Co-ordination Chemistry of Ruthenium with Chelating Amine Ligands: Synthesis and *X*-Ray Structural Study of the N_6-Co-ordinated Ruthenium(II) Complex of 1,4,8,11-Tetrakis(2-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane†

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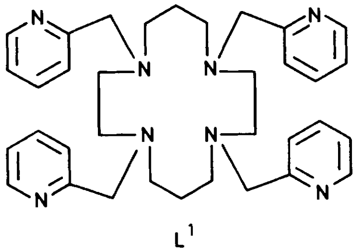
Reaction of $K_2[RuCl_5(H_2O)]$ with 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane (L^1) in ethanol yielded $[Ru^{II}(HL^1)][ClO_4]_3 \cdot H_2O$ (**1**). The $E_{\frac{1}{2}}$ value for the $Ru^{III/II}$ couple is 1.17 V *vs.* a normal hydrogen electrode and the optical spectrum shows an intense $d_\pi(Ru) \longrightarrow \pi^*$(pyridine) charge-transfer transition at 376 nm. The complex cation in (**1**) [space group $P\bar{1}$, a = 10.674(2), b = 14.211(3), c = 14.507(4) Å, α = 92.77(3), β = 107.28(3), γ = 105.65(2)°, U = 2 003.5(7) Å^3, Z = 2; R = 0.043 for 7 037 observed Mo-K_α data] is distorted octahedral with average Ru–N(tertiary amine) and Ru–N(pyridyl) bond distances of 2.191(3) and 2.075(3) Å respectively.

Binuclear ruthenium complexes with two ruthenium ions in close proximity are potential mediators for multi-electron transfer reactions. Tetra-aza macrocycles having four pendant co-ordinating groups attached to the four nitrogen atoms have been suggested as binucleating ligands for binuclear metal complexes.[1,2] Moore and co-workers[2] recently reported the synthesis of the ligand 1,4,8,11-tetrakis(2-pyridylmethyl)-1,4,8,11-tetra-azacyclotetradecane (L^1), and the corresponding binuclear copper(II) complexes. This ligand, which is easily synthesized from cyclam (1,4,8,11-tetra-azacyclotetradecane), has four pyridyl groups that should facilitate metal insertion reaction. We describe here the complexation behaviour of ligand L^1 with ruthenium. A mononuclear N_6-co-ordinated ruthenium(II), complex, similar to the (3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane)ruthenium(II) ion,[3] has been obtained by reacting $K_2[RuCl_5(H_2O)]$ with L^1 in refluxing ethanol, and characterized by *X*-ray crystallography.

Experimental

$K_2[RuCl_5(H_2O)]$ was obtained from Johnson Matthey and the ligand L^1 was prepared as described previously.[2]

Preparation of $[Ru^{II}(HL^1)][ClO_4]_3 \cdot H_2O$ (**1**).—An ethanolic solution of L^1 (0.37 g, 0.65 mmol in 200 cm^3) was added dropwise to an ethanolic suspension of $K_2[RuCl_5(H_2O)]$ (0.5 g, 1.3 mmol in 150 cm^3) under conditions of reflux and vigorous stirring. The addition process took 3 h for completion and the resulting solution was refluxed for 24 h, after which it was filtered to remove unreacted $K_2[RuCl_5(H_2O)]$. The filtrate was evaporated to dryness under vacuum. A yellow solid was obtained and dissolved in HCl (1 mol dm^{-3}, 20 cm^3) at room temperature. Upon addition of solid $NaClO_4$ (5 g) to the solution, an orange solid precipitated out. The crude product was recrystallized from water or ethanol, giving an overall yield of 25%. *X*-Ray crystallography revealed that one pyridyl group is protonated. Complex (**1**) is diamagnetic ($\mu_{eff.}$ = 0; Gouy method, crystalline sample, 25 °C). U.v.–visible in CF_3SO_3H: λ 376 nm (ε 11 000 dm^3 mol^{-1} cm^{-1}), 251 (16 300).



