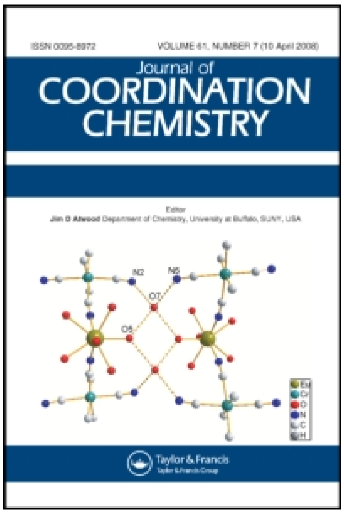

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TETRAETHYLPHYROPHOSPHITE AS A BRIDGING LIGAND IN A BIMETALLIC RUTHENIUM(II) - RUTHENIUM(II) COMPLEX

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The complex μ-TEPP-*trans-bis*$[P(OEt)_3Ru(NH_3)_4]_2(PF_6)_4$ has been prepared and characterized by microanalysis, vibrational and electronic spectroscopy (λ_{max} = 299 nm, $\varepsilon = 6.4 \times 10^2$ M^{-1} cm^{-1}; λ_{max} = 262 nm, $\varepsilon = 8.6 \times 10^2$ M^{-1} cm^{-1}), and cyclic voltammetry ($E^{\circ\prime} = +0.64$ V versus S.C.E., 25°, μ = 0.10 M $NaCf_3COO$, $C_H+ = 1 \times 10^{-3}$ M). In aqueous solutions, ($[H^+] > 1 \times 10^{-4}$ M), the binuclear species undergoes hydrolysis yielding the mononuclear species *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ with a specific rate constant of 2.4×10^{-5} sec^{-1} at 25°; $\Delta H^{\neq} = 84.5$ kJ mol^{-1}; $\Delta S^{\neq} = -49.4$ J mol^{-1} K^{-1}.

INTRODUCTION

During the investigation of the properties of ruthenium(II) tetraaminephosphite complexes we have described the synthesis and characterization of several mononuclear species.[1,2] The aquation[3] of these compounds, the "trans effect" and "trans influence" of the phosphorus ligands on these complexes and an extensive study of substitution reactions of the compound *trans.*$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ have been reported earlier.[1,4]

Since we consider the substitution reactions of these mononuclear species to be well-understood, we are now focussing our attention on the oxidation reactions of the mono and binuclear species. We present here the synthesis, characterization and properties of the first symmetrical binuclear species in which two ruthenium centers are bridged by a bidentate phosphorus ligand, tetraethylpyrophosphite.

EXPERIMENTAL

Chemicals and Reagents

All chemicals were of the highest quality available. Triethylphosphite ($P(OEt)_3$) and tetraethylpyrophosphite (TEPP) were purchased from Aldrich and used as supplied.

Ruthenium Complexes

$[Ru(NH_3)_5Cl]Cl_2$ and $[Ru(NH_3)_5(H_2O)](PF_6)_2$ were prepared following well known procedures.[5,6] *Trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$ was prepared from $[Ru(NH_3)_5(H_2O)](PF_6)_2$ 0.2 g) and triethylphosphite[1] (8 cm^3) by reaction in 10 cm^3 of acetone for 30 minutes in the absence of oxygen. The excess solvent was evaporated and the solid separated from the yellow liquid by adding ether (free from peroxide).

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Trans-$[Ru(NH_3)_4P(OEt)_3(H_2O)](PF_6)_2$: 0.5 g of *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2](PF_6)_2$ was dissolved in 110-130 cm^3 of 0.01 M trifluormethanesulfonic acid which had been previously degassed. After 72-76 hours under an argon atmosphere, the eliminated water was removed by evaporation.[1,2] The aquo-complex is collected as a yellow solid and used immediately in the synthesis of the μ-tetraethylpyrophosphite-*trans-bis*[(triethylphosphite tetraammine diruthenium(II)]hexafluorphosphate, μ-TEPP-*trans-bis*$[P(OEt)_3Ru(NH_3)_4]_2(PF_6)_4$.

