Triethyl phosphite as a ligand on Ru(III). Synthesis, characterization and properties of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$

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Abstract

The complex ion *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ was obtained through electrochemical and chemical oxidation of the corresponding Ru(II) complex ion. The compound *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ was isolated and characterized by means of micro-analysis, cyclic voltammetry, UV–Vis and electron paramagnetic resonance spectroscopy. The ion *trans*$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ decomposes in aqueous solution according to $4Ru(III) \Rightarrow 3Ru(II) + Ru(VI)$. The decay rate of the Ru(III) complex ion concentration is inversely proportional to the hydrogen ion solution concentration ($C_{H^+} = 1.0 \times 10^{-1}$ M, $k_{obs} = 4 \times 10^{-5}$ s^{-1}; $C_{H^+} = 10^{-12}$ M, $k_{obs} = 3.3$ s^{-1}; 25 °C, $\mu = 0.3$ $NaCF_3COO$).

Introduction

We have investigated ruthenium(II) tetraamines as models for the synthesis, characterization and substitution reactions of the monophosphite complex ions, *trans*-$Ru[(NH_3)_4P(OR)_3(H_2O)]^{2+}$ [1–6]. The results of these investigations provide knowledge of both the degree of $Ru(II) \Rightarrow P(III)$ backbonding and the effects of this strong interaction on the chemical properties of the phosphane and metal centers.

In the present work, our goal is to extend the investigation to a d^5 low spin system, the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ ion, where the metal ⇒ ligand backbonding is less extensive [1–6].

The substitution inertness [7, 8] of the monophosphite complexes of Ru(III) and Ru(II) provides a unique opportunity to study the changes in the chemical reactivity of the ligand and the metal centers just by changing the oxidation state of the metal. Besides providing knowledge of the basic chemistry of such systems, the possibility of establishing a new synthetic route for ruthenium complexes, similar to those described for sulfite [9] was a further incentive to undertake this work.

As part of a systematic study on the basic chemistry of phosphite ligands we report here the synthesis and some chemical properties of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ ion.

Experimental

Chemicals and reagents

The solvents employed were freshly distilled before use. Doubly distilled water was used throughout. All chemical reagents were of analytical grade purity.

Synthesis of the ruthenium compounds, $[Ru(NH_3)_5Cl]\ Cl_2$, $[Ru(NH_3)_5(H_2O)]\ (PF_6)_2$, *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](CF_3SO_3)_2$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]\ (CF_3SO_3)_2$ were done according to procedures already described [1–5].

trans-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$

A sample of 75–100 mg of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ salt was dissolved in 30–35 ml of degassed 10^{-1} M CF_3SO_3H solution. Electrochemical oxidation was performed at +0.70 V versus the SCE. When the oxidation was completed, the water was evaporated; the solid was filtered off, washed with two portions (3 ml) of cold degassed ethanol and three portions (6 ml) of cold degassed dry ether. The white solid obtained was unstable on storage even under vacuum conditions and in the absence of light, so it was always

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used within a two-day period. The yield was always better than 90%.

The analysis for *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ was performed through single sweep voltammetry and by spectrophotometry using plots of i_{p_a} versus C_{Ru} and absorbance at 365 nm versus C_{Ru}, respectively. The calibration plots were established employing *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ solutions of known concentration [1]. The MLCT band of the *trans*-$[Ru(NH_3)_4P(OEt)_3(isn)]^{2+}$ ion at 365 nm ($\epsilon = 4.8 \times 10^3$ M^{-1} cm^{-1}) [1] is more sensitive than the band at 316 nm ($\epsilon = 6.5 \times 10^2$ M^{-1} cm^{-1}) and to the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ species, and was used for the spectrophotometric measurements. In this case, the measurements were performed in the presence of 0.70 M isonicotinamide (isn) and 1.0×10^{-2} M CF_3SO_3H. The *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ solutions, in 1.0×10^{-2} M CF_3SO_3H, were treated with Zn(Hg) before the electrochemical measurements or the addition of isonicotinamide. The analytical results for the content of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ in the isolated solids, are $99.5 \pm 0.3\%$ (spectrophotometric data) and $99.6 \pm 0.4\%$ (voltammetric data) for three independent preparations.

