

Kinetics and Mechanism of Ligand Interchange in Pentacyano-L-osmate(II) Complexes (L = H₂O, NH₃, N-Heterocyclic Ligands)

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The new complex, K₃[Os(CN)₅NH₃]·2H₂O, a convenient precursor for the pentacyano-L-osmate(II) series, was prepared and characterized by chemical analysis, cyclic voltammetry, and IR and UV–vis spectroscopies. By controlled aquation in weakly acidic medium, the [Os(CN)₅H₂O]³⁻ ion was generated. Weak absorptions in the UV region for L = H₂O, NH₃, and CN⁻ were found at 287, 272, and 240 nm, respectively, and were assigned to d–d transitions, in terms of a model for tetragonally distorted ions also valid for the members of the iron and ruthenium series. The kinetics of the formation and dissociation reactions of the [Os(CN)₅L]ⁿ⁻ ions, L = pyridine (py), pyrazine (pz), *N*-methylpyrazinium (mpz⁺), etc., were studied. At 25.0 °C, the formation rate constants for the neutral ligands pz and isonicotinamide were ca. 0.13 M⁻¹ s⁻¹ and slightly increased for L = mpz⁺ and decreased for isonicotinate. The enthalpies of activation were ca. 22.0 kcal mol⁻¹, independently of the entering L, and the activation entropies were all positive, ca. 11–13 cal K⁻¹ mol⁻¹. The dissociation reactions showed a saturation rate behavior of *k*_{obs} (s⁻¹) as a function of the concentration of the scavenger ligand. The specific dissociation rate constant at 25.0 °C was 1.06 × 10⁻⁷ s⁻¹ for L = NH₃ and around 10⁻⁹ s⁻¹ for py, pz, and mpz⁺ (extrapolated to 25.0 °C from values measured in the range 60–95 °C). These small values are associated with high activation enthalpies (range 30–35 kcal mol⁻¹) and positive activation entropies (range 10–20 cal K⁻¹ mol⁻¹). The evidence for both the formation and dissociation processes shows that dissociative mechanisms are operative, as for the iron and ruthenium analogues.

Introduction

Work on the synthesis and spectroscopic properties of pentacyano-L-osmate(II) complexes with L = N-heterocyclic ligands¹ allowed us to obtain a comparative picture for the pentacyano complexes containing metals of the three transition series.^{2,3} Important differences were found for the osmium complexes, compared to the iron and ruthenium analogues, comprising the splitting of the characteristic metal-to-ligand charge-transfer (MLCT) bands, a fact that was

ascribed to the significantly greater spin–orbit coupling constant of the osmium center. This issue was recently considered, attempting to put the CT spectroscopic features of all these d⁶ low-spin complexes under a common theoretical framework.⁴

Preliminary experiments^{1a} also revealed that the osmium complexes were very inert toward the release of L, although a detailed mechanistic analysis of the ligand interchange reactions was not pursued because of the lack of adequate characterization of the aquapentacyanoosmate(II) ion, a key intermediate in these processes.

The work with the osmium cyano complexes still merits further expansion, given the limited set of L ligands used so far, in contrast to the extensive investigations carried out with the other metal analogues.⁵ Now we report the prepara-

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tion of new complexes of the $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ series with small inorganic ligands such as NH_3 and H_2O , which are suitable labile precursors for the synthesis of other members of the series. With the characterization of these complexes, we afford a kinetic and mechanistic study of the formation and dissociation reactions of a selected group of $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ complexes, thus allowing for comparisons with the results already available for the iron² and ruthenium⁶ series.

Experimental Section

Materials. Pyridine (py), pyrazine (pz), isonicotinamide (isn), isonicotinic acid, and dimethyl sulfoxide (dmsO) were purchased from Aldrich and were used as supplied. *N*-Methylpyrazinium (mpz^+) iodide was prepared by reaction of pz with iodomethane (Aldrich), as described in the literature.⁷ Other chemicals (hydrazinium chloride, sodium phosphates, sodium chloride, potassium iodide, ammonia, solvents) of analytical grade quality were used without further purification. House doubly distilled and deionized water was used in all the experiments.

