

The unusually fast reactions between ruthenium(III)-ammine complexes and NO revisited †

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The kinetics of the unusually fast reactions between $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}]^{(3-n)+}$ ($\text{X}^{n-} = \text{Cl}^-, \text{NH}_3, \text{H}_2\text{O}$) and NO were reinvestigated in acidic aqueous solution in order to clarify the underlying reaction mechanism. The measured second-order rate constants ($k_{\text{NH}_3} = 0.30 \pm 0.01 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{Cl}^-} = 0.75 \pm 0.03 \text{ M}^{-1} \text{ s}^{-1}$, $k_{\text{H}_2\text{O}} = 55.6 \pm 3.2 \text{ M}^{-1} \text{ s}^{-1}$ at 26 °C) are in good agreement with literature data for X = ammonia and halide. The activation parameters determined for the reactions are: $\Delta H^\ddagger = 41 \pm 2 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -114 \pm 7 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^\ddagger = -13.6 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Ru}(\text{NH}_3)_6]^{3+}$; $\Delta H^\ddagger = 34.4 \pm 1.0 \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = -132 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta V^\ddagger = -18.0 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ for $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$; and $\Delta H^\ddagger = 31.0 \pm 0.7 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -108 \pm 2 \text{ J K}^{-1} \text{ mol}^{-1}$ for $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. Bond formation with the entering nucleophile appears to be substantial in the transition state for the reaction. An associative substitution mechanism coupled to a concerted electron transfer process to produce $[\text{Ru}^{\text{II}}(\text{NH}_3)_5(\text{NO}^+)]^{3+}$ is proposed for all three reactions. Possible reasons for the significantly faster reaction observed in case of the aqua complex are discussed.

Introduction

The discovery that nitric oxide plays an important role in mammalian bioregulation and immunology, has stimulated intense interest in the chemistry of NO and its derivatives such as transition metal nitrosyl complexes. Such complexes have been intensively studied and a number of comprehensive reviews of the reactions and properties of nitrosyl complexes have been published over the past decades.¹⁻³ One of the most prominent features of transition metal nitrosyl chemistry, is the existence of numerous complexes where NO, as a result of its radical character in the ground state, binds to metal centres either as NO^- or as NO^+ .⁴ Such interactions were studied in parallel investigations performed in our laboratories, which concentrated on the reaction of NO with reduced vitamin B₁₂,⁵ metmyoglobin,⁶ a series of polyaminecarboxylate complexes of Fe^{II} (in order to remove NO from exhaust gases),⁷⁻⁹ and with aquated Fe^{II}, the classical “brown ring” test reaction for nitrate.¹⁰

A literature survey reveals that ruthenium ammine complexes have been investigated by several groups in a wide range of research areas. These complexes are of particular interest because of their ability to coordinate nitric oxide. In fact ruthenium forms more nitrosyl complexes than any other transition metal.¹¹ The common characteristics of these complexes are their octahedral stereochemistry and the presence of an extremely stable Ru–NO group which bears a formal charge of +3. Although many studies deal with the redox behaviour of ruthenium ammine nitrosyls, complex-formation reactions with NO and the underlying reaction mechanisms are still not well understood.¹² It is well known that $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is very inert and only undergoes very slow ligand substitution reactions, but an acidic solution of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ is rapidly and quantitatively converted to $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ in the presence of nitric oxide. In this rather surprisingly fast reaction, bond making by the entering nucleophile seems to form an important aspect of the overall ligand displacement process. Taube *et al.*¹² concluded that the experimental observations support an electrophilic substitution mechanism, in which NO was considered to be an

electrophile and the product complex was formally described as $\text{Ru}^{\text{IV}}\text{--NO}^-$. This suggestion is questionable in light of the detailed characterisation of the $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ complex (see below). Subsequently, Pell and Armor¹³ performed a detailed study of the kinetics of the reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ with NO in the pH range 3 to 11. In basic solution the reaction involves the attack of NO on the deprotonated ammine complex to produce $[\text{Ru}(\text{NH}_3)_5\text{N}_2]^{3+}$. In acidic solution, however, substitution of coordinated ammine is actually important and yields $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$. The reported activation parameters for the latter reaction, *viz.* $\Delta H^\ddagger = 35.6 \pm 3.3 \text{ kJ mol}^{-1}$ and $\Delta S^\ddagger = -138.1 \pm 12.6 \text{ J K}^{-1} \text{ mol}^{-1}$ led to the same conclusion as reached by Taube *et al.* in that a convenient bond making mechanism is operative in this reaction.

As a result of the unusually fast reaction between Ru^{III} ammine complexes and NO, we carefully reinvestigated the reactions of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}]^{(3-n)+}$ ($\text{X}^{n-} = \text{Cl}^-, \text{NH}_3, \text{H}_2\text{O}$) with NO in aqueous acidic solution. In this paper we present a detailed account of our results on the kinetics and mechanism of the formation of $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$, and discuss these in reference to the available literature.

Experimental

Materials

$[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was prepared from RuCl_3 (Alfa Aesar) by the method of Allen *et al.*¹⁴ and partly converted to the precursor complex $[\text{Ru}(\text{NH}_3)_5(\text{OSO}_2\text{CF}_3)](\text{OSO}_2\text{CF}_3)_2$ as previously described by Dixon *et al.*¹⁵ The precursor complex is dissolved in water and yields $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{OSO}_2\text{CF}_3)_3$ by precipitation with $\text{CF}_3\text{SO}_3\text{H}$. $[\text{Ru}(\text{NH}_3)_6]\text{Cl}_3$ was purchased from Alfa Aesar. All complexes were converted to the triflate salt by precipitating several times from water with $\text{CF}_3\text{SO}_3\text{H}$ to ensure a high purity. The complexes were characterised by using spectroscopic (UV-Vis) and analytical techniques. Analyses: calcd. for $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{OSO}_2\text{CF}_3)_3$: C, 5.53; H, 2.63; N, 10.75; S, 14.77; found: C, 5.54; H, 2.60; N, 10.43; S, 14.65. Absorption maximum at 268 nm, shoulder at ~322 nm. The molar absorptivity at 268 nm was determined from isolated crystals to be $\epsilon = 788 \pm 2 \text{ M}^{-1} \text{ cm}^{-1}$ (average of five determinations); lit.: 268 nm ($\epsilon = 719 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁶ ($\epsilon = 770 \text{ M}^{-1} \text{ cm}^{-1}$),¹⁷ ($\epsilon = 757 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁸ Analyses: calcd. for $[\text{Ru}(\text{NH}_3)_5\text{Cl}](\text{OSO}_2\text{CF}_3)_2$: C, 4.62; H, 2.91; N, 13.47; S, 12.34; found: C, 4.52; H, 2.83; N, 12.98; S,

† Electronic supplementary information (ESI) available: UV-Vis spectrum of $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ and titration curve for the acid dissociation of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. See <http://www.rsc.org/suppdata/dt/b210256k/>

12.31. Absorption maximum at 327 nm with $\epsilon = 1930 \text{ M}^{-1} \text{ cm}^{-1}$; lit.: 328 nm ($\epsilon = 1930 \text{ M}^{-1} \text{ cm}^{-1}$).¹⁹ Analyses: calcd. for $[\text{Ru}(\text{NH}_3)_6](\text{OSO}_2\text{CF}_3)_3$: C, 5.54; H, 2.79; N, 12.92; S, 14.79; found: C, 5.47; H, 2.72; N, 12.52; S, 14.74. Absorption maximum at 276 nm with $\epsilon = 530 \text{ M}^{-1} \text{ cm}^{-1}$ and shoulder at ~ 325 nm; lit.: 275 nm ($\epsilon = 467 \text{ M}^{-1} \text{ cm}^{-1}$),¹² ($\epsilon = 475 \text{ M}^{-1} \text{ cm}^{-1}$),²⁰ ($\epsilon = 530 \text{ M}^{-1} \text{ cm}^{-1}$)¹⁹ and 325 nm (shoulder).

