

Predominance of electron-withdrawing effect over angular strain in the metal-promoted hydrolysis of 2,4,6-tris(2-pyridyl)-1,3,5-triazine

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The reaction of 2,4,6-tris(2-pyridyl)-1,3,5-triazine (tptz) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ in refluxing ethanol–water (1 : 1) resulted in the hydrolysis of tptz to bis(2-pyridylcarbonyl)amide anion (bpca) and afforded a complex of composition $[\text{Rh}(\text{bpca})_2][\text{PF}_6]$ **1**. However, hydrolysis of tptz did not occur when it was treated with $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$ under similar condition, yielding instead the complex $[\text{Ru}(\text{tptz})_2][\text{PF}_6]_2 \cdot \text{H}_2\text{O}$ **2**. The molecular structures of **1** and **2** have been established by single-crystal X-ray analysis. In complex **1** the bis(2-pyridylcarbonyl)amido moiety functions as a tridentate ligand with nitrogen donor atoms and is bound to Rh^{III} in a mutually perpendicular fashion forming a distorted-octahedral geometry around the metal ion. In complex **2** two tridentate tptz are co-ordinated to Ru^{II} in a similar manner as found for **1**. From a comparison of bond lengths and angles in the co-ordination spheres of **1** and **2** it is suggested that the electron-withdrawing effect (L→M) of the metal ion is the predominant factor, rather than angular strain at the carbonyl carbon atoms, responsible for hydrolysis of tptz. Electrochemical studies of **1** revealed a metal-based two-electron couple ($\text{Rh}^{\text{III}}-\text{Rh}^{\text{I}}$) at -1.15 V and two ligand-based redox couples at -1.44 and -1.84 V. In the case of **2** the $\text{Ru}^{\text{II}}-\text{Ru}^{\text{III}}$ couple appears at $+1.77$ V and the ligand-based reduction at -0.62 and -0.80 V which are significantly positively shifted compared to those of free tptz.

2,4,6-Tris(2-pyridyl)-1,3,5-triazine (tptz) is of current interest because of its use as a spacer for designing multinuclear metal complexes.^{1–5} The compounds of this family, 2,4,6-triaryltriazines, are usually stable towards hydrolysis, concentrated mineral acid and temperatures above 150°C are required for their hydrolytic reaction.⁶ In fact tptz has been used as an analytical reagent for various metal ions.⁷ A number of transition-metal and lanthanide complexes of it have also been reported.^{8–20} Lerner and Lippard^{21,22} found that tptz and a similar compound 2,4,6-tris(pyrimidin-2-yl)triazine (tpmtz) undergo hydrolytic reaction in the presence of Cu^{II} in aqueous media. Crystal structures of copper(II) complexes of the hydrolytic products of tpmtz and tptz have also been reported.^{21–24} On the basis of the Cu–N bond distances and angles at the carbonyl carbon atoms within the chelate ring it was suggested that co-ordination of tptz induces an angular strain allowing nucleophilic attack at the carbon atoms of the triazine ring by the solvent resulting in the hydrolysis of tptz.^{21,24} In the case of ruthenium there is no report of metal-promoted hydrolysis of tptz^{1–5,19,20} and for mononuclear complexes, obtained by the reaction of $\text{K}_2[\text{RuCl}_5]$ or RuCl_3 with tptz, the electrochemistry of $[\text{Ru}(\text{tptz})_2][\text{ClO}_4]_3$,¹⁹ photophysical studies of $[\text{Ru}(\text{tptz})_2][\text{ClO}_4]_2 \cdot 3\text{H}_2\text{O}$ ²⁰ and ¹H NMR data for $[\text{Ru}(\text{tptz})_2][\text{PF}_6]_2$ ² have been reported.