L^1

Physical Measurements.—U.v.–visible spectra were recorded with a Shimadzu model 240 spectrophotometer. Infrared spectra were obtained as Nujol mulls on a Perkin-Elmer model 577 spectrophotometer. N.m.r. spectra were run on a JEOL model FX90Q spectrometer (90 MHz) at 298 K; $SiMe_4$ was used as an internal standard (δ = 0). Cyclic voltammetry was performed using a Princeton Applied Research (PAR) model 175 universal programmer, model 173 potentiostat, and model 179 digital coulometer.

X-*Ray Structural Study of* $[Ru^{II}(HL^1)][ClO_4]_3 \cdot H_2O$ (**1**).—Diffraction measurements were made on a Nicolet R3m four-circle diffractometer (graphite-monochromatized Mo-K_α radiation, λ = 0.710 69 Å); determination of the crystal class, orientation matrix, and accurate unit-cell parameters were performed according to established procedures.[4]

Intensities were recorded at 22 °C; data collection and processing parameters are summarized in Table 1. The raw intensities were processed using the learnt-profile procedure;[5] an absorption correction was applied by fitting a pseudo-ellipsoid to the azimuthal scans of selected strong reflections over a range of 2θ values.[6]

The structure of (**1**) was solved by Patterson and Fourier methods. One perchlorate group was found to exhibit two-fold disorder about a Cl–O bond; accordingly the two sets of disordered atoms, O(10)–O(12) and O(13)–O(15), were treated as isotropic, and their site occupancy factors were varied as g and $(1 - g)$, respectively. The remaining non-hydrogen atoms in the asymmetric unit were subjected to anisotropic refinement. The pyridyl and water hydrogens were located from a difference map, and the methylene and aromatic hydrogen atoms of the macrocyclic ligand were generated geometrically (C–H fixed at

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

0.96 Å) and allowed to ride on their respective parent carbon atoms. All H atoms were included in structure factor calculations with assigned isotropic thermal parameters.

Table 1. Data collection and processing parameters for (**1**)

Formula	$C_{34}H_{47}Cl_3N_8O_{13}Ru$
M	983.22
Cell constants	
a,b,c/Å	10.674(2), 14.211(3), 14.507(4)
α,β,γ/°	92.77(3), 107.28(3), 105.65(2)
U/Å^3	2 003.5(7)
Z	2
D_m/g cm^{-3} (flotation)	1.625
D_c/g cm^{-3}	1.630
Space group	$P\bar{1}$
μ/cm^{-1}	6.56
Crystal size (mm)	0.36 × 0.28 × 0.22
Mean μr	0.07
Transmission factors	0.782—0.930
Scan type and speed/° min^{-1}	ω—2θ; 2.02—8.37
Scan range	1° below K_{α_1} to 1° above K_{α_2}
Background counts	stationary; half of scan time at each end
Collection range	h, $\pm k$, $\pm l$; $2\theta_{max.} = 52°$
Unique data	7 488
Observed data with $\lvert F\rvert > 3\sigma(\lvert F\rvert)$, n	7 037
Variables, p	530
F(000)	1 012
$R = \Sigma\lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert/\Sigma\lvert F_o\rvert$	0.043
Weighting scheme	$w = [\sigma^2(\lvert F_o\rvert) + 0.0005\lvert F_o\rvert^2]^{-1}$
$R' = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/w\lvert F_o\rvert^2]^{\frac{1}{2}}$	0.062
$S = [\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2/(n - p)]^{\frac{1}{2}}$	2.082
Extrema in difference map (e Å^{-3})	+1.32 to −0.96

Computation was performed on a Data General Nova 3/12 minicomputer with the SHELXTL system.[7] Analytic expressions of neutral-atom scattering factors incorporating the real and imaginary components of anomalous dispersion were employed.[8] Blocked-cascade least-squares refinement converged to the R indices and other parameters listed in Table 1.[9]

Figure 1 shows a perspective view of the $[Ru^{II}(HL^1)]^{3+}$ complex cation and the atomic numbering scheme. The final atomic co-ordinates for compound (**1**) are listed in Table 2; bond distances, bond angles, and selected torsion angles are