As often recommended in the literature, we tried several times to precipitate the $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ complex as its perchlorate salt, but always found impurities of at least 3%. $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ is unstable in aqueous perchloric acid solution and its decomposition is accelerated by increasing the acid concentration. Even in the solid state stored under vacuum or an inert gas and protected from light, the complex is slowly oxidised by perchlorate.

Caution! Great care should be used when attempting to precipitate Ru complexes as their perchlorate salts, as they are explosive and present a safety hazard.

The same product, *viz.* $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$, is formed in the reaction of nitric oxide with all three investigated complexes. The $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ complex is diamagnetic, octahedrally coordinated with an approximate four-fold symmetry axis and formally considered to be $\text{Ru}^{\text{II}}\text{-NO}^+$.²¹ In acidic solution the complex appears to be indefinitely stable, a property characteristic of the highly stable $\text{Ru}^{\text{II}}\text{-NO}^+$ entity. The $\text{Ru}^{\text{II}}\text{-NO}^+$ entity was confirmed by ⁹⁹Ru Mössbauer studies²² on a series of ruthenium nitrosyl complexes, indicating that the isomer shift is consistent with a +2 charge on ruthenium. This can, furthermore, be confidently concluded from the high IR stretching frequency near 1900 cm^{-1} , which is characteristic for the linear coordination of the NO^+ ligand.²³ Analyses: calcd. for $[\text{Ru}(\text{NH}_3)_5\text{NO}](\text{OSO}_2\text{CF}_3)_3$: C, 5.43; H, 2.28; N, 12.67; S, 14.50; found: C, 5.50; H, 2.24; N, 12.56; S, 14.53. The molar absorptivity was determined from isolated crystals to be $\epsilon = 62.4 \pm 0.3 \text{ M}^{-1} \text{ cm}^{-1}$ at 306 nm and $\epsilon = 15.8 \pm 0.2 \text{ M}^{-1} \text{ cm}^{-1}$ at 455 nm (average of four determinations); lit.: 300 nm ($\epsilon = 67.2 \text{ M}^{-1} \text{ cm}^{-1}$), 460 nm ($\epsilon = 14.4 \text{ M}^{-1} \text{ cm}^{-1}$).¹²

All other chemicals were of analytical reagent grade, and deionized (Millipore) water was used throughout this study. $\text{CF}_3\text{SO}_3\text{H}$ (Alfa Aesar) and $\text{CF}_3\text{SO}_3\text{Na}$ (Sigma Aldrich) were used to adjust the ionic strength and to control the pH (between 1 and 2) of the solutions. All experiments were performed under strict exclusion of oxygen. Acidified solutions were deaerated for extended periods (in general, 1 min ml^{-1} of solution) with pure N_2 before being brought in contact with the Ru^{III} complexes or nitric oxide. A stock solution of nitric oxide was prepared in a gas-tight syringe by degassing an acidified solution, followed by saturation with nitric oxide to a final NO concentration of $1.43 \times 10^{-3} \text{ M}$ at 23°C . Dilutions of known concentration were prepared from this saturated solution by the use of syringe techniques. NO gas was purchased from Air Liquide in a purity of at least 99.5 vol% and cleaned from trace amounts of higher nitrogen oxides like N_2O_3 and NO_2 by passing it through an Ascarite II column (NaOH on silica gel, Sigma-Aldrich) *via* vacuum line techniques.

Instrumentation

pH measurements were performed on a Metrohm 632 pH-Meter with a Mettler Toledo inLab 422 glass electrode. The concentration of nitric oxide in solution was determined with an ISO-NOP electrode connected to an ISO-NO Mark II nitric oxide sensor from World Precision Instruments. The NO electrode consists of a membrane covered anode which selectively oxidizes NO to NO_3^- ions. The resulting current is proportional to the concentration of NO in solution. The NO electrode was calibrated daily with fresh solutions of sodium nitrite and potassium iodide according to the method suggested by the manufacturers. The calibration factor $\text{nA}/\mu\text{M}$ was determined with a linear fit program.

UV/Vis spectra and kinetic experiments were recorded on a Cary 5G spectrophotometer equipped with a thermostated cell compartment using a 1 cm quartz cuvette directly attached to a round flask with a sideways gas connection. This enabled the performance of different physical or chemical operations, like bubbling the solution with NO or N_2 , and the measurement of spectra under exclusion of dioxygen in the same vessel. The repetitive scan spectra reported in this study were obtained using this experimental set-up. The recorded spectra partly show initial absorbances that differ from zero, due to a different reference cuvette.

Kinetic measurements were performed by rapidly mixing solutions of the Ru^{III} complex with solutions of NO using a SX-18-MV (Applied Photophysics) thermostated ($\pm 0.1^\circ\text{C}$) stopped-flow spectrometer coupled to an online data acquisition system. The changes in absorbance were monitored at 268 nm for $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. Kinetic measurements were also performed on a Shimadzu UV-2100 spectrophotometer equipped with a thermostated high pressure cell and a pill-box cuvette²⁴ at ambient and under high pressure (up to 150 MPa). Absorbance changes were monitored at 276 nm for the reaction of NO with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and at 327 nm for $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$. The kinetic data were analysed with the OLIS KINFIT program. All kinetic experiments were performed under pseudo-first-order conditions and the reported rate constants are the mean values from at least five kinetic runs.

Cyclic voltammograms were recorded with an EG&G PARC potentiostat-galvanostat Model 263 controlled by a PC. The electrochemical cell was a conventional three electrode system: an Ag/AgCl reference electrode, a platinum sheet counter electrode, and a glassy carbon working electrode (all from BAS).

