# The Synthesis of an Aqua *trans*-Diphosphine Complex of Ruthenium: Crystal Structure of *trans*-$[Ru(H_2O)(PEt_3)_2(trpy)](ClO_4)_2 \cdot 3H_2O$

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## Abstract

The complexes *cis*- and *trans*-$[Ru(Cl)_2(PEt_3)(trpy)]$, *trans*-$[Ru(Cl)(PEt_3)_2(trpy)](Cl)$ and $[Ru(L)(PEt_3)_2(trpy)](ClO_4)_x$ (trpy = 2,2′,2″-terpyridine; L = $NO_2$, NO, $OH_2$; $x = 1-3$) were prepared. A novel synthetic strategy was employed to form the aqua *trans*-diphosphine complex because of the difficulty of forming it via a direct pathway. Characterization by electronic spectroscopy, electrochemistry and elemental analysis was conducted. The species $[Ru(H_2O)(PEt_3)_2(trpy)](ClO_4)_2 \cdot 3H_2O$ was further characterized by an X-ray structural analysis and is the first aqua *trans*-diphosphine complex of ruthenium to be synthesized. The complex $[Ru(H_2O)(PEt_3)_2(trpy)](ClO_4)_2 \cdot 3H_2O$ crystallized in the centrosymmetric monoclinic space group $P2_1/c$ with $a = 9.886(5)$, $b = 19.289(7)$, $c = 20.255(6)$ Å, $\beta = 92.88(3)^\circ$ and $Z = 4$. Diffraction data were collected on a Syntex $P2_1$ automated diffractometer and the structure refined to $R_F = 8.8\%$ for all 3407 reflections ($R_F = 7.5\%$ for those 2771 data with $I > 3\sigma(I)$). The structure contains a disordered $PEt_3$ ligand, highly librating $ClO_4^-$ ions and (possibly) a less than unit occupancy for certain $H_2O$ molecules of solvation. The $[Ru(H_2O)(PEt_3)_2(trpy)]^{2+}$ cation has the trpy ligand in *mer* configuration and mutually *trans* $PEt_3$ ligands. Metal–ligand distances are Ru–N = 2.091(9), 1.952(9), 2.087(8) Å; Ru–$PEt_3$ = 2.405(3), 2.411(4) Å; Ru–$H_2O$ = 2.218(4) Å.

## Introduction

We have reported the synthesis and characterization of a family of ruthenium complexes which utilize phosphine ligands, namely $[Ru(bpy)_2(O)(PR_3)]^{2+}$ and $[Ru(bpy)(biq)(O)(PR_3)]^{2+}$ (where bpy = 2,2′-bipyridyl, $PR_3$ = phosphine ligand, biq = 2,2′-biquinoline) [1, 2]. The presence of the phosphine ligand, *cis* to the oxo ligand, provides a means of affecting the reactivity of the (oxo)ruthenium center. For example, the phosphine ligands affect the rates of alcohol oxidation by (oxo)(phosphine)ruthenium complexes through a novel hydrophobic effect [3] and the presence of a phosphine ligand in the coordination sphere of (aqua)ruthenium complexes causes the ruthenium complexes to function as catalysts in the aerobic oxidation of cyclohexene [4]. In addition, we have recently reported the synthesis and characterization of a (nitro)ruthenium(III) complex which is stable as a solid and in solution [5]. We observed that a specific ligand environment, consisting of a 2,2′:6′,2″-terpyridine ligand in combination with *trans*-diphosphine ligands, causes stabilization of a (nitro)ruthenium(III) center.

To pursue these ligand effects further, we designed a complex which combines the ligand environment which stabilizes (nitro)ruthenium(III) centers with an (aqua)ruthenium center. In this paper we present the synthesis, characterization and the X-ray crystal structure of *trans*-(aqua)bis(triethylphosphine)(terpyridyl)ruthenium(II) perchlorate.

## Experimental

### *Materials*

$RuCl_3 \cdot 3H_2O$ was obtained from Johnson Matthey, 2,2′:6′,2″-terpyridine (trpy) and triethylphosphine ($PEt_3$) were obtained from GFS Chemicals and Strem Chemical Co., respectively. All solvents and reagents were used without further purification unless indicated.

### *Measurements*

Elemental analysis was performed by Schwarzkopf Microanalytical Laboratory. Electronic absorption spectra were measured with a Bausch and Lomb Spectronic 2000 spectrophotometer. The infrared spectrum was measured with a Perkin-Elmer 457 grating infrared spectrophotometer.

### *Electrochemical measurements in organic solvents*

Cyclic voltammograms were run either in reagent grade dichloromethane (dried over calcium hydride)

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or in acetonitrile (purified by literature methods) [6]. The supporting electrolyte was tetra-n-butylammonium tetrafluoroborate ($Bu_4NBF_4$) or tetraethylammonium perchlorate ($Et_4NClO_4$) and was used in 0.1 M concentration. A platinum working electrode (BAS Bioanalytical Systems), platinum wire auxiliary electrode and a saturated sodium chloride calomel (SSCE) reference electrode were used for all electrochemical experiments in dichloromethane or acetonitrile.

All electrochemical measurements were made on either a BAS 100 Electroanalytical System (Houston Instrument Hiplot DMP-40 series Digital Plotter) or on an IBM EC/225 Voltammetric Analyzer (Houston Instruments model 100 recorder).

### *Ru(Cl)$_3$(trpy)*

This complex was prepared by a literature procedure [7].

