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Properties of the mixed-valence binuclear complex ion, $[(NH_3)_5Ru^{III}\text{–}NC\text{–}Os^{II}(CN)_5]^-$ ☆

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Abstract

The mixed-valence ion, $[(NH_3)_5Ru^{III}\text{–}NC\text{–}Os^{II}(CN)_5]^-$, was prepared in solution from $[Ru(NH_3)_5H_2O]^{3+}$ and $[Os(CN)_6]^{4-}$ and was isolated as a potassium salt. A kinetic study of the formation reaction shows that a dissociative mechanism is operative, the process being rate-controlled by the loss of water from the Ru(III) moiety, as in related reactions with $[Fe(CN)_6]^{4-}$ and $[Ru(CN)_6]^{4-}$. The binuclear ion shows a distinctive intervalence band, associated to charge transfer from Os(II) to Ru(III), at 830 nm ($\epsilon = 3450$ M^{-1} cm^{-1}), with a noticeable asymmetry, probably associated to spin–orbit coupling. Shifts in the redox potentials at the metal centers on dimer formation are consistent with the Os(II)–Ru(III) formulation. By measuring solution Raman spectra in post-resonance conditions with respect to the IT band, activation of the bridging CN stretching, as well as of the terminal stretching modes, is observed; absolute distortion values for both of the modes can be calculated by applying a time-dependent analysis of the scattering problem. IR and Raman results of the solid samples are also presented. Theoretical models were applied to IT data, allowing an estimation of the delocalization parameter, α^2, and the electronic coupling parameter, H_{AB}. The results are compared with other valence-trapped binuclear systems.

Keywords: Ruthenium complexes; Osmium complexes; Ammine complexes; Cyano complexes; Mixed-valence complexes

1. Introduction

As a part of a broad investigation on the synthesis, spectroscopic and kinetic properties of mixed-valence systems [1], recent emphasis has been placed on the pentacyanoferrate-L-pentaammineruthenium series [2]; the work was pioneered by a study on the L-pyrazine-bridged species [3] and it has been followed by studies with other bridging ligands as well [3,4]. By using $[Ru(CN)_5]^{3-}$ instead of $[Fe(CN)_5]^{3-}$, closely related compounds have been obtained [5]. A particularly relevant system was described for $L = CN^-$, both with Fe [6] and Ru [5] as cyanide containing moieties.

In view of the current interest in cyanide-bridged systems [7], as well as considering the usefulness of extending the above mentioned studies in order to include the missing Os derivative (which was only briefly mentioned in the literature) [8], we report herein our studies on the preparation, kinetics of formation and electrochemical and spectroscopic properties (IR, UV–Vis, Raman) of the $[(NH_3)_5Ru^{III}\text{–}NC\text{–}Os^{II}(CN)_5]^-$ ion. The present work appears also to be relevant in the context of very recent developments on the synthesis and structural characterization of $Na_2Os(CN)_5NO \cdot 2H_2O$ [9], as well as related members of the $[Os(CN)_5L]^{n-}$ series.

2. Experimental

2.1. Materials

The synthesis of $[Ru(NH_3)_5Cl]Cl_2$ and of $[Ru(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ followed the literature procedures [10,11]. Potassium hexacyanoosmate was prepared according to a slightly modified procedure as described for $K_4Ru(CN)_6$ [12], starting from OsO_4

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(Johnson-Matthey) and potassium cyanide (Mallinckrodt). The purity was checked by comparing with published absorbance data [13]. The reagents for maintaining ionic strength ($NaClO_4$, Riedel-Häen) and buffers (acetic acid, sodium acetate (Merck)) were used as received. Water was distilled and purified with a Milli-Q system.

2.2. Kinetic measurements

A solution containing $[Ru(NH_3)_5OSO_2CF_3]^{2+}$ (6×10^{-5} M), buffer (pH range 4–5.2) and $I=0.1$ M was deaerated by flushing with argon, and a solution of $[Os(CN)_6]^{4-}$ (range 1.7–5×10^{-4} M) was added. The mixture was transferred in anaerobic conditions to a thermostated spectrophotometric cell in a Hewlett-Packard 8452A diode array spectrophotometer and the absorbance data at 820 nm were obtained as a function of time (no influence of dissolved oxygen was detected, however). The rate constants, k_{obs}, were calculated from a linear least-squares fit of ln $(A_\infty - A_t)$ versus time (A_∞ is a calculated value obtained by an iterative procedure).