We were interested to study the reactions of tptz with hydrated RhCl_3 and RuCl_3 under similar conditions. In the case of Rh^{III} , hydrolysis of tptz to bis(2-pyridylcarbonyl)amide anion (bpca) occurred under the reaction condition and for ruthenium a complex of Ru^{II} with intact tptz as found by earlier workers² was obtained. In this paper we report the crystal structures of both complexes together with electrochemical and spectroscopic data. To our knowledge this is the first report of a crystallographic characterisation of complexes where two hydrolysed tptz and two intact tptz are bound to metal ions. From the structural data we wish to emphasise mechanistic aspects of the hydrolytic reaction, particularly the role of the metal ion.

Experimental

Materials

The compound tptz, ammonium hexafluorophosphate and tetrabutylammonium tetrafluoroborate were obtained from Aldrich, hydrated rhodium trichloride and ruthenium trichloride from Arora Matthey.

Physical measurements

Elemental analyses (C, H and N) were performed on a model 2400 Perkin-Elmer Elemental Analyser. Infrared spectra were recorded on a Bio-Rad FTS-40 spectrometer as KBr pellets, UV/VIS spectra on a model 8452A Hewlett-Packard Diode-Array spectrophotometer. Electrochemical experiments were performed with a model 273A EG & G Princeton Applied Research potentiostat. All experiments were conducted in an argon atmosphere with a platinum working electrode, an Ag–AgCl electrode as reference and 0.1 mol dm^{-3} $[\text{NBu}^n_4][\text{BF}_4]$ as supporting electrolyte.

Synthesis of complexes

$[\text{Rh}(\text{bpca})_2][\text{PF}_6]$ **1.** A mixture of tptz (312 mg, 1 mmol) and $\text{RhCl}_3 \cdot 3\text{H}_2\text{O}$ (132 mg, 0.5 mmol) in ethanol–water (1 : 1, 50 cm^3) was refluxed for 30 h. The volume of the reaction mixture was reduced to ca. 25 cm^3 by rotary evaporation and an aqueous solution (5 cm^3) of KPF_6 (368 mg, 2 mmol) was added. The precipitate was filtered off and washed with water and diethyl ether. Recrystallisation of complex **1** from boiling acetonitrile afforded pale yellow crystals. Yield: 72% (Found: C, 41.1; H, 2.3; N, 12.0. Calc. for $\text{C}_{24}\text{H}_{16}\text{F}_6\text{N}_6\text{O}_4\text{PRh}$: C, 41.15; H, 2.3; N, 12.0%).

$[\text{Ru}(\text{tptz})_2][\text{PF}_6]_2 \cdot \text{H}_2\text{O}$ **2.** This complex was synthesized following the procedure of Thummel and co-workers.² During purification on an alumina column eluting with acetonitrile–toluene (1 : 1) a small purple fraction was eluted first, then the

desired complex separated as a dark red band. Yield: 75% (Found: C, 41.9; H, 2.4; N, 16.2. Calc. for $C_{36}H_{26}F_{12}N_{12}OP_2Ru$: C, 41.85; H, 2.55; N, 16.35%).

