Synthesis and Single-crystal *X*-Ray Structure Determination of *trans*-$[RhCl_2(tmc)]PF_6$ (tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane)†

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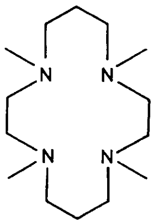
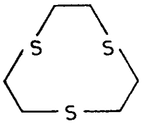
Reaction of $RhCl_3 \cdot 3H_2O$ with one molar equivalent of tmc (1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane) in refluxing MeOH affords the complex cation $[RhCl_2(tmc)]^+$. The complex $[RhCl_2(tmc)]PF_6$ crystallises in the orthorhombic space group *Pnma*, with each anion and each cation lying on a crystallographic mirror plane. The single-crystal *X*-ray structure of the octahedral complex shows the chloride ions mutually *trans* to one another, Rh–Cl 2.355(3) and 2.362(3) Å, with the tetra-aza macrocycle adopting an *RRSS* conformation with two methyl groups lying above, and two methyl groups lying below the RhN_4 plane [Rh–N 2.110(8) and 2.114(8) Å]. *trans*-$[RhCl_2(tmc)]^+$ shows a quasi-reversible Rh^{III}–Rh^{II} redox couple at $E_{\frac{1}{2}} = -0.99$ V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ in MeCN; slow loss of chloride occurs on electrochemical reduction of the complex.

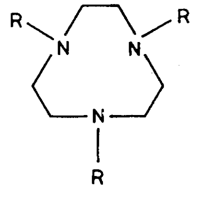
We have been investigating the synthesis and redox activation of macrocyclic complexes of the platinum group metals.[1] As part of this study, we have reported recently the stabilisation of Pt^{III} [2] and Pd^{III} [3,4] centres by polythia macrocycles, and the generation of Pd^{I} bound to tetra-aza ionophores.[5] We wished to extend this work to the complexation of Rh^{III} by N- and S-donor macrocyclic ligands, and to monitor their ability to stabilise d^7 Rh^{II} centres.[2,3] Our approach was based on the synthesis of mononuclear, octahedral Rh^{III} precursors incorporating redox-inactive tetra-aza ligands. On reduction, such complexes would therefore show potential metal-based redox activity, and could give the corresponding Jahn-Teller distorted mononuclear Rh^{II} species. The generation of univalent Cu,[6] Ni,[7] and Pd[5] complexes of tmc [tmc = 1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane (tetramethylcyclam)] has been reported previously. We reasoned that the stabilisation of reduced Rh centres might therefore be achieved using the same macrocyclic ligand system. A further impetus for this work has been the reported generation of mononuclear Rh^{II} porphyrin intermediates,[8] and the stabilisation of Rh^{II} by homoleptic hexathia co-ordination in $[Rh(L^1)_2]^{2+}$ (L^1 = 1,4,7-trithiacyclononane).[2,3,9]



tmc



L^1



L^2 : R = Me
L^3 : R = H

We report herein the synthesis, single-crystal *X*-ray structure determination, and preliminary redox data on the Rh^{III} macrocyclic complex $[RhCl_2(tmc)]^+$.

