Ligand Substitution Kinetics in Complexes of Pyridine and Pyrazine Derivatives with Pentacyanoruthenate(II)†

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The reactivity of the pentacyanoruthenate(II) complexes of derivatives of pyridine and pyrazine (L) are reported. The kinetics of dissociation of the complexes, measured in the presence of an excess of a scavenging ligand, show saturation behaviour with respect to this reactant. The limiting rates, k_{-L}, are in the range (2—10) × 10^{-5} s^{-1} (25 °C). A dissociative interchange mechanism is postulated, as in related pentacyanoferrate(II) complexes. The rates of formation, starting from $[Ru(CN)_5(H_2O)]^{3-}$, are typically first order with respect to the concentration of the ligands, with k = *ca.* 1 dm^3 mol^{-1} s^{-1} (25 °C) for neutral ligands and slightly higher and lower values for positively and negatively charged ligands, respectively. An ion-pair dissociative interchange mechanism is postulated. Activation parameter data are presented for both types of reactions and compared with those from related systems, $[Fe(CN)_5L]^{n-}$ and $[Ru(NH_3)_5L]^{n+}$.

The spectral and kinetic properties of low-spin d^6 complexes of general formula type MX_5L are of current interest, as shown by the extensive literature dealing with $[Co(NH_3)_5L]^{n+}$, $[Fe(CN)_5L]^{n-}$, and $[Ru(NH_3)_5L]^{n+}$ systems. A relevant property of the last two series is concerned with the π-donor ability of the M^{II} centre,[1,2] which may be observed when L has orbitals with appropriate energy and symmetry to engage in back-bonding interactions. Another important feature is the variety of ligands able to co-ordinate to the MX_5 moieties. Thus, the MX_5L systems are very suitable to perform systematic studies in which the bonding and reactivity of related complex ions are investigated.

Very limited information exists on the chemistry of ruthenium cyano complexes.[3] Recently, we synthesized the nitrosyl derivative of the $[Ru(CN)_5L]^{n-}$ series;[4] the sodium salt, which is isostructural with $Na_2[Fe(CN)_5(NO)]\cdot 2H_2O$, also presents a similar reactivity picture, thus allowing for a route to the synthesis of other $[Ru(CN)_5L]^{n-}$ ions, through attack of the co-ordinated NO group by suitable reagents. Also, Johnson and Shepherd [5,6] synthesized a series of $[Ru(CN)_5L]^{n-}$ ions, where L is a derivative of pyridine or pyrazine; these species show a characteristic intense band in the visible region, which is sensitive to the acceptor properties of L and has been assigned to a metal to ligand charge-transfer (m.l.c.t.) transition.[6]

In this work we present a kinetic and mechanistic study of the dissociation and formation reactions in the above mentioned $[Ru(CN)_5L]^{n-}$ system, equation (1). Previous

$$[Ru(CN)_5L]^{n-} + H_2O \underset{k_L}{\overset{k_{-L}}{\rightleftharpoons}} [Ru(CN)_5(H_2O)]^{3-} + L \quad (1)$$

studies with the $[Fe(CN)_5L]^{n-}$ series have demonstrated well that the value of k_{-L} is strongly related to the Fe–L bonding properties; π back-bonding effects are particularly relevant in determining these dissociation rates;[1] also, under particular circumstances, steric[7] and solvation[8] effects may also be in evidence. On the other hand, k_L values are nearly independent of the specific bonding properties of L for a wide range of ligands;[9] k_L is however influenced by the charge type of the entering ligand L.[10] Similar results have been found in substitution reactions with $[Ru(NH_3)_5L]^{n+}$ complexes.[11] Thus, our work explores the kinetic properties of the M–L bond towards ligand interchange, examining the influence of both changing the metal centre in the same total environment $[M(CN)_5L]^{n-}$ (M = Fe^{II} or Ru^{II}) as well as modifying the auxiliary ligands (X = CN^- or NH_3) in the MX_5L species.