Crystallography

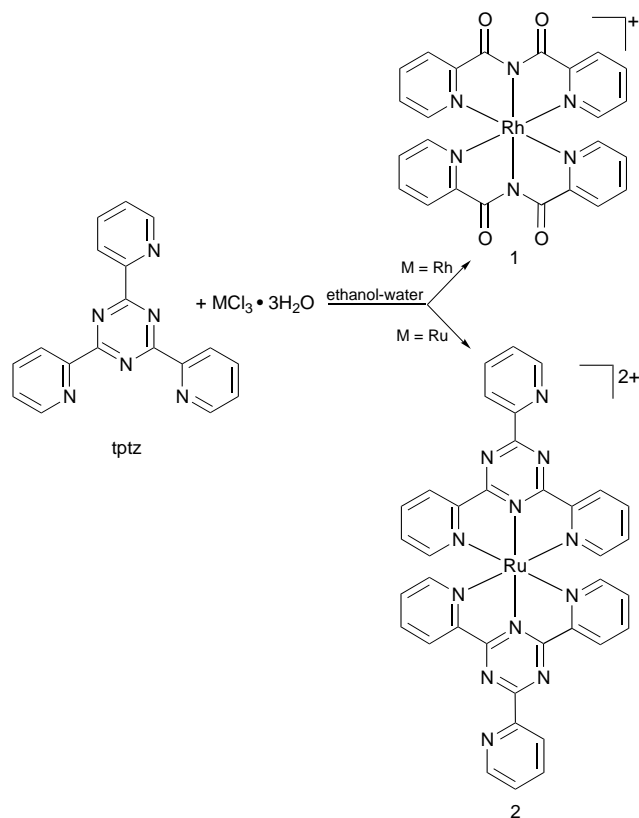
Preliminary data on the space group and unit-cell dimensions as well as intensity data were collected on an Enraf-Nonius CAD-4 X-ray diffractometer using graphite-monochromatised Mo-K α radiation ($\lambda = 0.7107 \text{ \AA}$) in the range θ 2–23°. Accurate cell dimensions were obtained using 25 reflections in the range θ 8–12°. The crystal orientation, refinement of cell parameters and intensity measurements were carried out using the program CAD-4 PC.²⁵ Intensities were corrected for Lorentz-polarisation effects but not for absorption. The Lorentz-polarisation correction and data reduction were carried out using the NRCVAX program.²⁶ The structures were solved by the heavy-atom method using the program SHELXS 86.²⁷ Crystallographic data for complexes **1** and **2** are summarised in Table 1.

For complex **1** the extensive disorder of the PF_6^- was obvious at the structure-solution stage itself. After locating all the non-hydrogen atoms of the cation in the Fourier-difference map, the peak for phosphorus appeared with the expected height of $\approx 13 \text{ e \AA}^{-3}$, whereas a large number of peaks appeared with heights ranging from 3 to 1.5 e \AA^{-3} joining the phosphorus atom and corresponding to F atoms. Isotropic full-matrix refinement of all the non-hydrogen atoms except F was carried out till convergence using the program SHELXL 93.²⁸ Attempts were made to fit the orientational disorder of PF_6^- by analysing the Fourier-difference map. However, it was not possible to resolve the orientation of each PF_6^- in the lattice due to the presence of a large number of peaks with heights of $\approx 2 \text{ e \AA}^{-3}$ in the Fourier difference map. Therefore, all the peaks with heights $> 2 \text{ e \AA}^{-3}$ were included at every stage only for their structure-factor contribution in the least-squares refinement, till the Fourier-difference map contained no significant peaks corresponding to F atoms and the peaks corresponding to H atoms started appearing. At this stage 24 peaks corresponding roughly to four major orientations of the PF_6^- with occupancy 0.25 were allowed to refine only for their thermal but not their positional parameters, as the peaks would merge into each other. The rest of the non-hydrogen atoms were refined anisotropically using the weighting scheme $w = 1/\sigma(|F|^2)^2$ in both **1** and **2**. Despite the extensive disorder of the PF_6^- , the Fourier-difference map at this stage contained almost all the hydrogen atoms which could even be refined isotropically (except one which was refined using a riding model). The inclusion of these 24 disordered F atoms significantly improved the refinement parameters such as R , wR and goodness of fit. This fact can be taken as correct treatment of the anion disorder, although a constrained or rigid model refinement was not possible in this case. The structure solution and the least-squares refinement of compound **2** proceeded smoothly, with no disorder of PF_6^- .

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/532.

Results and Discussion

The reaction of rhodium trichloride and tptz in refluxing ethanol-water resulted in the hydrolysis of tptz to bis(2-pyridylcarbonyl)amide (bpca) anion and afforded a complex of composition $[Rh(bpca)_2][PF_6]_2$ **1** with good yield. However, the hydrolysis of tptz did not occur when ruthenium trichloride reacted with tptz under similar conditions, and this reaction yielded a complex, $[Ru(tptz)_2][PF_6]_2 \cdot H_2O$ **2**, similar to that