Results and Discussion

Reaction of $RhCl_3 \cdot 3H_2O$ with one molar equivalent of tmc in refluxing MeOH for 1 h under N_2 affords a yellow solution. Addition of excess of NH_4PF_6 gave a yellow precipitate which could be recrystallised from MeCN. The i.r. spectrum of the product shows a single band at 280 cm^{-1} assigned to a rhodium–chloride stretching vibration, ν(Rh–Cl), in addition to bands assignable to co-ordinated tmc, and PF_6^- counter ion. The u.v.–visible spectrum shows absorbances at $\lambda_{max.}$ 227 (ε 39 900), 324 (241), and 452 nm (63 dm^3 mol^{-1} cm^{-1}); the low absorption coefficients for the *d–d* transitions at 324 and 452 nm are consistent with a *trans*-dichloro system as observed for a series of analogous complexes *trans*-$[RhX_2(cyclam)]^+$ (cyclam = 1,4,8,11-tetra-azacyclotetradecane).[10] The absorbance at 227 nm is assigned to a Cl→Rh ligand-to-metal charge-transfer transition. The fast-atom bombardment (f.a.b.) mass spectrum of the complex shows a peak with the correct isotopic distribution at $M^+ = 429$ assigned to $[^{103}Rh^{35}Cl_2(tmc)]^+$, with peaks at $M^+ = 394$ and 358 corresponding to $[^{103}Rh^{35}Cl(tmc)]^+$ and $[^{103}Rh(tmc - H)]^+$ respectively. This, together with analytical data, suggested the complex cation to be *trans*-$[RhCl_2(tmc)]^+$. The ^1H n.m.r. spectrum of the product in CD_3CN showed a single resonance at δ 2.78 p.p.m. assigned to four equivalent methyl groups of a symmetric isomer. A further four methyl resonances observed at δ 2.76, 2.75, 2.67, and 2.51 p.p.m. may be assigned to the methyl groups of an asymmetric isomer.[11] The ^{13}C DEPT n.m.r. spectrum of the isolated product likewise showed the presence of two isomers in solution. The symmetric isomer showed resonances at δ 50.69 (CH_3), 23.86, 61.52, and 63.10 p.p.m. (three types of CH_2). Fourteen further resonances were observed in the ^{13}C n.m.r. spectrum with δ 47.11, 47.95, 49.87, 53.63 p.p.m. for the four methyl carbon centres. From these data, the asymmetric isomer can be

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† *trans*-Dichloro(1,4,8,11-tetramethyl-1,4,8,11-tetra-azacyclotetradecane-*NN′N″N‴*)rhodium(III) hexafluorophosphate.

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

Table 1. Selected bond lengths (Å) and angles (°) with estimated standard deviations in parentheses for $[RhCl_2(tmc)]PF_6$

Rh(1)–Cl(1)	2.355(3)	P(1)–F(1)	1.569(12)
Rh(1)–Cl(2)	2.362(3)	P(1)–F(2)	1.551(11)
Rh(1)–N(1)	2.110(8)	P(1)–F(3)	1.608(12)
Rh(1)–N(4)	2.114(8)	P(1)–F(4)	1.582(14)
Rh(1)–N(4)–C(3)	105.1(6)	Rh(1)–N(1)–C(2)	101.6(6)
Rh(1)–N(4)–C(5)	107.2(7)	Rh(1)–N(1)–C(14)	109.4(6)
Rh(1)–N(4)–C(4N)	124.7(9)	Rh(1)–N(1)–C(1N)	119.8(8)
Rh(1)–N(4)–C(3′)	105.3(7)	Rh(1)–N(1)–C(2′)	100.1(7)
Rh(1)–N(4)–C(5′)	108.9(10)	Rh(1)–N(1)–C(14′)	116.0(9)
Rh(1)–N(4)–C(4N′)	114.0(10)	Rh(1)–N(1)–C(1N′)	111.8(9)
Cl(1)–Rh(1)–Cl(2)	178.04(11)	F(1)–P(1)–F(2)	89.6(6)
Cl(1)–Rh(1)–N(1)	88.78(23)	F(1)–P(1)–F(3)	89.1(6)
Cl(1)–Rh(1)–N(4)	90.33(22)	F(1)–P(1)–F(4)	178.4(7)
Cl(2)–Rh(1)–N(1)	89.91(23)	F(2)–P(1)–F(3)	175.5(6)
Cl(2)–Rh(1)–N(4)	91.05(22)	F(2)–P(1)–F(4)	91.4(7)
N(1)–Rh(1)–N(4)	86.9(3)	F(3)–P(1)–F(4)	89.7(7)

