Co-ordination of 6,13-Dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine to Platinum(II) and Palladium(II). Syntheses, Characterisation, and *X*-Ray Crystal Structures of the Perchlorate Salts of Both Complexes†

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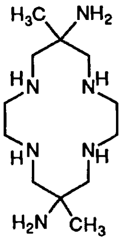
Both platinum(II) and palladium(II) complexes of 6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine (L^1) as a quadridentate ligand have been prepared in facile reactions as perchlorate salts, and characterised by electronic and n.m.r. spectroscopy, and voltammetry. The platinum(II) complex, $[Pt(H_2L^1)][ClO_4]_4$, represents the first structurally characterised with a saturated macrocyclic tetra-amine ligand. It crystallises in the triclinic space group $P\bar{1}$, with a = 10.006(4), b = 8.691(3), c = 8.173(2)Å, α = 75.74(2), β = 79.00(3), and γ = 83.54(3)°, as does the complex $[Pd(H_2L^1)][ClO_4]_4\cdot6H_2O$, with a = 11.123(5), b = 8.609(5), c = 8.541(3) Å, α =91.27(4), β = 96.09(3), and γ = 98.20(4)°. The cell of the palladium complex is derivative of that of the platinum simply by expansion, albeit with variations in some individual parameters. The Pt–N distances [2.045(7) and 2.043(6) Å] and Pd–N distances [2.044(3) and 2.036(3) Å] are slightly shorter than in non-cyclic $M^{II}N_4$ analogues.

The pendant-arm macrocycle 6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine (L^1) has been shown to be a versatile polyamine ligand when co-ordinated to transition-metal ions.[1–3] Depending on the degree of protonation of the pendant amino groups and the preferred co-ordination geometry of the metal ion, the ligand may occupy four, five, or six co-ordination sites when complexed. For example, it may act as quadridentate when complexed with copper(II)[4] and low-spin nickel(II)[5] which both prefer a square-planar co-ordination geometry. Moreover, the pendant groups, when protonated, may remain unco-ordinated in octahedral complexes of metal ions such as cobalt(III)[1] and rhodium(III).[3] Deprotonation of the pendant amines can lead to sexidentate co-ordination of the ligand to these metal ions.[1,3]

It is somewhat surprising that despite the vast array of platinum(II) and palladium(II) complexes in the literature there are very few tetra-aza macrocyclic complexes of platinum(II) extant, and more though still limited examples of palladium(II) tetra-aza macrocyclic species. The crystal structure of the palladium(II) complex of the unsubstituted 1,4,8,11-tetra-azacyclotetradecane (cyclam, L^2) has been reported.[6] However, the sole report of a saturated tetra-aza macrocyclic complex of platinum(II) gave little spectroscopic information, with the emphasis being on the biological activity of the complex.[7] Recently, the synthesis of $[PtL^2]^{2+}$, its palladium(II) relative, and some oxidation products of these complexes have been patented.[8] The diamide 5,7-dioxo-cyclam (L^3) has been reported as its platinum(II) complex;[9] this ligand must be deprotonated at each amide nitrogen before co-ordination and is therefore not strictly comparable with saturated tetra-aza macrocycles.

Here we report the synthesis, physical properties, and *X*-ray crystal structure of square-planar complexes as the perchlorate salts of platinum(II) and palladium(II) with the saturated macrocycle L^1.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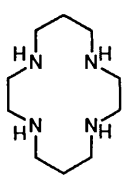
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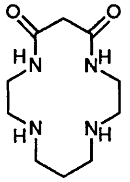
L^3

Experimental

Physical Methods.—N.m.r. spectra of compounds dissolved in D_2O were recorded on a JEOL FX-90Q FT-NMR spectrometer and chemical shifts in p.p.m. are cited relative to sodium 3-trimethylsilylpropionate and tetramethylsilane for ^1H and ^{13}C spectra respectively. Electronic spectra were recorded on a Hitachi 150-20 spectrophotometer, i.r. spectra of complexes dispersed in KBr discs on a Nicolet MX-1 FT-IR spectrometer. Polarography was performed using an AMEL model 457 controller employing a PAR 303 dropping mercury working electrode with platinum-counter and silver–silver chloride reference electrodes. Aqueous cyclic voltammetry was performed with the above apparatus and also with a BAS CV-27 controller coupled with a glassy carbon working electrode, and other electrodes as above. All measurements were made on nitrogen-purged solutions 0.1 mol dm^{-3} in $NaClO_4$. Non-aqueous cyclic voltammetry was performed with the BAS

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix—xxii.