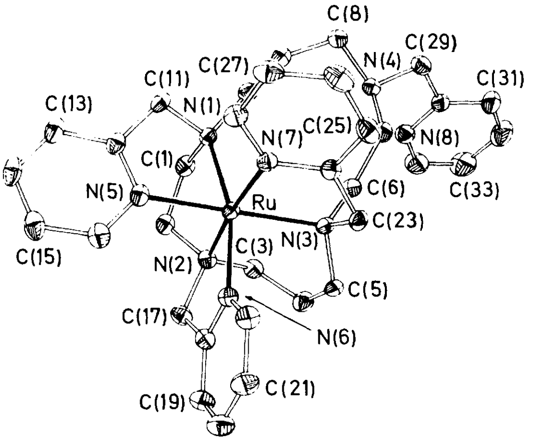

Figure 1. Perspective view of the $[Ru^{II}(HL^1)]^{3+}$ cation. Protonation of the macrocyclic ligand occurs at N(8), but all hydrogen atoms have been omitted for clarity

Table 2. Atomic co-ordinates (× 10^5 for Ru and Cl atoms; × 10^4 for other atoms) for (**1**)

Atom	x	y	z
(*a*) Cation			
Ru	37 321(2)	26 580(2)	15 338(2)
N(1)	4 730(3)	4 137(2)	2 496(2)
N(2)	5 287(3)	3 203(2)	911(2)
N(3)	4 780(3)	1 661(2)	2 339(2)
N(4)	6 291(3)	2 911(2)	4 962(2)
N(5)	2 584(3)	3 525(2)	774(2)
N(6)	2 983(3)	1 609(2)	318(2)
N(7)	2 283(3)	1 998(2)	2 176(2)
N(8)	8 965(3)	2 950(3)	5 301(2)
C(1)	5 811(4)	4 700(3)	2 082(3)
C(2)	5 585(4)	4 300(3)	1 039(3)
C(3)	6 590(3)	2 968(3)	1 399(3)
C(4)	6 522(4)	1 888(3)	1 409(3)
C(5)	5 396(4)	1 186(3)	1 702(2)
C(6)	5 908(3)	2 073(3)	3 312(2)
C(7)	5 513(4)	2 005(3)	4 246(2)
C(8)	5 420(4)	3 515(3)	5 103(3)
C(9)	4 560(4)	3 761(3)	4 145(3)
C(10)	5 431(4)	4 312(3)	3 600(2)
C(11)	3 570(4)	4 586(3)	2 309(3)
C(12)	2 752(4)	4 415(3)	1 249(3)
C(13)	2 175(4)	5 101(3)	804(3)
C(14)	1 386(4)	4 878(3)	−172(3)
C(15)	1 160(4)	3 954(3)	−658(3)
C(16)	1 755(4)	3 302(3)	−171(3)
C(17)	4 733(4)	2 789(3)	−144(3)
C(18)	3 663(3)	1 802(3)	−340(2)
C(19)	3 345(4)	1 155(3)	−1 171(3)
C(20)	2 267(4)	303(3)	−1 368(3)
C(21)	1 555(4)	111(3)	−721(3)
C(22)	1 924(4)	769(3)	108(3)
C(23)	3 631(3)	846(2)	2 465(3)
C(24)	2 516(3)	1 218(2)	2 627(3)
C(25)	1 746(4)	782(3)	3 194(3)
C(26)	701(4)	1 128(3)	3 306(3)
C(27)	441(4)	1 903(3)	2 818(3)
C(28)	1 230(3)	2 311(3)	2 265(3)
C(29)	7 027(4)	2 689(3)	5 906(3)
C(30)	8 368(4)	2 524(3)	5 922(3)
C(31)	9 040(5)	1 999(3)	6 576(3)
C(32)	10 276(6)	1 917(4)	6 571(4)
C(33)	10 867(6)	2 379(5)	5 886(4)
C(34)	10 209(5)	2 903(4)	5 281(4)
(*b*) Perchlorate groups			
Cl(1)	20 662(10)	80 923(7)	9 323(8)
O(1)	2 301(4)	7 441(3)	1 639(3)
O(2)	3 343(3)	8 760(3)	945(3)
O(3)	1 231(4)	8 639(3)	1 162(3)
O(4)	1 402(4)	7 520(3)	1(3)
Cl(2)	9 683(10)	46 008(7)	32 364(8)
O(5)	8 988(4)	3 891(4)	3 516(3)
O(6)	9 472(5)	5 416(3)	2 994(3)
O(7)	11 234(4)	4 902(3)	4 009(4)
O(8)	10 079(6)	4 166(4)	2 350(4)
Cl(3)	68 698(14)	95 614(8)	41 066(8)
O(9)	6 806(5)	8 590(3)	4 348(3)
O(10)	6 578(9)	10 066(5)	4 867(4)
O(11)	5 722(8)	9 457(6)	3 217(5)
O(12)	8 114(9)	10 083(8)	4 015(11)
O(13)	7 527(14)	9 810(8)	3 403(9)
O(14)	7 410(13)	10 298(5)	4 928(6)
O(15)	5 403(8)	9 526(8)	3 625(11)
(*c*) Water molecule			
O_w	5 050(4)	7 131(3)	2 483(3)

