)_5]^{3-}$ moiety. However, a preliminary study concerning the characterization and kinetic behaviour of the corresponding monomeric complexes seems to be in order, and is the subject of the present paper.

Experimental

Reagents.—Potassium hexacyanoruthenate(II) was obtained from Ventron; 3- and 4-cyanopyridine (Riedel) were used after purification by crystallization from hot, 95%, ethanol. Benzonitrile (C. Erba) was used as supplied. Other chemicals were of analytical grade. Doubly distilled water was used.

Preparation of Solid Complexes.—Using a modified technique previously employed for the preparation of $K_3[Ru(CN)_5(pyz)]$ [10] impure samples of $K_3[Ru(CN)_5(CN\text{-}py)]$ were isolated. Direct precipitation from the product reaction mixture {obtained by mixing $[Ru(CN)_6]^{4-}$ with bromine, KBr, and an excess of the desired ligand} could not be achieved with the aid of solvents (the use of acetone was precluded due to reaction with the cyanopyridines). The solutions showed characteristic bands in the visible–near-u.v. region (m.l.c.t. = metal to ligand charge transfer), as well as u.v. bands corresponding to intra-ligand transitions (see below); the latter could be identified after performing successive extractions of unreacted CN-py with diethyl ether.

On evaporating the solutions to dryness, the residue contained KBr and showed i.r. bands characteristic of the $[Ru(CN)_5]^{3-}$ moiety (2 040 and 550 cm^{-1}),[10,17] as well as a band at 2 250 cm^{-1} assigned to stretching of the nitrile group in CN-py (co-ordinated through the pyridine nitrogen).[1,3] Upon dissolution of the solids, the m.l.c.t. band was shifted to higher

Table 1. Pseudo-first-order rate constants for the formation and isomerization reactions of pentacyanoruthenate(II) complexes with 4- and 3-CN-py and the formation reaction with benzonitrile[a]

L	10^3c/mol dm^{-3}	10^3k/s^{-1}
4CN-py	1	1.2[b]
	2	2.3[b]
	4	4.8[b]
	10	0.86[c]
	20	0.87[c]
3CN-py	2	1.8[d]
	4	3.3[d]
	6	5.3[d]
	5	0.89[e]
	10	0.93[e]
	20	1.1[e]
PhCN[f]	2	2.8
	10	6.7
	15	9.0
	20	12.0

[a] $[Ru(CN)_5(H_2O)]^{3-}$ = 5 × 10^{-5} mol dm^{-3}, 25 °C, I = 0.1 mol dm^{-3} (LiCl). [b] Formation reaction, measured at 388 nm; from the plot of k *vs.* [CN-py]: $(k_f^N + k_f^{NC})$ = 1.2 dm^3 mol^{-1} s^{-1}. [c] Isomerization reaction, measured at 335 nm. [d] Formation reaction, measured at 342 nm; $(k_f^N + k_f^{NC})$ = 0.8 dm^3 mol^{-1} s^{-1}. [e] Isomerization reaction, measured at 317 nm. [f] Measured at 295 nm.

wavelengths, compared to the values obtained in the non-evaporated solutions. The magnitude of the shift was variable for different experiments and was particularly significant for the complex containing 4CN-py (up to 410 nm), suggesting the presence of mono- and di-meric species, the latter probably being bridged by CN-py.

Electronic Spectra.—The thermodynamically stable (pyridine-bonded) pentacyano(cyanopyridine)ruthenate(II) complexes were prepared in solution from freshly generated $[Ru(CN)_5(H_2O)]^{3-}$, as described above. Alternatively, a previously described[14] stoicheiometric reaction could be used, in which the $[Ru(CN)_5(NO)]^{2-}$ ion is attacked by hydrazine in the presence of an excess of CN-py. In either case, the electronic spectra were measured with a Shimadzu UV-210 A spectrophotometer, 20 h after mixing of the reactants, in order to ensure that only the desired stable isomer was present. The positions of the band maxima were the same for both procedures and the calculated molar absorbances were equal to within 5% error.