### *trans-Ru(Cl)$_2$(PEt$_3$)(trpy) (1)*

1.0 g (2.3 mmol) of Ru(Cl)$_3$(trpy) was slurried in 150 ml of $CH_2Cl_2$. The mixture was degassed and brought into an inert-atmosphere glove box and 1.1 g (9.3 mmol) of $PEt_3$ were added. The solution was then removed from the glove box, 5 ml of triethylamine ($NEt_3$) were added, and the solution was heated at reflux for 5 h. The solution volume was then reduced to 75 ml and passed down an activated alumina column with $CH_2Cl_2$ as the eluent. The blue band was collected and the solvent was removed by rotary evaporation; yield 0.90 g (75%). This complex was used without further purification in the synthesis of *cis*-Ru(Cl)$_2$(PEt$_3$)(trpy). $E_{1/2}$ = +0.44 V, $\Delta E_p$ = 0.10 V in $CH_2Cl_2$. Electronic spectrum (nm ($10^{-3}$ $\epsilon$ $M^{-1}$ $cm^{-1}$) in $CH_2Cl_2$); 634(1.5); 563(4.0); 410(4.7); 330(7.6); 318(15.7); 284(14.2).

### *cis-Ru(Cl)$_2$(PEt$_3$)(trpy) (2)*

0.9 g (1.7 mmol) of *trans*-Ru(Cl)$_2$(PEt$_3$)(trpy) was dissolved in 150 ml of $CH_2Cl_2$ and the solution was irradiated with a 150 W tungsten lamp for 5 h. The solvent was removed by rotary evaporation and the purple *cis*-Ru(Cl)$_2$(PEt$_3$)(trpy) was collected in quantitative yield. *Anal.* Calc. for $C_{21}H_{26}Cl_2N_3PRu$: C, 48.19; H, 5.01; N, 8.03. Found: C, 47.84; H, 4.89; N, 7.95%. $E_{1/2}$ = +0.58 V, $\Delta E_p$ = 0.10 V in $CH_2Cl_2$. Electronic spectrum (nm ($10^{-3}$ $\epsilon$ $M^{-1}$ $cm^{-1}$) in $CH_2Cl_2$): 560(4.1); 508(1.1); 373(4.6); 321(22.5); 275(19.3).

### *trans-[Ru(Cl)(PEt$_3$)$_2$(trpy)](Cl)·2H$_2$O (3)*

0.9 g (1.7 mmol) of *cis*-Ru(Cl)$_2$(PEt$_3$)(trpy) was dissolved in 150 ml of $CH_2Cl_2$ and the solution was degassed and brought into the inert-atmosphere glove box. 0.2 g (1.7 mmol) of $PEt_3$ was added and the solution was stirred overnight. The solvent was removed by rotary evaporation and the residue was slurried in hexanes to remove excess $PEt_3$. A red product was collected in quantitative yield. *Anal.* Calc. for $C_{27}H_{45}Cl_2N_3O_2P_2Ru$: C, 47.86; H, 6.69; N, 6.20. Found: C, 47.46; H, 6.54; N, 6.03%. $E_{1/2}$ = +0.73 V, $\Delta E_p$ = 0.07 V in $CH_3CN$. Electronic spectrum (nm ($10^{-3}$ $\epsilon$ $M^{-1}$ $cm^{-1}$) in $CH_3CN$): 509(4.9); 462(1.8); 351(2.6); 311(36.0); 273(20.8).

### *trans-[Ru(NO$_2$)(PEt$_3$)$_2$(trpy)](ClO$_4$)·H$_2$O (4)*

1.0 g (1.56 mmol) of *trans*-[Ru(Cl)(PEt$_3$)$_2$(trpy)](Cl) and 2.69 g (39 mmol) of $NaNO_2$ were dissolved in 150 ml of degassed 1:1 water/ethanol (95%). The solution was heated to reflux for 4 h under $N_2$. While the solution was still hot, 0.764 g (6.24 mmol) of $NaClO_4$ was added and the volume was slowly reduced by rotary evaporation until precipitation of the product initiated. The mixture was then cooled in an ice bath and the product filtered from solution; yield 0.74 g (65%). *Anal.* Calc. for $C_{27}H_{43}ClN_4O_7P_2Ru$: C, 44.17; H, 5.90; N, 7.63; P, 8.43. Found: C, 44.03; H, 5.55; N, 7.47; P, 8.62%. $E_{1/2}$ = +1.04 V, $\Delta E_p$ = 0.08 V in $CH_3CN$. Electronic spectrum (nm ($10^{-3}$ $\epsilon$ $M^{-1}$ $cm^{-1}$) in $CH_3CN$): 462(2.1); 438(5.4); 310(32.0); 274(19.1).

### *trans-[Ru(NO)(PEt$_3$)$_2$(trpy)](ClO$_4$)$_3$ (5)*

1.0 g (1.4 mmol) of *trans*-[Ru(NO$_2$)(PEt$_3$)$_2$(trpy)](ClO$_4$) was dissolved in 100 ml of 1:1 water/methanol. Concentrated $HClO_4$ was added until the color changed from dark red to light yellow. Cooling in an ice bath for 15 min resulted in the precipitation of the product; yield 1.17 g (91%). $E_{1/2}$ = +0.29 V, $\Delta E_p$ = 0.07 V in $CH_3CN$. Electronic spectrum (nm ($10^{-3}$ $\epsilon$ $M^{-1}$ $cm^{-1}$) in $CH_3CN$): 373(7.3); 305(sh); 288(19.3); IR ($cm^{-1}$; KBr) $\nu$(N–O) 1875.