Table 3. Bond distances (Å), bond angles (°), and selected torsion angles (°)

(*a*) Cation

Ru–N(1)	2.264(2)	Ru–N(2)	2.105(3)	C(1)–C(2)	1.516(5)	C(3)–C(4)	1.517(6)
Ru–N(3)	2.205(3)	Ru–N(5)	2.093(3)	C(4)–C(5)	1.522(5)	C(6)–C(7)	1.534(5)
Ru–N(6)	2.058(3)	Ru–N(7)	2.073(3)	C(8)–C(9)	1.536(5)	C(9)–C(10)	1.486(6)
N(1)–C(1)	1.515(5)	N(1)–C(10)	1.528(4)	C(11)–C(12)	1.496(5)	C(12)–C(13)	1.376(6)
N(1)–C(11)	1.501(5)	N(2)–C(2)	1.496(4)	C(13)–C(14)	1.385(5)	C(14)–C(15)	1.385(6)
N(2)–C(3)	1.496(5)	N(2)–C(17)	1.492(4)	C(15)–C(16)	1.369(6)	C(17)–C(18)	1.502(5)
N(3)–C(5)	1.512(5)	N(3)–C(6)	1.520(4)	C(18)–C(19)	1.376(5)	C(19)–C(20)	1.376(5)
N(3)–C(23)	1.506(4)	N(4)–C(7)	1.485(4)	C(20)–C(21)	1.367(6)	C(21)–C(22)	1.374(5)
N(4)–C(8)	1.474(6)	N(4)–C(29)	1.460(4)	C(23)–C(24)	1.498(6)	C(24)–C(25)	1.383(6)
N(5)–C(12)	1.351(5)	N(5)–C(16)	1.360(4)	C(25)–C(26)	1.381(7)	C(26)–C(27)	1.385(6)
N(6)–C(18)	1.359(5)	N(6)–C(22)	1.351(4)	C(27)–C(28)	1.368(6)	C(29)–C(30)	1.506(6)
N(7)–C(24)	1.357(4)	N(7)–C(28)	1.353(5)	C(30)–C(31)	1.386(6)	C(31)–C(32)	1.358(9)
N(8)–C(30)	1.331(5)	N(8)–C(34)	1.356(7)	C(32)–C(33)	1.423(9)	C(33)–C(34)	1.341(9)
N(1)–Ru–N(2)	82.7(1)	N(1)–Ru–N(3)	104.4(1)	C(24)–N(7)–C(28)	117.7(3)	C(30)–N(8)–C(34)	123.0(4)
N(2)–Ru–N(3)	93.4(1)	N(1)–Ru–N(5)	78.2(1)	N(1)–C(1)–C(2)	113.7(2)	N(2)–C(2)–C(1)	111.1(3)
N(2)–Ru–N(5)	90.9(1)	N(3)–Ru–N(5)	175.2(1)	N(2)–C(3)–C(4)	117.6(2)	C(3)–C(4)–C(5)	120.0(4)
N(1)–Ru–N(6)	160.6(1)	N(2)–Ru–N(6)	82.0(1)	N(3)–C(5)–C(4)	115.6(3)	N(3)–C(6)–C(7)	118.3(3)
N(3)–Ru–N(6)	88.4(1)	N(5)–Ru–N(6)	90.2(1)	N(4)–C(7)–C(6)	111.0(3)	N(4)–C(8)–C(9)	113.3(3)
N(1)–Ru–N(7)	100.5(1)	N(2)–Ru–N(7)	174.0(1)	C(8)–C(9)–C(10)	112.2(3)	N(1)–C(10)–C(9)	113.7(3)