Results

Repetitive scan spectra were recorded in the range 200 to 500 nm at intervals of 10 s to 15 min for the reactions of all three complexes with NO and under non-kinetic conditions. Fig. 1 represents the reaction of NO with $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$,

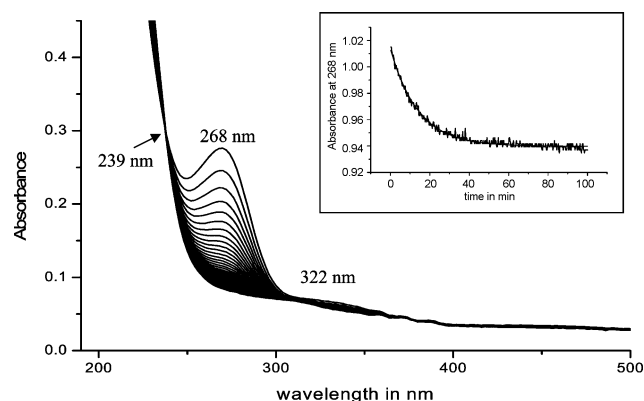


Fig. 1 UV-Vis spectra recorded for the reaction of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ with NO (using a tandem cuvette). Experimental conditions: $[\text{Ru}^{\text{III}}] \sim 0.5 \text{ mM}$, $[\text{NO}] \sim 0.5 \text{ mM}$, $T = 10^\circ\text{C}$, measurement intervals of 10 s, overall reaction time ~ 500 s. Inset: kinetic trace recorded at 268 nm for $[\text{Ru}^{\text{III}}] = 1.35 \text{ mM}$, $[\text{NO}] = 6 \times 10^{-5} \text{ M}$, $\text{pH} = 1$, $T = 26^\circ\text{C}$.

for which an isosbestic point is observed at 239 nm. After mixing with NO, there is an immediate rapid reaction as seen from the decrease in the absorbance maximum at 268 nm, which is complete within 500 s. Fig. 2 represents the reaction with $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$, for which an isosbestic point occurs at 276 nm. The decrease in absorbance at the maximum at 327 nm indicates that this reaction is clearly slower and takes *ca.* 3 h. Fig. 3 represents the reaction with $[\text{Ru}(\text{NH}_3)_6]^{3+}$, for which an isosbestic point is observed at 246 nm, which is in good agreement with that reported by Taube and coworkers, *viz.* 247 nm, $\epsilon = (3.0 \pm$

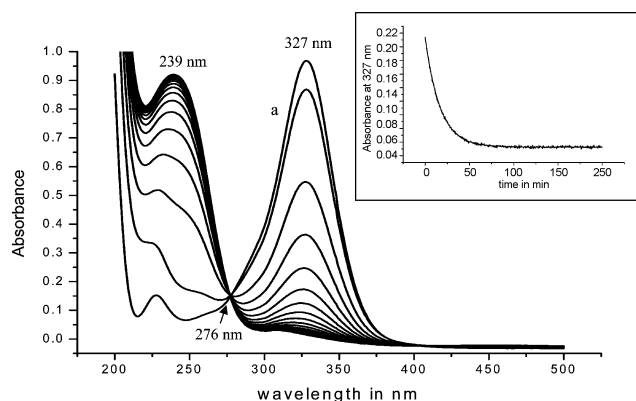


Fig. 2 UV-Vis spectra recorded for the reaction of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ with NO (using the reaction vessel–cuvette set-up). Experimental conditions: $[\text{Ru}^{\text{III}}] = 0.7 \text{ mM}$, 1 min saturation with NO, $T = 23 \text{ }^\circ\text{C}$, measurement intervals of 10 min, overall reaction time $\sim 3 \text{ h}$, (a) spectrum of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ without added NO. Inset: kinetic trace recorded at 327 nm for $[\text{Ru}^{\text{III}}] = 0.1 \text{ mM}$, $[\text{NO}] = 1.06 \text{ mM}$, $\text{pH} = 2$, $T = 26 \text{ }^\circ\text{C}$.

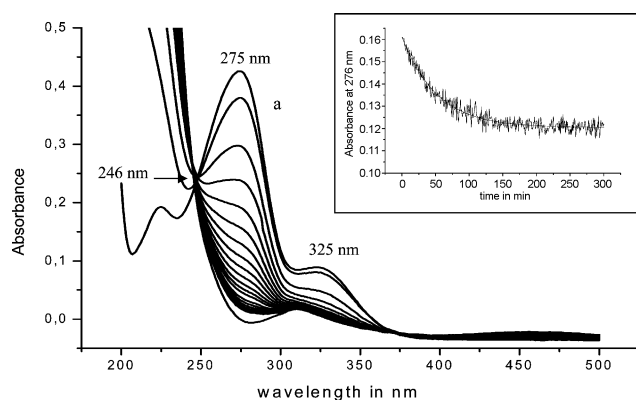


Fig. 3 UV-Vis spectra recorded for the reaction of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ with NO (using the reaction vessel–cuvette set-up). Experimental conditions: $[\text{Ru}^{\text{III}}] = 0.9 \text{ mM}$, 1 min saturation with NO, $T = 23 \text{ }^\circ\text{C}$, measurement intervals of 15 min, overall reaction time $\sim 5 \text{ h}$, (a) spectrum of $[\text{Ru}(\text{NH}_3)_6]^{3+}$ without added NO. Inset: kinetic trace recorded at 275 nm for $[\text{Ru}^{\text{III}}] = 0.1 \text{ mM}$, $[\text{NO}] = 1.06 \text{ mM}$, $\text{pH} = 2$, $T = 26 \text{ }^\circ\text{C}$.

$0.2) \times 10^2 \text{ M}^{-1} \text{ cm}^{-1}$.¹² The overall reaction time is *ca.* 5 h as seen from the decrease at the maximum at 275 nm.

The same new absorption bands were observed for all three reactions at ~ 300 and $\sim 450 \text{ nm}$, which were suggested by Taube and coworkers¹² to be characteristic for the $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$ complex. The UV-Vis spectrum of $[\text{Ru}(\text{NH}_3)_5(\text{NO})]^{3+}$ is shown in Fig. S1 (ESI†) with characteristic absorption bands at 306 and 455 nm. This is the only identifiable product isolated by precipitation from all three reactions discussed above.

It is known that Ru^{III} ammine complexes undergo disproportionation in alkaline solution.^{25,26} In most cases, studies on substitution and redox reactions of ruthenium ammines have been confined to acidic solution. $[\text{Ru}(\text{NH}_3)_6]^{3+}$ shows no spectral changes over the pH range $1 \leq \text{pH} \leq 3.5$, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$ over the pH range $1 \leq \text{pH} \leq 3.0$, and $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ with $\text{p}K_a = 3.95 \pm 0.01$ (see pH titration reported in Fig. S2) is the only form present in solution at $\text{pH} = 1$.