Experimental

Reagents.—$Na_2[Ru(CN)_5(NO)]\cdot 2H_2O$ was prepared from $RuCl_3$ (Johnson-Matthey), as recently described.[4] $K_4[Ru(CN)_6]\cdot 3H_2O$ was from Ventron. All other reagents, including the different *N*-heterocyclic ligands [4-methylpyridine (4Me-py), pyridine (py), isonicotinamide (ina), nicotinamide (na), pyrazine (pyz), nicotinic acid (Hnic)] were analytical grade. *N*-Methylpyrazinium iodide ($Hmpyz^+I^-$) was synthesized following known procedures.[12]

Dissociation Reactions.—The $[Ru(CN)_5L]^{n-}$ complexes were prepared in solution from sodium pentacyano(nitrosyl)ruthenate(II) dihydrate, by the reaction with aqueous hydrazine in a molar ratio 1:0.75, in the presence of at least a ten-fold excess of the ligand L, at pH 9. Under these conditions, reactions (2) and (3) are consecutive processes, the first reaction being rapidly followed by the second. Reactions (2) and (3) are

$$[Ru(CN)_5(NO)]^{2-} + 0.75N_2H_4 + OH^- \longrightarrow [Ru(CN)_5(H_2O)]^{3-} + 1.25N_2 + H_2O \quad (2)$$

$$[Ru(CN)_5(H_2O)]^{3-} + L \longrightarrow [Ru(CN)_5L]^{n-} + H_2O \quad (3)$$

favoured under gentle heating, but care must be taken in order to prevent any excess of hydrazine, as this compound is also able to co-ordinate to $[Ru(CN)_5(H_2O)]^{3-}$.

The dissociation kinetic runs were monitored on a UV-210 A Shimadzu double-beam spectrophotometer, in thermostatted 1-cm cells; the overall reaction corresponded to equation (4). In a

$$[Ru(CN)_5L]^{n-} + L' \longrightarrow [Ru(CN)_5L']^{n-} + L \quad (4)$$

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† *Non-S.I. unit employed*: cal = 4.184 J.

Table 1. Saturation rate constants for the release of ligands L from $[Ru(CN)_5L]^{n-}$ at different temperatures (°C)*

L	T	$10^5k_{-L}/s^{-1}$	L	T	$10^5k_{-L}/s^{-1}$
4Me-py	25.0	3.8	pyz	25.0	2.4
	32.0	9.5		32.0	8.2
	37.0	18.5		36.0	12.9
	41.0	32.0		43.0	33.0
	43.0	39.1		47.0	57.0
	47.0	62		50.0	84.7
py	25.0	3.4	$Hmpyz^+$	25.0	7.3
	32.0	8.6		34.0	31.4
	37.0	17.3		36.0	44.0
	41.0	29.5		40.0	80.0
	43.0	38.5		41.0	97.0
	45.0	59		47.0	229
	53.0	141		49.0	321
ina	25.0	2.8	na	25.0	5.0
	26.5	3.2		32.0	17.4
	33.0	10.0		37.0	39.1
	37.0	19.2		43.0	88.0
	41.0	29.0		47.0	145
	43.0	41.5		50.0	225
	50.0	110			
	56.0	226			

* pH 9.0, $I = 1$ mol dm^{-3} (NaCl).

Table 2. Specific formation rate constants in $[Ru(CN)_5L]^{n-}$ ions at different temperatures (°C)*

L	T	k_L/dm^3 mol^{-1} s^{-1}	L	T	k_L/dm^3 mol^{-1} s^{-1}
4Me-py	25.0	1.18	pyz	23.4	0.87
	31.0	2.35		25.0	0.96
	35.4	3.98		31.0	1.96
	40.3	5.62		35.5	2.47
	46.0	9.55		40.3	3.72
	49.8	12.02		45.3	6.06
				49.6	7.86
py	25.0	0.95		57.0	15.54
	30.4	1.75			
	35.3	2.78	$Hmpyz^+$	21.0	5.75
	40.5	4.62		25.0	8.64
	50.6	9.36		30.0	13.49
				35.0	17.23
na	25.0	1.21		40.0	33.28
	30.0	2.02		46.0	53.64
	36.0	3.59			
	40.5	5.25	nic	25.0	0.28
	46.0	8.33		31.0	0.43
	50.2	12.56		35.3	0.69
				40.5	1.06
ina	25.0	1.28		46.0	1.93
	31.0	1.76		49.8	3.04
	35.5	2.91			
	40.0	4.47			
	45.2	7.35			
	49.7	9.71			

* Unbuffered system (pH *ca.* 6—7), $I = 0.1$ mol dm^{-3} (LiCl).