### *trans-[Ru(H$_2$O)(PEt$_3$)$_2$(trpy)](ClO$_4$)$_2$·3H$_2$O (6)*

0.55 g (0.6 mmol) of *trans*-[Ru(NO)(PEt$_3$)$_2$(trpy)](ClO$_4$)$_3$ was dissolved in 200 ml of degassed, deionized $H_2O$. The solution was cooled in an ice bath, then 0.039 g (0.6 mmol) of $NaN_3$ were added to the solution, and the solution was stirred for 15 min under $N_2$. Precipitation of an orange solid was induced by adjustment of solution pH to 1 with $HClO_4$; yield 0.34 g (71%). *Anal.* Calc. for $C_{27}H_{49}Cl_2N_3O_{12}P_2Ru$: C, 38.53; H, 5.87; P, 7.36. Found: C, 38.87; H, 6.19; P, 7.43%. $E_{1/2}$ = +1.14 V, $\Delta E_p$ = 0.11 V in $CH_2Cl_2$; irreversible multiwave electrochemistry in $H_2O$, pH = 2, working electrode = glassy carbon electrode. Electronic spectrum (nm ($10^{-3}$ $\epsilon$ $M^{-1}$ $cm^{-1}$) in $CH_2Cl_2$): 484(4.4); 450(4.3); 310(39.3); 273(21.5); in $H_2O$: 472(3.5); 432(3.1); 299(29.4); 264(17.5). This complex was further characterized via X-ray structural analysis (*vide infra*).

TABLE 1. Experimental data for the X-ray diffraction study of $[Ru(trpy)(PEt_3)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$ at 24 °C (297 K)

| | |
|---|---|
| Unit cell data | |
| $a$ (Å) | 9.886(5) |
| $b$ (Å) | 19.289(7) |
| $c$ (Å) | 20.255(6) |
| $\beta$ (°) | 92.88(3) |
| $V$ (Å$^3$) | 3858(3) |
| Crystal system | monoclinic |
| Space group | $P2_1/c$ (No. 14) |
| $Z$ | 4 |
| Formula | $C_{27}H_{49}Cl_2N_3O_{12}P_2Ru$ |
| Molecular weight | 841.6 |
| $D_{calc}$ | 1.45 g/cm$^3$ |
| Collection of X-ray diffraction data | |
| Diffractometer | Syntex $P2_1$ |
| Radiation | Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710730 Å) |
| Monochromator | highly oriented (pyrolytic) graphite; equatorial mode with $2\theta$ (m) = 12.160°; assumed to be 50% perfect/50% ideally mosaic for polarization correction |
| Reflections measured | $+h, +k, \pm l$ for $2\theta$: 4.5 → 45.0°, yielding 3620 unique data |
| Scan type | coupled $\theta$(crystal)–$2\theta$(counter) |
| Scan width | $[2\theta(K\alpha_1)-1.0]° \rightarrow [2\theta(K\alpha_2)+1.0]°$ |
| Scan speed | 3.5 °/min ($2\theta$) |
| Backgrounds | stationary-crystal, stationary-counter at the two extremes of the $2\theta$ scan; each for one-quarter of the total scan time |
| Standard reflections | three approximately mutually orthogonal reflections collected before each set of 97 data points; no significant decay observed |
| Absorption correction | $\mu$(Mo K$\alpha$) = 6.7 cm$^{-1}$; corrected empirically by interpolation (in $2\theta$ and $\phi$) for 7 close-to-axial ($\psi$ scan) reflections |

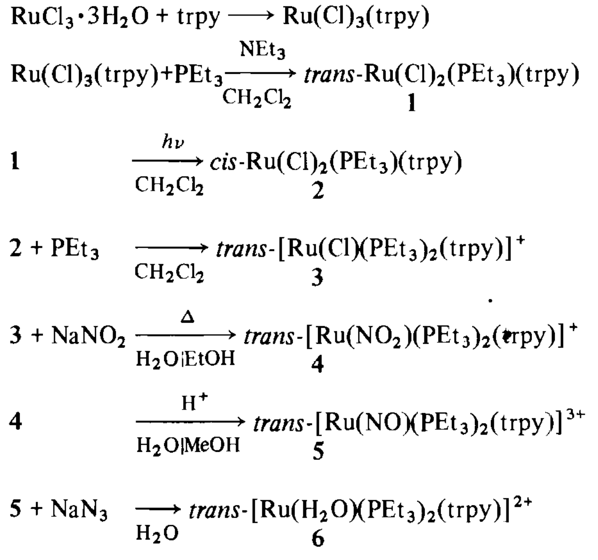
### *Collection of X-ray Diffraction Data for $[Ru(H_2O)(PEt_3)_2(trpy)](ClO_4)_2 \cdot 3H_2O$*

The crystals obtained from aqueous solution (*vide supra*) are noticeably efflorescent. Those of a size suitable for an X-ray diffraction study (<0.5 mm in diameter) rapidly lose their crystalline appearance and crumble to a fine powder after a few hours exposure to the atmosphere. The essential chemical identity of the material is maintained, since dissolution in water and recrystallization regenerates the original material. The crystal selected for the X-ray diffraction study defined a well-formed orange needle. It was carefully trimmed with a razor blade to form an equidimensional block of side ~0.3 mm. This was inserted and sealed into a thin-walled capillary while the crystal was still moist. The capillary was then mounted into a eucentric goniometer and the crystal was centered on a Syntex $P2_1$ automated four-circle diffractometer. Set-up operations (determination of diffraction symmetry, systematic absences, cell parameters and the orientation matrix) and data collection were carried out as described previously [8]; details appear in Table 1. The crystal possesses $2/m$ ($C_{2h}$) diffraction symmetry and is therefore monoclinic. The systematic absences $h0l$ for $l = 2n + 1$ and $0k0$ for $k = 2n + 1$ uniquely define the centrosymmetric monoclinic space group $P2_1/c$ ($C_{2h}^5$; No. 14) [9]. All data were adjusted for the effects of absorption (a very minor correction, since $\mu$(Mo K$\alpha$) = 6.7 cm$^{-1}$) and for Lorentz and polarization factors. Symmetry-equivalent reflections were averaged ($R(I)$ = 4.8% for 271 pairs of $0kl$ and $0k\bar{l}$ reflections). Data were converted to unscaled $|F_o|$ values, any datum with $I \leqslant 0$ being expunged from the file. Data were placed upon an approximately absolute scale by means of a Wilson plot, which also provided the average overall thermal parameter ($B$ = 3.98 Å$^2$). It should be noted that the set of diffraction data was not of the highest quality, probably as a result of the efflorescent nature of the material and/or of disorder (*vide infra*).