Scheme 1 Compound **2** was also reported earlier.^{2,20}

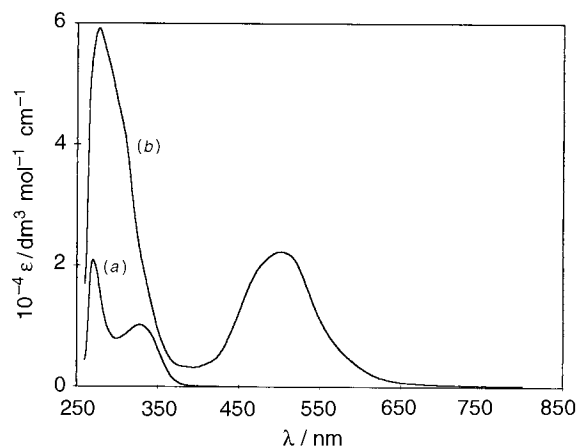


Fig. 1 Electronic absorption spectra of complexes **1** (a) and **2** (b) in dmf

obtained by Thummel and co-workers,² $[Ru(tptz)_2][PF_6]_2$. The difference is only the water of crystallisation. The other complexes of Ru^{II} and Ru^{III} , $[Ru(tptz)_2][ClO_4]_2 \cdot 3H_2O$ ²⁰ and $[Ru(tptz)][ClO_4]_3$,¹⁹ respectively were prepared by different methods. The ligand and complexes **1** and **2** are shown in Scheme 1.

The IR spectrum of complex **1** exhibits a strong band at 1720 cm^{-1} whereas **2** and free tptz do not show any band in that region. This band is assigned to $\nu(C=O)$ of the co-ordinated bpca chelate formed by the hydrolysis of tptz.^{21–24} Complexes **1** and **2** exhibit strong bands at 842 and 840 cm^{-1} respectively, which can be assigned to $\nu(PF_6^-)$. Their electronic spectra in dimethylformamide (dmf) are shown in Fig. 1. Complex **1** exhibits absorption bands at 328 (9800) and 272 nm (ϵ $20\,900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The band of **2** in the visible region in dmf (504 nm ; $22\,300 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) compares well with the reported value of 501 nm for $[Ru(tptz)_2][ClO_4]_2$ in water.²⁰ In the UV region complex **2** shows a band at 280 nm (ϵ $59\,100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The high-energy bands at 272 and 280 nm for **1** and **2**, respectively, are ligand centred and due to $\pi-\pi^*$ transition.^{4,5} The band at 504 nm of **2** is due to a metal-to-ligand

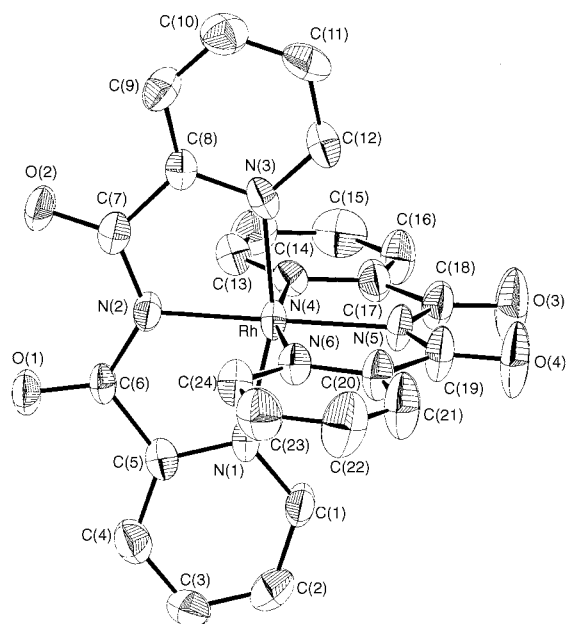


Fig. 2 An ORTEP (50% probability) view with atom labelling scheme for the cation of complex **1**; hydrogen atoms are omitted for clarity

Table 1 Summary of crystallographic data and parameters for complexes **1** and **2**