The spectra of the unstable, nitrile-bonded pentacyanoruthenate(II) isomers with 3- and 4-CN-py were obtained as follows.

Solutions of the $[Ru(CN)_5(H_2O)]^{3-}$ ion (5 × 10^{-5} mol dm^{-3}) were left for 5 min at 25 °C, then CN-py was added in a 500-fold excess. Successive spectra were recorded for a period of about 5 min. The spectra of the unstable isomers were obtained by extrapolating the curves of absorbance *vs.* time, for each wavelength, to the mixing time, and subtracting the absorbance contribution of the pyridine-bonded isomer, whose percentage in the initial mixture was calculated by an independent experiment (see below).

Kinetic and Stoicheiometric Measurements.—Rates of formation of the mixture of isomers were obtained under pseudo-first-order conditions for different concentrations of CN-py and temperatures (20—60 °C). (See footnotes to Table 1 for experimental details.)

Rates of dissociation for the stable pyridine-bonded complexes were measured by adding either dimethyl sulphoxide (dmso) or methylpyrazinium (mpyz) iodide to the solution of the desired complex. The measurements were carried out under pseudo-first-order conditions, by following the disappearance of the complex at its absorption maximum {or, in the case of methylpyrazinium, by following the build-up of the $[Ru(CN)_5(mpyz)]^{2-}$ ion at 524 nm}.[11] Rate constants were obtained at different concentrations of dmso (range 10^{-3} – 10^{-1} mol dm^{-3}). Activation parameters were obtained from $k_{exp.}$ values measured at saturation conditions ([dmso] = 0.1 mol dm^{-3}), in the temperature range 25—57 °C, I = 1 mol dm^{-3} (NaCl), pH 9.

Rates of dissociation for the unstable, nitrile-bonded isomers were calculated using measured values of the isomerization rate constant, k_{iso}, and f_N, the fraction of pyridine-bonded isomer.

Rates of isomerization of the nitrile-bonded isomers were measured by following the slow reaction, after the fast formation reaction, through the decrease in absorbance at the maxima for the unstable isomers (see Table 1).

The stoicheiometric fractions of each isomer obtained in the formation reaction were measured as follows. The cyanopyridine (5 × 10^{-3} mol dm^{-3}) was added to a solution of $[Ru(CN)_5(H_2O)]^{3-}$ (5 × 10^{-5} mol dm^{-3}). After waiting for completion of the formation reaction (5 min), a large excess of methylpyrazinium iodide was added (0.25 mol dm^{-3}) in order to quench the isomerization process. The increase in absorbance at 524 nm was followed and the plot of ln $(A_\infty - A_t)$ *vs.* time exhibited a curve, due to the occurrence of two kinetic processes with different time-scales. A linear region developed at longer times (*i.e.* when the unstable isomer had completely decayed), corresponding to dissociation of the stable isomer. Extrapolation of this line to zero time gave the absorbance corresponding to the stable isomer in the original mixture, and the desired fraction, f_N could be calculated.[3]

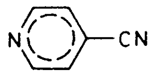
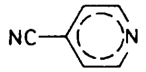
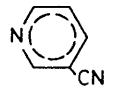
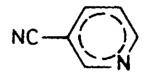
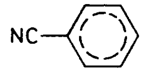
Complementary kinetic experiments with benzonitrile (PhCN) were performed in order to compare the results with those from the unstable isomers of CN-py complexes. The affinity of PhCN for $[Ru(CN)_5]^{3-}$ was shown to be lower than that observed for cyanopyridines, and the reaction of $[Ru(CN)_5(H_2O)]^{3-}$ with PhCN did not go to completion. A linear plot of ln $(A_\infty - A_t)$ *vs.* time {where A_t is the increasing absorption at 295 nm, the maximum for the $[Ru(CN)_5(PhCN)]^{3-}$ ion} was obtained. From the $k_{exp.}$ values, k_f and k_d were calculated using the relationship, $k_{exp.} = k_f\,[PhCN] + k_d$ (see Table 1).