## Results and Discussion

### *Synthesis and Characterization*

The (aqua)ruthenium species is synthesized by a seven step synthesis outlined in Scheme 1.



$$RuCl_3 \cdot 3H_2O + trpy \longrightarrow Ru(Cl)_3(trpy)$$

$$Ru(Cl)_3(trpy) + PEt_3 \xrightarrow[CH_2Cl_2]{NEt_3} \underset{1}{trans\text{-}Ru(Cl)_2(PEt_3)(trpy)}$$

$$1 \xrightarrow[CH_2Cl_2]{h\nu} \underset{2}{cis\text{-}Ru(Cl)_2(PEt_3)(trpy)}$$

$$2 + PEt_3 \xrightarrow[CH_2Cl_2]{} \underset{3}{trans\text{-}[Ru(Cl)(PEt_3)_2(trpy)]^+}$$

$$3 + NaNO_2 \xrightarrow[H_2O|EtOH]{\Delta} \underset{4}{trans\text{-}[Ru(NO_2)(PEt_3)_2(trpy)]^+}$$

$$4 \xrightarrow[H_2O|MeOH]{H^+} \underset{5}{trans\text{-}[Ru(NO)(PEt_3)_2(trpy)]^{3+}}$$

$$5 + NaN_3 \xrightarrow[H_2O]{} \underset{6}{trans\text{-}[Ru(H_2O)(PEt_3)_2(trpy)]^{2+}}$$

Scheme 1.

In the synthesis of (aqua)ruthenium complexes, a standard synthetic strategy is the direct replacement of a chloride ligand with an aqua ligand, with the use of silver cation [1–3]. This reaction did not yield a direct complex **3** to complex **6** interconversion, so we resorted to a more indirect route, via a nitrosyl complex [1]. The purification of the (aqua)ruthenium complex was also difficult, for purification by column chromatography proved ineffective. In addition, the cyclic voltammogram of the (aqua)ruthenium complex showed several waves, which were difficult to interpret relative to other known (aqua)ruthenium complexes. However, the complex did yield an acceptable elemental analysis, and the complex did form crystals suitable for X-ray structural analysis, which was conducted to determine the structure of the (aqua)ruthenium complex.

### *Spectroscopic and Electrochemical Characterization*

All complexes involved in the synthetic route to complex **6** were characterized by cyclic voltammetry and electronic spectroscopy. The cyclic voltammogram of complex **6** in pH = 2 aqueous solution shows evidence of at least three redox couples, which suggests possible decomposition of complex **6** upon oxidation in aqueous media.

### *Solution and Refinement of the Structure of $[Ru(H_2O)(PEt_3)_2(trpy)](ClO_4)\cdot 3H_2O$*

All calculations were performed by use of our locally-modified version of the Syntex XTL structure determination package [10]. The calculated structure factors were based upon the analytical form of the scattering factors for neutral atoms [11a]; both the real ($\Delta f'$) and imaginary ($\Delta f''$) components of anomalous dispersion were included for all non-hydrogen atoms [11b]. The function minimized during least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\{\sigma|F_o|)\}^2 + \{0.01|F_o|\}^2]^{-1}$.

The position of the ruthenium atom was determined from a Patterson synthesis. The positions of all remaining non-hydrogen atoms (including severely disordered ethyl groups on one of the $PEt_3$ ligands) were determined from a series of difference-Fourier maps. Full-matrix least-squares refinement of positional and thermal parameters (anisotropic for the central $RuN_3P_2O$ moiety and the atoms of the two $ClO_4^-$ anions) led to convergence with $R_F = 8.8\%$ and $R_{wF} = 9.1\%$ for the 3407 independent data with $I > 0$ ($R_F = 7.5\%$ and $R_{wF} = 8.9\%$ for those 2771 reflections with $I > 3\sigma(I)$)*. Hydrogen atoms of the trpy ligand were included in idealized positions with $d(C–H) = 0.95$ Å [12]; those of the $PEt_3$ ligands were not included in the calculations. A final difference-Fourier map showed no unexpected features. Final atomic coordinates are collected in Table 2.

### *Description of the Crystal and Molecular Structure of $[Ru(H_2O)(PEt_3)_2(trpy)](ClO_4)_2\cdot 3H_2O$*

The crystal consists of $[Ru(H_2O)(PEt_3)_2(trpy)]^{2+}$ cations, $ClO_4^-$ anions and $H_2O$ molecules in a 1:2:3 ratio. The labeling of atoms within the $[Ru(H_2O)(PEt_3)_2(trpy)]^{2+}$ cation is shown in Fig. 1 and the stereoview of the cation is shown in Fig. 2. Interatomic distances and angles (with e.s.d.s) are listed in Tables 3 and 4.

The precision of the crystallographic analysis is adversely affected by three phenomena. These are given below (not necessarily in order of importance).