All rate constants were measured under pseudo-first-order conditions: $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} = 0.66$ to 1.35 mM and $[\text{NO}] = 6 \times 10^{-5} \text{ M}$ at $\text{pH} 1$; $[\text{Ru}(\text{NH}_3)_6]^{3+} = 4.8 \times 10^{-5}$ to $1 \times 10^{-4} \text{ M}$, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+} = 4.6 \times 10^{-5}$ to $1 \times 10^{-4} \text{ M}$ and $[\text{NO}] = 3.97 \times 10^{-4}$ to $1.36 \times 10^{-3} \text{ M}$ at $\text{pH} 2$. These concentration ranges are controlled by solubility limitations of NO and the studied complexes. In the case of the $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ complex, the observed rate constants were measured under pseudo-first-order conditions with the complex in excess, due to the relatively low solubility of NO in aqueous solution ($[\text{NO}]_{\text{max}} =$

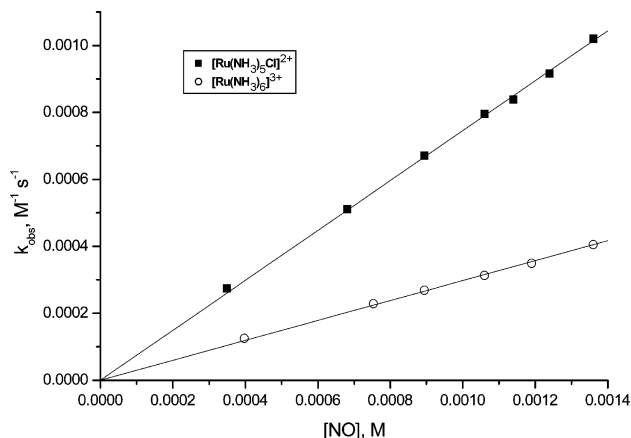


Fig. 4 Dependence of k_{obs} on $[\text{NO}]$ for reaction (1). Experimental conditions: $T = 26 \text{ }^\circ\text{C}$, $\mu = 0.1 \text{ M}$, $\text{pH} = 2.0$, $[\text{Ru}(\text{NH}_3)_6]^{3+} = 4.8 \times 10^{-5}$ to $1 \times 10^{-4} \text{ M}$, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+} = 4.6 \times 10^{-5}$ to $1 \times 10^{-4} \text{ M}$, $[\text{NO}] = 3.97 \times 10^{-4}$ to $1.36 \times 10^{-3} \text{ M}$.

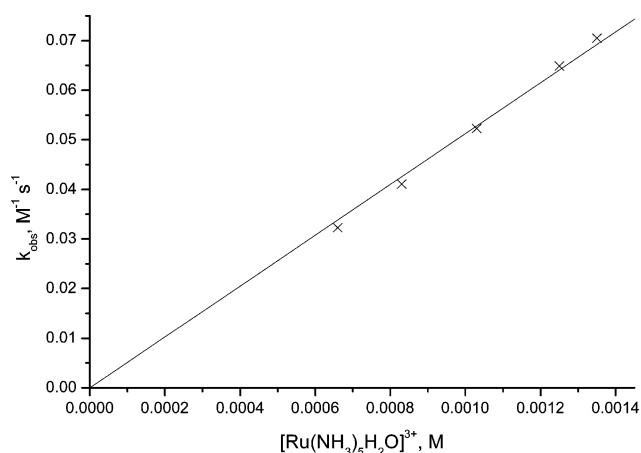
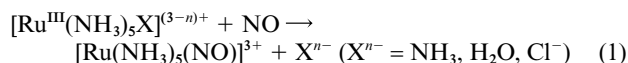


Fig. 5 Dependence of k_{obs} on $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ for reaction (1). Experimental conditions: $T = 26 \text{ }^\circ\text{C}$, $\mu = 0.1 \text{ M}$, $\text{pH} = 1.0$, $[\text{NO}] = 6 \times 10^{-5} \text{ M}$ and $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} = 0.66$ to 1.35 mM (line fitted through the origin).

$1.43 \times 10^{-3} \text{ M}$, which is diluted two times during the stopped-flow experiment) and the small absorbance changes associated with the reaction under these conditions. Plots of the observed rate constant *vs.* $[\text{NO}]$ (Fig. 4) or $[\text{Ru}^{\text{III}}]$ (Fig. 5) confirm that the reaction is first order in both Ru^{III} and NO as reported by Taube *et al.* before.¹² The plots in Fig. 4 and 5 exhibit no meaningful intercepts, indicating the absence of a reverse reaction and that the studied reactions all go to completion.

The overall reaction can be formulated as given in (1), for which the rate law is given in (2).



$$\text{rate} = k[\text{Ru}^{\text{III}}][\text{NO}], \text{ i.e. } k_{\text{obs}} = k[\text{NO}] \text{ or } k_{\text{obs}} = k[\text{Ru}^{\text{III}}] \quad (2)$$

The observed second order rate constants k are listed in Table 1 along with available literature data. The rate constants are in good agreement with those reported by Taube *et al.*,¹² except for the $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ complex which reacts much faster than the other two complexes.

Reduction potentials

The formal reduction potentials were measured by cyclic voltammetry and are listed in Table 2. For the complexes listed, reversible redox behaviour was concluded based on peak to peak separations between the cathodic and anodic waves of

Table 1 Second order rate constants for the reaction of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}]^{(3-n)+}$ ($\text{X}^{n-} = \text{Cl}^-, \text{NH}_3, \text{H}_2\text{O}$) with NO at 26 °C

Complex	$k/\text{M}^{-1} \text{s}^{-1}$	Ref.
$[\text{Ru}(\text{NH}_3)_6]^{3+}$	0.30 ± 0.01	this work
	0.2	12
$[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$	0.75 ± 0.03	this work
$[\text{Ru}(\text{NH}_3)_5\text{Br}]^{2+}$	0.7	12
$[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	55.6 ± 3.2	this work

Table 2 Formal reduction potentials of $\text{Ru}^{\text{III}}/\text{Ru}^{\text{II}}$ couples in aqueous solution determined by cyclic voltammetry

Couple	E_f/V vs. NHE	Medium	Ref.
$[\text{Ru}(\text{NH}_3)_6]^{3+/2+}$	0.039	<i>a</i>	this work
	0.051	<i>b</i>	27
$[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+/1+}$	-0.011	<i>c</i>	this work
	-0.042	<i>d</i>	27
$[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+/2+}$	0.057	<i>a</i>	this work
	0.066	<i>e</i>	27

a 25 °C, 5 mM complex in an aqueous solution of 0.01 M $\text{CF}_3\text{SO}_3\text{H}$, $\mu = 0.1$ M ($\text{CF}_3\text{SO}_3\text{Na}$). *b* 0.1 M NaBF_4 . *c* 25 °C, 5 mM complex in an aqueous solution of 0.01 M HCl, $\mu = 0.1$ M (NaCl). *d* 0.2 M $\text{CF}_3\text{CO}_2\text{Na}$. *e* Aqueous solution of 0.1 M $\text{CF}_3\text{CO}_2\text{H}/0.1$ M $\text{CF}_3\text{CO}_2\text{Na}$.

60 to 75 mV, which is close to the Nernst value of 57 mV. The E_f values differ from those of Lim, Barclay and Anson,²⁷ but the difference is sufficiently small to result from the difference in the selected experimental conditions.