typical experiment, to a solution containing the $[Ru(CN)_5L]^{n-}$ ion (final concentration 5×10^{-5} mol dm^{-3}) and an excess of the free ligand L (final concentration 5×10^{-3} mol dm^{-3}) was added the incoming ligand, L′, in sufficiently high concentration to ensure pseudo-first-order conditions ($[L'] = 5 \times 10^{-3}$ to 5×10^{-1} mol dm^{-3}). Values of pH 9 (sodium hydroxide–phosphate buffer) and $I = 1$ mol dm^{-3} (NaCl) were maintained in all of the experiments. These were monitored by measuring the decay of absorbance at the band maximum for $[Ru(CN)_5L]^{n-}$; L′ = dimethyl sulphoxide (dmso) was used as the incoming ligand, as it forms a very stable complex with $[Ru(CN)_5(H_2O)]^{3-}$, without a significant absorption in the visible–near-u.v. region.[13] Pseudo-first-order rate constants, $k_{obs.}$, were obtained from the plots of log $(A_t - A_\infty)$ *vs.* time, where A_t is the absorbance of the reactant at time *t*; the plots were rigorously linear over at least two half-lives (and usually up to 90% reaction) and duplicate runs were made for every experiment. The activation parameters were calculated by least-squares fitting from an Eyring plot; the temperature range employed covered 25 °C. Tabulated errors were determined by an analysis of variance about regression with 90% confidence limits. Results are shown in Table 1. Alternative measurements of the rate of the dissociation reaction could be made by following the increase of absorption of the product, $[Ru(CN)_5L']^{n-}$, when L′ was, for instance, a *N*-heterocyclic ligand absorbing at a different wavelength compared to $[Ru(CN)_5L]^{n-}$.

Formation Reactions.—The $[Ru(CN)_5(H_2O)]^{3-}$ ion ($\lambda_{max} = 310$ nm) was generated in solution following recently developed procedures:[5] equation (5). When the desired ligand L is added

$$[Ru(CN)_6]^{4-} + Br_2 \xrightarrow{H_2O} [Ru(CN)_5(H_2O)]^{3-} + BrCN + Br^- \quad (5)$$

to the product of reaction (5), the corresponding $[Ru(CN)_5L]^{n-}$ complex is rapidly formed. When the complex has an intense m.l.c.t. band, as in the present case with *N*-heterocyclic ligands,[6] the rate of formation may be followed by measuring the increase in absorption at the corresponding band maximum. A typical kinetic experiment was as follows. A solution of $[Ru(CN)_6]^{4-}$ (*ca.* 3×10^{-5}—6×10^{-5} mol dm^{-3}) was treated with a two-thirds excess of aqueous bromine and was left for 10—30 min, with argon bubbling; then a solution of the entering ligand L (final concentration 10^{-3}—10^{-2} mol dm^{-3}), containing the appropriate amount of LiCl to ensure final $I = 0.1$ mol dm^{-3}, was added. A pseudo-first-order behaviour was obtained by plotting log $(A_\infty - A_t)$ *vs.* *t*, where A_t is the absorbance of the product at time *t*. The measurements were made at different concentrations of L. Temperature was varied in the range 20—50 °C and in this way activation parameters were obtained from Eyring plots; a linear regression treatment was applied to the data, as in the case of the dissociation reaction. Results are shown in Table 2.

It was found that a pH lower than 10 and an ionic strength as low as possible were important factors in obtaining a convenient rate of formation of $[Ru(CN)_5(H_2O)]^{3-}$, according to equation (5); under these conditions, a rapid increase in the band at 310 nm was obtained in *ca.* 10—15 min at 25 °C. However, the intensity of this band decreased for longer periods of time. We were able to show that the decay of this band (which is accompanied by a shift of the maximum to lower wavelengths) is associated with a decrease in the concentration of $[Ru(CN)_5(H_2O)]^{3-}$, as shown by the decreasing A_∞ values obtained when a ligand L is added to an aliquot of the solution at increasing times after the addition of bromine. It is likely that a thermal decomposition process associated with cyanide release from $[Ru(CN)_5(H_2O)]^{3-}$ is occurring; the decay of $[Ru(CN)_5(H_2O)]^{3-}$ concentration follows a reasonably well behaved first-order law, with $k = ca.\ 10^{-5}\ s^{-1}$ (25 °C) and the aged solutions show a blue colour when air is present. The final products are most probably $[Ru(CN)_6]^{4-}$ and $[Ru(H_2O)_6]^{3+}$, with intermediate formation of mixed-ligand Ru^{II} complexes.