Some preliminary experiments were done with the addition of $[Os(CN)_6]^{3-}$ (obtained through oxidation of $[Os(CN)_6]^{4-}$ with Ce(IV), range 8×10^{-6} to 5×10^{-5} M); in these runs, no decrease but only a modest increase in k_{obs} was detected, directly related to the concentration of added reagent. In view of previous comments on the nature of this effect [6], no $[Os(CN)_6]^{3-}$ was added in subsequent experiments. All measurements were carried out at 25 °C.

2.3. Physical measurements

The absorption spectra in the UV–Vis and NIR regions were obtained with Hewlett-Packard 8452A and Shimadzu UV-160A instruments, respectively. The concentration of solutions ought to be 5×10^{-4} M or lower, in order to avoid precipitation. Solid samples of the potassium salt were obtained by mixing 10^{-3} M solutions of $[Os(CN)_6]^{4-}$ and aquated $[Ru(NH_3)_5OSO_2CF_3]^{2+}$. The precipitate was washed and further redissolved, passed through a Sephadex G-25 column and then evaporated to dryness and dried over silica gel. Analytical data for C, H, N were obtained with a Carlo Erba EA 1108 elemental analyzer; water content was determined by thermogravimetry. The results conformed to the formula $K[(NH_3)_5Ru\text{–}NC\text{–}Os(CN)_5]\cdot2H_2O$.

IR measurements were carried out with a FTIR Nicolet 150P spectrophotometer, in KBr pellets. The electrochemical titration experiment (square wave voltammetry) was performed with a PAR potentiostat, model 273 A, by using a 10^{-4} M solution, $I=0.1$ M, contained in a standard three electrode cell with a platinum wire and a platinum gauze as working and counter electrodes, respectively, and a calomel reference electrode. Successive voltammograms were obtained after mixing the monomeric reagents, up to the completion of reaction.

The resonance Raman spectra were recorded on a Jobin-Ivon U-1000 spectrometer (University of São Paulo), with a resolution of 6 cm^{-1}. Only the Ar^+ laser facilities (Spectra-Physics, model 165) could be employed. Solid samples were prone to partial decom-