N(3)–Ru–N(7)	80.9(1)	N(5)–Ru–N(7)	94.7(1)	N(1)–C(11)–C(12)	111.5(3)	N(5)–C(12)–C(11)	114.9(3)
N(6)–Ru–N(7)	95.8(1)	Ru–N(1)–C(1)	105.3(2)	N(5)–C(12)–C(13)	122.8(3)	C(11)–C(12)–C(13)	122.3(3)
Ru–N(1)–C(10)	126.6(2)	C(1)–N(1)–C(10)	105.2(2)	C(12)–C(13)–C(14)	119.2(4)	C(13)–C(14)–C(15)	118.6(4)
Ru–N(1)–C(11)	102.7(2)	C(1)–N(1)–C(11)	110.2(3)	C(14)–C(15)–C(16)	119.3(4)	N(5)–C(16)–C(15)	122.8(4)
C(10)–N(1)–C(11)	106.4(3)	Ru–N(2)–C(2)	105.9(2)	N(2)–C(17)–C(18)	112.3(3)	N(6)–C(18)–C(17)	116.4(3)
Ru–N(2)–C(3)	113.5(2)	C(2)–N(2)–C(3)	108.1(2)	N(6)–C(18)–C(19)	122.2(3)	C(17)–C(18)–C(19)	121.4(3)
Ru–N(2)–C(17)	107.8(2)	C(2)–N(2)–C(17)	110.8(3)	C(18)–C(19)–C(20)	119.3(4)	C(19)–C(20)–C(21)	119.0(4)
C(3)–N(2)–C(17)	110.7(3)	Ru–N(3)–C(5)	109.6(2)	C(20)–C(21)–C(22)	119.6(3)	N(6)–C(22)–C(21)	122.4(4)
Ru–N(3)–C(6)	119.0(2)	C(5)–N(3)–C(6)	106.8(3)	N(3)–C(23)–C(24)	112.2(3)	N(7)–C(24)–C(23)	116.5(3)
Ru–N(3)–C(23)	104.1(2)	C(5)–N(3)–C(23)	106.0(2)	N(7)–C(24)–C(25)	121.4(4)	C(23)–C(24)–C(25)	122.0(3)
C(6)–N(3)–C(23)	110.6(3)	C(7)–N(4)–C(8)	113.0(3)	C(24)–C(25)–C(26)	120.5(4)	C(25)–C(26)–C(27)	117.7(4)
C(7)–N(4)–C(29)	112.2(3)	C(8)–N(4)–C(29)	109.1(3)	C(26)–C(27)–C(28)	119.8(4)	N(7)–C(28)–C(27)	122.9(4)
Ru–N(5)–C(12)	116.8(2)	Ru–N(5)–C(16)	125.9(3)	N(4)–C(29)–C(30)	112.2(3)	N(8)–C(30)–C(29)	117.4(3)
C(12)–N(5)–C(16)	117.2(3)	Ru–N(6)–C(18)	114.4(2)	N(8)–C(30)–C(31)	118.8(4)	C(29)–C(30)–C(31)	123.8(4)
Ru–N(6)–C(22)	128.2(3)	C(18)–N(6)–C(22)	117.4(3)	C(30)–C(31)–C(32)	120.2(5)	C(31)–C(32)–C(33)	118.9(5)
Ru–N(7)–C(24)	114.8(2)	Ru–N(7)–C(28)	127.3(2)	C(32)–C(33)–C(34)	119.4(6)	N(8)–C(34)–C(33)	119.6(5)

