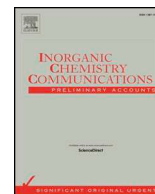




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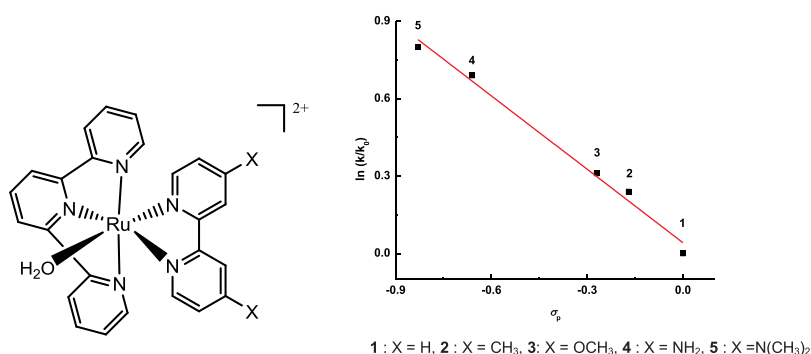
Trans-kinetic effects in ligand substitution processes of ruthenium polypyridyl complexes

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GRAPHICAL ABSTRACT



ABSTRACT

A concerted mechanism is disclosed when studying *trans*-kinetic effects in substitution processes of complexes of formula $[\text{Ru}(\text{trpy})(4,4'-(\text{X})_2\text{-bpy})(\text{H}_2\text{O})]^{2+}$, with $\text{trpy} = 2,2':6',2''\text{-terpyridine}$, $\text{bpy} = 2,2'\text{-bipyridine}$ and $\text{X} = \text{H}, \text{CH}_3, \text{OCH}_3, \text{NH}_2$ and $\text{N}(\text{CH}_3)_2$. The second order rate constants k_2 for substitution of water by acetonitrile increase with increasing donor ability of the X group. The correlation between $\ln k_2$ and Hammett substituent constants σ_p of X gives a slope of near 1, indicating high sensitivity of the kinetic parameters for water replacement to the donor ability of the para-substituent attached to a bipyridine *trans*- to the water ligand and considerably separated from it. Besides, the activation enthalpies decrease with increasing pK_a values of the $4,4'-(\text{X})_2\text{-bpy}$ ligands and the activation entropies have negative values almost one order of magnitude higher than those reported before in similar processes. These data indicate a concerted ligand interchange mechanism, infrequently found in substitution reactions of octahedral complexes which can be explained by the fact that H-bonds between the leaving ligand (H_2O) and the entering ligand (CH_3CN) will favor an intermediate transition state of increased order respect to the initial state. These results are pertinent for finding the best candidates in the quantitative detection of CH_3CN , an important contaminant in radiopharmaceuticals used in PET (positron emission tomography) studies.

Ruthenium polypyridyl complexes are relevant in systems involved in artificial photosynthesis [1]. Ligand substitution processes for the replacement of water by acetonitrile have already been studied in aquo (phosphine)ruthenium(II) complexes [2] and in complexes of the type $[\text{Ru}(\text{H}_2\text{O})(\text{N-N})(\text{trpy})]^{2+}$ (with N-N = diimine ligand and $\text{trpy} = 2,2':6',2''\text{-terpyridine}$) [3], where steric effects for bidentate

bipyridyl ligands were disclosed to be important in modulating the rate constants. However, since we were interested in detecting CH_3CN – an important contaminant in radiopharmaceuticals used in PET (positron emission tomography) studies [4] – by a rapid kinetic analytical method, we resorted to analyzing ligand substitution kinetics in similar complexes with 2,2'-bipyridines substituted in the 4,4'-positions with

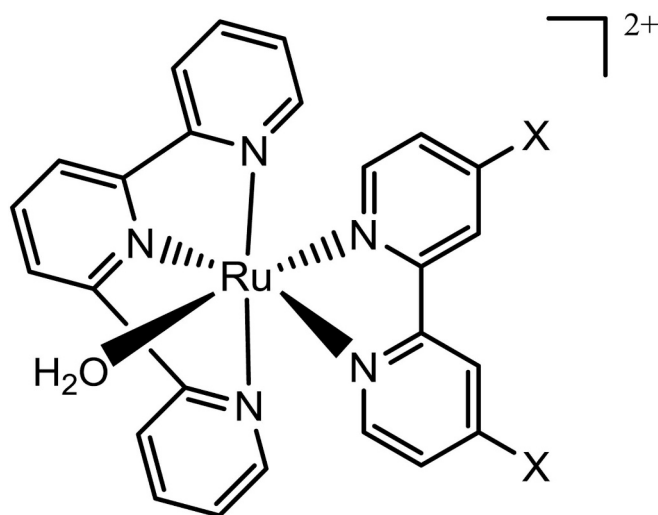
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Scheme 1. Structure of complexes **1** ($X = \text{H}$), **2** ($X = \text{CH}_3$), **3** ($X = \text{OCH}_3$), **4** ($X = \text{NH}_2$) and **5** ($X = \text{N}(\text{CH}_3)_2$).

groups of different donor abilities, processes that had not been studied before.