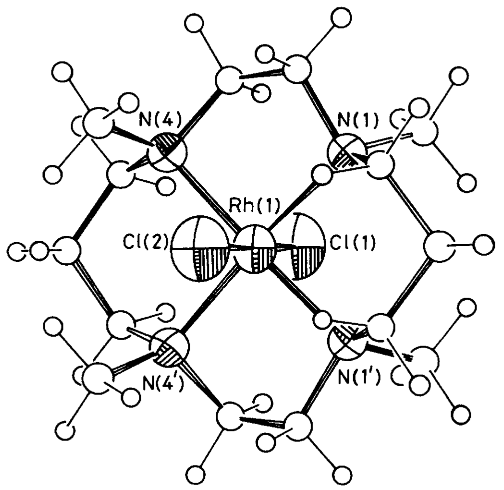

Figure. Structure of the $[RhCl_2(tmc)]^+$ cation with atomic numbering scheme adopted

assigned tentatively to a species with an *RSRR* configuration with three methyl groups above, and one methyl group below the RhN_4 plane, or to a solvated species. The ratio of the two isomers in solution appears to be near 50:50.

It was important to assign a configuration to the symmetric isomer which could be either *RRSS* (two methyls up, two methyls down) or *RSRS* (all methyls up). In view of the fact that no structural studies on Rh^{III} tetra-aza macrocyclic complexes have been previously reported, a crystallographic study was undertaken.

The complex was recrystallised from MeCN to yield orange rhomboid crystals of $[RhCl_2(tmc)]PF_6$. The cation is markedly disordered and the following discussion refers to the major component of that disorder. The *X*-ray structure shows four $[RhCl_2(tmc)]^+$ cations and four PF_6^- anions per unit cell, each bisected by a crystallographically-imposed mirror plane. The cation (see Figure) therefore possesses *m* symmetry with the mirror plane passing through the Rh and Cl atoms and through the central carbon atom of each propyl chain. The octahedral Rh^{III} atom is co-ordinated to two mutually *trans* Cl^- ligands and by a planar arrangement of four N-donors, Rh–Cl 2.355(3) and 2.362(3), Rh–N 2.110(8) and 2.114(8) Å. The structure shows the complex adopting an *RRSS* configuration (or *trans*-III in the notation used by Bosnich *et al.*[12]) with two methyl groups above, and two methyl groups below the RhN_4 co-ordination plane. The Rh atom is displaced by only 0.017 Å out of the N_4 plane confirming that the top and bottom faces of the complex appear identical to the co-ordinated Rh atom. This contrasts with the displacement of 0.082 Å of the Pd atom in the *RSRS* isomer of $[Pd(tmc)]^{2+}$.[5] Calculations indicate that the cavity size of the co-ordinated macrocycle in *trans*-$[RhCl_2(tmc)]^+$ [N(1)–N(4) 2.905(11), N(1)–N(1′) 3.146(11), and N(4)–N(4′) 2.983(11) Å] is slightly larger than that of $[Pd(tmc)]^{2+}$ [N(1)–N(4) 2.968(15), N(1)–N(1′) 2.860(16), and N(4)–N(4′) 2.946(17) Å].[5] Other platinum metal complexes of tmc that have been reported include *trans*-$[RuX_2(tmc)]^+$ (X = Cl, NCO, or NCS),[13] *trans*-$[Ru(O)_2(tmc)]^{2+/+}$,[14] *RSRR trans*-$[Ru(O)Cl(tmc)]^+$,[15] *RSRS trans*-$[Ru(O)(NCMe)(tmc)]^{2+}$,[16] and *trans*-$[Os(O)_2(tmc)]^{2+/+}$ [17] An *RRSS* configuration for co-ordinated tmc has been observed for $[Ni(tmc)(OH_2)_2]Cl_2 \cdot 2H_2O$, $[Ni(tmc)][CF_3SO_3]_2$,[18] $[\{Ni(tmc)(N_3)\}_2(\mu\text{-}N_3)]^+$,[19] and $[Ni(O_2COMe)_2(tmc)]$,[20] while the *RSRS* configuration has been found in $[Ni(O_2COMe)(tmc)]^+$,[20] $[Ni(tmc)][CF_3SO_3]_2 \cdot Me_2CO \cdot H_2O$,[21] and $[Ni(N_3)(tmc)]^+$.[22] Strain-energy minimisation analyses on Ni^{II} complexes by Hambley[21] suggest that the *RSRS* and *RRSS* conformations are preferred by four-co-ordinate square-planar and by six-co-ordinate octahedral complexes of tmc respectively. Our crystallographic studies on $[Pd(tmc)]^{2+}$,[5] $[Pd(tbc)]^{2+}$ [tbc = 1,4,8,11-tetrabenzyl-1,4,8,11-tetra-azacyclotetradecane (tetrabenzylcyclam)],[1,23] and *trans*-$[RhCl_2(tmc)]^+$ are in accord with these calculations.