μ-TEPP-*trans-bis*$[P(OEt)_3Ru(NH_3)_4]_2(PF_6)_4$: 0.3 g of *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)](PF_6)_2$ was dissolved in a minimum volume of degassed ethanol which had been previously dried over molecular sieves. Under continuous argon flow and absence of light 1.5 cm^3 of tetraethylpyrophosphite ligand (degassed) was added to the ethanolic solution. After 25-30 min. the ethanol was removed by evaporation.

The separation of the ruthenium binuclear complex from the excess of ligand is achieved by adding 150-200 cm^3 of ether. The precipitate obtained was filtered and washed with ether, and finally dried and stored under vacuum and protected from light. *Anal.;* Calcd for μ-TEPP-*trans-bis*$[P(OEt)_3Ru(NH_3)_4]_2(PF_6)_4$: C, 1.32%; H, 4.94%; N, 0.53%. Found: c, 1.40%, H, 5.14%; N, 0.53%. Yield better than 80%. Microanalyses were performed by the staff of the Microanalytical Laboratory of Instituto de Quimica da Universidade de São Paulo.

As judged from the electronic and voltammetric spectra, the binuclear comples does not exhibit any significant decomposition over a three-week period.

Methods

Manipulations were carried out in the absence of oxygen. All the complexes were stored in vacuum and protected from light.

Electronic spectra were recorded with a Varian Techtron model 635 spectrophotometer. The I.R. spectra were recorded using a Perkin Elmer 1320 spectrophotometer.

Cyclic voltammograms were obtained with a Princeton Applied Research (PAR) model 173 potentiostat/galvanostat, 175 Universal Programmer and a R.E. 0074-X-Y recorder. Glassy Carbon, Platinum wire and a S.C.E. were used as working, auxiliary and reference electrodes, respectively.

The kinetics of conversion of the binuclear species to *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ ions were studied by dissolving 12-14 mg of the complex in 15 cm^3 of a 0.10 M solution of $NaCF_3COO$ (at the desired hydrogen ion concentration) and transfering the solution rapidly through teflon tubing to a 1 cm path length quartz cell seated with a serum cap. The reaction was monitored following changes in absorbance at 316 nm. An isosbestic point at 298 nm was evident for more than four half-lives. First-order rate constants were determined graphically from plots of log $(A_\infty - A_t)$ versus t. The enthalpy of activation, $\Delta H^{\neq}$ was calculated following the usual procedure[7] from the slope of log k/T versus 1/T plots, and the entropy of activation, $\Delta S^{\neq}$, at 25°C, from the usual equation. During the experiments the temperature was controlled within ± 0.1°

RESULTS AND DISCUSSION

The infrared spectrum of the binuclear complex in the range 4000 - 600 cm^{-1} shows superposition of the bands present in tetraethylpyrophosphite plus the ruthenium ammine group, and is very similar[2] to that of the *trans*-$[Ru(NH_3)_4(P(OEt)_{32}](PF_6)_2$ complex. Aqueous solutions of the complex μ-tetraethylpyrophosphite-*trans-bis* [trietylphosphitetetraamine ruthenium(II)], exhibit two absorption bands at λ_{max}

$= 299$ nm(sh) ($\varepsilon = 6.4 \times 10^2$ M^{-1} cm^{-1}, ${}^1A_{1g} \longrightarrow {}^1B_{2g}, {}^1E_g$) and $\lambda_{max} = 262$ nm(sh) ($\varepsilon = 8.6 \times 10^2$ M^{-1} cm^{-1}, ${}^1A_{1g} \longrightarrow {}^1A_{1g}, {}^1E_g$). This behaviour is consistent with D_{4h} symmetry of the binuclear compelx.[8]

Investigation of the binuclear complex by cyclic voltammetry gave a single, well defined wave for the Ru(III)/Ru(II) couple in the title complex. The electrochemical process in acidic medium is reversible in the sense that the oxidation and reduction wave currents are equal.[9] The peak to peak separation, 63 mV, is the same observed for the *trans.* $[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ and *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ systems which are also known to be reversible. The formal reduction potential, E°′, for the Ru(III)/Ru(II) couple in the title complex is + 0.64 ± 0.01 V versus S.C.E. at 25°, $\mu = 0.10$ M $NaCF_3COO$, $C_{H+} = 1 \times 10^{-3}$ M CF_3COOH. Based on E°′ data,[1-3] the π acidity of TEPP is about the same as $P(OEt)_3$.