N(1)–C(1)–C(2)–N(2)	−47.4(4)	C(1)–C(2)–N(2)–C(3)	−72.4(4)	N(3)–C(6)–C(7)–N(4)	−141.3(3)
C(2)–N(2)–C(3)–C(4)	177.0(3)	N(4)–C(8)–C(9)–C(10)	−59.4(4)	C(7)–N(4)–C(8)–C(9)	−52.5(4)
C(3)–C(4)–C(5)–N(3)	−23.8(4)	C(9)–C(10)–N(1)–C(1)	−176.0(3)	C(8)–C(9)–C(10)–N(1)	151.2(3)
C(5)–N(3)–C(6)–N(7)	−142.4(3)	N(2)–C(3)–C(4)–C(5)	−47.4(5)	C(10)–N(1)–C(1)–C(2)	155.1(3)
C(6)–C(7)–N(4)–C(8)	110.8(4)	C(4)–C(5)–N(3)–C(6)	−66.4(3)		

(*b*) Perchlorate

Cl(1)–O(1)	1.427(4)	Cl(1)–O(2)	1.430(3)	Cl(3)–O(9)	1.429(4)	Cl(3)–O(10)	1.441(8)
Cl(1)–O(3)	1.426(5)	Cl(1)–O(4)	1.415(4)	Cl(3)–O(11)	1.460(7)	Cl(3)–O(12)	1.384(11)
Cl(2)–O(5)	1.414(4)	Cl(2)–O(6)	1.417(5)	Cl(3)–O(13)	1.409(15)	Cl(3)–O(14)	1.412(7)
Cl(2)–O(7)	1.417(4)	Cl(2)–O(8)	1.449(6)	Cl(3)–O(15)	1.499(8)		
O(1)–Cl(1)–O(2)	110.2(2)	O(1)–Cl(1)–O(3)	108.7(3)	O(9)–Cl(3)–O(10)	106.0(3)	O(9)–Cl(3)–O(11)	106.8(3)
O(2)–Cl(1)–O(3)	109.3(2)	O(1)–Cl(1)–O(4)	108.4(2)	O(10)–Cl(3)–O(11)	106.2(5)	O(9)–Cl(3)–O(12)	114.3(6)
O(2)–Cl(1)–O(4)	109.3(3)	O(3)–Cl(1)–O(4)	110.9(3)	O(10)–Cl(3)–O(12)	110.7(7)	O(11)–Cl(3)–O(12)	112.2(7)
O(5)–Cl(2)–O(6)	109.2(3)	O(5)–Cl(2)–O(7)	109.6(3)	O(9)–Cl(3)–O(13)	113.2(6)	O(9)–Cl(3)–O(14)	113.6(4)
O(6)–Cl(2)–O(7)	110.8(2)	O(5)–Cl(2)–O(8)	107.9(3)	O(13)–Cl(3)–(14)	111.7(6)	O(9)–Cl(3)–O(15)	104.9(5)
O(6)–Cl(2)–O(8)	106.4(3)	O(7)–Cl(2)–O(8)	112.8(3)	O(13)–Cl(3)–O(15)	105.5(8)	O(14)–Cl(3)–O(15)	107.2(8)

(*c*) Hydrogen bonding

N(8) $\cdots$ O(5)	2.974(7)	O(1) $\cdots$ O_w $\cdots$ O(9)	111.5(6)	Cl(1)–O(1) $\cdots$ O_w	121.9(6)
O_w $\cdots$ O(9)	3.079(6)	Cl(3)–O(9) $\cdots$ O_w	107.2(6)	Cl(2)–O(5) $\cdots$ N(8)	135.6(6)
O_w $\cdots$ O(1)	2.986(6)	C(30)–N(8) $\cdots$ O(5)	154.0(7)	C(34)–N(8) $\cdots$ O(5)	82.1(7)

given in Table 3. Additional material available from the Cambridge Crystallographic Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

Attempts to prepare binuclear ruthenium complexes by refluxing $K_2[RuCl_5(H_2O)]$ with ligand L^1 in ethanol resulted in the isolation of a N_6-co-ordinated ruthenium(II) complex, **(1)**, which is diamagnetic in accord with its formulation $[Ru^{II}, (t_{2g})^6]$. The structure of **(1)**, consisting of complex cation, counter anion, and solvent in a molar ratio of 1:3:1, has been established by *X*-ray crystallography. Interestingly, protonation of the macrocyclic ligand occurs at the pyridyl nitrogen atom N(8), which is normally less basic than the tertiary N(4) atom. The ruthenium ion, instead of being located at the centre of the