Preparation of Solid Complexes. $\text{K}_2[\text{Os}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ was first obtained from $\text{K}_4[\text{Os}(\text{CN})_6]$ (which was prepared similarly as $\text{K}_4[\text{Ru}(\text{CN})_6]$),⁸ by mixing with an excess of KNO_2 in diluted trifluoroacetic acid (pH 4) and irradiating for ca. 26 h (254 nm).^{1a} The photolyzed solution was evaporated to 2 mL, and purification was achieved by exclusion chromatography on a Sephadex G-25 column (length, 1.5 m, diameter, 2.5 cm). Elution with water provided two fractions: The first one, containing dimers and oligomers, was discarded. The second one, containing $[\text{Os}(\text{CN})_5\text{NO}]^{2-}$, was still contaminated with nitrite, which was oxidized to nitrate by acidification to pH 4 ($\text{CF}_3\text{CO}_2\text{H}$) and addition of excess H_2O_2 (20 vol). Upon standing for 1 h, the nitrosyl compound was precipitated with AgNO_3 . The solid was recovered by filtration, washed with abundant water, methanol, and ether, and dried in vacuo over silica gel. The $\text{Ag}_2[\text{Os}(\text{CN})_5\text{NO}]$ precipitate was suspended in 100 mL of water, and a slight defect of potassium bromide was added. The suspension was shaken for 2 h and filtered through a polyamide membrane (0.2 μm pore) to eliminate the yellow precipitate of silver bromide. The clear, yellow solution was evaporated to dryness, and the solid was dried in a vacuum over silica gel. Analytical data were as reported previously^{1a} for $\text{K}_2[\text{Os}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$, prepared by cation interchange from $\text{Na}_2[\text{Os}(\text{CN})_5\text{NO}]\cdot 2\text{H}_2\text{O}$.

$\text{K}_3[\text{Os}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$ was obtained by dissolving 0.2 g of $\text{K}_2[\text{Os}(\text{CN})_5\text{NO}]\cdot\text{H}_2\text{O}$ in 25 mL of concentrated ammonia, which was previously deoxygenated under argon flushing. A 1.5 equiv amount of hydrazinium chloride was added, and the mixture was left in the darkness with permanent stirring for 3 days. A saturated solution of potassium iodide in deoxygenated ethanol was added to the resulting pale yellow solution to induce a white precipitate. The solid was collected by filtration, washed with cold acetone, and dried under vacuum. Recrystallization was performed from a mixture of concentrated ammonia and acetone; the overall yield was 90%. All these procedures were performed under an argon atmosphere using Schlenk techniques, though the dry solid proved

to be air stable. Anal. Calcd for $\text{K}_3[\text{Os}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$: C, 12.14; H, 1.43; N, 17.14; K, 23.9. Found: C, 12.53; H, 1.71; N, 16.53; K, 23.69. Elemental analyses (C, H, N) were carried out at Inquimae, in a Carlo Erba Ea 1108 elemental analyzer. Potassium was measured by emission photometry.

$\text{K}_3[\text{Os}(\text{CN})_5\text{L}]\cdot 3\text{H}_2\text{O}$ (L = py, pz, etc) and $\text{K}_2[\text{Os}(\text{CN})_5\text{mpz}]\cdot 2\text{H}_2\text{O}$. A 0.2 mmol amount of $\text{K}_2[\text{Os}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$ was dissolved in 15 mL of argon-deoxygenated water containing a 10-fold excess of L. The mixture was kept at 80–90 °C for 3 h under argon and evaporated in a rotary evaporator at 25 °C down to 1 mL. The reaction mixture was purified by chromatography on Sephadex G-25 (length, 1.5 m; diameter, 2.5 cm). The first fraction containing small amounts of dinuclear material was discarded, and the fractions containing the mononuclear $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ compounds were collected and concentrated (Rotavap, room temperature). Slow addition of cold KI-saturated ethanol yielded solid compounds whose composition was equivalent to those described in ref 1.

Spectroscopic and Kinetic Measurements. IR spectra were taken in KBr pellets on a Nicolet 510P FTIR instrument. UV–vis spectra were obtained in diode-array Hewlett-Packard 8452A and 8453 spectrophotometers. The cyclic voltammetry (CV) was performed with a Princeton Applied Research 273A instrument, using a cell with platinum working and counter electrodes and Ag/AgCl as a reference, at 100 mV/s and $I = 0.1$ M (KNO_3). For the formation kinetics experiments, aqueous solutions of the $[\text{Os}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ ion were prepared by high-temperature aqution of the ammine complex. Dilute solutions of $\text{K}_2[\text{Os}(\text{CN})_5\text{NH}_3]\cdot 2\text{H}_2\text{O}$ in a phosphate buffer, pH 6.6 ($I = 0.1$ M, NaCl), were heated at 80 °C in a water bath for 2 h, under an argon atmosphere, and were immediately cooled to the desired temperature for the kinetic runs. Low concentrations (range $(1-2) \times 10^{-5}$ M) were used to prevent dimerization processes. Fresh solutions were preferentially used, although aged solutions of $[\text{Os}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ gave good results up to 24 h after being prepared.⁹ The studies were performed by mixing the solutions of the aqua ion with varying concentrations of the entering ligand (range 10^{-4} – 10^{-2} M), under pseudo-first-order conditions, and maintaining the above-mentioned ionic strength and pH. The entering L ligands used were isn, pz, mpz^+ , and the isonicotinate ion. The progress of the reactions was measured spectrophotometrically in the 300–600 nm interval. The temperature range studied was 10–40 °C (± 0.1 °C), and a complete set of experiments at the different concentrations of L was carried out for each temperature.