	1	2
Formula	C ₂₄ H ₁₆ F ₆ N ₆ O ₄ PRh	C ₃₆ H ₂₆ F ₁₂ N ₁₂ OP ₂ Ru
<i>M</i>	700.31	1031.68
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$	<i>Pbcm</i>
Crystal dimensions/mm	0.24 × 0.08 × 0.04	0.04 × 0.14 × 0.06
<i>a</i> /Å	8.890(4)	11.043(2)
<i>b</i> /Å	12.053(3)	16.747(2)
<i>c</i> /Å	14.013(2)	21.751(2)
α /°	109.48(1)	
β /°	102.11(3)	
γ /°	98.12(3)	
<i>U</i> /Å ³	1347.2(7)	4022.7(2)
<i>Z</i>	2	4
<i>D</i> _c /g cm ⁻³	1.762	1.704
<i>F</i> (000)	696	2056
Total reflections	3537	2638
Observed reflections	2653	1923
[<i>I</i> ≥ 2σ(<i>I</i>)]		
Parameters refined	410	344
Final (<i>R</i> 1) (on <i>F</i>)	0.060	0.031
Final (<i>wR</i> 2) (on <i>F</i> ²)	0.155	0.094
$R1 = \sum F_o - F_c / \sum F_o $; $wR2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)]^{1/2}$.		

charge-transfer (MLCT) transition.^{20,29} That of **1** at 328 nm may be MLCT in character^{30,31} but the possibility of σ bond-to-ligand charge-transfer (SBLCT) cannot be ruled out.^{32,33} The electrochemical behaviour of the complexes are discussed in a later section.

Crystal structures

Complex 1. A perspective (ORTEP³⁴) view of the complex cation along with the atom numbering is shown in Fig. 2. Selected bond distances and angles are presented in Table 2. The geometry of the rhodium(III) ion can be described as a distorted octahedron formed by the co-ordination of two bpca which functions as a tridentate ligand with nitrogen donor atoms. The complex cation has two perpendicular approximate planes of symmetry each containing the plane of one ligand and cutting the other through the Rh–N (amido) bond. The four nitrogen atoms N(2), N(4), N(5) and N(6) which comprise the equatorial co-ordination and the Rh show a high degree of

Table 2 Selected bond distances (Å) and angles (°) for complexes **1** and **2**

Complex 1

Rh–N(1)	2.015(7)	Rh–N(6)	2.020(7)
Rh–N(2)	1.996(6)	C(6)–O(1)	1.215(9)
Rh–N(3)	2.024(7)	C(7)–O(2)	1.230(9)
Rh–N(4)	2.048(6)	C(18)–O(3)	1.197(10)
Rh–N(5)	1.993(6)	C(19)–O(4)	1.205(10)
N(2)–Rh–N(4)	97.1(3)	N(2)–C(7)–C(8)	112.1(7)
N(4)–Rh–N(5)	81.4(3)	N(5)–C(18)–C(17)	111.1(7)
N(5)–Rh–N(6)	81.6(3)	N(5)–C(19)–C(20)	111.4(7)
N(6)–Rh–N(2)	100.0(3)	N(2)–C(6)–O(1)	128.0(7)
N(1)–Rh–N(3)	162.7(2)	N(2)–C(7)–O(2)	128.5(8)
N(2)–Rh–N(5)	178.4(3)	N(5)–C(18)–O(3)	128.7(9)
N(4)–Rh–N(6)	162.9(3)	N(5)–C(19)–O(4)	126.7(8)
N(5)–C(6)–C(5)	111.8(6)		

Complex 2

Ru–N(1)	2.099(3)	Ru–N(3)	2.100(3)
Ru–N(2)	1.973(3)		
N(2)–Ru–N(1A)	103.47(11)	N(1A)–Ru–N(3A)	155.09(11)
N(1A)–Ru–N(2A)	77.65(11)	N(2)–C(6)–C(5)	112.6(2)
N(2A)–Ru–N(3A)	77.44(11)	N(2)–C(7)–C(8)	112.4(3)
N(3A)–Ru–N(2)	101.44(12)	N(2)–C(6)–N(4)	122.5(3)
N(1)–Ru–N(3)	155.09(11)	N(2)–C(7)–N(5)	123.3(3)
N(2)–Ru–N(2A)	178.4(2)		