Activation parameters

In order to gain further insight into the mechanism of reaction (1), the rate constants were measured as a function of temperature in the range 20 to 40 °C at pH 2 for $[\text{Ru}(\text{NH}_3)_6]^{3+}$, in the range 10 to 30 °C at pH 2 for $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$, and in the range 15 to 35 °C at pH 1 for $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$. The Eyring plots for these data (see Fig. 6 and Table 3) demonstrate a linear

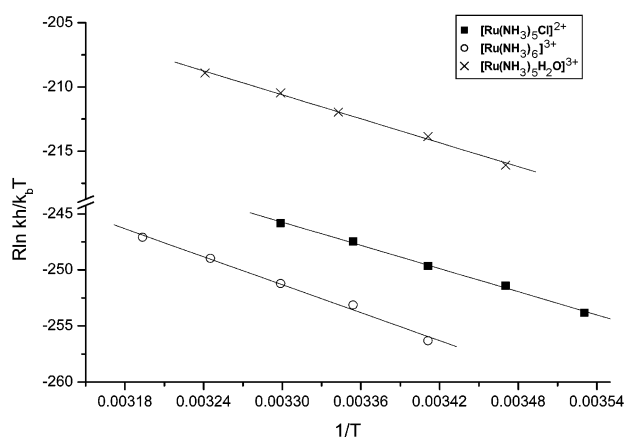


Fig. 6 Dependence of the second order rate constants for reaction (1) on temperature. Experimental conditions: $\mu = 0.1$ M, pH = 2.0, $[\text{Ru}(\text{NH}_3)_6]^{3+} = 1.43 \times 10^{-4}$ M, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+} = 1.5 \times 10^{-4}$ M and $[\text{NO}] = 1.36$ mM; $\mu = 0.1$ M, pH = 1.0, $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+} = 1.35$ mM and $[\text{NO}] = 1.13 \times 10^{-4}$ M.

Table 3 Activation parameters for the reaction of $[\text{Ru}^{\text{III}}(\text{NH}_3)_5\text{X}]^{(3-n)+}$ ($\text{X}^{n-} = \text{Cl}^-, \text{NH}_3, \text{H}_2\text{O}$) with NO

Complex	$\Delta H^\ddagger/\text{kJ mol}^{-1}$	$\Delta S^\ddagger/\text{J K}^{-1} \text{mol}^{-1}$	$\Delta V^\ddagger/\text{cm}^3 \text{mol}^{-1}$	Ref.
$[\text{Ru}(\text{NH}_3)_6]^{3+}$	41 ± 2	-114 ± 7	-13.6 ± 0.3	this work
	36 ± 3	-138 ± 13		13
$[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$	34.4 ± 1.0	-132 ± 3	-18.0 ± 0.5	this work
$[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$	31.0 ± 0.7	-108 ± 2		this work

behaviour within the error limits of the data, where the slope represents ΔH^\ddagger and the intercept ΔS^\ddagger . The reactions were also studied as a function of pressure over the range 0.1 to 150 MPa, for which $\ln k_{\text{obs}}$ appeared to be a linear function of pressure as shown in Fig. 7. From the slope of the plots ($-\Delta V^\ddagger/RT$) the

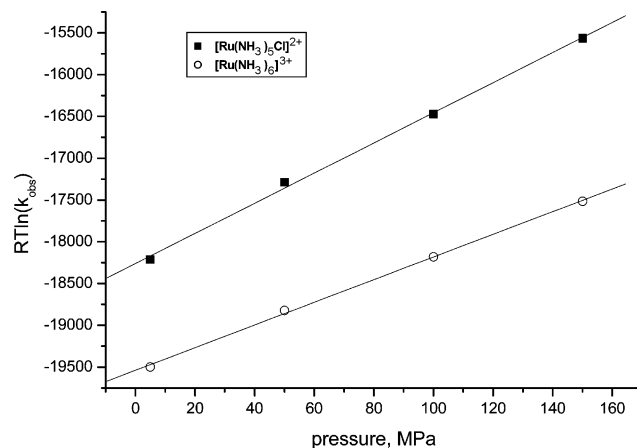


Fig. 7 Dependence of the observed rate constants for reaction (1) on pressure. Experimental conditions: $\mu = 0.1$ M, pH = 2.0, $[\text{Ru}(\text{NH}_3)_6]^{3+} = 1.43 \times 10^{-4}$ M at 20 °C, $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+} = 1.5 \times 10^{-4}$ M at 10 °C and $[\text{NO}] = 1.36$ mM.

volumes of activation, ΔV^\ddagger , were found to be $-13.6 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ for the reaction with $[\text{Ru}(\text{NH}_3)_6]^{3+}$ and $-18.0 \pm 0.5 \text{ cm}^3 \text{ mol}^{-1}$ for the reaction with $[\text{Ru}(\text{NH}_3)_5\text{Cl}]^{2+}$. It was not possible to study the effect of pressure on the reaction of NO with $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})]^{3+}$ due to technical reasons. Since this reaction is significantly faster than the others, a high pressure stopped-flow instrument had to be employed. Unfortunately, this reaction is characterised by very small absorbance changes at 268 nm under pseudo-first-order conditions (excess of the aqua complex), which could not be resolved accurately enough with the available instrumentation.

Discussion

It was the objective of this study to reinvestigate the fundamental kinetics of the formation of the $[\text{Ru}(\text{NH}_3)_5\text{NO}]^{3+}$ complex and to gain further insight into the mechanism of this reaction. Low spin $d^5 \text{Ru}^{\text{III}}$ complexes are substitution inert and thus undergo very slow substitution reactions as seen from the data collected in Table 4. The pentaammine triflate complex is a real exception since triflate is an extraordinary weak nucleophile. The reactions with NO studied here are unusually fast in comparison to the substitution data in Table 4. The substitution of Cl^- by NO is approximately as fast as the displacement of NH_3 , but both reactions are much slower than the displacement of water by NO which occurs ~ 200 times faster (compare data in Tables 1 and 4). From this comparison it was concluded that a classical ligand substitution process on the Ru^{III} ammine complexes cannot account for the observed kinetic data for reaction (1). This led to the suggestion that reaction (1) may involve a rate-determining outer-sphere electron transfer (OSET) process followed by a subsequently fast ligand substitution reaction on the more labile Ru^{II} centre as outlined in reactions (3) and (4), respectively.²⁸ The final reaction product has

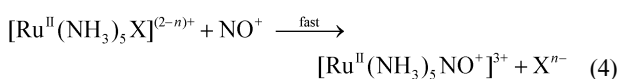
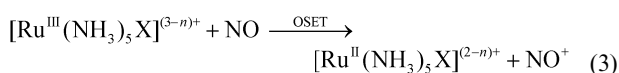
Table 4 Typical substitution data for Ru^{III} ammine complexes in aqueous solution

Reaction	Rate constant	Ref.
[Ru(NH ₃) ₅ Cl] ²⁺ + H ₂ O	3.1 × 10 ⁻⁶ s ⁻¹ at 35 °C	45
[Ru(NH ₃) ₅ Cl] ²⁺ + H ₂ O	3.28 × 10 ⁻⁴ s ⁻¹ at 80 °C	38
[Ru(NH ₃) ₅ Br] ²⁺ + H ₂ O	4.0 × 10 ⁻⁶ s ⁻¹ at 37 °C	45
[Ru(NH ₃) ₅ Br] ²⁺ + H ₂ O	3.99 × 10 ⁻⁴ s ⁻¹ at 80 °C	38
[Ru(NH ₃) ₅ I] ²⁺ + H ₂ O	1.64 × 10 ⁻⁴ s ⁻¹ at 80 °C	49
[Ru(NH ₃) ₅ (TFMS)] ²⁺ + H ₂ O	9.3 × 10 ⁻² s ⁻¹ at 25 °C	50
[Ru(NH ₃) ₅ (H ₂ O)] ³⁺ + H ₂ O	2.3 × 10 ⁻⁴ s ⁻¹ at 25 °C	51
[Ru(NH ₃) ₅ (H ₂ O)] ³⁺ + Br ⁻	1.32 × 10 ⁻³ M ⁻¹ s ⁻¹ at 55 °C	52
[Ru(NH ₃) ₅ (H ₂ O)] ³⁺ + I ⁻	7.4 × 10 ⁻⁴ M ⁻¹ s ⁻¹ at 55 °C	52
[Ru(NH ₃) ₅ (H ₂ O)] ³⁺ + Cl ⁻	2.1 × 10 ⁻³ M ⁻¹ s ⁻¹ at 55 °C	52
[Ru(NH ₃) ₅ (H ₂ O)] ³⁺ + Cl ⁻	8.7 × 10 ⁻⁵ M ⁻¹ s ⁻¹ at 40 °C	53
[Ru(H ₂ O) ₆] ³⁺ + H ₂ O	3.5 × 10 ⁻⁶ s ⁻¹ at 25 °C	57