trans-$[RhCl_2(tmc)]^+$ shows a quasi-reversible reduction at $E_{\frac{1}{2}} = -0.99$ V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$ in MeCN (0.1 mol dm^{-3} $NBu^n{}_4PF_6$) at platinum electrodes assigned tentatively to a Rh^{III}–Rh^{II} couple. Cyclic voltammetry confirmed that loss of Cl^- occurred on reduction of $[RhCl_2(tmc)]^+$, the $Cl^{-/0}$ couple being observed near +1.0 V, with a daughter product being detected near −0.35 V. Binding of Cl^- to the metal centre would be expected to be destabilised on reduction of rhodium(III) to rhodium(II), leading to the formation of five-co-ordinate or solvated product(s). This opens up the possibility of utilising the reduction of $[RhCl_2(tmc)]^+$ to generate an electron-rich rhodium centre which, on loss of Cl^-, has a vacant co-ordination site for binding of substrates such as CO, O_2, or alkene. More importantly, these results show that simple alkylated tetra-aza macrocycles could be important ligands for the stabilisation of rhodium(II) [and rhodium(I)] species.

Relatively few examples of mononuclear, rhodium(II) species have been reported in the literature.[8,9,24–26] An important example is $[Rh(L')]$ [L′ = porphyrinate(2−)] which readily dimerises to $[\{Rh(L')\}_2]$ involving a direct Rh–Rh bond.[8] Other examples include $[Rh(sep)]^{2+}$ [sep = 1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane (sepulchrate)] which shows[25] a Rh^{II} couple at $E_{\frac{1}{2}} = -0.71$ V *vs.* $[Fe(\eta\text{-}C_5H_5)_2]$–$[Fe(\eta\text{-}C_5H_5)_2]^+$. The related mixed-sandwich species $[Rh(\eta\text{-}C_5Me_5)(L)]^{2+}$ ($L = L^1$—L^3) likewise show reversible or quasi-reversible reductions on the cyclic voltammetric time-scale; the reduction products derived from these complexes are however unstable during the electrogeneration experiments at 293 K.[27]

Current work is aimed at the full electrochemical characterisation of the redox and chemical processes (ligand dissociation, dimerisation, O_2 binding) occurring in the Rh systems described herein, and the synthesis of the related complexes $[RhY_2(tmc)]^{3+}$ (Y = pyridine or PR_3).

Experimental

Infrared spectra were measured as Nujol mulls, KBr and CsI discs using a Perkin-Elmer 598 spectrometer over the range 200—4 000 cm^{-1}. U.v.–visible spectra were measured in quartz cells using a Pye Unicam SP8-400 spectrophotometer. Microanalyses were performed by the Edinburgh University Chemistry Department Microanalytical Service. Electrochemical measurements were performed on a Bruker E310 Universal Modular polarograph. All readings were taken using a three-electrode potentiostatic system in acetonitrile containing 0.1 mol dm^{-3} $NBu^n{}_4PF_6$ or $NBu^n{}_4BF_4$ as supporting electrolyte. Cyclic voltammetric measurements were carried out using a double platinum electrode and a Ag–AgCl reference electrode. Mass spectra were run by electron impact on a Kratos MS 902 and by fast-atom bombardment on a Kratos MS 50TC spectrometer.