The intensity of the anodic and cathodic currents in the binuclear complex suggests that the two symmetric ruthenium centers undergo electron transfer at the same potential. The complex ion *trans*-$[Ru(NH_3)_4(P(OEt)_3)_2]^{2+}$ is not the true monomer of the *trans*-$[P(OEt)_3(Ru(NH_3)_4)_2P(OEt)_2OP(OEt)_3]^{2+}$ ion, but can be considered as a very good model.

The bisphosphite complex and the binuclear species undergo electron transfer at E°′ = +0.642 and +0.650 V, respectively. These values are very close, and experimentally very difficult to distinguish since the experimental error is estimated to be ±10 mV. These observations suggest that very weak or no interaction is taking place between the two metal centers in the binuclear complex.[10] Departure from reversibility is observed if the hydrogen ion concentration of the medium is smaller than 10^{-6} M. At $C_{H+} < 10^{-10}$ M, only the anodic peak is observed. This behaviour is now under investigation.

The binuclear species is fairly stable in aqueous solutions. It is slowly converted into the monophosphite complex ion *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$. This conversion is quantitative at least as far as the electronic and voltammetric spectra are concerned. The kinetic data for this reaction are summarized in Table I.

Although no experimental data for the hydrolysis of tetraethylpyrophosphite (TEPP) are available it is expected that it should react with water following the same pattern as other phosphites. Trialkylphosphites (methyl to octyl) undergo hydrolysis in acid media with half-lives not greater than 1 minute but are reasonably stable in alkaline media.[3] These differences of stability account for the changes observed in specific rates (Table I) for the reaction in acid and base.

For the hydrolysis of the binuclear complex two possibilities could be envisaged. In one scheme we first assume a binuclear complex dissociation followed by hydrolysis of

TABLE I
Kinetic Data for the Reaction

$$[P(OEt)_3Ru(NH_3)_4P(OEt)_2OP(OEt)_2Ru(NH_3)_4P(OEt)_3]^{4+} + H_2O \xrightarrow[k_1]{} 2[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+} + H(O)P(OEt)_2$$

C_{H+}/M	k_1/sec^{-1}	Temp.
1.0‡	2.0×10^{-5}	25°
1.0×10^{-1}	2.0×10^{-5}	25°
1.0×10^{-2}	2.4×10^{-5}	25°
1.0×10^{-3}	2.3×10^{-5}	25°
1.0×10^{-4}	2.1×10^{-5}	25°
1.0×10^{-6}	1.7×10^{-5}	25°
1.0×10^{-9}	1.8×10^{-7}	25°
1.0×10^{-3}	7.7×10^{-5}	35°
1.0×10^{-4}	8.2×10^{-5}	35°
1.0×10^{-3}	2.4×10^{-4}	45°
1.0×10^{-6}	2.3×10^{-4}	45°

†$\mu = 0.1$ M ($NaCf_3COO$), $C_{Ru(II)} = 7 \times 10^{-4}$ M. ‡$\mu = 1.0$ M (CF_3COOH).

coordinated TEPP by attack at the P-O-P bond with subsequent aquation of the coordinated dialkyl phosphite molecule as shown below.

$$[(P(OEt)_3(NH_3)_4Ru)_2TEPP]^{4+} \xrightarrow[\text{slow}]{} [P(OEt)_3Ru(NH_3)_4(H_2O)]^{2+} + [P(OEt)_3Ru(NH_3)_4TEPP]^{2+}$$

$$[P(OEt)_3Ru(NH_3)_4TEPP]^{2+} + H_2O \xrightarrow[\text{fast}]{H^+} [P(OEt)_3Ru(NH_3)_4POH(OEt)_2] + POH(OEt)_2$$

$$[P(OEt)_3Ru(NH_3)_4POH(OEt)_2]^{2+} + H_2O \xrightarrow[\text{fast}]{H^+} P(OH)(OEt)_2 + [P(OEt)_3Ru(NH_3)_4(H_2O)]^{2+}$$

Another possiblity involves the P-O-P bond breaking in the binuclear complex. followed by the aquation of the coordinated $P(OH)(OEt)_2$ ligand in the mononuclear complex *trans*-$[P(OEt)_3Ru(NH_3)_4P(OH)(OEt)_3]^{2+}$.