CV-27 apparatus but with a gold-wire reference electrode. Potentials were calibrated by employing the ferrocene–ferrocenium couple (+0.10 V *versus* Ag–AgCl) as a standard. The solvent system was dry CH_3CN (0.1 mol dm^{-3} in $NaClO_4$) purged with nitrogen prior to measurement.

Syntheses.—The ligand 6,13-dimethyl-1,4,8,11-tetra-azacyclotetradecane-6,13-diamine hexahydrochloride (L^1·6HCl) was prepared as previously described.[1] Potassium tetrachloroplatinate(II) was prepared according to a literature synthesis.[10] Potassium tetrachloropalladate(II) was obtained from Strem Chemicals.

(13-*Ammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecan*-6-*amine*)*platinum*(II) *perchlorate*, $[Pt(HL^1)][ClO_4]_3$. To a refluxing solution of potassium tetrachloroplatinate(II) (1.0 g) in water (100 cm^3) was slowly added a solution of L^1·6HCl (1.3 g) in water (100 cm^3) which had been neutralised with sodium hydroxide. The solution was refluxed for 3 h to afford a pale yellow solution. This solution was cooled, neutralised, and sorbed on a column (15 × 3 cm) of Sephadex SP-C25 cation-exchange resin. The eluate was monitored at 270 nm *via* a flow-through spectrometer cell. The column was washed with 0.1 mol dm^{-3} $NaClO_4$ solution, the product eluted with 0.2 mol dm^{-3} $NaClO_4$ solution and evaporated to *ca.* 50 cm^3. Perchloric acid (1 cm^3, 5 mol dm^{-3}) was added and, upon standing, a colourless powder precipitated which was collected, washed with ethanol and diethyl ether, and dried in a vacuum desiccator (1.5 g, 83%) (Found: C, 19.2; H, 4.1; N, 10.95. Calc. for $C_{12}H_{31}Cl_3N_6O_{12}Pt$: C, 19.2; H, 4.15; N, 11.2%). Electronic spectrum (in water): $\lambda_{max.}$ 260 (ε 49) and 231 nm (ε 270 dm^3 mol^{-1} cm^{-1}), N.m.r. (D_2O): ^1H, δ 1.58 (s, 6 H), 3.11 (t, 8 H), and 3.29 (s, 8 H); ^{13}C (^1H-decoupled), δ 17.9, 44.9, 50.4, and 53.2 p.p.m.

(13-*Ammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecan*-6-*amine*)*palladium*(II) *perchlorate hydrate*, $[Pd(HL^1)][ClO_4]_3 \cdot H_2O$. A solution of L^1·6HCl (1.7 g) in water (50 cm^3) was neutralised with sodium hydroxide and added dropwise to a refluxing solution of potassium tetrachloropalladate(II) (1.0 g) in water (150 cm^3). A dark yellow precipitate formed immediately and reflux was continued for a further 90 min upon which the precipitate redissolved and the solution colour faded to pale yellow. The solution was cooled and filtered to remove traces of palladium metal and the filtrate sorbed on a column of Sephadex SP-C25 resin. The eluate was monitored spectrophotometrically at 300 nm. The column was washed with 0.1 mol dm^{-3} $NaClO_4$ solution and the product removed with 0.5 mol dm^{-3} $NaClO_4$ solution. The eluate was concentrated on a rotary evaporator to *ca.* 30 cm^3 and perchloric acid (2 cm^3, 5 mol dm^{-3}) added to aid precipitation of the off-white product which was collected, washed with ethanol and diethyl ether, then dried in a vacuum desiccator (1.55 g, 76%) (Found: C, 21.4; H, 5.2; N, 12.35. Calc. for $C_{12}H_{33}Cl_3N_6O_{13}Pd$: C, 21.15; H, 4.9; N, 12.3%). Electronic spectrum (in water): $\lambda_{max.}$ 276 (ε 430) and 200 nm (ε 20 400 dm^3 mol^{-1} cm^{-1}). N.m.r. (D_2O): ^1H, δ 1.38 (s, 6 H), 2.80, 3.17 (q, 8 H), 2.84, 3.00 (q, 8 H); ^{13}C (^1H-decoupled), δ 20.5, 54.8, 56.3, and 58.4 p.p.m.

Preparation of the palladium compound by crystallisation was also performed. Overall, the non-protonated, mono- and di-protonated macrocycle compounds were isolated as perchlorate salts, the first from basic solution, and the last two from $HClO_4$ solutions of increasing acidity.