(1) The $ClO_4^-$ anions are either disordered or are exhibiting extremely large amplitudes of librational motion. We attempted both a disordered model and full anisotropic refinement. The latter gave acceptable results and is the model selected. Nevertheless, the resulting anisotropic thermal parameters are extremely large. (Maximum $B_{ii}$ values, in Å$^2$, are 29.0(19) for O(11), 18.5(12) for O(12), 13.4(9) for O(13), 27.6(20) for O(14), 47.3(39) for O(21), 23.6(2) for O(22), 33.6(31) for O(23) and 33.0(3) for O(24).) Clearly, the use of an ellipsoid (rather than a partial toroid) in defining the thermal motion for each of these atoms is of limited validity.

(2) The ethyl groups of one $PEt_3$ group (that based on P(2)) are severely disordered.

(3) The water molecules of hydration are probably not at full occupancy. We treated these as being of full occupancy, thereby producing isotropic thermal parameters of 7.8(2) Å$^2$ for O(2), 9.6(3) Å$^2$ for O(3) and 14.9(5) Å$^2$ for O(4). Correlation difficulties

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*$R_F(\%) = 100\Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_{wF}(\%) = 100[\Sigma w(|F_o| - |F_c|^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE 2. Final positional parameters for $[Ru(trpy)(PEt_3)_2(H_2O)](ClO_4)_2{\cdot}3H_2O$[a]

| Positional and isotropic thermal parameters<br>Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| Ru | 0.04199(9) | 0.19952(5) | 0.20177(4) | |
| P(1) | −0.09833(32) | 0.27067(17) | 0.26784(16) | |
| P(2) | 0.19432(34) | 0.13685(20) | 0.13417(17) | |
| O(1) | 0.13903(72) | 0.29846(37) | 0.17452(35) | |
| N(1) | −0.11096(88) | 0.18906(48) | 0.12734(41) | |
| N(2) | −0.04351(80) | 0.11336(41) | 0.22825(44) | |
| N(3) | 0.15841(82) | 0.17612(43) | 0.28769(38) | |
| C(1) | −0.1432(13) | 0.23166(73) | 0.07643(71) | 6.22(31) |
| C(2) | −0.2499(15) | 0.21546(79) | 0.02932(73) | 7.26(35) |
| C(3) | −0.3159(15) | 0.15768(85) | 0.03428(75) | 7.58(37) |
| C(4) | −0.2869(13) | 0.11235(72) | 0.08541(68) | 6.43(32) |
| C(5) | −0.1832(12) | 0.13007(65) | 0.13247(58) | 4.78(26) |
| C(6) | −0.1465(12) | 0.08799(64) | 0.18982(58) | 4.86(26) |
| C(7) | −0.2092(13) | 0.02530(72) | 0.20849(67) | 6.16(31) |
| C(8) | −0.1642(14) | −0.00509(76) | 0.26501(75) | 7.32(36) |
| C(9) | −0.0593(13) | 0.02125(71) | 0.30402(65) | 5.98(30) |
| C(10) | 0.0054(11) | 0.08280(60) | 0.28549(56) | 4.31(24) |
| C(11) | 0.1165(11) | 0.11812(63) | 0.31749(57) | 4.72(26) |
| C(12) | 0.1844(13) | 0.09376(71) | 0.37701(65) | 6.10(30) |
| C(13) | 0.2916(14) | 0.13067(76) | 0.40282(69) | 6.78(33) |
| C(14) | 0.3343(12) | 0.18934(68) | 0.37382(64) | 5.91(30) |
| C(15) | 0.2645(11) | 0.21090(58) | 0.31532(55) | 4.30(24) |
| C(21) | −0.2368(17) | 0.32281(93) | 0.22760(87) | 9.32(45) |
| C(22) | −0.1833(19) | 0.3845(11) | 0.1926(10) | 11.22(54) |
| C(31) | 0.0111(14) | 0.33061(77) | 0.32018(70) | 6.80(33) |
| C(32) | −0.0702(16) | 0.38008(88) | 0.36542(84) | 9.36(45) |
| C(41) | −0.1968(15) | 0.22629(84) | 0.33145(79) | 8.32(40) |
| C(42) | −0.3232(17) | 0.18684(89) | 0.30128(85) | 9.27(44) |
| C(51) | 0.3445(37) | 0.1697(18) | 0.1084(22) | 6.000(0) |
| C(52) | 0.2588(28) | 0.2184(15) | 0.0391(15) | 8.000(0) |
| C(51′) | 0.2974(44) | 0.1871(25) | 0.0734(29) | 6.000(0) |
| C(52′) | 0.1536(40) | 0.2141(19) | 0.0091(18) | 8.000(0) |
| C(61) | 0.1023(22) | 0.0791(12) | 0.0725(12) | 5.49(60) |
| C(61′) | 0.1217(43) | 0.0610(24) | 0.0943(22) | 4.90(11) |
| C(62) | 0.2001(15) | 0.03272(80) | 0.03190(74) | 7.78(38) |
| C(71) | 0.2921(22) | 0.0558(12) | 0.1855(11) | 6.20(51) |
| C(71′) | 0.3671(37) | 0.1201(21) | 0.1679(20) | 7.48(95) |
| C(72) | 0.3994(19) | 0.0774(11) | 0.2207(10) | 10.75(51) |
| H(1) | −0.0937 | 0.2750 | 0.0729 | 6.0 |
| H(2) | −0.2734 | 0.2476 | −0.0058 | 6.0 |
| H(3) | −0.3861 | 0.1469 | 0.0003 | 6.0 |
| H(4) | −0.3402 | 0.0686 | 0.0889 | 6.0 |
| H(7) | −0.2841 | 0.0039 | 0.1804 | 6.0 |
| H(8) | −0.2070 | −0.0486 | 0.2779 | 6.0 |
| H(9) | −0.0290 | −0.0019 | 0.3447 | 6.0 |
| H(12) | 0.1532 | 0.0510 | 0.3988 | 6.0 |
| H(13) | 0.3393 | 0.1148 | 0.4431 | 6.0 |
| H(14) | 0.4105 | 0.2173 | 0.3930 | 6.0 |
| H(15) | 0.2944 | 0.2527 | 0.2929 | 6.0 |
| O(2) | 0.40037(91) | 0.32888(51) | 0.19218(47) | 7.77(24) |
| O(3) | 0.0855(10) | 0.11402(58) | 0.56958(55) | 9.58(29) |
| O(4) | 0.4543(15) | 0.08922(83) | 0.58503(76) | 14.93(47) |
| Cl(1) | 0.45727(38) | 0.39084(19) | 0.37201(17) | |
| Cl(2) | 0.75590(74) | 0.43189(35) | −0.02154(27) | |
| O(11) | 0.4598(19) | 0.40605(86) | 0.30549(64) | |
| O(12) | 0.5454(16) | 0.33884(80) | 0.38388(67) | |
| O(13) | 0.4796(62) | 0.45048(62) | 0.40765(60) | |