Apparatus and techniques

Following standard procedures [10], manipulations were carried out in the absence of oxygen, under a nitrogen or argon atmosphere. All the complexes were stored under vacuum and protected from light. The purity of the complexes was always checked by means of cyclic voltammetry and spectrophotometric measurements.

Ultraviolet and visible spectra were recorded either on a Cary model 14 or a Varian Techtron model 635 spectrophotometer.

During the experiments the temperature was controlled within ±0.2 °C.

EPR spectra of powdered samples and solutions were measured in a quartz tube at the X band on a Varian E-109 spectrometer equipped with the multipurpose E-231 cavity and the Varian E-257 temperature accessory. The experimental conditions were: modulation frequency, 100 kHz; microwave power, 10 mW, modulation amplitude, 5 Gauss; and a sample temperature of -150 ± 5 °C.

The cyclic voltammetric measurements and controlled potential electrolysis experiments were performed on a multifunctional system from Princeton Applied Research, potentiostat/galvanostat model 173, universal programmer 175, R.E. 0074-X-Y recorder and coulometer 379. A glassy carbon electrode (area of 0.51 cm^2), platinum wire and SCE were used in cyclic voltammetric experiments as the working, auxiliary and reference electrodes, respectively. During the electrolysis, a platinum net (area of 13.6 cm^2) or a gold electrode (area of 1.0 cm^2) was used as the working electrode.

The fast kinetics experiments were performed on an Aminco Morrow stopped-flow apparatus equipped with a Tektronix R5103M oscilloscope.

Kinetic measurements

Deaerated solutions of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ with pH and ionic strength previously adjusted were prepared in a flask. After 1–2 min, the solution was transferred rapidly through a teflon tube by gas pressure to a 1 cm path length quartz cell sealed with a serum cap. The reaction was monitored following the changes in absorbance at 316 and 325 nm, respectively.

The appearance of the component absorbing at $\lambda_{max} = 316$ nm follows simple first-order kinetics. Good agreement was observed for first-order rate constants determined graphically from plots of $\log(A_\infty - A_t)$ versus t, for absorbance data obtained at 316 and 325 nm. When the solution hydrogen ion concentration was lower than 10^{-8} M, an Aminco-Morrow stopped-flow apparatus was used for monitoring the absorbance changes.

Results and discussion

In acidic media, the complex ion *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ undergoes a one electron oxidation process by controlled potential electrolysis or by reaction with chemical oxidizing reagents.

The controlled potential electrolysis of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_2$ solution, at +0.70 V versus SCE, has been followed through changes in the electronic and voltammetric spectra. As shown in Fig. 1, the final product exhibits absorption at 285 nm ($\epsilon = 8.1 \pm 0.3 \times 10^2$ M^{-1} cm^{-1}). An isosbestic point is detected at 309 nm. Neglecting the differences of the diffusion coefficients for the Ru(II) and Ru(III) species ($D_{Ru(II)} = 6.1 \times 10^{-6}$ cm^2 s^{-1}, $D_{Ru(III)} = 3.7 \times 10^{-6}$ cm^2 s^{-1}), the voltammetric spectra of the solutions are the same, prior to and after the electrolysis.

The electronic and voltammetric data indicate that the treatment of the Ru(III) complexes solution with zinc amalgam regenerates the original Ru(II) complex ion quantitatively. No oxidation of the coordinate phosphite molecule was observed, even when the oxidation was performed with ceric ions, bromine or hydrogen peroxide, although the high reactivity

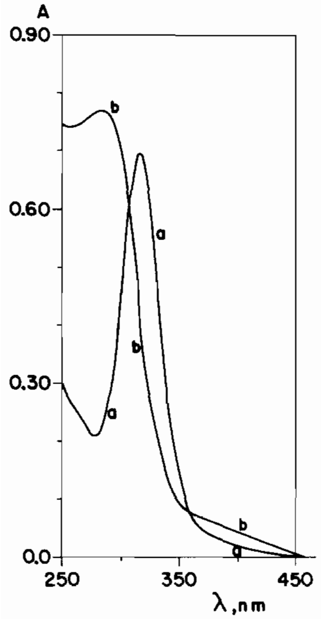

Fig. 1. Changes in electronic spectra associated with the oxidation in aqueous solutions of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$: a, before oxidation; b, after oxidation is completed. $C_{Ru}=9.5\times10^{-4}$ M; $\mu=0.10$ $NaCF_3COO$; pH = 2.4.