Results

Electronic Spectra.—The absorption maxima and molar absorbances in the visible–near-u.v. region for the complexes of pentacyanoruthenate(II) with 4- and 3-CN-py and PhCN are shown in Table 2, together with data for related pentacyanoferrate(II) and penta-ammineruthenium(II) complexes.[1–3, 18] A direct comparison, based on consideration of relative energies and intensities, shows that the bands of the pentacyanoruthenate(II) complexes may be assigned to m.l.c.t. transitions, from predominantly ruthenium(II) orbitals to π*(CN-py) orbitals, as in the case of the related $[MX_5(CN\text{-}py)]$ complexes.

The comparisons are also valuable for identifying the linkage isomers in the $[Ru(CN)_5(CN\text{-}py)]^{3-}$ complexes. Pyridine-bonded isomers have been shown to absorb at longer wavelengths than nitrile-bonded isomers for both 4- and 3-CN-py in the pentacyanoferrate(II) complexes,[3] as well as in the penta-ammine(4-cyanopyridine)ruthenium(II) system.[1] Additional evidence is as follows. (*i*) A higher wavelength is found for the m.l.c.t. band in the 4-substituted pyridine complexes, compared to the 3-substituted ones. (*ii*) The wavelengths found for the pentacyanoruthenate(II) complexes with any of the ligands in Table 2 are the lowest of all (a discussion concerning energy shifts in m.l.c.t bands for MX_5L complexes may be found elsewhere).[11–14] (*iii*) In the spectra of the solutions free of excess CN-py, additional bands are found at 265 nm {for

Table 2. M.l.c.t. transitions for MX_5L complexes with L = pyridine- and nitrile-bonded cyanopyridines and benzonitrile.

L	MX_5								
	$Ru^{II}(CN)_5$ [a]			$Fe^{II}(CN)_5$ [b]			$Ru^{II}(NH_3)_5$		
	λ/nm	$\tilde{\nu}/\mu m^{-1}$	ε [c]	λ/nm	$\tilde{\nu}/\mu m^{-1}$	ε [c]	λ/nm	$\tilde{\nu}/\mu m^{-1}$	ε [c]
	388	2.58	5 900	477	2.10	5 700	500	2.00	
	333	3.00	2 000 [d]	405	2.47	7 400	425 [e]	2.35	5 370
	342	2.92	5 500	414	2.42	3 200			
	317	3.15	2 000 [d]	370	2.70	6 000	401 [e]	2.49	5 620
	295	3.39	5 400	341	2.93	5 100	376 [f]	2.66	8 500

[a] This work. [b] Ref. 3. [c] Molar absorbances in $dm^3\ mol^{-1}\ cm^{-1}$. [d] Estimated value. [e] Ref. 1. [f] Ref. 18.

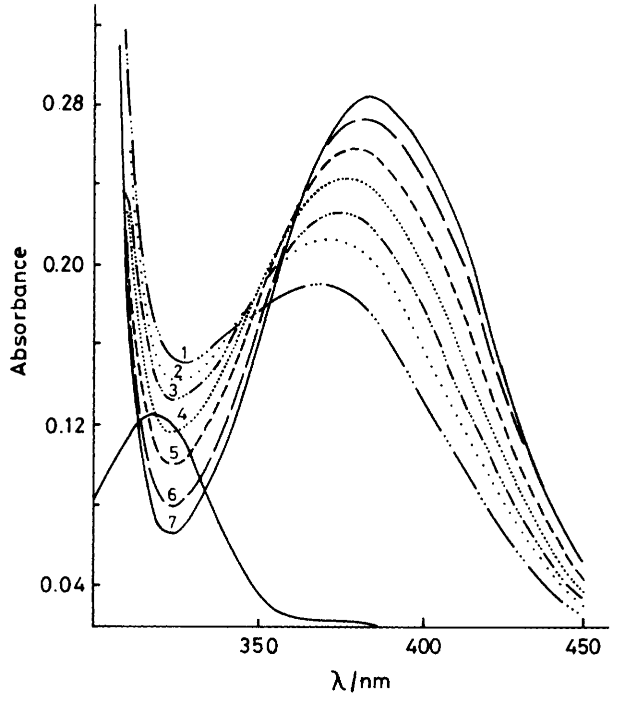
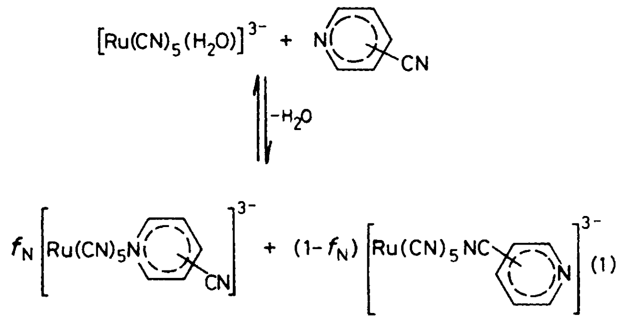