For the dissociation kinetics experiments, solutions of the $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ complexes were prepared by dissolution of the corresponding salts for L = NH_3 , py, pz, and mpz^+ , at ca. 10^{-5} M, adding a slight excess of L (ca. 2×10^{-4} M), and varying concentrations of a scavenger ligand, dmsO (or pz for L = NH_3), in the range 10^{-3} – 10^{-1} M, with $I = 1$ M (NaCl). Complementary experiments with mpz^+ as a scavenger ligand were also performed. The kinetic data were collected running successive spectra in the 190–820 nm range. All the experiments were performed in a quartz cuvette (1 cm), tightly closed and thermostated with a RC6 Lauda external water bath. Due to the high temperatures (range 60.0–95.0 °C) and long reaction periods (1–96 h, depending on the temperature), a calibrated thermistor placed inside the cuvette was used to monitor the temperature. Along the reaction period the fluctuations proved to be lower than ± 0.1 °C. The pseudo-first-

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Table 1. Electronic Spectra [$\lambda_{\text{max}}/\text{nm}$ ($\epsilon/\text{M}^{-1} \text{cm}^{-1}$)]^a in the UV–Vis Region (MLCT and d–d Transitions) for $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ Ions (L = H₂O, NH₃, CN⁻) in Aqueous Solution

H ₂ O ^b	NH ₃ ^b	CN ^{-c}	assgnt ^d
195 (25 000)	196 (17 000)	192 (42 900)	$^1A_{1g} \rightarrow ^1T_{1u}^{(2)} (^1E^{(2)})$
207 (32 000)	208 (28 000)	213 (47 400)	$^1A_{1g} \rightarrow ^1T_{1u}^{(1)} (^1E^{(1)})$
240 (3500)	230 (7000)	240 (3000)	$^1A_{1g} \rightarrow ^1T_{1g} (^1A_2)$
288 (2000)	272 (2500)		$^1A_1 \rightarrow ^1E^{(1)}$
	310 (600)	340 (300)	$^1A_{1g} \rightarrow ^3T_{2g} (^1E^{(2)})$
342 (400)	370 (100)	430 (100)	$^1A_{1g} \rightarrow ^3T_{1g} (^1E^{(1)})$

^a Quoted values of ϵ in this work are roughly estimated values, associated with weak shoulders protruding from the intense CT bands. ^b This work. Values for iron analogues: cf. refs 12 and 25. For ruthenium analogues: cf. refs 12 and 26. ^c This work. CT data in the far-UV region are from ref 12. ^d In parentheses: symmetry of the excited state for the tetragonally distorted species.

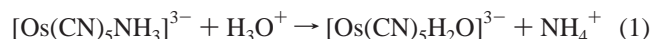
order rate constants were obtained by nonlinear least-squares fitting of the spectral output at the absorption maxima for the relevant MLCT bands.

Activation parameters were obtained for both the formation and dissociation reactions, by fitting to $\ln(k/T)$ against $1/T$.

Results

Characterization of $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ Complexes (L = NH₃, H₂O, CN⁻). (a) L = NH₃. The IR spectrum of solid $\text{K}_3[\text{Os}(\text{CN})_5\text{NH}_3] \cdot 2\text{H}_2\text{O}$ shows characteristic water absorptions¹⁰ at 3343 and 1618 cm^{-1} , two bands in the cyanide-stretching region¹⁰ (a strong one at 2040 cm^{-1} and a medium intense one at 2001 cm^{-1}), and weak bands at 1290, 554, and 407 cm^{-1} . From the UV–vis spectrum of an aqueous solution of the complex, band energies and intensities were estimated by Gaussian deconvolution (Figure S1). The cyclic voltammogram in aqueous solution shows a reversible wave at 0.55 V (vs NHE).

(b) L = H₂O. The complex was generated in solution by aquation of $[\text{Os}(\text{CN})_5\text{NH}_3]^{3-}$ (see Experimental Section). The stoichiometry described by eq 1 is supported by the spectra of the initial reactant and of the product at full conversion (Figure S2).



(c) L = CN⁻. Although the $[\text{Os}(\text{CN})_6]^{4-}$ complex has already been described in the literature,¹¹ only CT bands in the UV region, around 200 nm, have been reported.^{12,13} New absorptions have been found in the present work in the near UV–vis region, although some of them appear as poorly defined shoulders. Table 1 displays the absorption maxima and estimated molar absorptivities for the complexes with L = NH₃, H₂O, and CN⁻.

Kinetic Studies. The kinetics of the formation and dissociation reactions can be described by eq 2.