(6,13-*Diammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*palladium*(II) *trichloride–tetrachloropalladate*(II)–*water* (1/0.5/2.5), $[Pd(H_2L^1)]Cl_3 \cdot [PdCl_4]_{0.5} \cdot 2.5H_2O$. Palladium chloride (0.4 g, 2.26 mmol) was refluxed in concentrated HCl until dissolved, and the solution rotary evaporated to dryness. The residue of H_2PdCl_4 was dissolved in a small volume of water and $L^1 \cdot 3.5H_2O$ (0.5 g, 1.56 mmol) added, the solution boiled for a few minutes, then filtered while hot. The solution was cooled slowly, when lustrous brown crystals of the product separated; they were collected, washed with ethanol, and air dried (0.9 g, 60%) (Found: C, 22.5; H, 6.0; Cl, 27.3; N, 13.1. Calc. for $C_{24}H_{74}Cl_{10}N_{12}O_5Pd_3$: C, 22.5; H, 5.8; Cl, 27.6; N, 13.1%).

(6,13-*Diammonio*-6,13-*dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*)*palladium*(II) *perchlorate hexahydrate*, $[Pd(H_2L^1)][ClO_4]_4 \cdot 6H_2O$. Ivory coloured crystals of the product were obtained when the chloropalladate salt was recrystallised from hot dilute aqueous perchloric acid. These were collected, washed with ethanol, and air dried (Found: C, 16.7; H, 4.9; N, 9.7. Calc. for $C_{12}H_{44}Cl_4N_6O_{22}Pd$: C, 16.5; H, 5.3; N, 9.6%).

(6,13-*Dimethyl*-1,4,8,11-*tetra-azacyclotetradecane*-6,13-*diamine*)*palladium*(II) *perchlorate hemihydrate*, $[PdL^1][ClO_4]_2 \cdot 0.5H_2O$. The product was formed by recrystallising the previous compound from hot dilute aqueous ammonia. The beige coloured crystals were collected, washed with ammonia solution, and dried (Found: C, 25.4; H, 5.7; N, 15.2. Calc. for $C_{12}H_{31}Cl_2N_6O_{8.5}Pd$: C, 25.4; H, 5.4; N, 14.8%). A mixed chloride–tetrachloropalladate salt of $[PdL^1]^{2+}$ can be prepared in the same manner, from the protonated precursor described above.

Crystals suitable for *X*-ray work, rather than the powders isolated above, were grown by dissolving *ca.* 0.1 g of each of the above complexes in water (50 cm^3), adding perchloric acid (5 cm^3, 5 mol dm^{-3}), and permitting slow evaporation. In both cases, colourless crystals of the form $[Pt(H_2L^1)][ClO_4]_4$ and $[Pd(H_2L^1)][ClO_4]_4 \cdot 6H_2O$ were obtained from the strongly acidic solutions, with both pendant primary amines protonated. These compounds were spectroscopically identical with those isolated in the general syntheses above.

Structure Determination.—*Crystal data.* $C_{12}H_{32}Cl_4N_6O_{16}Pt$, M = 853.3, triclinic, space group $P\bar{1}$ (C_i^1, no. 2), a = 10.006(4), b = 8.691(3), c = 8.173(2) Å, α = 75.74(2), β = 79.00(3), γ = 83.54(3)°, U = 674.6 Å^3, $D_c(Z = 1)$ = 2.10 g cm^{-3}, $F(000)$ = 420, μ_{Mo} = 67.4 cm^{-1}, specimen, colourless plate, 0.10 × 0.40 × 0.40 mm; $A^*_{min.,max.}$ = 1.93, 8.94; Syntex $P2_1$ diffractometer, $2\theta_{max.}$ = 50°, N = 2 389, N_o = 2 389; R = 0.024, R' = 0.038, n_w = 3.

$C_{12}H_{32}Cl_4N_6O_{16}Pd \cdot 6H_2O$, M = 872.8, triclinic, space group $P\bar{1}$, a = 11.123(5), b = 8.609(5), c = 8.541(3) Å, α = 91.27(4), β = 96.09(3), γ = 98.20(4)°, U = 804.3 Å^3, $D_c(Z = 1)$ = 1.81 g cm^{-3}, $F(000)$ = 448, μ_{Mo} = 9.1 cm^{-1}; specimen, colourless, 0.05 × 0.20 × 0.10 mm; $A^*_{min.,max.}$ = 1.05, 1.21; Enraf-Nonius CAD-4 diffractometer, $2\theta_{max.}$ = 55°, N = 3 671, N_o = 3 329; R = 0.038; R' = 0.049, n_w = 4.