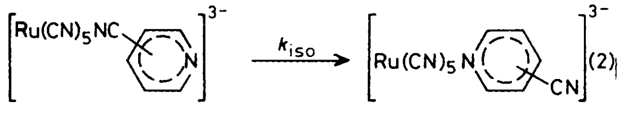
Figure. Successive electronic spectra obtained after mixing $[Ru(CN)_5(H_2O)]^{3-}$ (5×10^{-5} mol dm^{-3}) with 4CN-py. Spectrum number (time after mixing, in min): 1(5); 2(8); 3(11); 4(15); 5(20); 6(30); 7(160). The spectrum of initial $[Ru(CN)_5(H_2O)]^{3-}$ is also shown

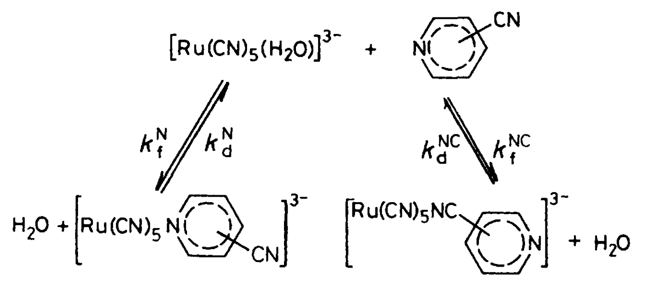


$[Ru(CN)_5(4CN\text{-}py)]^{3-}\}$ and 260 nm {for $[Ru(CN)_5(3CN\text{-}py)]^{3-}$}; they are only slightly shifted to higher energies when compared to the corresponding bands in the free ligands (271 and 265 nm, respectively).[19] In contrast, the bands in the $[Ru(NH_3)_5(CN\text{-}py)]^{2+}$ complexes are shifted to 253 (4CN-py) and 255 nm (3CN-py).[1] The shifts are consistent with the intraligand character of the transition; they are certainly expected to be higher for the latter complexes, due to the higher degree of Ru–CN-py π* interaction.

Kinetics of the Formation and Isomerization Reactions.—The Figure shows successive spectra for solutions obtained after mixing $[Ru(CN)_5(H_2O)]^{3-}$ with 4CN-py; a similar shape is obtained with 3CN-py. We propose rapid formation of the mixture of isomers as given in reaction (1) (*cf.* spectrum 1).

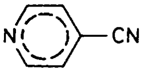
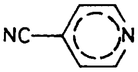
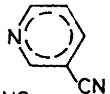
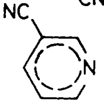
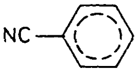
The shift of the maximum toward higher wavelengths is assigned to the isomerization reaction involving conversion of the nitrile-bonded isomer into the pyridine-bonded one [equation (2)]. This interpretation is supported by the fact that the rate of reaction (1) is dependent on the concentration of CN-py (first order), whereas that of reaction (2) shows no such dependence (Table 1).





Scheme.