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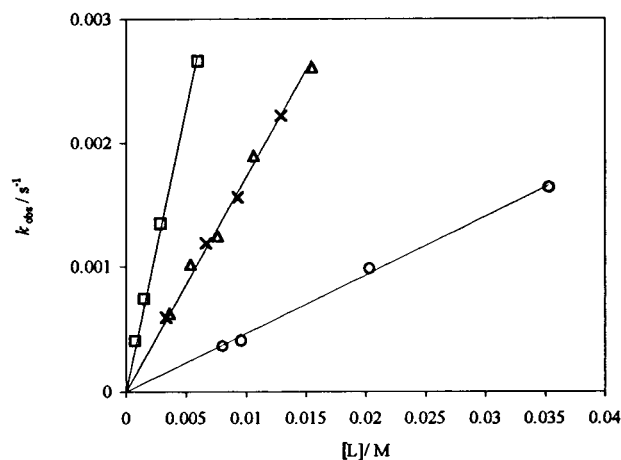
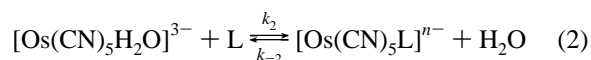


Figure 1. Dependence of k_{obs} on ligand concentration for the substitution reactions of $[\text{Os}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ (25.0 °C, $I = 0.1 \text{ M}$, NaCl). Ligands: (□) *N*-methylpyrazinium ion; (Δ) pyrazine; (×) isonicotinamide; (○) isonicotinate ion.

Addition of an excess of L to the aqua complex results in intense absorptions in the near UV–vis region, which have been well characterized for different *N*-heterocyclic ligands in a previous work and assigned as MLCT transitions.¹ The stoichiometry of eq 2 has been demonstrated on the basis of the weighed amount of the precursor ammine complex (eq 1) and the known molar absorptivities of the $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ products.¹



Under pseudo-first-order conditions, the formation of $[\text{Os}(\text{CN})_5\text{L}]^{n-}$ followed the rate expression in eq 3.

A good fit was obtained, up to 3 half-lives. Figure 1 shows the linear plots of k_{obs} against the concentration of L, for each ligand under study, according to $k_{\text{obs}} = k_2[\text{L}] + k_{-2}$. The zero intercept anticipates that the reverse dissociation rate process in eq 2, k_{-2} , should be very slow (see below).

$$\frac{d}{dt}[[\text{Os}(\text{CN})_5\text{L}]^{n-}] = -\frac{d}{dt}[[\text{Os}(\text{CN})_5\text{H}_2\text{O}]^{3-}] = k_{\text{obs}}[[\text{Os}(\text{CN})_5\text{H}_2\text{O}]^{3-}] \quad (3)$$

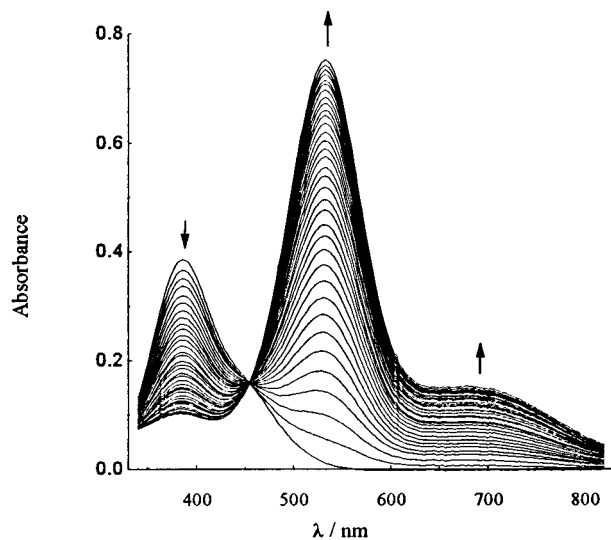
Table 2 displays the rate and activation parameters for the formation reactions. Also included are the corresponding values previously measured for the iron and ruthenium analogues.^{2,6} For the osmium complexes, the rate constant, k_2 , is invariant for the neutral L ligands, while a significant dependence on the charge of the ligand is observed. The activation enthalpies are constant, within experimental error, for all the four studied complexes, a result that is also supported by the data for the other metal complexes. However, the activation enthalpy values for the osmium complexes are greater by ca. 4–5 kcal mol^{-1} when compared to those observed in the ruthenium series and by ca. 5–7 kcal mol^{-1} if compared with the iron series. The activation entropy values for the osmium complexes are more positive than those found for the other related series. An increasing trend from iron to osmium is observed, although the differences are close to the experimental uncertainties.

Table 2. Rate and Activation Parameters for the Formation Reactions in Aqueous Solution:^a

$$[\text{M}(\text{CN})_5\text{H}_2\text{O}]^{3-} + \text{L} \xrightarrow{k_2} [\text{M}(\text{CN})_5\text{L}]^{n-} + \text{H}_2\text{O}$$

L	Fe ^b			Ru ^c			Os ^d		
	10 ⁻² k ₂ , M ⁻¹ s ⁻¹	ΔH [‡] , kcal/mol ^e	ΔS [‡] , cal mol ⁻¹ e ⁻¹	10 ⁻¹ k ₂ , M ⁻¹ s ⁻¹	ΔH [‡] , kcal/mol ^e	ΔS [‡] , cal K ⁻¹ mol ⁻¹ e ⁻¹	10k ₂ , M ⁻¹ s ⁻¹	ΔH [‡] , kcal/mol ^f	ΔS [‡] , cal K ⁻¹ mol ⁻¹ f ⁻¹
mpz ⁺	5.50	16.8	10	4.70	17.3	7	3.73	21.9	13
pz	3.80	15.4	5	1.09	17.2	4	1.32	22.6	13
isn	2.96	15.8	6	0.54 ^g	17.9 ^g	4 ^g	1.37	22.1	12
isonic ⁻	0.60 ^h			0.35	17.5	3	0.42	22.6	11