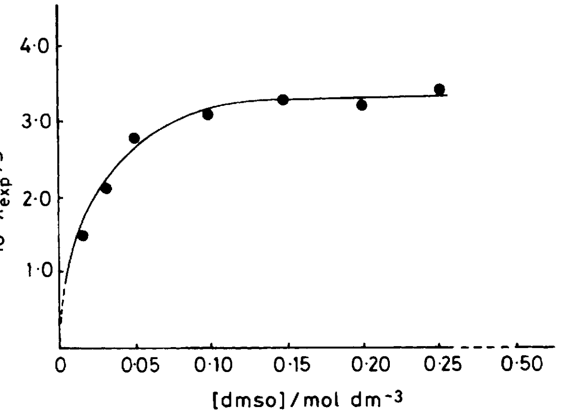

Figure 1. Plot of experimental pseudo-first-order rate of dissociation of pyridine from $[Ru(CN)_5(py)]^{3-}$, $k_{exp.}$, against concentration of the incoming ligand, dmso: $[Ru(CN)_5(py)^{3-}] = 5 \times 10^{-5}$; $[py] = 2 \times 10^{-3}$ mol dm^{-3}; pH 9.0; $I = 1$ mol dm^{-3} (NaCl); $T = 25$ °C. With other incoming ligands (L = pyz or $Hmpyz^+$), the same value of $k_{exp.}$ in the saturation region was obtained

Our observations do in fact show that substitution-inert species are formed, as expected for $[Ru(CN)_6]^{4-}$; the blue colour is presumably associated with the appearance of an outer-sphere intervalence charge-transfer absorption between the Ru^{II} and Ru^{III} decomposition products. A similar thermal decomposition process has been shown recently to be operative with the $[Fe(CN)_5(H_2O)]^{3-}$ ion.[14]

When concentrations of $[Ru(CN)_6]^{4-}$ higher than 10^{-4} mol dm^{-3} are used, disturbing slow processes are developed in the kinetic traces; a similar result has been observed with solutions of $[Fe(CN)_5(H_2O)]^{3-}$ when measuring substitution reactions of similar rate, and they have been ascribed to the presence of dimers.[9] On the other hand, the presence of dissolved air did not affect the kinetic results, and argon was bubbled into the solutions.

Results and Discussion

Dissociation Reactions.—A pseudo-first-order process was measured for the rate of L release from $[Ru(CN)_5L]^{n-}$ when reaction (4) was carried out. It was found that $k_{obs.}$ depends on the concentration of the entering ligand, L′, and a limiting rate is achieved at high L′ concentrations. This is shown in Figure 1 for the dissociation behaviour of $[Ru(CN)_5(py)]^{3-}$; a similar situation is found for the other ligands L. It was also found that the value of $k_{obs.}$ in the saturation region is independent of the type of entering ligand L′ for a given $[Ru(CN)_5L]^{n-}$ complex. This kinetic behaviour resembles the previous work with related dissociation processes in the $[Fe(CN)_5L]^{n-}$ systems.[1] Thus, a similar dissociative mechanism is proposed: equations (6)—(8).

$$[Ru(CN)_5L]^{3-} \underset{k_6}{\overset{k_{-6}}{\rightleftharpoons}} [Ru(CN)_5]^{3-} + L \qquad (6)$$

$$[Ru(CN)_5]^{3-} + H_2O \overset{K}{\rightleftharpoons} [Ru(CN)_5(H_2O)]^{3-} \qquad (7)$$

$$[Ru(CN)_5]^{3-} + L' \underset{k_{-8}}{\overset{k_8}{\rightleftharpoons}} [Ru(CN)_5L']^{3-} \qquad (8)$$