Table 3. Rate constants for the formation and dissociation, and stability constants of pentacyanoruthenate(II) complexes with 4- and 3-cyanopyridine (pyridine- and nitrile-bonded isomers) and benzonitrile[a]

L	k_f/dm^3 mol^{-1} s^{-1} [b]	10^4k_d/s^{-1} [c]	$10^{-3}K_{st}$/dm^3 mol^{-1}
	0.76	0.25	30
	0.44	13[d]	0.32
	0.35	0.6	6.5
	0.45	24[d]	0.20
	0.49	18	0.28

[a] $T = 25$ °C. [b] $I = 0.1$ mol dm^{-3} (LiCl). [c] $I = 1$ mol dm^{-3} (NaCl), except for benzonitrile where $I = 0.1$ mol dm^{-3}. [d] Calculated from $k_{iso} = k_d^{NC}f_N$.

Table 4. Temperature dependence of the pseudo-first-order rate constants for the formation and dissociation reactions of pentacyanoruthenate(II) complexes with 4- and 3-CN-py[a]

Formation reaction

4CN-py[b]				3CN-py[c]			
T/°C	10^3k/s^{-1}	T/°C	10^3k/s^{-1}	T/°C	10^3k/s^{-1}	T/°C	10^3k/s^{-1}
25.0	2.17	45.3	11.2	17.3	1.86	35.2	7.58
31.0	3.28	50.6	15.7	21.0	2.99	40.4	12.3
36.0	4.52	57.0	29.6	24.7	3.26	46.0	17.6
40.7	6.36			29.3	4.84	50.6	19.5
				30.0	5.38		

Dissociation reaction

4CN-py				3CN-py			
T/°C	10^3k/s^{-1}	T/°C	10^3k/s^{-1}	T/°C	10^3k/s^{-1}	T/°C	10^3k/s^{-1}
25.0	0.254	42.5	4.62	25.0	0.600	36.0	3.19
34.0	1.11	49.5	14.3	26.0	0.928	39.5	4.96
37.5	2.01	57.0	35.7	31.5	1.84	50.0	24.1

[a] $I = 0.1$ mol dm^{-3} (LiCl), formation reaction; 1 mol dm^{-3} (NaCl), dissociation reaction. [b] [4CN-py] = 1.8×10^{-3} mol dm^{-3}. [c] [3CN-py] = 4.1×10^{-3} mol dm^{-3}.

From the linear dependence of k [reaction (1)] *vs.* concentration of CN-py, values of $(k_f^N + k_f^{NC})$ may be obtained from the slopes, where k_f^N and k_f^{NC} are defined in the Scheme. The results are shown in Table 1. Individual values for k_f^N and k_f^{NC} were calculated from $k_f^N + k_f^{NC}$ and the fraction of each isomer; these k_f values are shown in Table 3, which also includes the value for the PhCN complex.

The fractions of the stable isomers, $f_N = k_f^N/(k_f^N + k_f^{NC})$, were $f_N = 0.63$ (for 4CN-py) and 0.44 (for 3CN-py).

Activation parameters for reaction (1) were: $\Delta H_f^\ddagger = 64 \pm 7$ kJ mol^{-1}, $\Delta S_f^\ddagger = -80 \pm 21$ J K^{-1} mol^{-1} (for 4CN-py); and $\Delta H_f^\ddagger = 54 \pm 4$ kJ mol^{-1}, $\Delta S_f^\ddagger = -110 \pm 12$ J K^{-1} mol^{-1} (for 3CN-py) (see data in Table 4).

Kinetics of the Dissociation Reactions.—The first-order rate constants for the disappearance of the pyridine-bonded complexes (for 4- and 3-CN-py) increased with the concentration of the scavenger ligand, dmso or mpyz$^+$; but limiting values were reached when the concentration was higher than 0.02 mol dm^{-3}. This behaviour resembles a well known pattern for the dissociative reactions of MX_5L systems.[12–14,20] Under these saturation conditions, $k_{exp.} = k_d$, the dissociation rate constant of the pyridine-bonded isomer. Values of k_d are shown in Table 3.

Activation parameters were $\Delta H_d^\ddagger = 125 \pm 3$ kJ mol^{-1}, $\Delta S_d^\ddagger = 88 \pm 8$ J K^{-1} mol^{-1} (for 4CN-py); and $\Delta H_d^\ddagger = 109 \pm 7$ kJ mol^{-1}, $\Delta S_d^\ddagger = 44 \pm 22$ J K^{-1} mol^{-1} (for 3CN-py) (see data in Table 4).