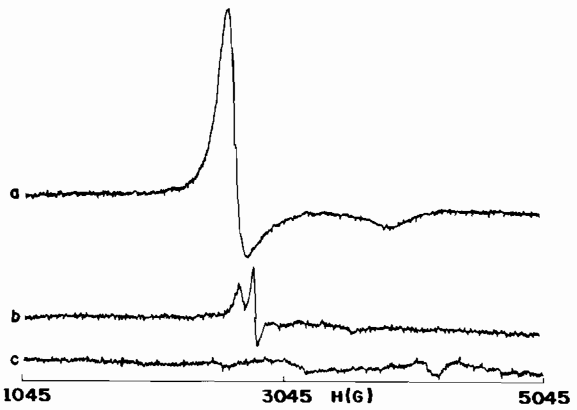

Fig. 2. EPR spectra of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]$-$(CF_3SO_3)_3$ solutions as function of hydrogen ion concentration: a, $C_{H^+}=10^{-1}$ M; b, $C_{H^+}=10^{-11}$ M; c, b after reacidification to $C_{H^+}=1.0\times10^{-3}$ M. $\mu=0.10$ $NaCF_3COO$; gain 8×10^3; time constant, 0.032 s; scan time, 2 min; scan range, 4000 gauss; $t=-150\pm5$ °C.

of the free phosphite molecules is well known [11]. This chemical behaviour of triethyl phosphite when coordinated to the ruthenium center is remarkable, reflecting the effect of the metal center on the electron density at the phosphorus atom [1, 6].

The EPR spectra of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ compound are identical both in acidic solutions and in powder form, see Fig. 2. The experimental values of $g_\perp$ and $g_\parallel$ are 2.429 and 1.675, respectively, at −150 °C, which are similar to those of other Ru(III) complexes [12–18]. The features of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ ion EPR spectra are consistent with axial symmetry C_{4v}. The complex ion *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ also belongs to the C_{4v} point group [2]. Therefore corroborating the electronic and the voltammetric data, the EPR spectra strongly suggest that the coordination sphere remained unchanged during the oxidation process.

Since none of the ligands on the coordination sphere are π-donor ligands, a destabilization of the d_{xz} and d_{yz} orbitals with respect to d_{xy} is expected [17–19]. No superhyperfine structure was observed in any of the recorded EPR spectra.

Assuming $\Delta_\parallel=35.088$ cm^{-1} and $\lambda=1000$ cm^{-1} [13], $g_\parallel$ was estimated as being 1.774 using the expression

$$g_\parallel=2.0023\left(1-\frac{4\lambda}{\Delta_\parallel}\right)$$

The $g_\parallel$ value is quite different from the experimental value of 1.675 which corresponds to a crystal field energy of 24.470 cm^{-1}.

A very careful analysis of the spectrum of Fig. 1 leads to the identification of an absorption band at 390±5 nm (ϵ $9\pm1\times10$ M^{-1} cm^{-1}) compatible with the value of 408 nm calculated from the experimental $g_\parallel$ value. Therefore it is unlikely that the band at 285 nm is associated with a d–d transition, being instead probably of a charge transfer character.

From the experimental $g_\perp$ value of 2.429 and the expression $g_\perp=2.0023$ $(1-\lambda/\Delta_\perp)$, $\Delta_\perp$ was estimated as 4681 cm^{-1}. As predicted by the theory [13], this transition was not observed in the 200–800 nm region of the spectrum.

The instability of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ ion in aqueous solution is quite pH dependent. With addition of sodium hydroxide until the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ solution reaches a pH ≅ 11, changes are observed in the EPR, electronic and voltammetric spectra. The changes in intensities and number of EPR lines suggest that not only the concentration of the paramagnetic species, but also their structures, are altered. As shown in Fig. 2, at pH ≅ 11, not more than 10% of the original EPR signal remains.

The electronic spectrum of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ solution at $C_{H^+}<10^{-8}$ M shows a decrease in absorbance at 285 nm with a simultaneous increase in absorbance at 316 nm.