Direct evidence favouring one of these two possibilities has proved difficult to obtain. For several bisphosphite complexes the conversion into the corresponding monophosphite species involves the dissociation of the coordinated phosphite followed by the hydrolysis of the free ligand.[2,3]

The activation parameters, $\Delta S^{\neq}$ and $\Delta H^{\neq}$ are -49.4 J K^{-1} mol^{-1} and 84.5 kJ mol^{-1}, respectively. The data fit very well on an isokinetic[3] plot for the aquation of several complexes of the *trans*-$[Ru(NH_3)_4P(OR_1)_3P(OR_2)_3]$ type, where $R_1 = R_2$ or $R_1 \neq R_2$, (Fig. 1). Thus we conclude that the same mechanism is operative for all these complexes.

The reactivity of free trialkylphosphite molecules toward hydrolysis and oxidation is explained by the favourable energy balance during $P = O$ bond formation.[11] However when coordinated to the Ru(II) centre, the phosphites are quite resistant to hydrolysis and oxidation. This increase in stability has been explained[12] on the basis of the relative stabilities of $4d_{\pi}(Ru) \ldots 3d_{\pi}(P)$ and $3d_{\pi}(P) \ldots 2p_{\pi}(O)$ bonds. The Ru(II) center at one corner of the phosphorus tetrahedron will serve to stabilize the ligand. Therefore, the TEPP molecule, as long as it has the two phosphorus linkages to the ruthenium(II)

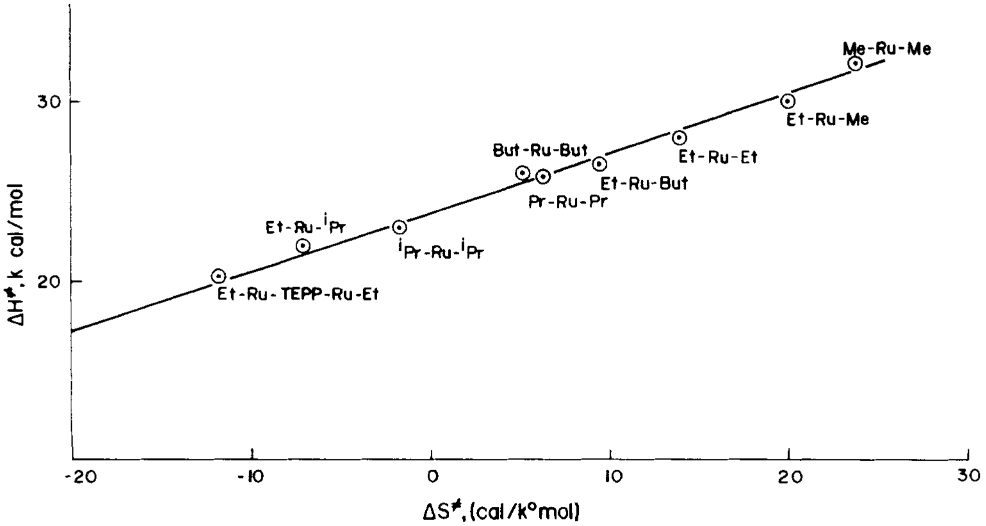

FIGURE 1 Isokinetic plot for the aquation of phosphite complexes of Ru(II).

centers is expected to be stable. However, since the other phosphorus is not bridging, this will exhibit the same reactivity associated with the hydrolytic instability characteristic of the P-O-P linkage.[11]

The above considerations suggest that the breaking of the Ru-P bond is the rate-determining step of the reaction. Since the complex *trans*-$[Ru(NH_3)_4P(OEt)_3(H_2O)]^{2+}$ is the only ruthenium species detected in solution after the binuclear complex is split, the breaking of the Ru-P bond should occur selectively at the Ru-TEPP linkage.

Work on electron transfer reactions of binuclear complexes containing phosphorus molecules as bridging ligands is in progress in our laboratory and results will be reported later.

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