Rate constants for the dissociation of the nitrile-bonded isomers and the $[Ru(CN)_5(PhCN)]^{3-}$ complex are also shown in Table 3.

Discussion

The spectral and substitution-kinetic properties of pentacyano(cyanopyridine)ruthenate(II) complexes appear to be closely related to those of the pentacyanoferrate analogues. The present work is supported by a similar experimental strategy, results, and line of argument to those used by Szecsy *et al.*[3] The Scheme is representative of the reactions studied.

In the Scheme, k_f^N, k_f^{NC} are the formation rate constants and k_d^N, k_d^{NC} are the dissociation rate constants for the stable and unstable linkage isomers, respectively; it is also assumed that the relation $k_{iso} = k_d^{NC}k_f^N/(k_f^N + k_f^{NC})$ holds, provided that the isomerization process occurs exclusively *via* an intermolecular mechanism, as was the case for the pentacyanoferrates.[3]

The formation rate constants of pentacyanoruthenate complexes of CN-py and PhCN fall in the range 0.4—0.8 dm^3 mol^{-1} s^{-1} per ligand binding site (Table 3). These values agree with those previously found for the entry of several *N*-heterocyclic ligands into $[Ru(CN)_5]^{3-}$.[14] The poor sensitivity of k_f to the nature of the entering ligand is one piece of evidence favouring the assignment of an ion-pair dissociative interchange mechanism to the formation reaction, according to equations (3) and (4).

$$[Ru(CN)_5(H_2O)]^{3-} + L \overset{K_{ip}}{\rightleftharpoons} \{Ru(CN)_5(H_2O)^{3-},L\} \quad (3)$$

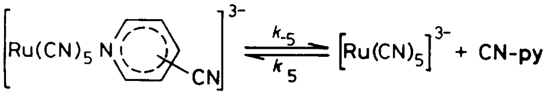
$$\{Ru(CN)_5(H_2O)^{3-},L\} \overset{k_{-H_2O}}{\rightleftharpoons} [Ru(CN)_5L]^{3-} + H_2O \quad (4)$$

In this mechanism, $k_f = k_{-H_2O}K_{ip}$; the loss of water [reaction (4)] is rate determining in the, probably concerted, process involving movement of the ligand L from the second to the first co-ordination sphere. Thus, constancy of not only k_f, but also of activation parameters, is expected within a series of reactions with different (although equally charged) entering ligands. The values for $\Delta H_f^\ddagger$ and $\Delta S_f^\ddagger$ are in close agreement with the values found for the reaction of $[Ru(CN)_5(H_2O)]^{3-}$ with other substituted pyridines and pyrazines.[14]

The result for $f_N = 0.44$ (3CN-py) suggests that both isomers are formed with very comparable rates. For 4CN-py, however, $f_N = 0.63$ and a higher k_f obtains for the pyridine-bonded isomer; the latter result compares well with data from the $[Fe(CN)_5(CN\text{-}py)]^{3-}$ complexes.[3] It is possible that a more favourable orientation of the 4CN-py ligand is obtained with the *N*-pyridine site pointing toward the metal, thus maximizing long-range π interactions (*i.e.* a higher K_{ip} value obtains for the pyridine-bonded isomer).

In contrast to the formation rate constants, the dissociation rate constants depend on the nature of the ligand, L. This behaviour is typical of dissociative reactions in MX_5L systems,[20] and has recently been confirmed for a group of $[Ru(CN)_5L]^{n-}$ complexes.[12–14] As seen in Table 3, k_d values for pyridine-bonded complexes are about 50 times lower than k_d values for nitrile-bonded ones; the latter values are similar to k_d for the $[Ru(CN)_5(PhCN)]^{3-}$ ion, as expected. Also, for both types of isomers, k_d values for complexes containing 4CN-py are lower than values for complexes containing 3CN-py. All of these results are strongly indicative of the importance of Ru^{II}–π^* interactions in determining the dissociation rate behaviour, as well as the electronic spectral tendencies. As has been fully discussed previously, lower energies for the m.l.c.t. transition and lower k_d values are related to a higher degree of back-bonding M–L interactions within a series of MX_5L complexes.[11,19,20]

Activation parameters for the dissociative reactions of the stable isomers are within the same range as those previously found for several pentacyano(*N*-heterocyclic)ruthenate(II) complexes.[14] These results, taken together with the saturation rate behaviour and the independence of k_d on the type of scavenger ligand, point to the operation of a dissociative mechanism, as shown by equations (5)—(7).