Unique data sets were measured at *ca.* 295 K to the specified $2\theta_{max.}$ limits and on the machines as recorded; N independent reflections were obtained, N_o with $I > 3\sigma(I)$ being considered 'observed' and used in the full-matrix least-squares refinement after analytical absorption correction (monochromatic Mo-K_α radiation, λ = 0.71069 Å; cells were calibrated on the same machine on the same day. Anisotropic thermal parameters were refined for the non-hydrogen atoms; hydrogen atoms were located in difference maps and included with (x, y, z, U_{iso}) constrained at estimated values. Residuals at convergence on $|F|$ are conventional R, R'; statistical reflection weights, derivative of $\sigma^2(I) = \sigma^2(I_{diff.}) + 0.000n_w\sigma^4(I_{diff.})$, were used. Neutral atom scattering factors were employed;[11] computation used the XTAL 2.6 program system[12] implemented by S. R. Hall. Pertinent results are given in the Tables and Figures.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates and thermal parameters.

Results and Discussion

The syntheses of the platinum(II) and palladium(II) complexes of

L^1 were found to generate each complex in high yield with no other species being detectable by spectroscopy during column chromatography. Both complexes were stable in aqueous acid solution for extended periods with no dissociation or disproportionation reactions being observed. Infrared spectra of the isolated complexes essentially replicated those of other metal(II) complexes of L^1.[13] Refluxing stoicheiometric amounts of metal salt and ligand avoids the less-efficient traditional method for the syntheses of platinum(II) and palladium(II) tetra-amines where an intermediate $[PtCl_4]^{2-}$ or $[PdCl_4]^{2-}$ salt of the complex is isolated and treated with more ligand to generate the desired complex. As mentioned in the Experimental section, the tetrachloropalladate salt of the palladium(II) complex may be isolated by shortening the reaction time; this may be converted into the perchlorate salt by recrystallisation from dilute perchloric acid if required.

The ^1H-decoupled ^{13}C n.m.r. spectra of both complexes are consistent with the same C_{2h} symmetry, there being only four magnetically distinct sets of carbon atoms. The pendant methyl groups account for the low-field resonance, with peaks assigned to the carbons in the five-membered rings, the tertiary carbons to which the pendants are attached, and the remaining methylene carbons of the six-membered rings appearing in turn to higher field. The ^1H n.m.r. spectra differ slightly in their resolution of the proton–proton coupling. The spectrum of the platinum(II) complex comprises a low-field singlet, corresponding to the methyl groups, a broad triplet from coupling between protons in the five-membered rings, and a singlet from the isolated methylene groups in the six-membered rings. The spectrum of the palladium(II) complex is much clearer with two AB quartets being resolved from geminal coupling of the protons on the two types of non-equivalent methylene groups. The reason for the poorer resolution in the platinum(II) spectrum is most probably a result of unresolved coupling with the ^{195}Pt nucleus (*ca.* 30% abundance).

The electronic spectra of both complexes are consistent with an $^1A_{1g}$ ground state. The low-energy maximum (260 nm) of the platinum(II) complex is assigned as a $^1A_{2g} \leftarrow {}^1A_{1g}$ transition.[14] The analogous transition is not resolved in the spectrum of the palladium(II) analogue. Both spectra display $^1B_{1g} \leftarrow {}^1A_{1g}$ transitions, at 276 nm for the palladium(II) and 231 nm for the platinum(II) complex. The intense peak at 200 nm in the spectrum of the palladium(II) complex is presumably a charge-transfer transition.

Cyclic voltammetry and polarography were employed to study the redox properties of both complexes. Aqueous d.c. polarography indicated that the platinum(II) complex of L^1 undergoes a one-electron oxidation at +0.15 V (*versus* Ag–AgCl) whereas the palladium(II) analogue is oxidised in a clear two-electron process at +0.10 V, from wave-height comparisons with standards. Cyclic voltammetry (scan rate 100 mV s^{-1}, mercury drop working electrode) in water of both complexes showed these waves to be totally irreversible, but the positive potential limit imposed by using Hg (*ca.* +0.4 V *versus* Ag–AgCl) did not allow examination of any further processes at more positive potentials. On glassy carbon, a single anodic wave at −0.10 V (*versus* Ag–AgCl) is observed when scanning up to +0.8 V in the voltammogram of the platinum complex, indicating that the initially formed platinum(III) transient is unstable to disproportionation on the voltammetric time-scale and does not survive long enough to enable observation of a Pt^{III}–Pt^{IV} wave. Disproportionation is most probably the mechanism by which the platinum(III) transient decays. A cathodic wave is observed at −0.12 V which is the reduction of the putative platinum(IV) product of the disproportionation. As this species is the result of a chemical reaction following the oxidation [electrochemical-chemical (e.c.) mechanism] it is not surprising that the position of the cathodic wave is well removed from that of the forward wave. A similar situation is observed in acetonitrile, although the cathodic wave is shifted to −0.60 V (*versus* Ag–AgCl). The behaviour of the palladium(II) complex at a glassy carbon electrode is not significantly different from that observed at a mercury drop electrode. Metal(II)–metal(I) couples were outside the limit set by the acetonitrile solvent system (*ca.* −2 V *versus* Ag–Ag(Cl). It is possible that N-methylation of the ligand may stabilise the palladium(I) state,[15] but this was not pursued. The outcome of chemical oxidations is being probed, however, and will be reported subsequently.