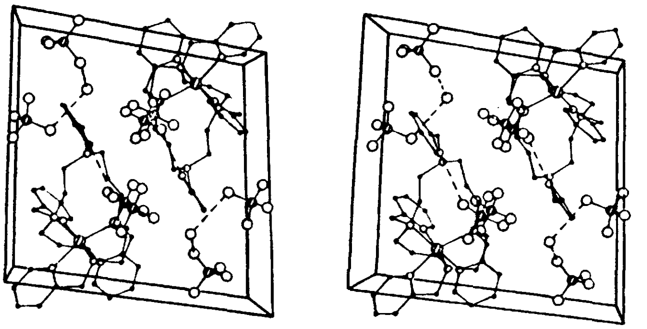

Figure 2. Stereodrawing of the crystal structure of $[Ru^{II}(HL^1)][ClO_4]_3 \cdot H_2O$. The origin of the unit cell lies at the lower left corner, with *a* pointing upwards out of the page, *b* from left to right, and *c* upwards. For clarity the disordered perchlorate group is shown in its preferred orientation

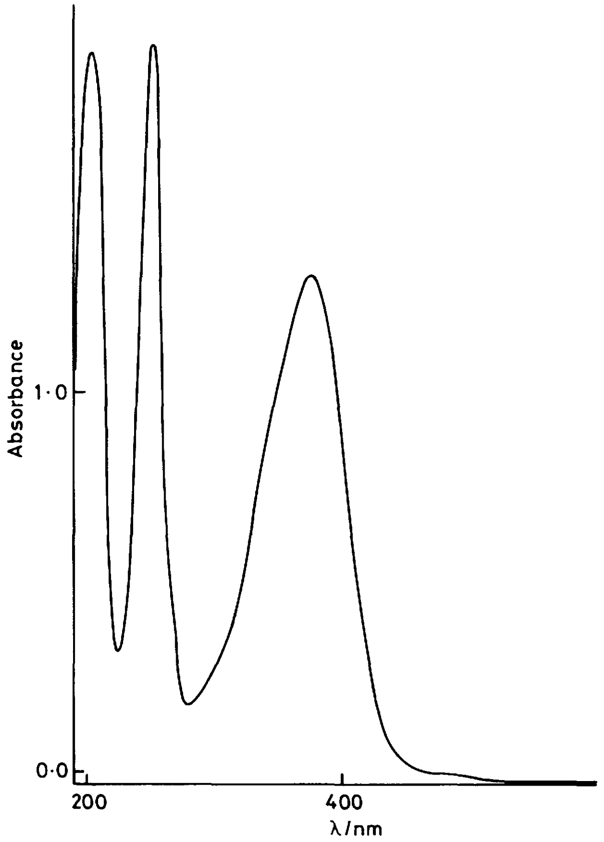

Figure 3. Optical spectrum of $[Ru^{II}(HL^1)]^{3+}$ in 0.1 mol dm^{-3} CF_3SO_3H

macrocyclic ring, co-ordinates to the three tertiary amino groups [N(1), N(2), and N(3)] and three pyridyl groups [N(5), N(6), and N(7)], in accord with the preference of Ru^{II} binding to a π-aromatic amine rather than a σ-saturated tertiary amine. The co-ordination geometry about the metal ion is highly distorted from octahedral, with the tertiary amino and pyridyl groups positioned *trans* to each other. For individual pairs of *cis* ligand atoms, the N–Ru–N bond angles fall in the range 78.2(1)—104.4(1)°, the latter value being associated with the nine-membered chelate ring generated by ligand sites at N(1) and N(3) (Figure 1). This mode of co-ordination is probably in a constrained state since the six-membered chelate ring anchored at N(2) and N(3) is in the twist boat conformation. Unlike $[Ru(L^2)_2][BPh_4]_2 \cdot 2Me_2SO$ (L^2 = 1,4,7-trithiacyclononane)[10] and $[Ru(NH_3)_6]^{2+}$ [11] where virtually identical metal–ligand bond lengths are found, the Ru–N(tertiary amine) and Ru–N(pyridyl) bonds in (**1**) vary over a wide range. The deviation in Ru–N(tertiary amine) bond distances is quite substantial, 2.105(3)—2.264(2) Å, possibly due to this constrained co-ordination mode in addition to steric overcrowding. The average Ru–N(tertiary amine) bond distance of 2.191(3) Å is significantly longer than the average Ru–N(pyridyl) bond, 2.075(3) Å, but comparable to the Ru–N bonds in $[Ru(NH_3)_6]^{2+}$ (2.144 Å).[11] The stronger Ru–N(pyridyl) than Ru–N(tertiary amine) bonding is no doubt due to metal-to-ligand(pyridyl) π back bonding.