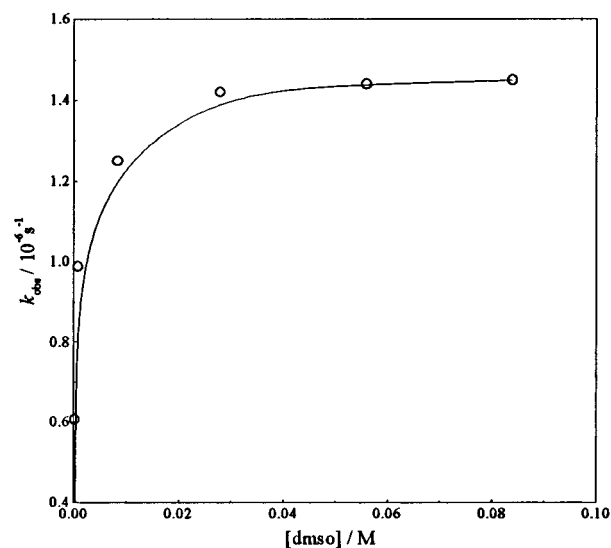
^a T = 25.0 °C. ^b Reference 2b (I = 0.5 M, except for mpz⁺, where I = 1.0 M). ^c Reference 6a (I = 0.1 M, pH 7–9). ^d This work (I = 0.1 M, pH 6.6–8). ^e Errors in ΔH[‡] and ΔS[‡] are ±0.5 and ±2, respectively. ^f Errors in ΔH[‡] and ΔS[‡] are in the range ±0.3–0.8 and ±1–3, respectively. ^g Data for L = py. ^h Reference 6b.

**Figure 2.** Consecutive spectra in the dissociation reaction of pyrazine from the [Os(CN)₅pz]³⁻ ion, in the presence of 0.1 M *N*-methylpyrazinium ion (I = 1 M NaCl; T = 25.0 °C).

The dissociation reactions of the [Os(CN)₅L]ⁿ⁻ complexes (reverse of eq 2) were studied using an excess of another ligand L', to scavenge the aqua ion by formation of a stable complex. Figure 2 shows a typical result for the dissociation of pz, the latter being replaced by mpz⁺. The absorbance traces fitted to a first-order behavior essentially up to full conversion. The isosbestic point in Figure 2 shows that the dissociation process (eq 4) evolves without any interference of other reactions.



Figure 3 shows the *k*_{obs} (s⁻¹) values for the release of pz against the concentration of the scavenger ligand, dmsO. It can be seen that *k*_{obs} increases up to a constant saturation value, as already found with the dissociation processes in iron and ruthenium cyanocomplexes.^{2,6} The same saturation value was obtained for *k*_{obs} using mpz⁺ as the scavenger ligand. Table 3 displays the saturation values of *k*_{obs} for several L ligands, for complexes comprising the three transition series, and includes the p*K*_a values of the L ligands.^{14–16} The observed dissociation rate constants for the osmium complexes are significantly smaller than those for the corresponding ruthenium and iron complexes. The variation of *k*_{-L} with L follows a similar trend for the osmium

**Figure 3.** Plot of observed rate of dissociation of pyrazine from the [Os(CN)₅pz]³⁻ ion, *k*_{obs}, against dimethyl sulfoxide concentration (T = 60.0 °C, I = 1 M, NaCl).

and ruthenium series, in contrast with the monotonic decreasing trend found for the iron series.

Table 3 also presents the activation parameter data. The positive entropies are fairly constant in the osmium series, showing a behavior similar to the found in related complex series, with no definite trends. On the other hand, the activation enthalpies are significantly larger for the osmium complexes by a factor that is even greater than that found for the formation reactions.

Discussion

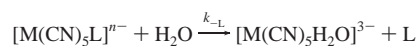
The K₃[Os(CN)₅NH₃]·2H₂O compound is a key member of the [Os(CN)₅L]ⁿ⁻ series, adding to the previously well characterized compounds with L = CN⁻,¹¹ NO⁺,¹⁷ N₂H₅⁺,^{1a} and *N*-heterocyclic ligands.¹ The ammine complex is a clean precursor for synthesizing any other member of the series by a substitution reaction, better than the previously reported hydrazinium complex, which is highly unstable in aerobic

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Table 3. Rate and Activation Parameters for the Dissociation Reactions in Aqueous Solution:^a