The *X*-ray crystal structures of the perchlorate salts of both complex cations confirm a square-planar arrangement of the four secondary amino groups about the metal ion which lies on a centre of symmetry in each case. The ligand is unequivocally the *anti* isomer where the protonated pendant ammonio groups are

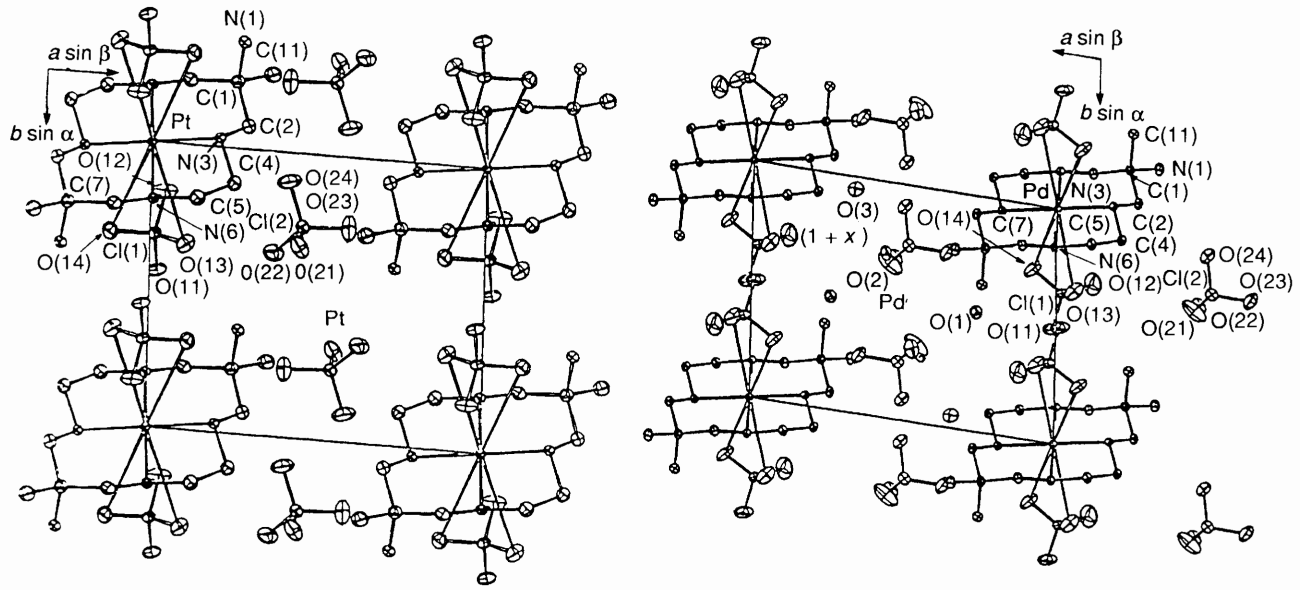

Figure 1. Unit-cell projections, *c* away from and toward the reader respectively, for $[Pt(H_2L^1)][ClO_4]_4$ and $[Pd(H_2L^1)][ClO_4]_4 \cdot 6H_2O$. Thermal ellipsoids (20%) are shown for the non-hydrogen atoms, together with labelling