Therefore, we report here the kinetic parameters of substitution of water (H_2O) by acetonitrile (CH_3CN) in complexes of formula $[\text{Ru}(\text{trpy})(4,4'-(X)_2\text{-bpy})(\text{H}_2\text{O})]^{2+}$, with $\text{trpy} = 2,2':6',2''$ -terpyridine, $\text{bpy} = 2,2'$ -bipyridine and $X = \text{H}, \text{CH}_3, \text{OCH}_3, \text{NH}_2$ and $\text{N}(\text{CH}_3)_2$. The structure of complexes **1**–**5** are disclosed in [Scheme 1](#).

All chemicals used in this work were analytical-reagent grade. Acetonitrile was freshly distilled over P_4O_{10} prior to use. Water used in all experiments was triply distilled; the second distillation was performed over KMnO_4 on a slightly basic media. Chemical analyses were carried out at INQUIMAE, University of Buenos Aires, Argentina, with an estimated error of $\pm 0.5\%$. $[\text{Ru}(\text{terpy})\text{Cl}_3]$ was prepared by following reported techniques [5]. All the $[\text{Ru}(\text{trpy})(4,4'-(X)_2\text{-2,2'-bpy})\text{Cl}]\text{Cl}$ complexes were synthesized as described before, by heating at reflux $\text{Ru}(\text{terpy})\text{Cl}_3$ and the corresponding $4,4'-(X)_2\text{-bpy}$ ligand for 3 h in ethylene glycol [6]. The recrystallization in concentrated $\text{HCl}_{(\text{aq})}$ was avoided for the bipyridines substituted with ammine groups; instead, a recrystallization in ethanol/ether was done. The reaction yields were between 70% and 80%.

In order to synthesize complexes of formula $[\text{Ru}(\text{trpy})(4,4'-(X)_2\text{-2,2'-bpy})(\text{H}_2\text{O})](\text{CF}_3\text{SO}_3)_2$, 100 mg of the corresponding $[\text{Ru}(\text{trpy})(4,4'-(X)_2\text{-2,2'-bpy})\text{Cl}]\text{Cl}$ complex were poured onto 10 mL of an acetone/water (3:1) mixture. Then, an equivalent quantity of $\text{Ag}(\text{CF}_3\text{SO}_3)$ was added, and the resulting solution was refluxed for 4 h under subdued light. The precipitated AgCl was then removed by filtration and the filtrate was roto-evaporated to dryness. The obtained solid was recrystallized twice in acetone/ether. The reaction yields were between 60% and 75%. Complex **1** has been characterized before [7]. Anal. % found (calculated) for $(2)\cdot(\text{CF}_3\text{SO}_3)_2\cdot 5/2(\text{CH}_3)_2\text{CO}$ or $\text{C}_{36.5}\text{H}_{40}\text{F}_6\text{N}_5\text{O}_{9.5}\text{RuS}_2$: C, 44.6 (44.7); N, 7.5 (7.2); H, 4.0 (4.1); for $(3)\cdot(\text{CF}_3\text{SO}_3)_2\cdot \text{H}_2\text{O}$ or $\text{C}_{29}\text{H}_{27}\text{F}_6\text{N}_5\text{O}_{10}\text{RuS}_2$: C, 39.0 (39.4); N, 7.7 (7.9); H, 3.1 (3.1); S, 7.6 (7.3); for $(4)\cdot(\text{CF}_3\text{SO}_3)_2\cdot 4\text{H}_2\text{O}\cdot 2(\text{CH}_3)_2\text{CO}$ or $\text{C}_{33}\text{H}_{43}\text{F}_6\text{N}_7\text{O}_{13}\text{RuS}_2$: C, 38.4 (38.7); N, 9.0 (9.6); H, 3.4 (4.2); S, 6.0 (6.3); for $(5)\cdot(\text{CF}_3\text{SO}_3)_2\cdot 2\text{H}_2\text{O}$ or $\text{C}_{31}\text{H}_{35}\text{F}_6\text{N}_7\text{O}_9\text{RuS}_2$: C, 39.9 (40.1); N, 10.5 (10.6); H, 3.7 (3.8); S, 6.8 (6.9).

Electrochemical experiments were performed using a BAS Epsilon EC equipment, with vitreous C as working electrode, Pt wire as auxiliary electrode and Ag/AgCl (3 M KCl) as reference electrode. The cyclic voltammograms were measured at a scan rate of 100 mV/s, in aqueous solutions at $\text{pH} = 1$ (0.1 M HNO_3) and $[\text{complex}] \sim 10^{-3}$ M. Only the redox potentials on the oxidative side were determined.