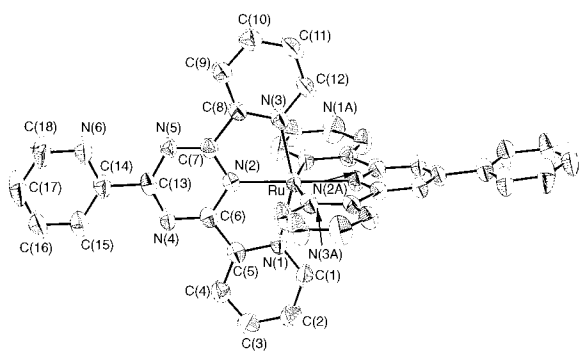
planarity (maximum deviation 0.003 Å). The axial nitrogen atoms [N(1) and N(3)] and Ru make an angle of 162.7° which deviates significantly from the ideal value of 180° as they are constrained to be part of the five-membered chelate rings. For the same reason, two angles at the equatorial base N(4)–Ru–N(5) and N(5)–Ru–N(6) having values 81.4(3) and 81.6(3)°, respectively, are significantly smaller than the ideal value of 90°. The Ru–N bond distances, a shorter Ru–N (amido) and longer Ru–N (pyridyl) bonds (Table 2), are comparable to the values for copper(II) complexes with the same ligand.^{21–24} Though both the ligands are co-ordinated in a similar fashion there is a significant difference in their conformations. This can be seen by dividing each ligand into two halves. The two halves consisting of N(4), C(13)–C(18), N(5), O(3) and N(5), C(19)–C(24), N(6), O(4) of the bpca which comprises the equatorial base are quite planar (maximum deviation 0.03 Å) and exhibit an angle of 3.43° to each other. However, the two halves of the other ligand, N(1), C(1)–C(6), N(2), O(1) (maximum deviation 0.11 Å) and N(2), C(7)–C(12), N(3), O(2) (maximum deviation 0.10 Å) make a dihedral angle of 11.8°. The PF₆⁻ in the molecule is severely disordered occupying four positions as discussed in the Experimental section. The molecular packing shows the C–H...O interactions listed in Table 3.

Complex 2. An ORTEP view of the complex cation along with the atom numbering is shown in Fig. 3. The complex molecule occupies a special position (crystallographic two-fold axis) in the unit cell and therefore only half of it and the three symmetry-related co-ordinated nitrogen atoms, N(1A), N(2A) and N(3A), are labelled. The two PF₆⁻ anions also occupy the special positions in the unit cell. Selected bond distances and angles are presented in Table 2.

The co-ordination of two tridentate tptz to the ruthenium(II) ion in a mutually perpendicular fashion provides a distorted octahedral geometry. Three co-ordinated nitrogen atoms of one tptz and one [N(2A)] of the other ligand form the equatorial base of the octahedron; N(1) and N(3) of the latter are in axial positions. The four nitrogen atoms of the equatorial base and Ru^{II} show excellent planarity (maximum deviation 0.012 Å). The axial nitrogen atoms and Ru^{II} make an angle of 155.09° which is slightly smaller than that of complex **1**. The two pyridyl rings and triazine moiety which are involved in co-