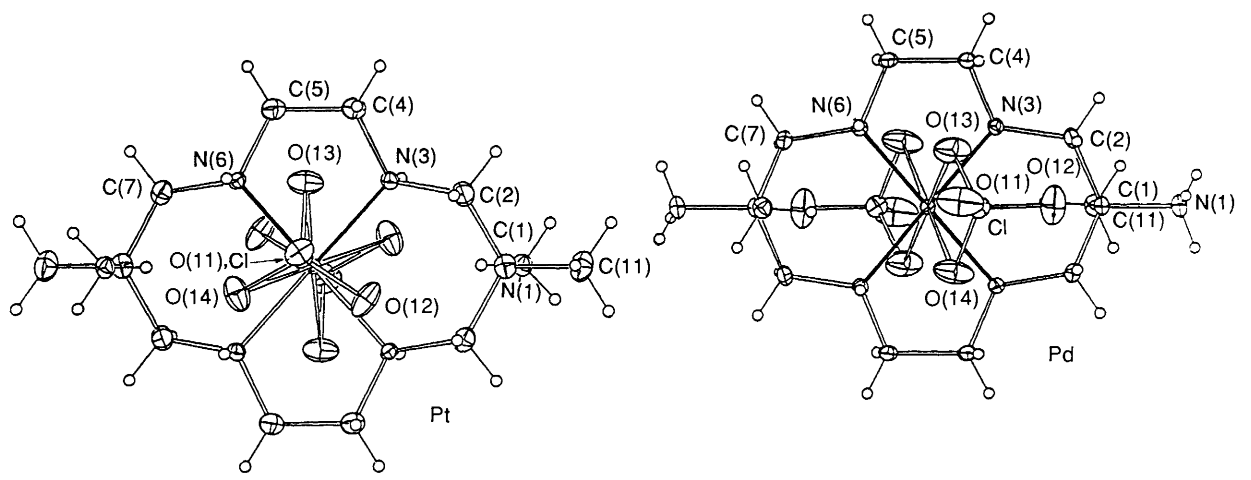

Figure 2. Projections of the two cations $[Pt(H_2L^1)]^{4+}$ and $[Pd(H_2L^1)]^{4+}$ normal to the N_4 co-ordination planes; hydrogen atoms have arbitrary radii of 0.1 Å. The relationship of the perchlorates in each case is shown, the metal atom being located on an inversion centre

Table 1. Non-hydrogen atom co-ordinates for $[Pt(H_2L^1)][ClO_4]_4$ and $[Pd(H_2L^1)][ClO_4]_4 \cdot 6H_2O$

	M = Pt			M = Pd		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
M	0	0	0	0	0	0
C(1)	0.253(1)	−0.232(1)	0.186(1)	−0.233 8(3)	−0.212 0(4)	−0.228 1(4)
N(1)	0.270 2(8)	−0.371 4(8)	0.101(1)	−0.331 1(3)	−0.235 8(4)	−0.367 2(4)
C(11)	0.356(1)	−0.265(1)	0.308(2)	−0.242 9(4)	−0.364 8(5)	−0.141 0(5)
C(2)	0.287(1)	−0.078(1)	0.052(1)	−0.264 1(3)	−0.075 4(5)	−0.128 5(5)
N(3)	0.204 6(7)	−0.031 1(8)	−0.086 7(9)	−0.182 8(3)	−0.046 1(3)	0.021 3(3)
C(4)	0.249(1)	0.120(1)	−0.211(1)	−0.212 5(3)	0.088 6(5)	0.115 7(5)
C(5)	0.139(1)	0.182(1)	−0.321(1)	−0.122 7(3)	0.124 9(5)	0.250 6(5)
N(6)	0.005 7(7)	0.196 5(7)	−0.198 6(8)	0.005 8(3)	0.160 8(3)	0.180 2(3)
C(7)	−0.111(1)	0.224(1)	−0.295(1)	0.113 7(3)	0.172 2(5)	0.299 6(4)
Cl(1)	0.014 1(3)	0.314 7(2)	0.219 1(3)	−0.021 75(9)	0.347 4(1)	−0.263 2(1)
O(11)	0.023 7(9)	0.438 4(8)	0.301 9(9)	0.011 7(5)	0.504 8(5)	−0.293 7(7)
O(12)	0.045(1)	0.164 9(8)	0.324(1)	−0.120 2(5)	0.288 7(8)	−0.373 1(7)
O(13)	0.107(1)	0.343(1)	0.061(1)	−0.059 4(4)	0.331 8(6)	−0.112 9(5)
O(14)	−0.119 7(9)	0.318(1)	0.183(1)	0.077 4(4)	0.265 2(5)	−0.278 5(5)
Cl(2)	0.453 4(3)	0.252 7(3)	0.267 7(3)	−0.515 1(1)	0.252 3(1)	−0.209 4(1)
O(21)	0.446(1)	0.322(1)	0.091(1)	−0.455 0(6)	0.334 7(7)	−0.075 9(5)
O(22)	0.369(1)	0.347(1)	0.366(1)	−0.469 5(4)	0.317 2(6)	−0.345 1(4)
O(23)	0.592(1)	0.244(1)	0.286(1)	−0.642 9(4)	0.254 5(6)	−0.219 5(6)
O(24)	0.410(1)	0.099(1)	0.316(2)	−0.499 2(4)	0.092 8(5)	−0.197 9(6)
O(1)				0.260 8(3)	0.485 6(4)	−0.440 3(4)
O(2)				0.559 3(3)	0.297 4(4)	0.259 4(4)
O(3)				−0.336 6(4)	0.053 9(5)	−0.508 1(4)

on opposite sides of the macrocycle. This is in agreement with all structures of L^1 complexes determined so far (at least eighteen),[1–5,16] adding weight to the view that the synthesis of the ligand is stereospecific towards the *anti* isomer.