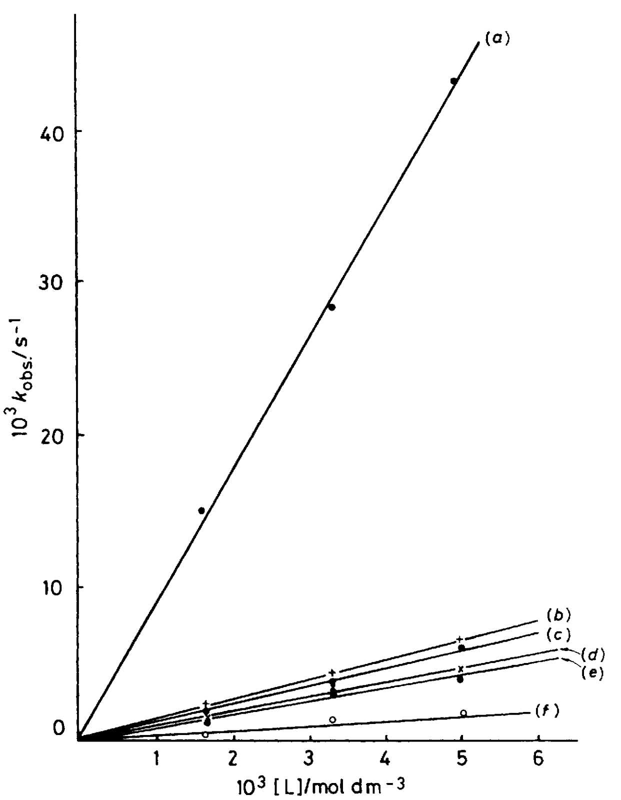

Figure 2. Plot of experimental pseudo-first-order rate of formation of $[Ru(CN)_5L]^{n-}$, $k_{obs.}$, against concentration of the entering ligand L: $[Ru(CN)_5(H_2O)^{3-}] = (3—6) \times 10^{-5}$ mol dm^{-3}; pH *ca.* 6; $I = 0.1$ mol dm^{-3} (LiCl); $T = 25$ °C. (*a*) $Hmpyz^+$, (*b*) ina, (*c*) 4Me-py, (*d*) pyz, (*e*) py, (*f*) nic

Equations (6)—(8) represent the accepted interchange mechanism, although equilibrium (7) might not be a separate step.[8,15] In equilibria (6)—(8), if the steady-state approximation is applied to $[Ru(CN)_5]^{3-}$, this gives equation (9). When the concentration of L′ is sufficiently high, rate saturation is predicted by equation (9), *i.e.*, $k_{obs.}$ must be equal to $k_{-6} = k_{-L}$, the dissociation rate constant from $[Ru(CN)_5L]^{n-}$. On the other hand, as the concentration of L′ approaches zero, $k_{obs.}$ should tend toward k_{-8}. Both predictions are verified in Figure 1 by the saturation behaviour of L′ (dmso) and by the fact that when extrapolating to L′ = 0, $k_{obs.}$ tends toward k_{-dmso}. Equation (9) also predicts the independence of k_{-6} at saturation

$$-d[Ru(CN)_5L^{3-}]/dt = k_{obs.}\{[Ru(CN)_5L^{3-}]_t - [Ru(CN)_5L^{3-}]_\infty\}$$

where $$k_{obs.} = \frac{k_6k_{-8}[L] + k_{-6}k_8[L']}{k_6[L] + k_8[L']} \qquad (9)$$

conditions on the nature of the entering ligand L′, as found in our experiments.

The dissociation rate constants, k_{-L}, and the corresponding activation parameters are given in Table 3 for several ligands L. Data for related $[Fe(CN)_5L]^{n-}$ complexes are also presented. In Table 3, the complexes have been ordered in terms of the π-acceptor capability of the ligand L from the M^{II} centre, which increases downwards. As shown by previous work, changes in the degree of M–L π interaction may be demonstrated, for instance, by the shift of the m.l.c.t. band to lower energies when the back-bonding interaction increases. This is known to occur for the $[Fe(CN)_5L]^{n-}$ [10] and $[Ru(NH_3)_5L]^{n+}$ [16] systems and has been shown recently to be operative also for the $[Ru(CN)_5L]^{n-}$ series.[6]

The higher π interaction has a direct relation with lower k_{-L} and higher $\Delta H_d^\ddagger$ values, as expected for a dissociative mechanism. Positive $\Delta S_d^\ddagger$ values are also in agreement with the accepted dissociative scheme.[1] This pattern is clearly shown for