Cyclic voltammograms at $C_{H^+}<10^{-8}$ M become irreversible with an increase in the anodic current with respect to the cathodic component (Fig. 3).

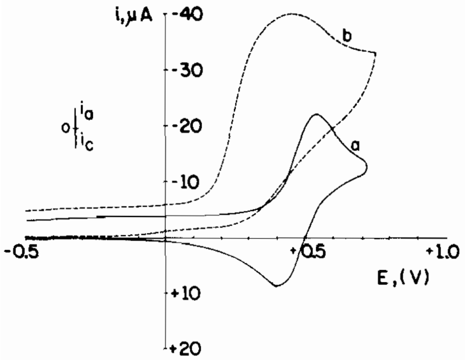

Fig. 3. Changes in the voltammetric spectra of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ solutions as function of the hydrogen ion solution concentration: a, $C_{H^+}=1.0\times10^{-3}$ M; b, $C_{H^+}=1.0\times10^{-11}$. $C_{Ru(II)}=1.0\times10^{-3}$ M; $\mu=0.10$ $NaCF_3COO$; 25 °C; scan rate = 220 mV s^{-1}.

When the solution hydrogen ion concentration is 1×10^{-11} M, the cathodic component cannot be observed and the anodic current is about four times the value observed for the same ruthenium concentration in acidic medium, $C_{H^+}=1.0\times10^{-3}$ M. Exhaustive controlled potencial coulometry of 1.00×10^{-3} *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ ions in aqueous alkaline solutions, $C_{H^+}\cong1.0\times10^{-11}$ M, are consistent with a four electron oxidation of the Ru(II) center.

The EPR and electronic spectra of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](CF_3SO_3)_3$ in solution are not regenerated by reacidification. However, the electronic spectra of the reacidified solutions are similar to those of the solution containing the original *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ complex ion. From absorbance measurements at 316 nm, or after the addition of isonicotinamide and measuring the amount of *trans*-$[Ru(NH_3)_4P(OEt)_3isn]^{2+}$ complex formed, it was possible to estimate that about 74–77% of the original Ru(III) complex was in the form of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ complex ion. Species such as *trans*-$[Ru(NH_3)_4(isn)_2]^{2+}$ and *cis*-$[Ru(NH_3)_3P(OEt)_3(isn)_2]^{2+}$ are not present in these solutions as judged by the electronic spectra. The treatment with zinc amalgam, after the solution reacidification, increased to about 85–91% the regeneration of the Ru(II) monophosphite complex ion, *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$.

The voltammetric spectrum of the reacidification solution shows the presence of 89–92% of the starting ruthenium monophosphite complex. No other electroactive species other than the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+/2+}$ couple are detected in the range of −0.8 to 1.2 V versus SCE. As judged from the electronic and voltammetric spectra data about 10% of the starting *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ complex ion is converted into other unidentified ruthenium species.

The absorbance increase rate at 316 nm was studied as a function of the hydrogen ion concentration. The plot of k_{obs} or log k_{obs} versus pH is similar to the profile for acid–base titration curves (see Fig. 4) suggesting that an acid–base equilibrium is involved [20–22].

Assuming tentatively the scheme

$$AH \overset{K_{AH}}{\rightleftharpoons} A^- + H^+$$

$$A^- \xrightarrow{k_A} \text{products}$$

$$AH \xrightarrow{k_{AH}} \text{products}$$

and that $k_{obs}=K_{AH}$ when $[H^+]\gg K_{AH}$ and $k_{obs}=k_A$, with $[H^+]\ll K_{AH}$ it is possible to estimate the orders of magnitude for k_A and k_{AH}, as being 3 s^{-1} and 4×10^{-7} s^{-1}, respectively. Attempts to estimate K_{AH} through the equation

$$k_{obs}=\frac{k_{AH}-k_A}{1+K_{AH}[H^+]^{-1}}+k_A$$

led to scattered values in the 10^{-8} to 10^{-11} range.