Surprisingly, in view of the identical method employed for growing the crystals, the palladium(II) complex is a hexahydrate whereas the platinum(II) complex is anhydrous. Also, remarkably, the unit cell of the palladium(II) complex is derivative of that of the platinum(II) compound simply by expansion, albeit with fairly radical variations in some of the individual parameters, with the triobtuse setting becoming triacute. The similarity may be apprehended from a comparison of the two cell diagrams (Figure 1), and the tabulated co-ordinates where, in the settings given, for corresponding atoms, $(x, y, z)_{Pd} \approx (\bar{x}, y, \bar{z})_{Pt}$ (Table 1). A notable exception to this is the pair of substituents on the tertiary carbon, C(1), which have opposite assignments in the two structures (Figure 2). If one considers the conformation of the six-membered rings it is clear that the chair conformer is observed in both structures, but the amine pendant in the palladium(II) complex is equatorial whereas in the platinum(II) complex it is axial. This assignment is supported by quite unambiguous refinement behaviour; in the palladium structure N(1) and C(11) if interchanged adopt grossly disparate thermal envelopes, while *R*, *R′* rise to 0.042, 0.055. Similar changes are observed in the platinum structure. Examples with the amine either axial or equatorial have been reported; in the crystal structures of the perchlorate salts of $[CuL^1]^{2+}$ and $[Cu(H_2L^1)]^{4+}$, the amines are axial and equatorial respectively,[4,17] for example. A further noteworthy feature is that the 'tridentate' perchlorate of the platinum structure is hinged about two oxygens, becoming 'bidentate' in the palladium structure, a variation which may invalidate direct comparability of the metal environments in the two structures. The mechanism of the perchlorate reorientation is consistent with the above assignment of N(1) and C(11). In the platinum(II) structure, intracation hydrogen contacts are observed

Table 2. Non-hydrogen interatomic distances (Å) for $[Pt(H_2L^1)][ClO_4]_4$ and $[Pd(H_2L^1)][ClO_4]_4{\cdot}6H_2O$

	M	
	Pt	Pd
M–N(3)	2.045(7)	2.044(3)
M–N(6)	2.043(6)	2.036(3)
C(1)–N(1)	1.52(1)	1.509(5)
C(1)–C(11)	1.52(2)	1.522(6)
C(1)–C(2)	1.53(1)	1.532(6)
C(1)–C(7)	1.53(1)	1.525(5)
C(2)–N(3)	1.48(1)	1.480(5)
N(3)–C(4)	1.50(1)	1.493(5)
C(4)–C(5)	1.52(2)	1.507(5)
C(5)–N(6)	1.52(1)	1.502(5)
N(6)–C(7)	1.49(1)	1.481(4)
Cl(1)–O(11)	1.425(8)	1.391(4)
Cl(1)–O(12)	1.410(7)	1.392(5)
Cl(1)–O(13)	1.428(8)	1.395(4)
Cl(1)–O(14)	1.42(1)	1.408(5)
Cl(2)–O(21)	1.43(1)	1.385(5)
Cl(2)–O(22)	1.39(1)	1.409(4)
Cl(2)–O(23)	1.42(1)	1.418(5)
Cl(2)–O(24)	1.39(1)	1.414(5)
M–O(12)	3.429(9)	4.29(1)
M–O(13)	3.45(1)	3.170(5)
M–O(14)	3.45(1)	3.421(5)

Table 3. Non-hydrogen interbond angles (°) for $[Pt(H_2L^1)][ClO_4]_4$ and $[Pd(H_2L^1)][ClO_4]_4{\cdot}6H_2O$