Table 3. Limiting rate constants for ligand dissociation and activation parameters in $[M(CN)_5L]^{n-}$ ions[a]

$[Fe(CN)_5L]^{n-}$ [b]				$[Ru(CN)_5L]^{n-}$		
$10^4k_{-L}/s^{-1}$	$\Delta H_d^\ddagger$/kcal mol^{-1}	$\Delta S_d^\ddagger$/cal K^{-1} mol^{-1}	L	$10^5k_{-L}/s^{-1}$	$\Delta H_d^\ddagger$/kcal mol^{-1}	$\Delta S_d^\ddagger$/cal K^{-1} mol^{-1}
11.5	24.0	9	4Me-py	3.8	23.8	3
11.0	24.8	11	py	3.4	24.9	5
7.3	26.0	14	ina[c]	2.8	27.2	12
4.2	26.4	14	pyz	2.4	28.4	13
2.8	27.5	18	Hmpyz$^+$	7.3	29.3	21

[a] Errors in $\Delta H_d^\ddagger$ and $\Delta S_d^\ddagger$ in the $[Ru(CN)_5L]^{n-}$ system are ± 1.0 kcal mol^{-1} and ± 3 cal K^{-1} mol^{-1} respectively. [b] Data taken from ref. 1. [c] Data for the 3-substituted isomer (na) are: $k_{-L} = 5.0 \times 10^{-5}$ s^{-1}, $\Delta H_d^\ddagger = 28.1$ kcal mol^{-1}, $\Delta S_d^\ddagger = 16$ cal K^{-1} mol^{-1}.

the $[Fe(CN)_5L]^{n-}$ series and also in our $[Ru(CN)_5L]^{n-}$ series, thus giving support to the proposed mechanism. The influence of the π interaction is also shown by the lower k_{-L} value found for isonicotinamide compared to the 3-substituted derivative, nicotinamide.*

For a given ligand L, the rate of release from the $[Ru(CN)_5]^{3-}$ centre is *ca.* 20—30 times slower than from $[Fe(CN)_5]^{3-}$. The differences seem to be associated mainly with an activation enthalpy effect. Higher values for $\Delta H_d^\ddagger$ in Ru^{II} *vs.* Fe^{II} cyano complexes are consistent with the higher ligand-field effects and back-bonding interactions in the Ru^{II} system.[6] The similarity in activation entropy values for both Fe^{II} and Ru^{II} systems also suggests that the geometry of the transition state is roughly the same in both series.

The important influence of $\Delta H_d^\ddagger$ may be confirmed when analysing data found for $[Ru(NH_3)_5L]^{n+}$ complexes. In the case of L = py, a value of $k_{-py} = 4.6 \times 10^{-9}$ s^{-1} is estimated;[17] this is about four orders of magnitude lower than the corresponding k_{-py} in $[Ru(CN)_5(py)]^{3-}$. Recently,[18] ΔH° values have been measured calorimetrically for reaction (10).

$$[Ru(NH_3)_5(H_2O)]^{2+} + L \rightleftharpoons [Ru(NH_3)_5L]^{n+} + H_2O \quad (10)$$

The results show that the exothermicity of reaction (10) increases when L is a better π-acceptor, the increasing trend from py to pyz reflecting the contribution of back-bonding to the metal–ligand interaction. As the activation enthalpy for the forward reaction is essentially independent of the type of L,[11] this implies that an increasing trend is also operative for $\Delta H_d^\ddagger$, the activation enthalpy for the backward dissociation reaction; thus, a value of 28.8 kcal mol^{-1} is calculated for L = py and 34.3 kcal mol^{-1} for L = pyz. These values are noticeably higher than corresponding ones for the $[Ru(CN)_5L]^{n-}$ complexes (see Table 3) and confirm our previous discussion concerning $\Delta H_d^\ddagger$ values for Fe^{II} and Ru^{II} cyano complexes. When NH$_3$ is the auxiliary ligand, the Ru^{II} centre is able to interact strongly with L, while in the case of $[Ru(CN)_5L]^{n-}$, the cyanide ligands compete for the π-electron density and the Ru–L back-bonding is considerably lower. It also results that in the $[Ru(NH_3)_5L]^{n+}$ series, the sensitivity of $\Delta H_d^\ddagger$ to the change in acceptor properties of L is much greater than in either of the other series [*cf.* the value $\Delta(\Delta H_d^\ddagger)$ for py and pyz complexes].