Table 5 Typical substitution data for Ru^{II} ammine complexes in aqueous solution

Reaction	Rate constant at 25 °C	Ref.
[Ru(NH ₃) ₆] ²⁺ + H ₃ O ⁺	1.24 × 10 ⁻³ M ⁻¹ s ⁻¹	54
[Ru(NH ₃) ₅ (H ₂ O)] ²⁺ + N ₂	7.3 × 10 ⁻² M ⁻¹ s ⁻¹	55
[Ru(NH ₃) ₅ (H ₂ O)] ²⁺ + NCS ⁻	4.0 M ⁻¹ s ⁻¹	43
[Ru(NH ₃) ₅ Br] ²⁺ + H ₂ O	5.4 s ⁻¹	56
[Ru(NH ₃) ₅ Cl] ²⁺ + H ₂ O	6.3 s ⁻¹	56
[Ru(H ₂ O) ₆] ²⁺ + H ₂ O	1.8 × 10 ⁻² s ⁻¹	57

been identified to have a Ru^{II}-NO⁺ character as discussed above.



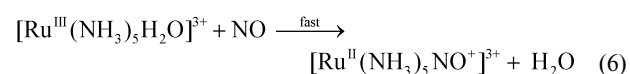
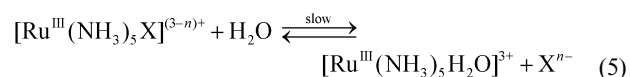
Ru^{II} amines are significantly more labile (see Table 5), show unusual reactivity with respect to substitution and redox processes,²⁹ and display a very rich photochemistry³⁰ that is dominated by substitution reactions.³¹ The mechanism of ligand substitution in [Ru(NH₃)₅(H₂O)]²⁺ is characterised by an insensitivity to the nature of the incoming nucleophile, on which basis a predominantly dissociative mechanism (I_d or D) was suggested.³² Displacement of water in [Ru(NH₃)₅(H₂O)]²⁺ by a neutral entering ligand shows rate constants in the range of 10⁻² M⁻¹ s⁻¹, whereas an anionic ligand reacts ~100 times faster and a cationic ligand ~10 times slower (see Table 5).³³ The suggested outer-sphere electron transfer mechanism seems to be inadequate to account for the observed kinetic behaviour since electron transfer must be the rate-determining step, followed by a rapid substitution reaction. Obviously this does not fit with the expected rate constant for substitution of NO⁺ on the relatively labile d⁶ low spin Ru^{II} ammine centre. So there would be a strong tendency for the formed NO⁺ to diffuse away before substitution could occur, since the reactants in reaction (4) are both positively charged. Furthermore, if this was to happen, other reaction products besides [Ru(NH₃)₅NO]³⁺ should be observed, which is not the case since [Ru(NH₃)₅NO]³⁺ is the only observable product in all three reactions. It also has been calculated that the lifetime of the nitrosonium ion in water must be very short, about 3 × 10⁻¹⁰ s.³⁴ This is based on the equilibrium constant for [NO⁺]/[HNO₂][H⁺], which has been determined spectrophotometrically as 3 × 10⁻⁷ mol⁻¹ dm³ at 25 °C.³⁴ Moreover, in the case of an initial electron transfer step the observed rate constants should follow the order of the reduction potentials (see Table 2), *i.e.* $k_{\text{Cl}^-} > k_{\text{NH}_3} > k_{\text{H}_2\text{O}}$, which is clearly not the case.

Another argument that speaks against an initial electron transfer reaction followed by a rapid ligand substitution reac-

tion, is that reduction of Ru^{III} ammine complexes are in general accompanied by a significant volume increase due to a decrease in electrostriction of the water molecules that solvate the ammine ligands on decreasing the overall charge of the complex. Tregloan and coworkers³⁵ determined the reaction volumes for redox reactions of metal complexes using high-pressure cyclic voltammetry. For the couple [Ru(NH₃)₆]^{3+/2+} in aqueous solution the reaction volume, ΔV^o, was calculated to be +30.3 cm³ mol⁻¹ (based on a contribution of -13 cm³ mol⁻¹ from the Ag/AgNO₃ reference electrode), of which +27.7 cm³ mol⁻¹ was assigned due to the decrease in electrostriction.³⁵ Thus a mechanism that involves the prior reduction of the Ru^{III} ammine complex would require the observed volume of activation to be significantly positive, and not negative as found in the present study (see Table 3).

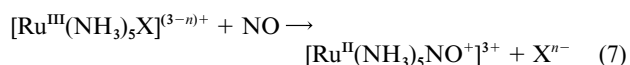
Several studies in ruthenium chemistry suggest that ligand substitution processes at Ru^{III} centres in aqueous solution may be associatively activated. These include the substitution of water in [Ru^{III}(edta)H₂O]⁻ with a series of entering ligands³⁶ including nitric oxide,³⁷ the aquation rates of Ru^{III} haloammine complexes,³⁸ and the isotopic exchange reaction of [RuCl₆]³⁻ that is controlled by the rate and mechanism of aquation of the metal centre.³⁹ Even the effect of pressure on the aquation of [Ru(NH₃)₅Cl]²⁺,⁴⁰ the anation of [Ru(NH₃)₅(H₂O)]³⁺,⁴¹ and the deammonation-anation of Ru^{III} hexaammine halides⁴² in the solid state, support evidence for a seven-coordinate intermediate, *i.e.* an associative substitution mechanism.

Another mechanistic suggestion results from the fact that substitution reactions of hexaammine complexes of M^{III} = Ru, Cr, Co are known to proceed *via* a two-step mechanism. In the case of substitution of [Ru(NH₃)₆]³⁺ by chloride, aquation of this complex is the slow, rate-determining step, followed by fast anation of [Ru(NH₃)₅(H₂O)]³⁺ by chloride.²⁵ In general, Ru^{III} hexaammine complexes almost certainly undergo spontaneous aquation reactions *via* an associative mechanism (I_a or A). Substitution studies on Ru^{III} pentaammine complexes show the same two-step mechanism, *viz.* slow formation of the aqua complex followed by rapid substitution, and have been interpreted in terms of the associative nature of the aquation reaction.^{38,43} There is complete retention of configuration in these reactions. This proposal would result in reactions (5) and (6) to account for the kinetic data found for reaction (1).



