Acceleration of Ligand Exchange by Coordinated Nitrate in Polypyridyl Ruthenium Complexes

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Abstract:

The rate of substitution of L by a chloride ion or acetonitrile in cis-[Ru(bpy)$_2$ (L)(X)]$^+$ (X = NO$_3$; L = pyridine, acetonitrile ; bpy = 2,2'-bipyridine) in low polarity solvents, is greatly enhanced over the rates observed for complexes with X = Cl, NO$_2$, CF$_3$CO$_2$ and p-CH$_3$C$_6$H$_4$SO$_3$. For X = NO$_3$, rate constants and a mechanism for formation of the final product, *cis*-Ru(bpy)$_2$Cl$_2$ or *cis*-Ru(bpy)$_2$(CH$_3$CN)$_2$]$^{2+}$, are presented. The rate enhancement for the nitrato complex is attributed to its ability to act as a bidentate ligand.

Article:

The influence of non-exchanging ligands on the rate of ligand substitution in coordination complexes has been studied extensively.[1] Often the influence can be related to the effect of donor or acceptor properties of the non-exchanging ligand on the electronic nature of the metal centre. The thermal and photochemical substitution reactions of polypyridyl ruthenium complexes are usually predictable and well-behaved, exhibiting trends expected in comparison to other systems.[2-4] In general, ruthenium(II) and ruthenium(III) complexes are relatively inert.[3] Facile ligand exchange occurs thermally only for solvent complexes, especially oxygen donor solvents, and complexes with weakly coordinating anions in polar solvents.[2]

The facile substitution of nitrato ligands of the complexes, [Ru(bpy)$_2$(L)(NO$_3$)]$^+$ (L = CH$_3$CN, pyridine (py) ; bpy = 2,2'-bipyridine), by anions in low polarity solvents is described here. However, surprisingly, the nitrato ligand induces rapid substitution of relatively inert ligands, such as acetonitrile and pyridine, in the subject complexes.

EXPERIMENTAL

Ruthenium complexes were prepared by literature methods.[4-6†] Acetonitrile and dichloromethane were purified by standard methods.[7] Other chemicals were reagent grade and used as received.

Spectral and kinetic data were obtained on a Varian DMS-100 spectrophotometer equipped with a thermostatable, programmable multicell holder and a Houston Model 164 recorder; temperature was controlled with a Neslab RTE-8 bath/circulator. Cyclic voltammetry experiments were performed with a Bioanalytical Systems model CV-1B analyzer using electrolyte solutions of 0.1 M tetraethylammonium perchlorate in acetonitrile, or 0.2 M tetrabutylammonium hexafluorophosphate in dichloromethane. All manipulations were performed under reduced light conditions because of the light sensitivity of these compounds.[4]

Rate constants at 25.0 ± 0.2°C were determined from absorbance (A) vs time (t) data taken from recorded spectra at appropriate wavelengths. Data showed that all reactions were first-order in ruthenium complex for two or more half-lives. Linear least-squares fitting at ln (A — A_0) vs t was used to obtain first-order rate constants. Where consecutive reactions occurred, the rate constants were different enough to avoid interference when data was carefully selected. Reported rate constants are the average of three or more trials with a typical standard deviation of < 20% of the reported values.

For the reaction of [Ru(bpy)$_2$(py)(NO$_3$)]+ with Cl⁻, the infinity values for runs with less than a stoichiometric amount of chloride were obtained from identical runs with more than the stoichiometric amount of chloride, such that the infinity values are those expected for complete transformation to Ru(bpy)$_2$Cl$_2$. In doing so, the data fit first-order behaviour very well.
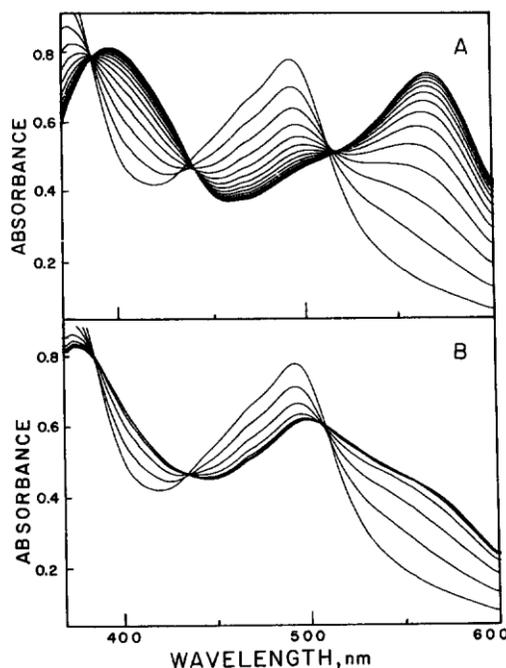

Fig. 1. Reaction of cis-[Ru(bpy)$_2$(py)(NO$_3$)]$^+$ with chloride ion in acetone at 25°C, recorded at 44 min intervals. Concentration of cis-[Ru(bpy)$_2$(py)(NO$_3$)]$^+$ = 1.2 × 10^{-4} M. (A) [Cl⁻] = 4.8 × 10^{-4} M; (B) [Cl⁻] = 0.96 × 10^{-4} M.