Formation Reactions.—In the presence of an excess of the entering ligand L, the kinetics of formation of the complexes is described by a first-order rate law for at least two half-lives, equation (11). The specific rates, k_L, are obtained by plotting

$$-d[Ru(CN)_5(H_2O)^{3-}]/dt = d[Ru(CN)_5L^{n-}]/dt = k_{obs.}[Ru(CN)_5(H_2O)^{3-}] \quad (11)$$

$k_{obs.}$ *vs.* the concentration of L (Figure 2). k_L Values and corresponding activation parameters are shown in Table 4; data for $[Fe(CN)_5L]^{n-}$ and $[Ru(NH_3)_5L]^{n+}$ systems are included for the sake of comparison. The following conclusions can be extracted.

(*a*) k_L Values are very similar for all the neutral ligands L; they do not depend on the nature and basicity of the donor atom in the entering group. Similarly, $\Delta H_f^\ddagger$ and $\Delta S_f^\ddagger$ are broadly constant in each series.

(*b*) The charge of L has a minor but significant influence on k_L; thus, higher and lower values are found for Hmpyz$^+$ and nicotinate anion, respectively, compared to the value for neutral ligands. This is in accord with previous results for the $[Fe(CN)_5L]^{n-}$ [9,10] and $[Ru(NH_3)_5L]^{n+}$ [11] systems.

(*c*) The rate of formation is more rapid in $[Fe(CN)_5L]^{n-}$ compared to $[Ru(CN)_5L]^{n-}$ for a given ligand L. While the activation enthalpy is constant for both series (within experimental error), the negative activation entropies appear to be responsible for the lower k_L values for the $[Ru(CN)_5L]^{n-}$ complexes.

Table 4. Specific formation rate constants and activation parameters in MX$_5$L ions (M = Fe^{II} or Ru^{II}, X = CN$^-$ or NH$_3$)[a]

	k_L/dm^3 mol^{-1} s^{-1}	$\Delta H_f^\ddagger$/ kcal mol^{-1}	$\Delta S_f^\ddagger$/ cal K^{-1} mol^{-1}
$[Fe(CN)_5L]^{n-}$ [b]			
4Me-py	360	15.1	4
py	365	16.1	7
ina	296	15.8	6
pyz	380	15.4	5
Hmpyz$^+$	550	16.8	10
$[Ru(CN)_5L]^{n-}$ [c]			
4Me-py	1.2	17.2	−11
py	0.95	16.4	−15
ina	1.3	16.1	−16
pyz	0.96	15.8	−18
na	1.2	16.9	−13
Hmpyz$^+$	8.6	16.2	−12
nic	0.28	17.6	−14
$[Ru(NH_3)_5L]^{n+}$ [d]			
py	0.093	16.9	−6.6
ina	0.105		
pyz	0.056	17.5	−5.7
Hmpyz$^+$	0.024	18.4	−10

[a] Errors in $\Delta H_d^\ddagger$ and $\Delta S_d^\ddagger$ in the $[Ru(CN)_5L]^{n-}$ system are ± 1.0 kcal mol^{-1} and ± 3 cal K^{-1} mol^{-1} respectively. [b] Ref. 9. [c] This work. [d] Ref. 11.

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* The value of $\Delta H_d^\ddagger$ was unexpectedly found to be lower for isonicotinamide; however, the difference is within the range of experimental error. An 'anomalously' high value of k_{-L} was found for Hmpyz$^+$, although the activation parameters agree with the expected order.

Our experimental results may be associated with the ion-pair dissociative interchange mechanism in equations (12) and (13). In the previous scheme, equations (6)—(8), the rate-

$$[Ru(CN)_5(H_2O)]^{3-} + L \xrightleftharpoons{K_{IP}} \{Ru(CN)_5(H_2O)^{3-}, L\} \quad (12)$$

$$\{Ru(CN)_5(H_2O)^{3-}, L\} \xrightleftharpoons[k_{H_2O}]{k_{-H_2O}} [Ru(CN)_5L]^{n-} + H_2O \quad (13)$$

determining step, k_{-H_2O}, is preceded by outer-sphere association of the reactants; neglecting the reverse (k_{H_2O}) step, the rate law (14) is obtained. Under our conditions, saturation is

$$k_{obs.} = \frac{K_{IP}k_{-H_2O}[L]}{1 + K_{IP}[L]} \quad (14)$$

not expected to occur, as $K_{IP}[L] \ll 1$. Thus, equation (14) becomes (15) with $k_L = K_{IP}k_{-H_2O}$.