L ^b	Fe ^c			Ru ^d			Os ^e		
	10 ⁴ k ₋₁ , M ⁻¹ s ⁻¹	ΔH [‡] , kcal/mol ^f	ΔS [‡] , cal K ⁻¹ mol ⁻¹ ^f	10 ⁵ k ₋₁ , M ⁻¹ s ⁻¹	ΔH [‡] , kcal/mol ^g	ΔS [‡] , cal K ⁻¹ mol ⁻¹ ^g	10 ⁹ k ₋₁ , M ⁻¹ s ⁻¹	ΔH [‡] , kcal/mol ^h	ΔS [‡] , cal K ⁻¹ mol ⁻¹ ^h
NH ₃ ⁱ	175	22.2	8	37			106	30.7	13
py	11.0	24.8 ^f	11 ^f	3.34	25.6	7	4.80	34.7	20
pz	4.2	26.4	14	1.77	22.4	-5	3.40	33.5	15
mpz ⁺	2.8	27.5	18	6.31	24.5	5	13.0	31.2	10

^a T = 25.0 °C. ^b pK_a's of the L ligands, from top to bottom: 9.25; 5.25; 0.65; <6. ^c Reference 19 for L = NH₃ and ref 2a for others (I = 0.5 M, except I = 1.0 M for mpz⁺). ^d Reference 6b, except for L = NH₃ (ref 26), I = 0.1 M. ^e This work. I = 1 M (NaCl). ^f Errors in ΔH[‡] and ΔS[‡] are ±0.5 and ±2, respectively. ^g Errors in ΔH[‡] and ΔS[‡] are in the range ±0.2–2 and ±1–5, respectively. ^h Errors in ΔH[‡] and ΔS[‡] are in the range ±0.3–0.8 and ±1–3, respectively. ⁱ Reference 19 for iron, I = 1 M, errors in ΔH[‡] and ΔS[‡] are ±1–3 and ±4, respectively. Reference 26 for ruthenium, I = 1 M.

medium. It is also a precursor for the aqua ion, as already found for the iron analogue.^{18,19}

The identity of the ammine complex is confidently supported by analytical, spectroscopic, and electrochemical results. The reversible CV peak at 0.55 V (vs NHE) can be assigned to the Os^{III,II} redox process, the potential being 0.1 V lower than the one found for the hexacyanide(III,II) couple at 0.64 V.²⁰ The same difference was observed for the Fe^{III,II} corresponding couples.^{20,21} More conclusive is the appearance of the band at 1290 cm⁻¹, corresponding to a deformation mode of bound ammonia.¹⁰ The intense band at 2040 cm⁻¹ is similar to that found at 2036 cm⁻¹ for K₄[Os(CN)₆],²² but the medium-intensity one at 2001 cm⁻¹ merits a special comment. While being hardly assignable to an isotopic ¹³C component because of its great intensity, it could be assigned to a split mode corresponding to the cyanide stretching trans to ammonia. No such intense band was observed for the hexacyanide anion.²² By replacement of a cyanide ligand with NH₃, more electron density can be transferred to the *trans*-cyanide ligand, thus increasing the population of the π*(CN) orbital and decreasing the IR absorption wavenumber. This is consistent with the assignment of the band at 407 cm⁻¹ to an Os–C stretching mode,²³ appearing at a significantly greater value than for the hexacyanide species, 390 cm⁻¹.²² The shift is consistent with the increased back-bonding, which strengthens the Os–C bond. The above interpretation is additionally supported by recent crystallographic evidence showing that the Fe–C bond trans to NH₃ is shorter than the equatorial Fe–C bonds, by 0.05 Å, in the Na₃[Fe(CN)₅NH₃]·7H₂O complex.²⁴

The UV–vis spectral results (Figures S1 and S2; see Table 1 for the MLCT and d–d assignments) are important because no d–d bands have been reported yet for any member of the [Os(CN)₅L]ⁿ⁻ series,¹³ in contrast with the results for the iron²⁵ and ruthenium²⁶ series. The band shapes of the

MLCT transitions to the π*(CN) orbitals are independent of L and are also similar to those found with the iron and ruthenium complexes.¹² For the [Os(CN)₆]⁴⁻ ion, only a shoulder at ca. 240 nm can be observed with intermediate intensity. Although ligand field theory predicts two spin-allowed d–d bands, from the ¹A_{1g} ground state to the ¹T_{1g} and ¹T_{2g} excited states,¹³ we assign the shoulder tentatively to the ¹A_{1g} → ¹T_{1g} transition. The second transition, ¹A_{1g} → ¹T_{2g}, is probably buried below the intense CT band. The assignment of the ¹A_{1g} → ¹T_{1g} transition implies a stronger ligand field for the osmium complex as compared to the ruthenium one, in agreement with expected trends.¹³ Table 1 also show two additional much weaker bands in the near UV–visible region, which we assign to spin-forbidden transitions.¹³