Table 3 Hydrogen-bonding parameters in complexes **1** and **2**

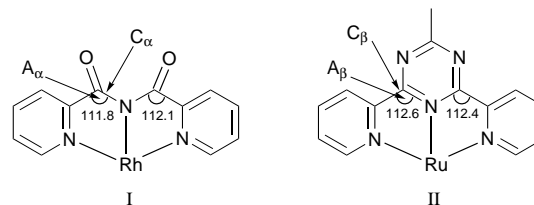
Complex	Donor (D)	Hydrogen	Acceptor (A)	D–A/Å	H...A/Å	D–H...A/°	Symmetry code
1	C(1)	H(1)	O(3)	2.97(1)	2.37(8)	129(7)	1 – x, –y, –z
	C(1)	H(1)	O(4)	3.26(1)	2.68(8)	127(7)	1 – x, –y, –z
	C(24)	H(24)	O(1)	3.39(1)	2.57(8)	138(6)	1 – x, 1 – y, 1 – z
	C(24)	H(24)	O(2)	3.12(7)	2.29(6)	140(6)	1 – x, 1 – y, 1 – z
2	O(1w)	H(10w)	N(5)	3.065(3)	2.38(5)	136(4)	x, y, z
	O(1w)	H(10w')	N(6)	2.947(5)	2.16(5)	150(4)	x, y, z
	C(9)	H(9)	O(1w)	3.197(6)	2.17(4)	165(3)	x, y, z
	C(1)	H(1)	F(5)	3.109(5)	2.73(4)	111(3)	x, y, z
	C(2)	H(2)	F(4)	3.120(5)	2.59(4)	123(3)	1 – x, –y, 1 – z
	C(12)	H(12)	F(1)	3.319(5)	2.46(4)	164(4)	x, y, z
							x, y, z

**Fig. 3** An ORTEP view (50% probability) with the atom labelling scheme for the cation of complex **2**; hydrogen atoms are omitted for clarity

ordination comprise a plane (maximum deviation 0.08 Å) but the free pyridyl ring is not in the same plane and is rotated by 6.4° about the C(13)–C(14) bond. The angles at the metal formed by the nitrogen atoms of the equatorial co-ordination sites are quite similar to those found around Rh^{III} in **1**. The Ru–N(2)/(2A) bond distances are comparable to the Rh–N (amido) distances but the Ru–N (pyridyl) bond lengths are slightly longer than the corresponding Rh–N (pyridyl) distances (Table 2). Unlike in complex **1**, the PF₆ anions do not show any disorder. The packing shows channels for the PF₆ anion and a water molecule. There are hydrogen-bonding interactions with N(5), N(6) and C(9) with the oxygen atom O(1w) of the water molecule. The PF₆ anion makes short contacts with C(1), C(2) and C(12) as shown in Table 3.

Electrochemistry

The Osteryoung square-wave and cyclic voltammograms of complex **1** in dmf show three reductions at –1.15 ($\Delta E = 92$), –1.44 (87) and –1.84 V; the last peak is poorly resolved in the cyclic voltammogram but well resolved in square wave. The first reduction is metal-centred and is in fact a composite wave corresponding to two electrons and assigned to the Rh^{III}–Rh^I couple.^{35–38} The resolution of the composite wave into two components at high scan rate ($>10 \text{ V s}^{-1}$) as found for some complexes^{35,36} could not be observed when the scan rate was increased to 20 V s^{-1} . The other two reductions are ligand based. It is interesting that in the cyclic voltammogram at low scan rate the anodic waves are small compared to the cathodic waves but they increased with increasing sweep rate. When the potential scan was reversed just after the first cathodic peak the first redox couple was almost reversible even at low scan rate (100 mV s^{-1}). These observations are consistent with no chemical change after metal reduction, but with a chemical change after ligand reductions. At high scan rate probably the electrochemical process becomes faster compared to the chemical change and thus the reversibility increases with increasing scan rate. The electrochemical study of complex **2** was carried out in acetonitrile because in dmf at positive potential a metal-based

**Scheme 2** Drawings showing the relevant structural portions of complexes **1** (I) and **2** (II)

redox couple is obscured by the edge of the solvent window. The acetonitrile solution of **2** shows two reversible ligand-based redox couples at –0.62 ($\Delta E = 64$) and –0.80 V (65 mV).^{4,5} Free tptz under the same conditions exhibits a reversible redox couple at –1.41 V, indicating a significant anodic shift of the reduction potential for both tptz co-ordinated to Ru^{II}. A quasi-reversible wave found at +1.77 V ($\Delta E = 120 \text{ mV}$) is assigned to the Ru^{II}–Ru^{III} couple.^{4,5}