$$k_{obs.} = K_{IP}k_{-H_2O}[L] \quad (15)$$

The charge of the reactants is expected to influence K_{IP} rather than k_{-H_2O}. In fact, the changes in rate measured for neutral and charged ligands are in the range expected from estimations of K_{IP} using the Fuoss equation.[19] Thus, K_{IP} values of 18, 1.6, and 0.1 $dm^3 mol^{-1}$ are calculated for unipositive, neutral, and uninegative ligands, respectively, when interacting with $[Ru(CN)_5(H_2O)]^{3-}$; these values should roughly explain the minor variations observed in our experimental k_L values. The ion-pair mechanism was shown to be useful in the interpretation of amino-acid interactions with the $[Fe(CN)_5]^{3-}$ moiety.[20]

The constant activation enthalpy for the whole series of ligands L is interpreted by assuming that $\Delta H^{\ddagger}$ in equation (12) is not very sensitive to the nature of L. Similarly, the dissociative loss of water in the outer-sphere complex (k_{-H_2O}) should be independent of the type of L. However, the similarity of $\Delta H_f^{\ddagger}$ values found for Fe^{II} and Ru^{II} cyano complexes is remarkable, as higher ligand-field effects are operative in the case of the Ru^{II} species (see below).

The negative activation entropies in the $[Ru(CN)_5L]^{n-}$ series are in contrast with the positive ones found in related $[Fe(CN)_5L]^{n-}$ ions. In fact, these noticeable differences had already been noted[9] when comparing the last series with the $[Ru(NH_3)_5L]^{n+}$ series. One interpretation of the differences in $\Delta S_f^{\ddagger}$ was related to the more 'associative' character of the activation process in the case of $[Ru(NH_3)_5L]^{n+}$. Alternatively, by assuming a truly *D* mechanism, differences in $\Delta S_f^{\ddagger}$ were taken as indicative of dissociative pathways involving a different geometry for the five-co-ordinate intermediate. Following Swaddle,[21] the first interpretation should be included in a more general picture where associative contribution to the activation in ligand substitution is considered normal. Bond formation by the incoming ligand serves to reduce $\Delta H_f^{\ddagger}$, but associated with a lower $\Delta S_f^{\ddagger}$, because of the lower degree of free rotation of the ligand L. The previous interpretation should favour the I_d over the *D* mechanism when assigning finer details to the k_{-H_2O} step. Thus, the behaviour of Ru^{II} in promoting specific association effects {a fact which has been demonstrated even in the electrostatically unfavourable association of $[Ru(NH_3)_5(H_2O)]^{2+}$ with $Hmpyz^+$}[22] should explain the striking differences in $\Delta S_f^{\ddagger}$ values for both M^{II} centres. In this context, it is probable that a compensation effect is operative in determining $\Delta H_f^{\ddagger}$ values, *i.e.* the above mentioned lowering of $\Delta H_f^{\ddagger}$ acting in the opposite way to ligand-field effects, which are known to be higher in Ru^{II} compared to Fe^{II} complexes.

The lability of water from $Ru^{II}X_5$ centres is shown to be little influenced by the nature of the auxiliary ligands, X. k_L Values are shown to be about an order of magnitude higher in the cyanide complexes compared to the ammine ones (see Table 4). Labilizing effects from *trans*-cyanide groups have been previously accounted for in Ru^{II} ammine complexes.[23] An estimation of k_{-H_2O} in $[Ru(CN)_5(H_2O)]^{3-}$ by using experimental k_L and calculated K_{IP} values leads to k_{-H_2O} = 0.4—0.6 s^{-1}. Similarly, if the same mechanism is accepted for the release of water in the $[Ru(NH_3)_5(H_2O)]^{2+}$ ion, k_{-H_2O} values of 0.1—1.5 s^{-1} are obtained. It is concluded that, after correction of charge effects, no significant influence on water lability exists when changing the auxiliary ligands in our $Ru^{II}X_5$ complexes.

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