	M	
	Pt	Pd
N(3)–M–N(6)	85.0(3)	85.3(1)
N(3)–M–N(6′)	95.0(3)	94.7(1)
N(1)–C(1)–C(11)	107.0(8)	106.9(3)
N(1)–C(1)–C(2)	110.1(8)	105.7(3)
N(1)–C(1)–C(7)	110.5(8)	105.0(3)
C(11)–C(1)–C(2)	107.9(9)	112.3(3)
C(11)–C(1)–C(7)	107.2(9)	113.3(3)
C(2)–C(1)–C(7)	113.8(8)	112.8(3)
C(1)–C(2)–N(3)	116.5(9)	112.5(3)
M–N(3)–C(2)	113.5(5)	115.7(2)
M–N(3)–C(4)	107.9(5)	106.3(2)
C(2)–N(3)–C(4)	111.5(8)	111.8(3)
N(3)–C(4)–C(5)	108.0(8)	107.2(3)
C(4)–C(5)–N(6)	106.9(8)	107.1(3)
M–N(6)–C(5)	107.6(5)	106.7(2)
M–N(6)–C(7)	115.7(5)	115.7(2)
C(5)–N(6)–C(7)	109.5(7)	112.6(3)
N(6)–C(7)–C(1)	115.5(8)	112.5(3)
O(11)–Cl(1)–O(12)	110.3(5)	107.4(3)
O(11)–Cl(1)–O(13)	107.6(5)	110.7(3)
O(11)–Cl(1)–O(14)	110.5(5)	109.5(3)
O(12)–Cl(1)–O(13)	111.4(5)	108.3(3)
O(12)–Cl(1)–O(14)	108.6(6)	110.3(3)
O(13)–Cl(1)–O(14)	108.4(6)	110.6(3)
O(21)–Cl(2)–O(22)	107.9(6)	110.0(3)
O(21)–Cl(2)–O(23)	107.4(6)	111.3(4)
O(21)–Cl(2)–O(24)	110.7(8)	108.6(3)
O(22)–Cl(2)–O(23)	113.1(7)	109.5(3)
O(22)–Cl(2)–O(24)	109.4(6)	111.4(3)
O(23)–Cl(2)–O(24)	108.3(7)	105.9(3)

Table 4. Cation ligand torsion angles (°) (M = Pt or Pd). [Atoms are denoted by number (*N* italicised)]

	M	
Atoms	Pt	Pd
C(7′)–C(1)–C(2)–*N*(3)	−65.4(6)	−71.0(4)
C(1)–C(2)–*N*(3)–C(4)	179.2(8)	179.2(3)
C(2)–*N*(3)–C(4)–C(5)	−165.8(8)	−179.9(3)
N(3)–C(4)–C(5)–*N*(6)	54.8(5)	58.0(4)
C(4)–C(5)–*N*(6)–C(7)	−168.5(5)	−170.3(3)
C(5)–*N*(6)–C(7)–C(1′)	176.6(5)	−178.8(3)
C(2′)–C(1′)–C(7)–*N*(6)	−62.1(7)	−71.3(4)

between O(12), O(13), O(14), and H(5B′, 7B′) 2.6 Å, H(4A, 6) 2.5, 2.4 Å, and H(3′, 1B′) 2.2, 2.1 Å respectively, the contact to the pendant ammonio group being the shortest. In the palladium(II) analogue the intracation contacts are differently disposed: O(13) ··· H(4B) 2.6 Å, O(14) ··· H(5A) 2.7 Å, and O(12) bifurcated between H(2B) and H(7A′) 3.1, 3.1 Å. The more immediate cause of the change in disposition, however, is likely to be the multifarious O ··· H interactions with the water molecules in the latter structure.

As expected, the metal–nitrogen bond lengths in both structures are significantly shorter than in comparable acyclic platinum(II) and palladium(II) tetra-amines. For example, the Pt–N bond lengths in the structure of $[PtL^4{}_2]Br_2$ (L^4 = 1,4,7-triazacyclononane),[18] where the ligand is bidentate, are 2.077(9) and 2.074(9) Å. The same bond lengths in $[Pt(H_2L^1)][ClO_4]_4$ are 2.045(7) and 2.043(6) Å. A similar observation is made when the Pd–N distances in $[PdL^4(HL^4)][PF_6]_2NO_3$, average 2.056(6) Å,[19] are compared with those in $[Pd(H_2L^1)][ClO_4]_4$, 2.044(3) and 2.036(3) Å. The Pd–N bond lengths in the structure of $[PdL^2][ClO_4]_2$ [2.057(7) and 2.044(7) Å][6] are similar to those reported here for the L^1 complex. Non-hydrogen, cation interatomic distances and angles for both complexes are presented in Tables 2 and 3. Cation ligand torsion angles are presented in Table 4, and are similar to those reported[4] for the structure of the copper(II) complex of L^1, $[Cu(H_2L^1)][ClO_4]_4$.

The simple and high-yielding syntheses of platinum(II) and palladium(II) complexes of L^1 have provided quite rare examples of tetra-aza macrocyclic complexes of these metals. Moreover, the crystal structure of the platinum(II) complex is, we believe, the first reported for a saturated tetra-aza macrocycle. The ready availability of the pendant primary amines on the ligand may lead to their co-ordination upon oxidation of both metal centres to the octahedral, tetravalent state. This chemistry is currently being pursued.

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