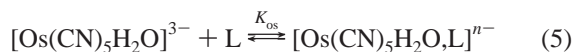
For the tetragonally distorted [Os(CN)₅L]ⁿ⁻ ions, we rely on a previous analysis made by Toma et al. for the iron analogues,²⁵ successfully applied later to the ruthenium complexes.²⁶ Both the ¹T_{1g} and ¹T_{2g} states split under C_{4v} symmetry, although we neglect the transitions to the split ¹T_{2g} because of overlap with the CT bands (see above). The ¹T_{1g} excited state splits into the ¹A₂ and ¹E(1) levels.²⁵ As the transition ¹A₁ → ¹A₂ is orbitally forbidden, a weak intensity is predicted; besides, its energy should be relatively insensitive to changes in L. This is not the case for the allowed ¹A₁ → ¹E transition, which lies at lower energies than the ¹A₁ → ¹A₂ if L has a weaker ligand field than cyanide. The results in Table 1 follow this prediction, as previously found for the Fe and Ru complexes.²⁷ We then assign the bands at 272 nm (L = NH₃) and 287 nm (L = H₂O) to the ¹A₁ → ¹E(1) transitions. A weak absorption reported for the [Os(CN)₅pz]³⁻ ion at ca. 280 nm,^{1a} consistent with similar measurements for the ruthenium (282 nm)^{3a} and iron²⁵ (ca. 380 nm) analogues, may also have the same origin.

For the formation reactions (Table 2), the dependence of the rate constants, k₂, on the charge of the entering L ligands

- (18) Toma, H. E. *Inorg. Chim. Acta* **1975**, *15*, 205–211.
 (19) Toma, H. E.; Malin, J. M. *Inorg. Chem.* **1973**, *13*, 1772–1774.
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 (21) Parise, A. R.; Pollak, S.; Slep, L. D.; Olabe, J. A. *An. Asoc. Quim. Argent.* **1995**, *83*, 211–223.
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 (25) Toma, H. E.; Giesbrecht, E.; Malin, J. M.; Fluck, E. *Inorg. Chim. Acta* **1975**, *14*, 11–15.

- (26) Olabe, J. A.; Zerga, H. O.; Gentil, L. A. *J. Chem. Soc., Dalton Trans.* **1987**, 1267–1269.
 (27) Some of the estimated molar absorptivities in Table 1 appear as too high for being considered as d–d transitions. However, intensity stealing from, and mixing with, overlapping CT bands may contribute to the enhanced intensities. Note that even the orbitally forbidden ¹A₁ → ¹A₂ transitions have been assigned for the aqua and amino complexes.

suggest an ion-pair, dissociative scheme:^{5,28}

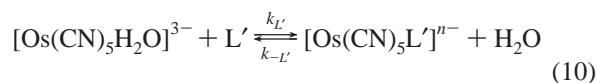
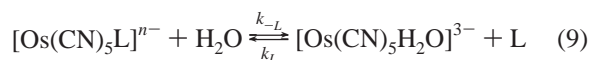


The fast preequilibrium involving association of the reactants (eq 5) depends on the size and charge of L and on the ionic strength of the medium. The rate-determining loss of water in the outer-sphere complex, eq 6, is followed by a fast conversion to the final product, eq 7. The rate and equilibrium constants are related to the observed rate constant k_{obs} (s^{-1}) by

$$k_{\text{obs}} = \frac{k_{-w}K_{\text{os}}[\text{L}]}{1 + K_{\text{os}}[\text{L}]} \quad (8)$$

k_{obs} reduces to $k_{-w}K_{\text{os}}[\text{L}]$, if $K_{\text{os}}[\text{L}] \ll 1$, with reaction 7 being irreversible. Thus, the experimental second-order rate constant, k_2 ($\text{M}^{-1} \text{s}^{-1}$), can be associated to the product $k_{-w}K_{\text{os}}$. By assuming an Eigen–Fuoss expression,²⁹ a value of ca. 1 M^{-1} was calculated for K_{os} for the osmium complex, and the water-exchange rate constant, k_{-w} , was ca. 0.3 s^{-1} (25 °C). This is significantly smaller than the quoted values for the ruthenium and iron complexes, ca. 10 and 400 s^{-1} , respectively.^{6a,25} The validity of the mechanism is supported by the constancy of the activation enthalpy values for the different ligands.³⁰ This was observed also for the iron and ruthenium analogues. The enthalpy values, however, are much greater for the osmium series. The latter fact, partly compensated by the greater entropy values, explains the sharp decrease of the rate constants in the osmium system. Activation entropies are constant in the series, within experimental error, and also support a dissociative mechanism.^{5,28}

In the dissociation kinetics reactions, the saturation behavior of k_{obs} (s^{-1}) for the release of pz (Figure 3) is typical of the pentacyanometalate systems.⁵ This evidence, together with the fact that k_{obs} at saturation is independent of the type of entering ligand L', supports a dissociative mechanism:



The mechanism predicts the following expression for the observed rate constant:

(28) Langford, C. H.; Gray, H. B. *Ligand Substitution Processes*; W. A. Benjamin: New York, 1965.