Any value of K_{AH} in the range 10^{-8} to 10^{-11} is considered too high for the dissociation constant of the acid *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$. The pK_a for the $[Ru(NH_3)_5(H_2O)]^{3+}$ species [7, 8] is 4.5, and since little backbonding is operative in the Ru(III)–P(III) bond [1–6], the pK_a for the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ acid should be in the 3.5–5.5 range. Therefore, as judged from the kinetic experiments, probably further deprotonation occurs from a *trans*-$[Ru(NH_3)_4P(OEt)_3(OH)]^{2+}$ complex ion when the solution hydrogen ion concentration is smaller than 10^{-6} M.

In agreement with the kinetic data, the experiments on stoichiometry strongly suggest a disproportion-

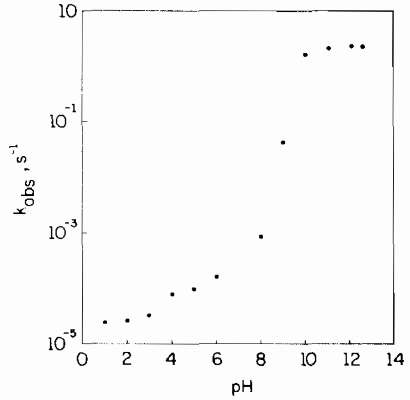

Fig. 4. The pH dependence of the rate k_{obs} for *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ decay. $\mu=0.10$ $NaCF_3COO$; $t=25.0\pm0.2$ °C.

ation reaction yielding Ru(II) and Ru(VI) as the major products.

$$4Ru(III) \Rightarrow 3Ru(II) + Ru(VI)$$

In the monophosphite complexes, in alkaline solutions, the Ru(II) and Ru(VI) centers are expected to be more stable than Ru(III). The phosphite strongly stabilizes [1, 6] Ru(II) by $4d_\pi \Rightarrow 3d_\pi$ back-bonding, and O^{2-} and NH_2^- will stabilize Ru(IV), (V) or (VI) through $3p_\pi \Rightarrow 4d_\pi$ interactions [23–27].

The disproportionation reaction above also provides an explanation for the voltammetric spectrum of the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+/2+}$ ions in alkaline solution, see Fig. 3. The Ru(II) oxidized at the electrode surface to Ru(III) rapidly disproportionates generating Ru(VI) and more Ru(II). Therefore, an increase in the current correspondent to the anodic peak, $Ru(II) \Rightarrow Ru(III) + e^-$, is observed. The cathodic segment is not detected on the reversal sweep since the ruthenium centers at higher oxidation states are not reduced in the range of potential investigated (-0.80 to $+1.2$ V versus SCE).

As pointed out before, about 90% of the starting *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ was recovered as the corresponding Ru(II) complex, after the treatment with zinc amalgam. This amount of ruthenium corresponds mainly to the species which do not undergo the loss of protons from the NH_3 ligands.

If any deprotonation occurred at the NH_3 ligands, because of the strong imido group *trans* labilizing effect and *trans* influence [20–23], some loss of ammonia ligand should be observed and species such as *trans*-$[Ru(NH_3)_3P(OEt)_3(H_2O)_2]^{2+}$ should be detected as products.

It is difficult at the moment to offer a clear explanation about the nature of the remaining 10% ruthenium species not recovered as *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ ions. These species probably contain the metal center in higher oxidation states. These compounds are probably ammonia deficient, and the ruthenium in higher oxidation states would likely exist in solution mainly as binuclear or trinuclear species containing bridges of oxo ligands [23–27].

The higher stability of these species, due to the oxo formation and strong $3d_\pi$–$4d_\pi$ interaction [23, 27] could account for our failure to detect these ruthenium species spectrophotometrically, after the treatment with zinc amalgam and isonicotinamide, or through the voltammetric spectra. The strong electron delocalization between metal centers bridged through oxygen atoms could explain the EPR spectrum after reacidification.

The chemistry of the higher oxidation state systems is complex and remains an open subject [24–28]. It is claimed that the oxo-species of Ru(VI) and Ru(V) are able to oxidize water [27, 29–33] and the oxo-species of Ru(VI) are of great interest as oxo-transfer reagents [27, 29–34]. Preliminary experiments show that *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ in solution is able to oxidize pyrazine and isonicotinamide. These facts are additional incentives to pursue work aiming at a better characterization of the species involved in the *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{3+}$ ion disproportionation reaction.

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