RESULTS

When tetrabutylammonium chloride is added to dichloromethane or acetone solutions of [Ru(bpy)$_2$(py)(NO$_3$)]$^+$, the solution spectrum (Fig. 1) changes smoothly from that of the nitrato complex (λ_{max} = 486 nm) to that of Ru(bpy)$_2$Cl$_2$ (λ_{max} = 562 nm), with isosbestic points at 365, 422 and 510 nm. This suggests that the one step transformation shown in the following equation has occurred.

$$[Ru(bpy)_2(py)(NO_3)] + 2Cl⁻ \rightarrow Ru(bpy)_2Cl_2 + py + NO⁻_3.$$
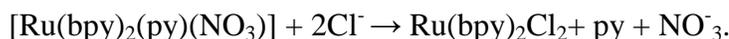
The reaction is first-order (k = 7.3 × 10^{-5} s^{-1} at 25.0°C) in ruthenium complex but zero-order in chloride. An interesting feature of the reaction kinetics is that with less than a 1 : 2 mole ratio of ruthenium to chloride, the spectral changes follow typical first-order behaviour until all chloride is depleted. The reaction then comes to an immediate halt [Fig. 1(B)]. The reaction is not influenced by elimination of atmospheric oxygen, the presence of hydroquinone or ascorbic acid as reducing agents, by solvent purification, or by use of different samples of the ruthenium complex. Under the same conditions, [Ru(bpy)$_2$(CH$_3$CN)(NO$_3$)]$^+$ reacts extremely rapidly with the chloride ion and two well separated steps are observable. The first is complete on an ordinary mixing time scale, giving an intermediate with λ_{max} = 535 nm. This species reacts more slowly with chloride by a first-order reaction (k = 3.0 × 10^{-4} s^{-1} at 25°C) to give Ru(bpy)$_2$Cl$_2$. With more polar solvents, like ethanol, solvolysis of the nitrato ligand occurs rapidly and [Ru(bpy)$_2$(L)(S)]$^{2+}$ (S = solvent) and/or [Ru(bpy)$_2$(L)Cl]$^+$ are obtained as the products.

Other anions, such as Br⁻ and SCN⁻, substitute similarly to chloride giving Ru(bpy)$_2$X$_2$ (X = Br, SCN) as final products. Related complexes, [Ru(bpy)$_2$(py)(X)]$^+$ (X = Cl, p-CH$_3$C$_6$H$_4$SO$_3$, CF$_3$CO$_2$, NO$_2$) are unreactive or at least much less reactive ($t_{1/2}$ > 5 days) than the nitrato complex under the same conditions.

The reaction of $[Ru(bpy)_2(L)(NO_3)]^+$ (L = CH_3CN, py) with chloride in acetonitrile solution yields a mixture of products but, in pure acetonitrile, $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ (λ_{max} = 425 nm) is the observed product. For L = CH_3CN, a one step reaction is observed. With L = py, two steps are observed (Fig. 2) with an intermediate which has a spectrum very similar to that of $[Ru(bpy)_2(CH_3CN)(NO_3)]^+$ in acetonitrile. The rate of the first step ($k = 7.2 \times 10^{-5}$ s^{-1}) is identical to that for chloride substitution. The rate at which the intermediate is transformed to $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ is the same as for $[Ru(bpy)_2(CH_3CN)(NO_3)]^+$ ($k = 7.5 \times 10^{-6}$ s^{-1}).
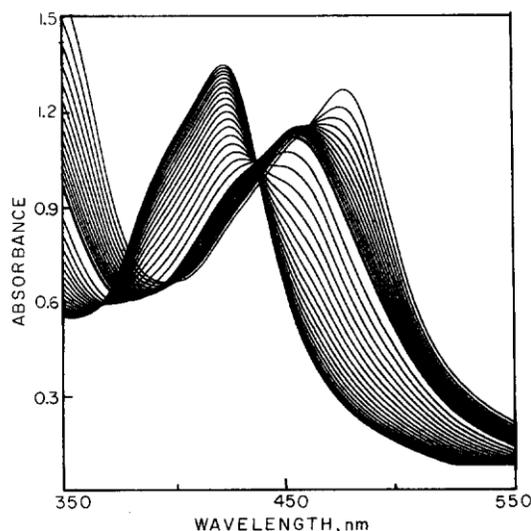
Fig. 2. Reaction of *cis*-$[Ru(bpy)_2(py)(NO_3)]^+$ with acetonitrile solvent at 25°C, recorded at 30 min, then 120 min intervals.