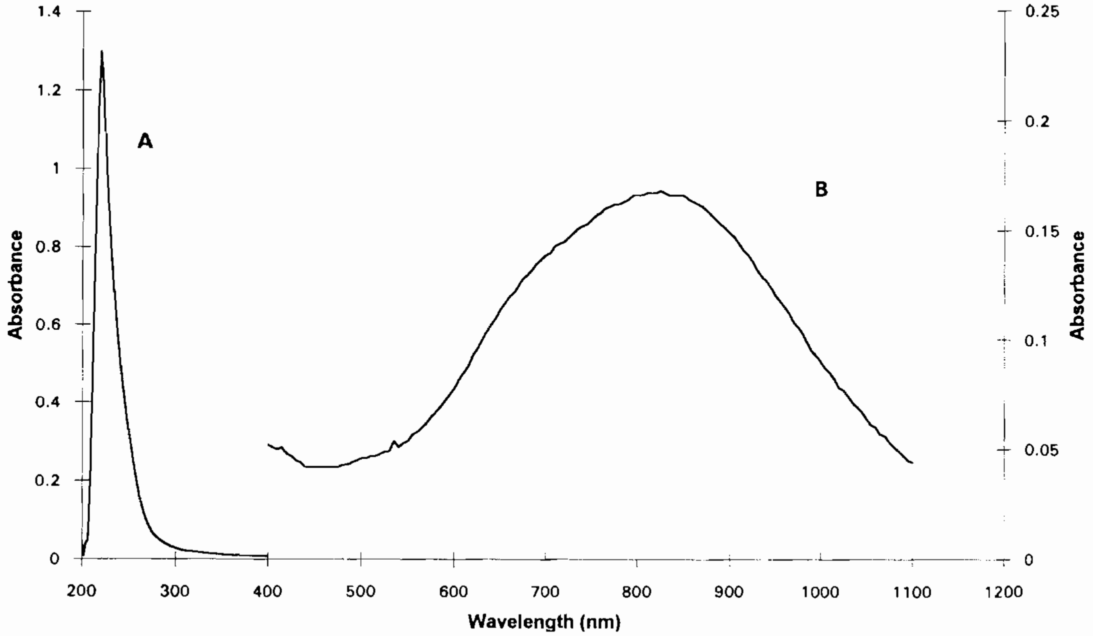


Fig. 1. A: UV spectrum of an aqueous solution of $K[(NH_3)_5Ru^{III}\text{–}NC\text{–}Os^{II}(CN)_5]$, 6×10^{-6} M (left scale). B: Vis–NIR spectrum of the same solution, 6×10^{-5} M (right scale).

position, even in a rotating cell at low exciting power (10 mW). Aqueous solutions could be handled in dilute conditions ($\sim 10^{-4}$ M) with 50 mW laser radiation, in a spinning cell.

3. Results and discussion

When $[Ru(NH_3)_5OSO_2CF_3](CF_3SO_3)_2$ is dissolved in an aqueous medium (pH 4–6), the triflate anion dissociates rapidly (5 min) and is quantitatively replaced by water (in fact, a mixture of $[Ru(NH_3)_5H_2O]^{3+}$ and $[Ru(NH_3)_5OH]^{2+}$ can be present, as the pK_a of the first species is 4.1 (cf. Ref. [6])). If a solution of $[Os(CN)_6]^{4-}$ is added, a blue color develops over a period of hours.

We propose that reaction (1) is operative

$$[Ru(NH_3)_5OH_2]^{3+} + [Os(CN)_6]^{4-} \rightleftharpoons [(NH_3)_5Ru^{III}\text{–}NC\text{–}Os^{II}(CN)_5]^- + H_2O \quad (1)$$

Fig. 1 shows the spectrum of the product of reaction (1), named hereafter as **I**. The band at 830 nm ($\epsilon = 3450$ M^{-1} cm^{-1}), which is absent in either of the reacting ions, is presently assigned as a MM′CT transition, from Os(II) to Ru(III). The intense UV band at 220 nm is close to that found in $[Os(CN)_6]^{4-}$ (MLCT, $Os(II) \rightarrow \pi^*(CN^-)$) [14]. That the Os(II),Ru(III) formulation, but not the one for the redox isomer Os(III),Ru(II) is present predominantly in the solution, seems therefore to be well proved, and is consistent with predictions based on the redox potentials of the monomeric reactants in reaction (1) ($[Os(CN)_6]^{4-}$, $E° = 0.63$ V [15]; $[Ru(NH_3)_5OH_2]^{3+}$, $E° = 0.1$ V [16]).

It can be seen that the shifts in the energy of the IT band for the three related complexes, $[(NH_3)_5Ru\text{–}NC\text{–}M(CN)_5]^-$ (M = Fe, Ru, Os), are in direct correspondence with the shifts in the redox potential for the respective hexacyanometallate ions, as shown in Table 1.

The kinetics of reaction (1) were studied as a function of $[H^+]$ and the results are shown in Fig. 2. The saturation behavior and the decrease of k_{obs} with decreasing $[H^+]$ are consistent with the previous results obtained for the iron and ruthenium derivatives [6] and allow us to sustain again the mechanism depicted in Scheme 1, from which Eq. (2) is derived.

The values of k_{obs} were fitted to Eq. (2) by means of a non-linear least-squares treatment, taking estimated, reliable values for K_{IP}^b (2.0×10^2 M^{-1}) and K_{IP}^a (2.1×10^3 M^{-1}) [6], as well as literature values for K_a^{Ru} (7.9×10^{-5} M^{-1}) [16] and K_a^{Os} (1.58×10^{-3} M^{-1}) [17]. We obtained $k = 6.5 \pm 0.5 \times 10^{-4}$ s^{-1}, a value in very close agreement with those obtained for the corresponding ruthenium and iron mixed-valence complexes, $7.8 \pm 0.9 \times 10^{-4}$ and $6.9 \pm 0.7 \times 10^{-4}$ s^{-1}, respectively [5,6]. As pointed out previously [6], they are consistent with a water–ligand interchange mechanism in the respective ion pairs $[Ru(NH_3)_5OH_2]^{3+}$ $[M(CN)_6]^{4-}$ (M = Fe, Ru, Os) and appear to be also in agreement with the estimated rate constant in the water-exchange reaction of $[Ru(NH_3)_5H_2O]^{3+}$, 5×10^{-4} s^{-1} [18].