*(continued)*

TABLE 2. *(continued)*

Positional and isotropic thermal parameters

| Atom | $x$ | $y$ | $z$ | $B$ (Å$^2$) |
|---|---|---|---|---|
| O(14) | 0.3258(15) | 0.37207(79) | 0.3754(10) | |
| O(21) | 0.7547(31) | 0.4533(13) | 0.0385(11) | |
| O(22) | 0.8648(19) | 0.3927(12) | −0.03744(89) | |
| O(23) | 0.6455(23) | 0.3913(13) | −0.0217(14) | |
| O(24) | 0.7302(26) | 0.4858(16) | −0.0599(14) | |

Anisotropic thermal parameters

| Atom | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|
| Ru | 4.319(50) | 3.411(49) | 2.956(46) | −0.186(39) | 0.346(32) | −0.138(39) |
| P(1) | 4.99(16) | 3.98(16) | 4.60(17) | 0.71(13) | 0.32(13) | −0.55(13) |
| P(2) | 4.95(17) | 6.85(21) | 4.60(18) | 0.13(15) | 1.26(14) | −1.46(16) |
| O(1) | 6.12(41) | 3.63(37) | 4.42(38) | −1.52(33) | 0.31(31) | 0.48(32) |
| N(1) | 5.36(49) | 4.84(54) | 3.01(44) | −0.06(43) | −0.20(37) | −0.33(40) |
| N(2) | 3.79(43) | 2.73(42) | 4.92(49) | −0.36(35) | 0.39(37) | −1.10(39) |
| N(3) | 4.11(44) | 3.69(47) | 2.82(41) | −0.25(35) | −0.09(34) | 0.41(35) |
| Cl(1) | 6.53(20) | 5.64(20) | 5.17(19) | 0.82(17) | −0.64(15) | 0.29(16) |
| Cl(2) | 13.27(44) | 9.88(37) | 7.36(30) | 2.24(33) | 1.53(29) | 0.96(27) |
| O(11) | 29.0(19) | 14.3(12) | 7.11(78) | 9.0(12) | −0.39(92) | 0.72(77) |
| O(12) | 18.5(12) | 15.7(11) | 12.4(10) | 12.2(11) | −6.43(88) | −4.05(86) |
| O(13) | 13.36(90) | 8.69(72) | 11.96(88) | −2.27(64) | −0.94(69) | −5.74(70) |
| O(14) | 10.8(10) | 12.6(11) | 27.6(20) | −1.93(84) | 4.4(11) | −1.7(12) |
| O(21) | 47.3(39) | 22.0(22) | 13.1(15) | −2.9(22) | 0.4(18) | −10.3(16) |
| O(22) | 17.5(14) | 23.6(20) | 15.2(13) | 5.6(14) | −1.5(11) | −5.4(13) |
| O(23) | 16.6(16) | 20.1(21) | 33.6(31) | −2.2(15) | 4.2(17) | −6.0(21) |
| O(24) | 25.6(23) | 33.0(30) | 29.6(27) | 11.3(22) | 6.9(20) | 20.1(25) |

[a] The anisotropic thermal parameters are in standard XTL format and enter the expression for the calculated structure factor in the form: $\exp[-0.25(h^2a^{*2}B_{11} + k^2b^{*2}B_{22} + l^2c^{*2}B_{33} + 2hka^*b^*B_{12} + 2hla^*c^*B_{13} + 2klb^*c^*B_{23})]$.

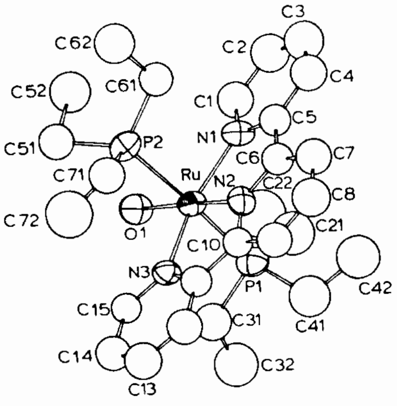

Fig. 1. The *trans*-$[\mathrm{Ru(trpy)(PEt_3)_2(OH_2)}]^{2+}$ cation; only the principal component for the disordered $PEt_3$ group is shown (ORTEP-II diagram).

between occupancy and thermal parameters for these atoms negates the possibility of simultaneous refinement of both.

Despite this rather impressive list of crystallographic misfortunes, which may well be interrelated, the coordination sphere about the central d$^6$ ($t_{2g}^6$) Ru(II) atom is well defined and can be discussed with confidence.