Synthesis of trans-$[RhCl_2(tmc)]PF_6$.—$RhCl_3{\cdot}3H_2O$ (0.15 g, 0.5 mmol) was treated with one molar equivalent of tmc (0.15 g, 0.59 mmol) in refluxing MeOH under N_2 for 1 h. Addition of excess of NH_4PF_6 gave a golden microcrystalline product which was collected, recrystallised from MeCN, and dried *in vacuo*. Yield: 230 mg, 70% (Found: C, 29.0; H, 5.7; N, 9.7. Calc. for $C_{14}H_{32}Cl_2F_6N_4PRh$: C, 29.2; H, 5.6; N, 9.7%). I.r. spectrum: 3 000, 2 940, 1 450, 1 380, 1 290, 1 260, 1 240, 1 200, 1 170, 1 150, 1 110, 1 050, 1 030, 980, 920, 840, 800, 790, 750, 720, 555, and 280 cm^{-1}. U.v.-visible spectrum: $\lambda_{max.}$ 227 (ε 39 900), 324 (241), and 452 nm (63 dm^3 mol^{-1} cm^{-1}). F.a.b. mass spectrum: found M^+ 429, calc. for $[^{103}Rh^{35}Cl_2(tmc)]^+$ M^+ 429; found M^+ 394, calc. for $[^{103}Rh^{35}Cl(tmc)]^+$ M^+ 394; found M^+ 358, calc. for $[^{103}Rh(tmc - H)]^+$ M^+ 358. ^1H N.m.r. spectrum (CD_3CN, 293 K, 200 MHz): δ 2.78 (s, CH_3, 12 H) and 2.2—3.5 p.p.m. (m, CH_2, 20 H) (symmetric isomer); δ 2.76, 2.75, 2.67, 2.51 (s, CH_3, 12 H) and 2.2—3.5 p.p.m. (m, CH_2, 20 H) (asymmetric isomer). ^{13}C DEPT n.m.r. (CD_3CN, 293 K, 50.32 MHz): δ 23.86 ($CH_2\mathit{C}H_2CH_2$, 2 C), 50.69 (CH_3, 4 C), 61.52 ($N\mathit{C}H_2CH_2\mathit{C}H_2N$, 4 C), 63.10 p.p.m. ($N\mathit{C}H_2\mathit{C}H_2N$, 4 C) (symmetric isomer); δ 23.55, 24.36 ($NCH_2\mathit{C}H_2CH_2N$, 2 C), 47.11, 47.95, 49.87, 53.63 (CH_3, 4 C), 55.21, 56.12, 60.80, 60.94, 62.93 (two overlapping resonances), 63.58, 64.40 p.p.m. (NCH_2, 8 C) (asymmetric isomer).

Addition of $NaBPh_4$ in place of NH_4PF_6 afforded the BPh_4^- salt $[RhCl_2(tmc)]BPh_4$ (Found: C, 61.4; H, 7.0; N, 8.1. Calc. for $C_{38}H_{52}BCl_2N_4Rh$: C, 60.9; H, 7.0; N, 7.5%).

Single-crystal X-Ray Structure of trans-$[RhCl_2(tmc)]PF_6$.—Recrystallisation from MeCN yielded orange, rhomboid crystals suitable for a crystallographic study.

Crystal data. $C_{14}H_{32}Cl_2F_6N_4PRh$, M = 575.3, orthorhombic, space group *Pnma*, a = 14.952(4), b = 10.687(3), c = 13.487(4) Å, U = 2 155 Å^3 (by least-squares refinement on diffraction angles for 17 centred reflections), Z = 4, λ = 0.710 73 Å, D_c = 1.773 g cm^{-3}. Crystal dimensions 0.79 × 0.54 × 0.46 mm, $F(000)$ = 1 168, $\mu(Mo\text{-}K_\alpha)$ = 11.09 cm^{-1}.