Table 1
Intervalence band energies (E_{IV}) in the $[(NH_3)_5Ru^{III}\text{–}NC\text{–}M^{II}(CN)_5]^-$ ions and redox potentials ($E°$) of the corresponding $[M(CN_6)]^{4,3-}$ couples (M^{II} = Fe, Ru, Os)[a]

M^{II}	$E°$ [b] (V)	E_{IV}	
		(cm^{-1})	(eV)
Fe	0.42	10200[c]	(1.265)
Ru	0.94	14700[d]	(1.824)
Os	0.63	12000	(1.489)

[a] The value of $E°$ for the reduction at the pentaammine-ruthenium site in the dimers was only measured for the presently reported complex ($E° = 0.00$ V), but not in the iron- and ruthenium-pentacyano species.

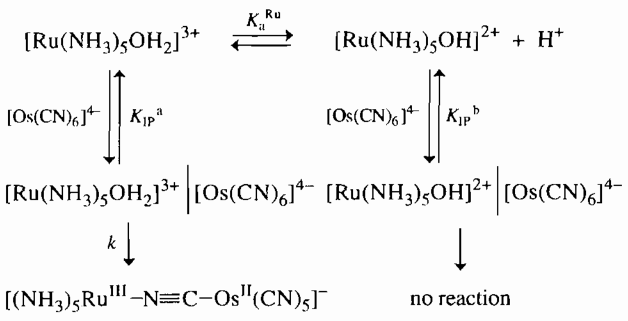
[b] vs. NHE; Ref. [15].

[c] Ref. [6].

[d] Ref. [5].

$$k_{obs} = \frac{\left\{\dfrac{kK_{IP}{}^{a}[H^+]K_a{}^{Os}[Os(CN)_6{}^{4-}]}{[H^+]+K_a{}^{Os}}\right\}}{([H^+]+K_a{}^{Ru}) + \left\{\dfrac{(K_{IP}{}^{a}[H^+]+K_{IP}{}^{b}K_a{}^{Ru})K_a\mathrm{Os}[Os(CN)_6{}^{4-}]}{[H^+]+K_a{}^{Os}}\right\}} \quad (2)$$

In the formation reaction of the iron analog of **I**, an alternative catalytic path was proposed, initiated by the rapid outer-sphere reaction between $[Fe(CN)_6]^{4-}$ and $[Ru(NH_3)_5H_2O]^{3+}$. Thus, one of the products, $[Fe(CN)_6]^{3-}$, could oxidize the fully reduced bridged complex, previously formed through the entry of $[Fe(CN)_6]^{4-}$ into the substitution-labile species $[Ru(NH_3)_5H_2O]^{2+}$. The new path was demonstrated through the decrease of k_{obs} when increasing amounts of $[Fe(CN)_6]^{3-}$ were added, up to a certain limit. We were unable to detect any drop in the k_{obs} values by



Scheme 1.