Each of the above reactions was also monitored by cyclic voltammetry.‡ All species involved exhibit at least pseudo-reversible behaviour. The cyclic voltammetry results confirmed the spectral analyses. Reaction of $[Ru(bpy)_2(py)(NO_3)]^+$ ($E_{1/2}$ = 0.94 V) with chloride in dichloromethane, showed a one step transformation to $Ru(bpy)_2Cl_2$ ($E_{1/2}$ = 0.36 V). The same reaction for $[Ru(bpy)_2(CH_3CN)(NO_3)]^+$ exhibits an intermediate ($E_{1/2}$ = 0.56 V) which then reacts to form $Ru(bpy)_2Cl_2$ at rates consistent with spectral data. In acetonitrile, $[Ru(bpy)_2(py)(NO_3)]^+$ reacts to form an intermediate ($E_{1/2}$ = 0.98 V) which then produces $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ ($E_{1/2}$ = 1.41 V). In this case, a second product, probably $[Ru(bpy)_2(py)(CH_3CN)]^{2+}$ ($E_{1/2}$ = 1.3 V) is observed, possibly the result of the higher ruthenium complex or supporting electrolyte concentration used for cyclic voltammetry compared to spectral analysis. A one step reaction is observed for the reaction of $[Ru(bpy)_2(CH_3CN)(NO_3)]^+$ ($E_{1/2}$ = 0.98 V) with acetonitrile to form $[Ru(bpy)_2(CH_3CN)_2]^{2+}$ ($E_{1/2}$ = 1.41 V).

In pure dichloromethane or acetone, $[Ru(bpy)_2(py)(NO_3)]^+$ is stable for days. However, $[Ru(bpy)_2(CH_3CN)(NO_3)]^+$ is reasonably stable in acetone but a significant amount of green oxo-bridged species is formed in a matter of hours in dichloromethane. Chloride ion substitution into $[Ru(bpy)_2(py)(H_2O)]^{2+}$ in acetone occurs in a reaction which is first-order in complex and zero-order in chloride ($k = 1.0 \times 10^{-3}$ s^{-1}).

DISCUSSION
The nitrato complexes $[Ru(bpy)_2(L)(X)]^+$ (L = py, CH_3CN ; X = NO_3) undergo relatively rapid ($t_{1/2} < 200$ min) ligand exchange, as shown in the following equation,

$$[Ru(bpy)_2(L)(NO_3)]^+ + 2L' \longrightarrow$$

$$[Ru(bpy)_2(L')_2]^{n+} + L + NO_3^-$$

$$[L = py, CH_3CN ; L' = Cl \ (n = 0);$$
$$L' = CH_3CN \ (n = 2)],$$
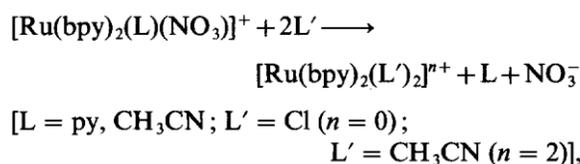
whereas, similar species (L = py ; X = Cl, NO_2, CF_3CO_2, p-$CH_3C_6H_4SO_3$) are unreactive, showing little to no reaction in 5 days. The spectral data and kinetic results are consistent with the mechanism shown in Scheme 1.

$$[Ru(bpy)_2(L)(NO_3)]^+ \underset{k_{-1}}{\overset{k_1}{\rightleftharpoons}} I + L \qquad (1)$$

$$I + L' \overset{k_2}{\longrightarrow} [Ru(bpy)_2(L')(NO_3)]^+ \qquad (2)$$

$$[Ru(bpy)_2(L')(NO_3)]^+ + L' \overset{k_3}{\longrightarrow}$$

$$[Ru(bpy)_2(L')_2]^{2+} + NO_3^-. \qquad (3)$$
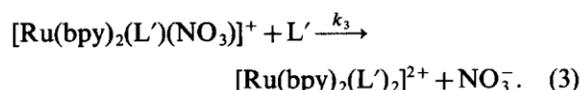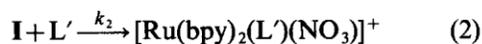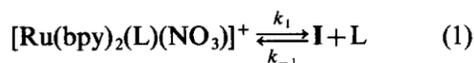
Scheme 1.