Data collection and processing. Stoe-Siemens AED2 four-circle diffractometer, ω–θ mode, 1 650 data ($+h, k, l$) measured to $2\theta = 45°$, giving 1 265 with $F \geqslant 6\sigma(F)$. No significant crystal decay, no absorption correction.

Structure analysis and refinement. The Rh position was deduced from a Patterson synthesis and the remaining non-hydrogen atoms from iterative rounds of least-squares refinement and difference Fourier synthesis.[28] Anisotropic thermal parameters were refined for Rh, Cl, P, F, and N. During refinement, some disorder of the macrocyclic ligand became obvious and could only be modelled by refining the minor isomer as an idealised, rigid group and, for the major isomer, constraining all C–C and C–N bonds to a common value of 1.523(20) Å and all macrocyclic angles to be tetrahedral. The discussion of the structure refers to the major component [66.3(13)%] of the disorder. We believe that the disorder arises from rotation of one component relative to the other, although the presence of a minor isomer in the solid state cannot be entirely discounted. At convergence, R, R' = 0.0715, 0.1153 respectively, S = 1.369 for 126 parameters, and the final difference Fourier synthesis showed no feature above 1.26 or below −0.74 e Å^{-3}. The weighting scheme $w^{-1} = \sigma^2(F) + 0.000\,811F^2$ gave satisfactory agreement analyses. Illustrations were prepared using ORTEP,[29] molecular geometry calculations utilised CALC,[30] and scattering factor data were inlaid[28] or taken from ref. 31. Fractional atomic co-ordinates are given in Table 2.

Table 2. Fractional atomic co-ordinates with estimated standard deviations in parentheses for $[RhCl_2(tmc)]PF_6$

Atom	*x*	*y*	*z*
Rh(1)	0.150 94(6)	0.25	0.125 14(7)
Cl(1)	0.024 92(22)	0.25	0.020 41(25)
Cl(2)	0.274 05(25)	0.25	0.234 9(3)
N(1)	0.092 2(5)	0.102 8(7)	0.206 5(7)
N(4)	0.211 7(5)	0.110 4(7)	0.036 8(5)
C(2)	0.155 9(8)	−0.004 9(15)	0.184 5(7)
C(3)	0.172 1(11)	−0.012 6(13)	0.073 1(7)
C(5)	0.182 8(14)	0.133 7(4)	−0.069 9(10)
C(6)	0.229 6(18)	0.25	−0.109 4(11)
C(13)	0.039 4(14)	0.25	0.336 8(12)
C(14)	0.095 4(12)	0.133 7(4)	0.316 7(9)
C(4N)	0.310 7(7)	0.077 4(24)	0.039 2(15)
C(1N)	−0.003 3(6)	0.062 5(15)	0.183 7(16)
C(2′)	0.089 5(7)	0.001 4(17)	0.127 2(9)
C(3′)	0.182 2(9)	−0.013 5(12)	0.081 8(12)
C(5′)	0.312 9(7)	0.122 8(19)	0.045(3)
C(6′)	0.341 7(10)	0.25	0.005(4)
C(13′)	−0.004 1(17)	0.25	0.301 4(25)
C(14′)	−0.002 1(7)	0.126 6(20)	0.245 0(18)
C(1N′)	0.151 7(16)	0.060 3(20)	0.291 7(13)
C(4N′)	0.184 5(22)	0.114 8(25)	−0.072 0(10)
P(1)	0.571 4(4)	0.25	0.864 0(4)
F(1)	0.650 4(8)	0.25	0.940 7(11)
F(2)	0.526 4(7)	0.141 8(8)	0.922 2(7)
F(3)	0.623 7(8)	0.354 3(10)	0.800 6(8)
F(4)	0.493 8(11)	0.25	0.784 3(12)

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters, remaining bond lengths and angles, H-atom co-ordinates.

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