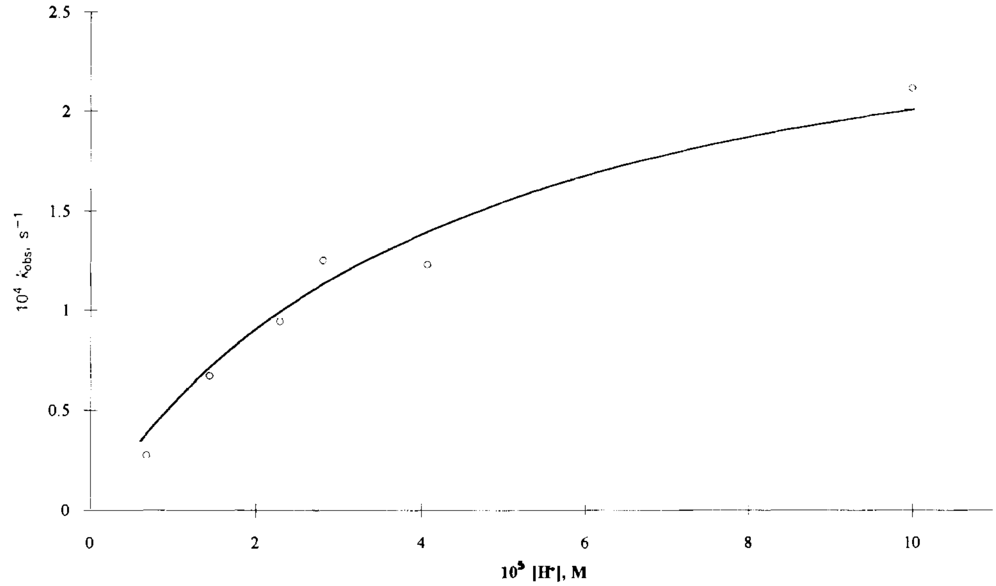


Fig. 2. k_{obs} vs. [H^+]: points, experimental values; solid line, calculated from Eq. (2) and the parameters given in the text. Measurements were taken at 25 °C, $I=0.10$ M, $[Os(CN)_6]^{4-}=3.6\times10^{-4}$ M.

increasing the concentration of added $[Os(CN)_6]^{3-}$; the result is feasible, because the potential of the $[Os(CN)_6]^{4,3-}$ couple is 0.2 V less reducing than the one for $[Fe(CN)_6]^{4,3-}$ [15], and this should mimimize the significance of the catalytic path. Probably for the same reason, we did not find any influence of oxygen either on the rate of reaction (1), or on the nature of products (i.e. no $[Os(CN)_6]^{3-}$ was found.)

The degree of advancement of reaction (1) was also followed through an electrochemical titration; the peaks of $[Os(CN)_6]^{4-}$ and $[Ru(NH_3)_5H_2O]^{3+}$ disappeared and new peaks developed at 0.84 and 0.00 V. The positive shift of the potential at the Os site in the dimer with respect to that in the $[Os(CN)_6]^{4,3-}$ couple (0.63 V) is consistent with similar shifts measured for the related dimers $[(NC)_5Fe\text{–}L\text{–}Ru(NH_3)_5]^-$ (L = pz, 4,4′-bpy) [3]. No direct comparisons can be made between the potentials of $[Ru(NH_3)_5H_2O]^{3,2+}$ (0.1 V) [16] and the negatively shifted value at the Ru site in the dimer. The shift is however consistent with the π-donor influence of the $[Os(CN)_6]^{4-}$ moiety, as was discussed elsewhere [3].

An additional insight on the electronic structure of **I** comes from the IR and Raman results with the solid potassium salt. Three bands at 2041, 2081 and 2114 cm^{-1} appear clearly defined in the C–N stretching region of the IR spectrum. The first (more intense) band is close to the values found in $Na_4Os(CN)_6\cdot10H_2O$ for the splitted components of the F_{1u} mode (2023, 2050, 2067 cm^{-1}) [14]; thus, it can be assigned to the terminal, equatorial stretching modes in the axially distorted bridged complex. This band, as well as the weaker 2081 cm^{-1} band (probably a terminal, axial C–N stretching) are diagnostic of Os(II) character in the mixed-valence complex. Finally, the very weak absorption at 2114 cm^{-1} can be assigned to the bridged C–N stretching, by comparison with Raman results discussed below. The statistical weight (1:5) may not be the only explanation for the weakness of the latter band; the C–N bridge oscillation should be associated with a lower change in the transition moment (but not in the polarizability) with respect to the terminal C–N stretching vibrations. Finally, the peak at 1298 cm^{-1} is diagnostic of NH_3 coordination (rocking mode) to a Ru(III) center [2].