The Ru(II) atom is in a rather distorted octahedral environment consisting of a tridentate trpy ligand (which takes up its required meridional position), two $PEt_3$ ligands (in mutually *trans* sites) and an aqua ($H_2O$) ligand. The cation is fully described as *mer*, *trans*-$[\mathrm{Ru(trpy)(PEt_3)_2(H_2O)}]^{2+}$. The trpy ligand imposes some rigid constraints upon the system and is associated with the following irregularities within the coordination sphere. (i) Angles between mutually *cis* nitrogen atoms are reduced substantially from the ideal value of 90°, with N(1)–Ru–N(2) = 79.0(3)° and N(2)–Ru–N(3) = 79.3(3)°. (ii) The angle between the mutually *trans* nitrogen atoms is reduced from the ideal value of 180°, with N(1)–Ru–N(3) = 158.3(3)°. (iii) The central Ru–N bond is significantly shorter than the outer Ru–N bonds, with Ru–N(2) = 1.952(9) Å *vis-à-vis* Ru–N(1) = 2.091(9) Å and Ru–N(3) = 2.087(8) Å (average Ru–N(outer) = 2.089 ± 0.003 Å).

The two Ru–$PEt_3$ linkages are equivalent, with Ru–P(1) = 2.405(3) and Ru–P(2) = 2.411(4) Å (average Ru–P = 2.408 ± 0.004 Å), and are associated with a *trans* angle of P(1)–Ru–P(2) = 175.1(1)°.

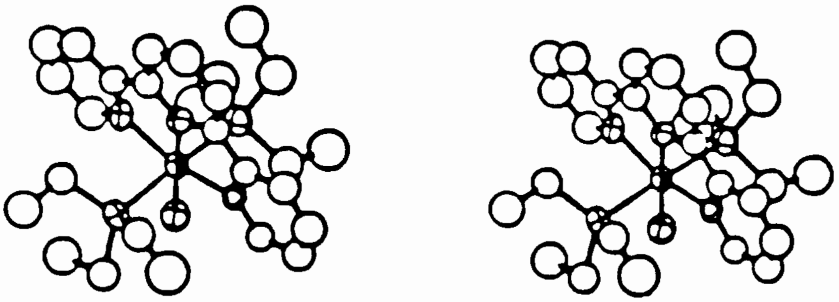

Fig. 2. Stereoview of the $[Ru(trpy)(PEt_3)_2(OH_2)]^{2+}$ cation.

TABLE 3. Selected interatomic distances (Å) for $[Ru(trpy)(PEt_3)_2(H_2O)](ClO_4)_2 \cdot 3H_2O$

| | | | |
|---|---|---|---|
| Ruthenium–ligand bond lengths | | | |
| Ru–P(1) | 2.405(3) | Ru–N(1) | 2.091(9) |
| Ru–P(2) | 2.411(4) | Ru–N(2) | 1.952(9) |
| Ru–O(1) | 2.218(4) | Ru–N(3) | 2.087(8) |
| N–C distances within the trpy ligand | | | |
| N(1)–C(1) | 1.344(17) | N(2)–C(10) | 1.367(14) |
| N(1)–C(5) | 1.350(15) | N(3)–C(11) | 1.346(15) |
| N(2)–C(6) | 1.342(14) | N(3)–C(15) | 1.343(14) |
| | | Average | 1.349 ± 0.009 |
| C–C distances within aromatic rings | | | |
| C(1)–C(2) | 1.421(20) | C(8)–C(9) | 1.370(19) |
| C(2)–C(3) | 1.298(22) | C(9)–C(10) | 1.408(18) |
| C(3)–C(4) | 1.375(21) | C(11)–C(12) | 1.430(17) |
| C(4)–C(5) | 1.407(18) | C(12)–C(13) | 1.359(19) |
| C(6)–C(7) | 1.419(18) | C(13)–C(14) | 1.352(19) |
| C(7)–C(8) | 1.342(20) | C(14)–C(15) | 1.404(17) |
| | | Average | 1.382 ± 0.040 |
| C–C distances between rings | | | |
| C(5)–C(6) | 1.448(17) | C(10)–C(11) | 1.421(16) |
| | | Average | 1.435 ± 0.019 |
| Distances within the ordered $PEt_3$ ligand | | | |
| P(1)–C(21) | 1.854(18) | C(21)–C(22) | 1.496(27) |
| P(1)–C(31) | 1.875(15) | C(31)–C(32) | 1.572(22) |
| P(1)–C(41) | 1.862(16) | C(41)–C(42) | 1.561(23) |
| Average | 1.864 ± 0.011 | Average | 1.543 ± 0.041 |
| P–C distances within the disordered $PEt_3$ ligand | | | |
| P(2)–C(51) | 1.72(4) | P(2)–C(61′) | 1.80(5) |
| P(2)–C(51′) | 1.90(5) | P(2)–C(71) | 2.09(3) |
| P(2)–C(61) | 1.87(3) | P(2)–C(71′) | 1.84(4) |
| | | Average | 1.87 ± 0.12 |
| Cl–O distances in $ClO_4^-$ anions | | | |
| Cl(1)–O(11) | 1.380(14) | Cl(2)–O(21) | 1.285(23) |
| Cl(1)–O(12) | 1.343(16) | Cl(2)–O(22) | 1.368(21) |
| Cl(1)–O(13) | 1.370(13) | Cl(2)–O(23) | 1.344(25) |
| Cl(1)–O(14) | 1.354(16) | Cl(2)–O(24) | 1.316(31) |
| | | Average | 1.345 ± 0.031 |
| O···O distances < 3 Å | | | |
| O(1)···O(2)$(x, y, z)$ | 2.656(12) | | |
| O(1)···O(3)$(x, +\frac{1}{2} - y, -\frac{1}{2} + z)$ | 2.745(13) | | |
| O(2)···O(4)$(x, +\frac{1}{2} - y, -\frac{1}{2} + z)$ | 2.758(18) | | |
| O(2)···O(11)$(x, y, z)$ | 2.774(17) | | |
| O(4)···O(23)$(x, +\frac{1}{2} - y, +\frac{1}{2} + z)$ | 2.965(30) | | |
| O(4)···O(24)$(1 - x, -\frac{1}{2} + y, +\frac{1}{2} - z)$ | 2.733(33) | | |