This mechanism is also unlikely since the observed rate constants are too fast compared to the rate constants for the aquation process. It can be estimated that the half-life for the spontaneous aquation of [Ru(NH₃)₆]³⁺ to form [Ru(NH₃)₅(H₂O)]³⁺ is approximately 3 years at 25 °C.^{12,44} In the case of the [Ru(NH₃)₅Cl]²⁺ complex, the rate of aquation is 3.1 × 10⁻⁶ s⁻¹ at 35 °C⁴⁵ (see Table 4), which suggests a half-life of approximately 25 days under our experimental conditions.

The unusually fast reaction of nitric oxide with the investigated Ru^{III} ammine complexes can be accounted for in terms of a unique combination of associative ligand binding and concerted electron transfer as indicated in reaction (7).^{28,46}



The versatility of nitric oxide as a coordinating ligand arises from its unusual electronic structure. According to simple molecular orbital (MO) theory, the odd electron on NO

occupies an antibonding π -MO. Removal of this electron is relatively easy and indeed the ionization potential (9.5 eV) is appreciably lower than that of other diatomic molecules.⁴⁷

A convenient bond-formation pathway is available for the entering group: Ru^{III} has a low-spin d⁵ electronic configuration and consequently the ability to accept an electron, giving the t_{2g}⁶ configuration. The unpaired electron occupies the t_{2g} orbital, which is essentially nonbonding, and can be engaged by the odd electron of nitric oxide in forming a bond. Thus a seven-coordinate intermediate can rather easily be produced in this particular case during the course of the reaction. The subsequent formal reduction of the metal centre occurs as a result of the nucleophilic attack by NO and so stabilizes the reaction product. In terms of the intimate mechanism of this concerted substitution/electron transfer process, two scenarios are possible. In the first, the investigated ruthenium ammine complexes are 17-electron species that produce seven-coordinate 19-electron species as a result of the nucleophilic attack by NO. In the concerted process, the metal centre is subsequently reduced due to the ability of NO to donate a third electron to the metal, generating a 18-electron species by loss of the leaving ligand. The second, kinetically equivalent mechanism suggested by a reviewer, involves an intramolecular ligand exchange between coordinated NO and the leaving ligand. In this case, NO first binds as a one-electron donor to form a seven-coordinate, 18-electron intermediate in which NO is coordinated in a bent mode. Subsequently, coordinated NO changes from a one- to a three-electron donor *via* interconversion from a bent to a linear bonding mode and the displacement of the leaving ligand to generate a 6-coordinate, 18-electron species. In this case the unusual reactivity of these systems is a consequence of the ability of nitric oxide to bind initially as a one-electron donor that changes to a three-electron donor. In general most nucleophiles bind as two-electron donors in such systems to give 19-electron intermediates.

Further support for the suggested mechanism comes from the reported activation parameters. The extraordinary high rate constants for the reactions with NO are accompanied by relatively low activation enthalpies (ΔH^\ddagger), large and negative activation entropies (ΔS^\ddagger), as well as large and negative activation volumes (ΔV^\ddagger). These all favour easy bond formation accompanied by a substantial decrease in entropy and a significant volume collapse. The proposed mechanism is essentially similar to that proposed by Taube *et al.*¹² in that NO combines with the Ru centre prior to loss of X in reaction (7). Taube *et al.* consider NO to be an electrophile which then coordinates formally as Ru^{IV}-NO⁻, whereas we consider NO to be a nucleophile which formally coordinates as Ru^{II}-NO⁺, in agreement with the characterisation of this entity.^{22,23}

Finally, the differences observed in the measured rate constants (see Table 1) also require some discussion. The [Ru(NH₃)₅Cl]²⁺ complex reacts with NO ~2.5 times faster than the [Ru(NH₃)₆]³⁺ complex, whereas the [Ru(NH₃)₅(H₂O)]³⁺ complex reacts ~80 times faster with NO than [Ru(NH₃)₅Cl]²⁺ and ~200 times faster than [Ru(NH₃)₆]³⁺. The displacement of Xⁿ⁻ by H₂O during the aquation of [Ru(NH₃)₅X]⁽³⁻ⁿ⁾⁺ (Xⁿ⁻ = Cl⁻, Br⁻, I⁻), follows the order Br⁻ ≥ Cl⁻ > I⁻³⁸ and was interpreted in terms of an associative aquation mechanism (see Table 4 and discussion above). By way of comparison, water exchange on [Ru(NH₃)₅(H₂O)]³⁺ is ~100 times faster than the aquation of [Ru(NH₃)₅Cl]²⁺. Thus ligand displacement by an entering nucleophile is expected to depend to some extent on the lability of the leaving group even when the reaction follows an associative mechanism. In terms of the reactions with NO studied here, this effect could partially account for the higher reactivity of the aqua complex, but is not in agreement with the small difference in rate constants observed for the hexaammine and chloropentaammine complexes. Clearly, the nucleophilic attack by NO coupled to the concerted reduction of the metal centre,

as discussed in more detail above, cannot be compared directly with a simple ligand substitution process.

There are a number of reports in the literature on ligand substitution reactions that are induced by NO⁺,⁴⁸ and it is in principle possible that a redox reaction between the investigated Ru^{III} complexes and NO could result in the production of this species that subsequently catalyses the ligand substitution process. In terms of such a mechanism, the aqua complex could exhibit a higher reactivity due to the possible formation of a nitrito intermediate formed by the attack of NO⁺ on the coordinated water molecule. However, we presently have no evidence that could support such a mechanism.

We conclude that the ligand substitution reactions of the investigated Ru^{III} ammine complexes with NO occur *via* an associative mechanism. The electronic structure of both NO and the d⁵ Ru^{III} centre obviously favours the unusually fast reaction, which results from associative bond formation coupled to a concerted electron transfer step to produce the stable Ru^{II} nitrosyl complex.