The Raman results (solid spectra, 2116, 2056 and 546 cm^{-1}) are consistent with the IR data; the lower energy band at 546 cm^{-1} (Raman) is close to the band measured in the IR spectrum (552 cm^{-1}), probably a mixing of Os–C stretching and OsCN bending modes. In the resonance Raman experiments in solution, two bands appeared in the C–N stretching fundamental region, at 2130 and 2040 cm^{-1}, with an intensity ratio of 3:1. The latter results were obtained with an excitation wavelength of 514.5 nm (post-resonance conditions, cf. the maximum of the IT band) and both bands disappeared if the 457.9 nm line was employed.

By comparison with the results on related cyanide-bridged complexes [19] and particularly with those containing $(Fe(CN)_5)^{3-}$ and $[Ru(CN)_5]^{3-}$ as donor moieties [20,21], it is straightforward to assign the 2130 cm^{-1} band to the bridging C–N stretching. As pointed out by Doorn and Hupp [21], enhanced scattering under post-resonance conditions is observed from both ends of the mixed-valence ion, based on a single electronic excitation. Unfortunately, we could not observe enhanced bands associated to stretchings and bendings in the $[Ru(NH_3)_5]^{3+}$ moiety, as was the case with the above mentioned related complexes. But the appearance of both bridged and terminal C–N stretchings is significant indeed. The variations in Raman intensity among the modes can be connected to normal-coordinate distortions by a time-dependent analysis of the scattering problem [22]. This was accomplished by Hupp and co-workers for the iron and ruthenium analogs of the present complex [20,21], and absolute distortion values, $|\Delta a|$, for the different modes were obtained. Our calculated values for $|\Delta a|$, 0.060 and 0.017 Å for the bridging and terminal stretching, respectively, are in keeping with the calculated values for the iron and ruthenium analogs. It should be pointed out that individual contributions to vibrational reorganization energy can be calculated from these bond distortion data.

Table 2 shows the energy, half-width and molar absorbance for the intervalence band in **I**, as well as for related dimers. Also included are the values for the delocalization parameter α^2, and the electronic coupling parameter, H_{AB}, calculated through application of theoretical models [1]. The H_{AB} value for **I** shows that some delocalization occurs ($\sim 2\%$) and that the coupling associated to cyanide bridging appears to be nearly constant in the series of related species. The value of H_{AB} is also significantly higher than the one found for related pyrazine-bridged complexes (~ 3–5×10^2 cm^{-1}) [3]; this is consistent with the lower distance of CN^- over pyrazine, the favorable overlapping ability of its π^* orbitals and, probably, a direct πd–πd overlap between metal centers [6].

A final comment should be added concerning the asymmetry of the IT band in **I**. This is in contrast with the results found for the related Ru and Fe species [5,6] but is consistent with the measurements in the $[(NH_3)Os^{III}\text{–}NC\text{–}M^{II}(CN)_5]^-$ series (M = Fe, Ru, Os) [23]. An asymmetric spectrum was found only for M = Os. The energy and intensity of the shoulder, as compared to the maximum of the band, are similarly related both in **I** and in $[(NH_3)_5Os^{III}\text{–}NC\text{–}Os^{II}(CN)_5]^-$. We assign the splitting as arising from spin–orbit coupling effects associated to the d^5 core in the Os(III)–Ru(II) excited state. In a related dimer $[(bpy)_2ClOs\text{–}CN\text{–}Ru(NH_3)_5]^{3+}$, two bands associated to IT transitions were also detected in water, but three components were resolved in nitrobenzene solution [7a], in agreement with theory [24].

Table 2
Intervalence absorption data and calculated parameters (Hush model) for the related $[(NH_3)_5Ru^{III}\text{–}NC\text{–}M^{II}(CN)_5]^-$ ions (M^{II} = Fe, Ru, Os)

M^{II}	$\Delta\nu_{1/2\,exp}$ (cm^{-1})	$\alpha^2 \times 10^2$	10^{-3} H_{AB} (cm^{-1})	ϵ_{max} (M^{-1} cm^{-1})
Fe	4100	2.20	1.5	3000
Ru		1.17	1.9	2800
Os	6700^a	1.86	1.6	3450

^{a}Calculated from the more intense peak, obtained from Gaussian analysis of the IT band (λ_{max} = 825 nm).

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