TABLE 4. Angles (°) involving the ruthenium atom

| | | | |
|---|---|---|---|
| Ligand–Ru–ligand angles | | | |
| P(1)–Ru–P(2) | 175.1(1) | P(2)–Ru–N(1) | 89.5(3) |
| P(1)–Ru–N(1) | 92.3(3) | P(2)–Ru–N(2) | 91.2(3) |
| P(1)–Ru–N(2) | 93.6(3) | P(2)–Ru–N(3) | 91.8(2) |
| P(1)–Ru–N(3) | 88.2(2) | P(2)–Ru–O(1) | 90.0(2) |
| P(1)–Ru–O(1) | 85.2(2) | O(1)–Ru–N(1) | 102.1(3) |
| N(1)–Ru–N(2) | 79.0(3) | O(1)–Ru–N(2) | 178.4(3) |
| N(1)–Ru–N(3) | 158.3(3) | O(1)–Ru–N(3) | 99.6(3) |
| N(2)–Ru–N(3) | 79.3(3) | | |
| Other angles involving the Ru atoms | | | |
| Ru–N(1)–C(1) | 129.0(8) | Ru–P(2)–C(51) | 124.2(13) |
| Ru–N(1)–C(5) | 113.1(7) | Ru–P(2)–C(51′) | 118.8(15) |
| Ru–N(2)–C(6) | 118.5(7) | Ru–P(2)–C(61) | 112.3(7) |
| Ru–N(2)–C(10) | 117.4(7) | Ru–P(2)–C(61′) | 114.5(14) |
| Ru–N(3)–C(11) | 112.6(7) | Ru–P(2)–C(71) | 112.3(6) |
| Ru–N(3)–C(15) | 128.7(7) | Ru–P(2)–C(71′) | 118.2(12) |
| Ru–P(1)–C(21) | 119.6(6) | | |
| Ru–P(1)–C(31) | 109.5(5) | | |
| Ru–P(1)–C(41) | 117.3(5) | | |

The aqua ligand is associated with a rather long Ru–O bond, with Ru–O(1) = 2.218(4) Å. It lies strictly *trans* to the central nitrogen atom of the trpy ligand (O(1)–Ru–N(2) = 178.4(3)°) and is in a rather exposed location; thus, *cis* angles (in decreasing order) are: O(1)–Ru–N(1) = 102.1(3), O(1)–Ru–N(3) = 99.6(3), O(1)–Ru–P(2) = 90.0(2) and O(1)–Ru–P(1) = 85.2(2)° (average O(1)–Ru–(*cis* ligand) = 94.2°).

Other items of interest include the following.

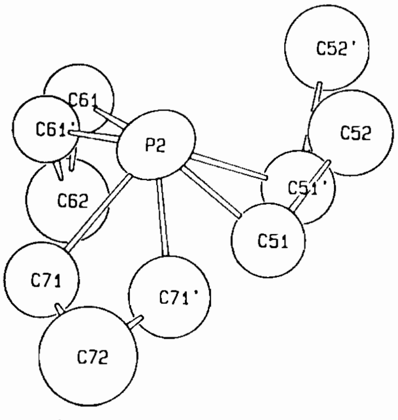

Fig. 3. Disordered $PEt_3$ ligand on the $[Ru(trpy)(PEt_3)_2(OH_2)]^{2+}$ cation.

(1) The aqua ligand, the $H_2O$ molecules of hydration and the $ClO_4^-$ anions are clearly involved in hydrogen bonding. Although the hydrogen atoms of interest were not located, we observe the following O···O distances <3 Å: O(1)···O(2) = 2.656(12), O(1)···O(3)($x, \frac{1}{2} - y, -\frac{1}{2} + z$) = 2.745(13), O(2)···O(4)($x, \frac{1}{2} - y, -\frac{1}{2} + z$) = 2.758(18), O(2)···O(11) = 2.774(17), O(4)···O(23)($x, \frac{1}{2} - y, \frac{1}{2} + z$) = 2.965(30) and O(4)···O(24)($1 - x, -\frac{1}{2} + y, \frac{1}{2} - z$) = 2.733(33) Å.

(2) Despite extraordinarily large 'thermal parameters', the $ClO_4^-$ anions appear to be reasonably well defined. Atom Cl(1) is associated with Cl–O distances of 1.343(16)–1.380(14) Å and O–Cl–O angles of 99.9(10)–116.6(8)°; analogous values for Cl(2) are 1.285(23)–1.368(21) Å and 98.2(17)–116.5(15)°.

(3) The $PEt_3$ ligand centered on P(1) is ordered with P–C = 1.854(18)–1.875(15) Å and C–C = 1.496(27)–1.572(22) Å. The $PEt_3$ ligand centered on P(2) is severely disordered. The disorder is illustrated in Fig. 3: there are two sites for each α-carbon and a common site for the β-carbon atoms in two of the ethyl groups. A symmetrical pattern of $C_{3v}$ symmetry is destroyed by a further disorder of one β-position (atoms C(52) and C(52′).

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