Kinetic measurements were carried out on a Hewlett-Packard 8453 Diode-Array Spectrophotometer connected to a bath thermostated

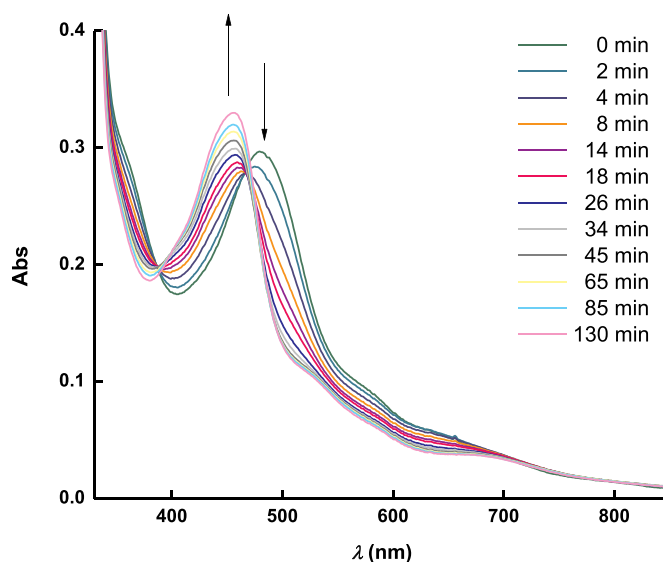


Fig. 1. Changes of absorbance with time for complex **3** ($X = \text{OCH}_3$), at $C \sim 4.5 \times 10^{-5}$, $[\text{CH}_3\text{CN}] = 0.74$ M and $T = 50$ °C.

to ± 0.5 °C. An aqueous solution of NaClO_4 0.1 M was used to adjust the ionic strength. The complex concentrations were about 4.6×10^{-5} M. The measured pH values for all solutions were between 4.7 and 4.9. The experiments were developed at different acetonitrile concentrations (0.74, 1.42 and 2.05 M) and for each concentration, the absorbance changes were determined at 50°, 60°, 70° and 80 °C. The pseudo-first order constants (k_{obs}) for the substitution were obtained by fitting an exponential function for the decay obtained at 4 selected wavelengths and computing the average values. All experiments were done by duplicate. Activation parameters were obtained by using the Eyring equation [8]:

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^*}{RT} + \ln\frac{k_B}{h} + \frac{\Delta S^*}{R} \quad (1)$$

where k is the rate constant at temperature T , k_B is the Boltzmann constant, h is the Planck constant, R is the universal gas constant, ΔH^* is the activation enthalpy and ΔS^* is the activation entropy. Errors in activation parameters are estimated to be $\pm 5\%$ in ΔH^* and $\pm 20\%$ in ΔS^* .

The substitution of water by acetonitrile is disclosed by changes in the UV/absorption spectra, as shown in [Fig. 1](#), for the case of $X = \text{OCH}_3$ as a representative example. The maximum absorption wavelengths (in nm) in aqueous solutions of the initial complexes $[\text{Ru}(\text{trpy})(4,4'-(X)_2\text{-bpy})(\text{H}_2\text{O})]^{2+}$ are: $\lambda_{\text{max}} = 475$ nm ($X = \text{H}$), 476 nm ($X = \text{CH}_3$), 482 nm ($X = \text{OCH}_3$), 485 nm ($X = \text{NH}_2$) and 493 nm ($X = \text{N}(\text{CH}_3)_2$). These bands can be assigned to metal-to-ligand charge transfer (MLCT) transitions $d_\pi(\text{Ru}) \rightarrow \pi^*(\text{bpy}, \text{trpy})$ [7]. As expected, the HOMO-LUMO gap decreases with increasing donor ability of the substituent X . The corresponding values in acetonitrile solutions for the final complexes $[\text{Ru}(\text{trpy})(4,4'-(X)_2\text{-bpy})(\text{CH}_3\text{CN})]^{2+}$ are: $\lambda_{\text{max}} = 454$ nm ($X = \text{H}$), 456 nm ($X = \text{CH}_3$), 457 nm ($X = \text{OCH}_3$), 467 nm ($X = \text{NH}_2$) and 463 nm ($X = \text{N}(\text{CH}_3)_2$).

In all cases, substitution of water by acetonitrile causes an hypsochromic shift of the absorption band maxima. Since CH_3CN is a good π -acceptor, in contrast to H_2O , it competes for the metal electronic density with the polypyridyl ligands and thus the HOMO-LUMO gap increases, as already discussed in a previous work on the hydrolysis of coordinated acetonitrile in $[\text{Ru}(\text{trpy})(\text{bpy})(\text{CH}_3\text{CN})]^{2+}$ [9].

Isosbestic points are detected in all cases (as shown in [Fig. 1](#) for $X = \text{OCH}_3$ and in [Supplementary Fig. 1](#) for the other complexes) and indicate the co-existence of two species in solution, according to the substitution process:

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