Mechanistic aspects of hydrolytic reaction

In copper(II) complexes with hydrolysed tptz and tpmtz the values of the angles at the carbonyl carbon atoms within the chelate ring, A_α (structure I of Scheme 2), are in the range 110.0–111.7°, ^{21–24} which is compressed considerably from the ideal value of 120°, and on the basis of these data it was suggested that the metal-induced angular strain at C_α (structure I) is responsible for the hydrolytic reaction. It is important to note that for mechanistic speculations the angular strain (A_α) at C_α of the hydrolysed ligands is cited,^{22,24} but nucleophilic attack occurs at the carbon atoms of the triazine ring of unhydrolysed tptz (C_β , structure II of Scheme 2). The geometry after hydrolysis of the ligand may not be the true picture at the time when intact tptz is bound to the metal ion. After hydrolysis C_α is no longer in a ring and therefore it is expected that the value of the N– C_α –O angle would be higher compared to N– C_β –N and this effect allows the pyridine moiety to come closer to the metal ion which results in a lower value of A_α and shorter M–N distances. In fact the angles N– C_α –O in the copper(II) complexes are in the range 128–130°^{22–24} which is significantly high compared to the ideal value of 120°. Therefore, for the discussion of mechanism the angular strain at C_β should be considered. The rhodium(III) and ruthenium(II) ions have a charge difference of unity only, but probably that alone also cannot make much difference in the activation of the ligand,³⁹ there are many examples of complexes of Cu^{II} and Ni^{II} which activate ligands making carbon atoms susceptible to nucleophilic attack.^{40–43}

In complex **1** the values of A_α (average 111.6°) and Rh–N distances (Table 2) are comparable to those of the copper(II) complexes. In the case of **2** the average value of A_β is 112.5° which is close to A_α indicating a similar angular strain at C_β to that found at C_α . Therefore, the stability of **2**, which resists hydrolysis of tptz, cannot be explained by the strain alone. We suggest a different factor assists the hydrolytic reaction. The co-ordination of tptz to the metal ion leads to destabilisation of

the triazine ring by enhancing the electron deficiency (L→M σ donation) upon it and this makes C _{β} susceptible to nucleophilic attack. Though Rh^{III} and Ru^{II} are isoelectronic, Ru^{II} has the ability to form π -back bonds to unsaturated ligands; this interaction serves to increase the electron density on the triazine ring, compensating at least partially for the σ -electron-withdrawing effect; a similar interaction (π -back bonding) for Rh^{III} is apparently not effective. Kinetics and NMR studies^{38,44} have demonstrated that the rate of base hydrolysis of co-ordinated nitriles (which also requires electron deficiency at the carbon atom of the nitrile) in rhodium(III) complexes is more than four orders of magnitude greater than structurally analogous ruthenium(II) complexes.³⁹ In the ¹H NMR spectra the downfield shift of the nitrile resonances is larger for the rhodium(III) than for the analogous ruthenium(II) complexes indicating that there is less electron density at the nitrile protons of the former complexes.⁴⁴ We also made similar observations for the chemical shift of the protons in complexes **1** and **2** attached to carbon atoms adjacent to co-ordinated nitrogens of pyridyl moieties.† For free tptz they appeared at δ 8.98, and in **1** and **2** the same proton appeared at δ 8.27 and 7.75, respectively. In some other rhodium(III) complexes with unhydrolysed tptz⁴⁵ it appeared in the range δ 8.6–9.0. These data show that the shielding of these protons in the ruthenium(II) complex is higher than in the rhodium(III) complex, consistent with the electron deficiency on the protons and also at the attached carbon atoms for rhodium(III) being greater compared to that in ruthenium(II) complexes. It is worth mentioning that rhodium(III) ion is capable of promoting hydrolysis of two co-ordinated tptz. This contrasts with the inference drawn earlier that once the hydrolysed tptz is bound to Cu^{II} the metal ion loses its ability to promote hydrolysis of any more tptz. In the present case we, therefore, suggest that the electron-withdrawing effect of the metal ion is the predominant factor, rather than angular strain, in hydrolysis of metal-bound tptz.

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† As there is no proton in the triazine ring, we have chosen these protons which after co-ordination of tptz to the metal ion would be most affected in view of the electron density upon it.

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