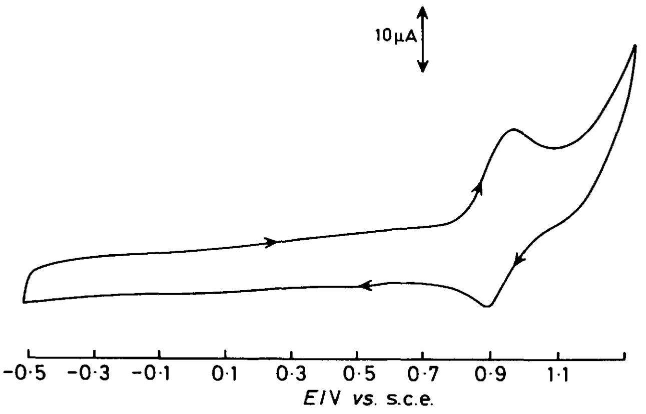

Figure 4. Cyclic voltammogram of $[Ru^{II}(HL^1)]^{3+}$ in 0.1 mol dm^{-3} CF_3SO_3H. Working electrode, pyrolytic graphite; scan rate, 100 mV s^{-1} s^{-1}

A stereodrawing of the crystal structure of (**1**), illustrating the hydrogen-bonding interactions (Table 3), is shown in Figure 2. The complex cation is linked to a perchlorate group *via* donor hydrogen bonding by the protonated N(8) atom of the pendant pyridyl group. The remaining perchlorate groups are bridged by the water molecule to form a $(ClO_4 \cdots H_2O \cdots ClO_4)^{2-}$ aggregate, and the well behaved (*i.e.* not disordered) O(9) atom of the disordered perchlorate group is involved in acceptor hydrogen bonding.

Figure 3 shows the optical spectrum of (**1**) in 0.1 mol dm^{-3} CF_3SO_3H. As expected for ruthenium(II)–pyridine complexes, it shows an intense absorption band at 376 nm, attributed to the allowed $d_\pi(Ru) \longrightarrow \pi^*(pyridine)$ charge-transfer transition.[12] The cyclic voltammogram of (**1**) (Figure 4) in 0.1 mol dm^{-3} CF_3SO_3H reveals only one reversible oxidation couple ($\Delta E_p \approx 60$ mV, $i_{pa}/i_{pc} = 1$; scan rate, 50—200 mV s^{-1}; n = 1.0 ± 0.1 by coulometry) at 1.17 V *vs.* normal hydrogen electrode, which is due to the oxidation of Ru^{II} to Ru^{III}. No reduction of (**1**) has been observed. The $E_{\frac{1}{2}}$ value of the $Ru^{III/II}$ couple for (**1**) is much higher than that for $[Ru(NH_3)_6]^{2+}$ (0.051 V)[13] and (3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane)ruthenium(II) (0.29 V),[3] in accord with the fact that metal-to-ligand(pyridine) π back bonding stabilizes the electron-rich Ru^{II} state. However, the $E_{\frac{1}{2}}$ value for (**1**) is even comparable to that for $[Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridyl; 1.26 V in H_2O).[14] The high redox stability of (**1**) is remarkable and reflects a matching of stereochemical and electronic features of the ligand L^1 with those of d^6 Ru^{II}.

Acknowledgements

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