Reaction (1) represents reversible formation of a short-lived intermediate, I. No net reaction occurs for $[Ru(bpy)_2(py)(NO_3)]^+$ when L' is absent. For L = CH_3CN, I may provide a pathway for decomposition to oxo-bridged products as well as substitution. When L' is present, reaction (1) becomes rate-controlling as I reacts rapidly with L'. The rate of this reaction depends on the identity of L but very little on L'. For L = py, k_1 (L' = Cl) is 7.3×10^{-5} s^{-1} and k_1 (L' = CH_3CN) is 7.2×10^{-5} s^{-1}. For L = CH_3CN, k_1 is very fast. For L = py and L' = Cl, k_2 and k_3 are presumably greater than k_1, so only starting complex and final product are spectrally observable. For L = CH_3CN and L'= Cl, k_1 and k_2 are greater than k_3, so the intermediate, $Ru(bpy)_2(Cl)NO_3$, accumulates during the reaction.

For acetonitrile substitution (L' = CH_3CN), k_3 is slower than for chloride substitution, probably a reflection of the charge effect in low polarity solvent. In this case, steps (1) and (2) lead to no net reaction for L = CH_3CN. For L = py, steps (1) and (2) lead to the formation of $[Ru(bpy)_2(CH_3CN)(NO_3)]^+$, which then undergoes the same transformation as when this species is the starting material.

The question arises as to what feature of the nitrato ligand leads to such facile substitution of pyridine and acetonitrile in $[Ru(bpy)_2(L)(NO_3)]^+$. Since the spectral properties of $[Ru(bpy)_2(py) (NO_3)]^+$ are very similar to those of the other $[Ru(bpy)_2(py)(X)]^+$ complexes,[4] the electronic nature of the ruthenium centre in the ground state reactants appears to be similar. The rates of various reactions would be consistent with solvation of the nitrato ligand followed by anation. However, the products are not the same for the nitrato reaction as for reaction of the aquo complex. Thus, this reaction pathway can be ruled out.

Two features which distinguish nitrate from the other X ligands are its ability to act as a bidentate ligand and its behaviour as an oxidizing agent. Nitrate has been shown to be capable of oxidizing $[Ru(bpy)_2(py)(H_20)]^{2+}$ in aqueous acidic solution.[8] Thus, a short-lived ion-paired redox species, such as $[Ru(bpy)_2(L)(O)^{2+},NO_2^-]$, may be generated. Ion pairing is undoubtedly important in the low polarity solvents used. Following substitution by L', recombination of the oxo moiety with NO_2^- would lead to the net substitution observed, including the absence of oxidized products. Substitution reactions carried out by redox intermediates are quite common in coordination chemistry.[9] Many are characterized by unusual kinetic features,[2c,9] but the net process involves unusually rapid substitution. The lack of influence by reducing agents and what appears to be a reasonably robust' coordination sphere in $[Ru(bpy)_2(py)(O)]^{2+}$ would argue against this mechanism.

Although nitrite and trifluoroacetate may behave as bidentate ligands, the tendency of these and other X ligands to do so is less than that of nitrate." With the relatively small bite angle of the nitrato ligand, the monodentate nitrato ligand of $[Ru(bpy)_2(py)(NO_3)]^+$ may bind to produce a pseudo-seven coordinate transition state. Loss of L and formation of a bidentate nitrato ligand leads to a six coordinate intermediate, I. The intermediate would then accept L' to generate $[Ru(bpy)_2(L')(NO_3)]^+$. A strongly ion-paired chloride or an acetonitrile from the solvent cage is readily available for coordination. Further substitution of the nitrato ligand by L' would give the final product. Other examples[11,12] of nitrate acceleration of *cis* ligand substitution have been reported for chromium(III)-amine and cobalt(III)-amine and -oxalato complexes. It is not obvious in all cases that a nitrato ligand in the coordination sphere of the metal is the active species.[12] When coordinated nitrate is thought to be present, a chelating mechanism similar to that proposed for I in Scheme 1 was proposed. In the present case, there appears to be no doubt that nitrate is coordinated during L substitution, since it remains in the coordination sphere after L substitution, and the presence of coordinated nitrate accelerates the rate of L substitution.

In summary, the nitrato ligand induces significant labilization of the ligands *cis* to it in *cis*-[Ru(bpy)$_2$(L)(NO$_3$)]$^+$ complexes. A three step mechanism, involving an intermediate which is extremely susceptible to ligand addition, leads to facile substitution of the nitrato ligand and its neighbour.

Notes
† Spectral analyses suggest that all ruthenium complexes involved are in the *cis* configuration.
‡ Reduction potentials differ by small amounts from literature values due to differences in solvent and /or added electrolyte.

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