(5)

$$[Ru(CN)_5]^{3-} + H_2O \rightleftharpoons [Ru(CN)_5(H_2O)]^{3-} \qquad (6)$$

$$[Ru(CN)_5]^{3-} + L' \underset{k_{-7}}{\overset{k_7}{\rightleftharpoons}} [Ru(CN)_5L']^{3-} \qquad (7)$$

Under the above-mentioned conditions, $k_{-5} = k_d$. A similar mechanism is also expected to hold in the case of the dissociation of the nitrile-bonded complexes, as well as in the isomerization process. Note that the values for k_{iso} are of the same order as k_d^{NC}.

From the stated values of k_f and k_d, the stability constants, K_{st}, were calculated for each member of Table 3. The higher values for the pyridine-bonded isomers (and noticeably for 4CN-py) are associated with lower values for k_d. A correlation of K_{st} with k_d was also found with the pentacyanoferrate complexes.[3,*] However, in the latter system, K_{st} values were about an order of magnitude higher than the values for the pentacyanoruthenate(II) complexes.[3] The difference may be traced to higher differences in k_f values when going from complexes of Ru^{II} to those of Fe^{II} [$k_f(Fe)/k_f(Ru)$ = *ca.* 500], compared to differences in k_d values [$k_d(Fe)/k_d(Ru)$ = *ca.* 50]. As shown recently,[14] strikingly low values of k_f for pentacyanoruthenate complexes were related to negative activation entropies for the formation reaction, in contrast to positive values found for the pentacyanoferrate(II) system.[20] The interpretation of activation parameter data concerning the mechanism of the formation reaction of pentacyanoruthenate(II) complexes is, however, still open to question, in the light of recent work.[13]

The $[Ru(CN)_5(CN\text{-}py)]^{3-}$ complexes are also less stable than the corresponding $[Ru(NH_3)_5(CN\text{-}py)]^{2+}$ ones. While k_f values are of the same order in both groups,[2] a value for k_d of about four orders of magnitude lower is estimated for the $[Ru(NH_3)_5(4CN\text{-}py)]^{2+}$ ion, assuming for the latter a similar value to that for the $[Ru(NH_3)_5(py)]^{2+}$ ion.[21] The difference in stability should be ascribed to the nature of the auxiliary ligands; with $X = NH_3$, the ruthenium(II) centre is able to interact strongly with CN-py, while in the case of $X = CN^-$ the cyanide ligands compete for the π electron density and the Ru^{II}–CN-py back bonding is considerably lower (*cf.* previous analysis of the spectral results).[9] An additional interesting feature of the $[Ru(NH_3)_5(4CN\text{-}py)]^{2+}$ system is that the most stable isomer is the nitrile-bonded one, probably because of steric hindrance between *ortho* hydrogens and ammine hydrogens in the case of the pyridine-bonded isomer.[1] Thus, it is expected that species of the type $[(NC)_5RuNC_5H_4CN\text{-}Ru(NH_3)_5]^n$ should be readily formed. An investigation of the latter and other related complexes is currently under way in our laboratory.

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[*] An interesting case of reversal of stability was found with the $[Fe(CN)_5(2CN\text{-}py)]^{9-}$ ion,[3] in which the nitrile-bonded isomer was found to be the more stable. Unfortunately, we were unable to detect the presence of the $[Ru(CN)_5(2CN\text{-}py)]^{3-}$ analogue, probably because of the high rates of dissociation of both isomers and the low solubility of 2CN-py, which did not allow the determination of higher rates of formation of the complex.