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References

- 1 M. Hoshino, L. Laverman and P. C. Ford, *Coord. Chem. Rev.*, 1999, **187**, 75.
- 2 D. M. P. Mingos and D. J. Sherman, *Adv. Inorg. Chem.*, 1989, **34**, 293.
- 3 J. A. McCleverty, *Chem. Rev.*, 1979, **79**, 53.
- 4 B. A. Averill, *Chem. Rev.*, 1996, **96**, 2951.
- 5 M. Wolak, G. Stochel, A. Zahl, T. Schnepfensieper and R. van Eldik, *J. Am. Chem. Soc.*, 2001, **123**, 9780.
- 6 L. E. Laverman, A. Wanat, J. Oszejca, G. Stochel, P. C. Ford and R. van Eldik, *J. Am. Chem. Soc.*, 2001, **123**, 285.
- 7 T. Schnepfensieper, S. Finkler, A. Czap, R. van Eldik, M. Heus, P. Nieuwenhuizen, C. Wreesmann and W. Abma, *Eur. J. Inorg. Chem.*, 2001, 491.
- 8 T. Schnepfensieper, A. Wanat, G. Stochel, S. Goldstein, D. Meyerstein and R. van Eldik, *Eur. J. Inorg. Chem.*, 2001, 2317.
- 9 T. Schnepfensieper, A. Wanat, G. Stochel, A. Zahl and R. van Eldik, *Inorg. Chem.*, 2002, **41**, 2565.
- 10 A. Wanat, T. Schnepfensieper, G. Stochel, R. van Eldik, B. Eckhard and K. Wiegardt, *Inorg. Chem.*, 2002, **41**, 4.
- 11 (a) F. Bottomley, *Coord. Chem. Rev.*, 1978, **26**, 7; (b) T. W. Hayton, P. Legzdins and W. B. Sharp, *Chem. Rev.*, 2002, **102**, 935.
- 12 J. N. Armor, H. A. Scheidegger and H. Taube, *J. Am. Chem. Soc.*, 1968, **90**, 5928.
- 13 S. Pell and J. N. Armor, *J. Am. Chem. Soc.*, 1973, **95**, 7625.
- 14 A. D. Allen, F. Bottomley, R. O. Harris, V. P. Reinsalu and C. V. Senoff, *Inorg. Synth.*, 1970, **12**, 3.
- 15 N. E. Dixon, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 846; N. E. Dixon, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem.*, 1984, **23**, 2940.
- 16 D. K. Lavalley, C. Lavalley, J. C. Sullivan and E. Deutsch, *Inorg. Chem.*, 1973, **12**, 570.
- 17 J. A. Broomhead, F. Basolo and R. G. Pearson, *Inorg. Chem.*, 1964, **3**, 826.
- 18 J. Endicott and H. Taube, *J. Am. Chem. Soc.*, 1962, **84**, 4985.
- 19 H. Hartmann and C. Buschbeck, *Z. Phys. Chem.*, 1957, **11**, 120.
- 20 T. J. Meyer and H. Taube, *Inorg. Chem.*, 1968, **7**, 2369.
- 21 A. F. Schreiner, S. W. Lin, P. J. Hauser, E. A. Hopcus, D. J. Hamm and J. D. Gunter, *Inorg. Chem.*, 1972, **11**, 880.
- 22 M. S. Goodman, M. J. DeMarco, M. S. Haka, S. A. Toorongian and J. Fridmann, *J. Chem. Soc., Dalton Trans.*, 2002, 117.
- 23 E. E. Mercer, W. A. McAllister and J. R. Durig, *Inorg. Chem.*, 1966, **5**, 1881.
- 24 M. Spitzer, F. Gartig and R. van Eldik, *Rev. Sci. Instrum.*, 1988, **59**, 2092.
- 25 P. A. Lay, *Comments Inorg. Chem.*, 1991, **11**, 235.
- 26 P. D. Rudd and H. Taube, *Inorg. Chem.*, 1971, **10**, 1543.
- 27 H. S. Lim, D. J. Barclay and F. C. Anson, *Inorg. Chem.*, 1972, **11**, 1460; T. Matsubara and P. C. Ford, *Inorg. Chem.*, 1976, **15**, 1107.

- 28 T. W. Swaddle, *Comments Inorg. Chem.*, 1991, **12**, 237.
29 H. Taube, *Surv. Prog. Chem.*, 1973, **6**, 1.
30 P. C. Ford, *Adv. Chem. Ser.*, 1978, **168**, 73.
31 E. Tfouni, *Coord. Chem. Rev.*, 2000, **196**, 281.
32 H. Taube, *Comments Inorg. Chem.*, 1981, **1**, 17.
33 M. A. Blesa and M. C. Geldstein, *Inorg. Nucl. Chem.*, 1977, **39**, 1641.
34 J. H. Ridd, *Adv. Phys. Org. Chem.*, 1978, **16**, 1; M. Feelisch and J. S. Stamler, *Methods in Nitric Oxide Research*, John Wiley & Sons, Chichester, 1996.
35 J. L. Sachinidis, R. D. Shalders and P. A. Tregloan, *Inorg. Chem.*, 1996, **35**, 2497.
36 T. Matsubara and C. Creutz, *Inorg. Chem.*, 1979, **18**, 1956; T. Matsubara and C. Creutz, *J. Am. Chem. Soc.*, 1978, **100**, 6255.
37 A. Wanat, T. Schneppensieper, A. Karocki, G. Stochel and R. van Eldik, *J. Chem. Soc., Dalton Trans.*, 2002, 941.
38 J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1968, **7**, 2519.
39 M. G. Adamson, *J. Chem. Soc. A*, 1968, 1370.
40 M. T. Fairhurst and T. W. Swaddle, *Inorg. Chem.*, 1979, **18**, 3241.
41 A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata and J. Oda, *J. Bull. Chem. Soc. Jpn.*, 1975, **48**, 262.
42 A. Ohyoshi, S. Hiraki, T. Odate, S. Kohata and J. Oda, *J. Bull. Chem. Soc. Jpn.*, 1975, **48**, 230.
43 Md. M. Rahman, *J. Indian Chem. Soc.*, 1999, **76**, 188.
44 J. N. Armor and H. Taube, *Inorg. Chem.*, 1971, **10**, 1570.
45 B. Anderes, S. T. Collins and D. K. Lavalley, *Inorg. Chem.*, 1984, **23**, 2201.
46 P. C. Ford and I. M. Lorkovic, *Chem. Rev.*, 2002, **102**, 993.
47 B. F. G. Johnson and J. A. McCleverty, *Prog. Inorg. Chem.*, 1966, **7**, 277.
48 D. A. Buckingham, I. I. Olsen and A. M. Sargeson, *Inorg. Chem.*, 1967, **6**, 1807; D. A. Buckingham, I. I. Olsen, A. M. Sargeson and H. Satrapa, *Inorg. Chem.*, 1967, **6**, 1027; D. A. Buckingham, J. D. Edwards and G. M. McLaughlin, *Inorg. Chem.*, 1982, **21**, 2770.
49 E. A. Seddon and K. R. Seddon, *The Chemistry of Ruthenium*, Elsevier, Amsterdam, 1984.
50 N. E. Dixon, G. A. Lawrance, P. A. Lay and A. M. Sargeson, *Inorg. Chem.*, 1983, **22**, 847.
51 H. Doine, K. Ishihara, H. R. Krouse and T. W. Swaddle, *Inorg. Chem.*, 1987, **26**, 3240.
52 J. A. Broomhead and L. Kane-Maguire, *Inorg. Chem.*, 1971, **10**, 85.
53 C. W. B. Bezerra, S. C. da Silva, M. T. P. Gambardella, R. H. A. Santos, L. M. A. Plicas, E. Tfouni and D. W. Franco, *Inorg. Chem.*, 1999, **38**, 5660.
54 P. C. Ford, J. R. Kuempel and H. Taube, *Inorg. Chem.*, 1968, **7**, 1967.
55 J. N. Armor and H. Taube, *J. Am. Chem. Soc.*, 1970, **92**, 6170.
56 G. N. Coleman, J. W. Gesler, F. A. Shirley and J. R. Kuempel, *Inorg. Chem.*, 1973, **12**, 1036.
57 I. Rapaport, L. Helm, A. E. Merbach, P. Bernhard and A. Ludi, *Inorg. Chem.*, 1988, **27**, 873.