(29) (a) Eigen, M. *Z. Phys. Chem. (Munich)* **1954**, *1*, 176. (b) Fuoss, R. M. *J. Am. Chem. Soc.* **1958**, *80*, 5059–5061.

(30) In the proposed mechanism, the measured activation enthalpy contains corresponding values for eqs 5 and 6. As we can assume that the value for eq 5 is near to zero,^{6a} the experimental value can be supposed to correspond to eq 6.

$$k_{\text{obs}} = \frac{k_{-L}k_{L'}[\text{L}'] + k_Lk_{-L'}[\text{L}]}{k_L[\text{L}] + k_{L'}[\text{L}']} \quad (11)$$

Under saturation conditions, $k_{L'}[\text{L}'] \gg k_L[\text{L}]$ and $k_{-L}k_{L'}[\text{L}'] \gg k_{-L}k_L[\text{L}]$, k_{obs} tends to k_{-L} , the specific dissociation rate constant for L.

Table 3 includes k_{-L} values extrapolated to 25.0 °C. The osmium complexes appear as very inert, compared to the iron and ruthenium analogues, for a given ligand. For the three series, NH_3 dissociates faster than the N-heterocyclic ligands. The values of the dissociation rates appear to be controlled mainly by the activation enthalpies, which show the greatest values for the osmium complexes. The values of ΔH^\ddagger among the N-heterocyclic ligands show a distinctive picture for Os compared to Ru and Fe systems. In the latter case, it was suggested that the monotonic increase from py to pz and mepz^+ could be related to the increasing back-bonding interactions. This would overcompensate the decrease in basicity favoring weaker bonds.^{2b} The different trend found in the osmium system suggests that basicities could be determinant. In fact, it has been proposed that the back-bonding contributions in the $[\text{M}(\text{CN})_5\text{L}]^{n-}$ complexes for L = py and pz and derivatives can be considered negligible in aqueous solutions.^{1,4,31} The picture should not be oversimplified, however, because the kinetic trends in ligand dissociation rates can depend on other factors, including solvation. Table 3 shows that NH_3 dissociates faster than the N-heterocyclic ligands, despite its greater basicity. Finally, the activation entropies displayed in Table 3 show positive values, supporting the dissociative mechanism, although no definite trends can be observed by changing L or the metal centers.

Resuming the interpretation of the kinetic results for the osmium complexes, we propose that dissociative mechanisms are operative in both the formation and dissociation processes. For the formation reactions, an ion-pair contribution responsible for the slight variations of the rate constants with the charge of the entering ligands was detected. The constancy of the activation parameters for the different entering L ligands and the positive activation entropies are diagnostic of a dissociative behavior for water release. For the dissociation reactions, additional support is provided by the rate-saturation behavior, high activation enthalpies (strongly dependent on L), and positive activation entropies. The picture is consistent with previous results observed for the iron and ruthenium analogues. We avoid a discrimination between D or I_d mechanisms,²⁸ although some evidence has been advanced in favor of the D situation for the iron pentacyano complexes.³² A central feature is the sharp decrease in the rates for the osmium systems, observed with the “ σ -only” NH_3 ligand, as well as with the potentially σ – π binding N-heterocyclic ligands. The comparisons suggest that

(31) Slep, L. D.; Pollak, S.; Olabe, J. A. *Inorg. Chem.* **1999**, *38*, 4369–4371.

(32) (a) Stochel, G.; Chatlas, J.; Martínez, P.; van Eldik, R. *Inorg. Chem.* **1992**, *31*, 5480–5483. (b) Maciejowska, I.; van Eldik, R.; Stochel, G.; Stasicka, Z. *Inorg. Chem.* **1997**, *36*, 5409–5412.

σ -interactions are mainly responsible for the trends. Relativistic effects are probably a reason for the great strength of the Os–L bonds, as compared to Ru–L and Fe–L bonds. The contraction of the 6s orbital makes it a better acceptor, while the expansion of the 5d orbitals contributes to a stronger overlap with L orbitals.^{33,34}

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(34) Similar trends have been found for the aquation reactions of the $[M^{III}(\text{NH}_3)_5\text{Cl}]^{2+}$ ions (M = Co, Rh, Ir). Values of $k_{-\text{Cl}^-}$ (s^{-1} , 25 °C) were 1.7×10^{-6} (Co), 6×10^{-8} (Rh), and 1×10^{-10} (Ir) (cf. ref 33, p 372).

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Supporting Information Available: Figure S1 showing the UV–vis spectrum of $\text{K}_3[\text{Os}(\text{CN})_5\text{NH}_3] \cdot 2\text{H}_2\text{O}$ in aqueous solution, with a multiple Gaussian fitting, and Figure S2, showing the electronic spectra corresponding to the conversion of $[\text{Os}(\text{CN})_5\text{NH}_3]^{3-}$ into $[\text{Os}(\text{CN})_5\text{H}_2\text{O}]^{3-}$ in aqueous solution. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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