Synthesis of Binuclear Platinum Metal N_4O_2-Compartmental Complexes: the Structures of the Protonated Metal-free Macrocycle $[LH_4](PF_6)_2{\cdot}MeNO_2$ and of $[Pd_2(L)](BF_4)_2{\cdot}2MeNO_2$

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Reaction of $[LH_4](PF_6)_2$, formed by condensation of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol in the presence of HBr followed by addition of NH_4PF_6, with platinum metal salts in the presence of base affords $[M_2(L)]^{2+}$ (M = Pd, Pt) and $[M_2Cl_4(L)]$ (M = Rh); the structure of $[LH_4](PF_6)_2{\cdot}MeNO_2$ shows a folded conformation incorporating both inter- and intra-molecular π–π interactions between phenyl rings; in contrast, the structure of $[Pd_2(L)](BF_4)_2{\cdot}2MeNO_2$ shows the binucleating macrocycle to be planar with intermolecular π-ring stacking.

In 1970, Robson and Pilkington reported the template synthesis of L^{2-}† around a series of first row transition metal ions.[1] Since then a wide range of metal complexes of L^{2-} and related compartmental ligands have been reported, their syntheses being based on *in situ* template condensation of dialdehydes and diamines in the presence of labile transition metal and main group metal ions.[2-5] Particular emphasis has been placed on the synthesis of polynuclear complexes of biological importance.[4] We wished to develop routes to platinum metal complexes of L^{2-}. In general, however, the

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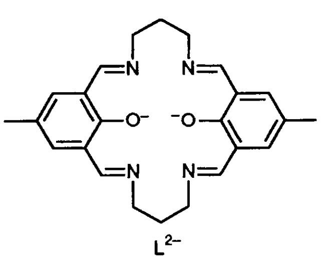
† L^{2-} is the dianion of 11,23-dimethyl-3,7,15,19-tetraazatricyclo[19.3.1.1^{9,13}]hexacosa-2,7,9,11,13(26),14,19,21(25),22,24-decaene-25,26-diol.



L^{2-}

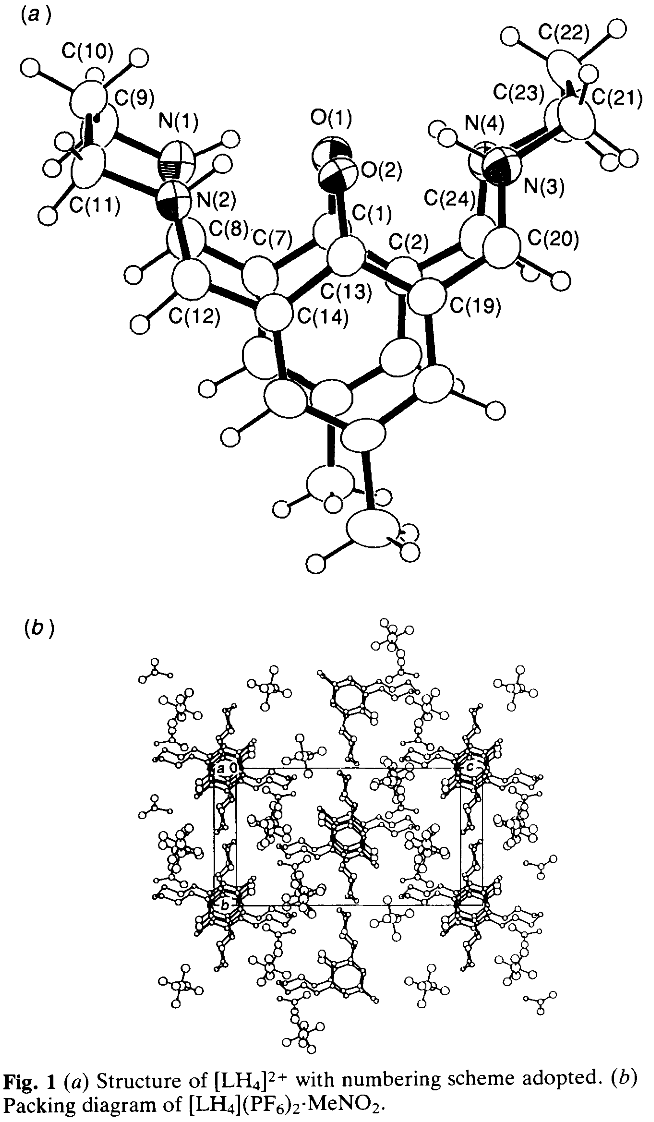


Fig. 1 (*a*) Structure of $[LH_4]^{2+}$ with numbering scheme adopted. (*b*) Packing diagram of $[LH_4](PF_6)_2{\cdot}MeNO_2$.

synthesis of Schiff-base macrocyclic complexes incorporating relatively inert metal ions requires metal insertion into a preformed ligand.[6] We report herein the preparation of the metal-free compartmental ligand $[LH_4]^{2+}$ and the synthesis of a range of platinum metal complexes.

Reaction of 1,3-diaminopropane and 2,6-diformyl-4-methylphenol[7] in MeOH in the presence of 48% HBr followed by addition of Br_2[3] affords the insoluble salt $[LH_4](Br_3)_2$. Metathesis of this salt with NH_4PF_6 or $NaBF_4$ in MeOH affords the protonated 2 + 2 condensation species $[LH_4](PF_6)_2$ or $[LH_4](BF_4)_2$‡ as orange products. Red crystals of $[LH_4](PF_6)_2$ were grown from $MeNO_2$.§ The single crystal X-ray structure of $[LH_4](PF_6)_2$ shows [Fig. 1(*a*)] the protonated Schiff-base macrocycle to adopt a highly unusual folded conformation with the two phenyl rings involved in inter- and intra-molecular [Fig. 1(*b*)] stacking interactions. The conformation of $[LH_4]^{2+}$ is reminiscent of that of calixarenes[8] and related Schiff-base macrocycles[5] with the ring folded downwards to leave the N- and O-donor atoms on an exposed face.

$[LH_4](PF_6)_2$ and $[LH_4](BF_4)_2$ are useful starting materials for the synthesis of complexes of inert metal ions such as those of the platinum metal group. Thus, reaction of $[LH_4](BF_4)_2$ with MCl_2 (M = Pt, Pd) or $[Pd(OAc)_2]_3$ in the presence of a tenfold molar excess of Et_3N in MeCN affords $[M_2(L)]^{2+}$ (M = Pd, Pt) in up to 75% yield. Reaction with $RhCl_3{\cdot}3H_2O$ with one molar equivalent of $TlPF_6$ under the same conditions affords $[Rh_2Cl_4(L)]$.‡ Crystals of $[Pd_2(L)](BF_4)_2{\cdot}2MeNO_2$ were grown from $MeNO_2$–Et_2O and a single crystal X-ray structural determination undertaken.¶ The structure of the complex shows [Fig. 2(*a*)] each square planar Pd^{II} centre bound to two O-donors, Pd–O(1) 2.016(4), Pd–O(1a) 2.014(4) Å, and to two N-donors, Pd–N(1) 1.981(4), Pd–N(2) 1.993(4) Å, <O(1)–Pd–N(1) 93.30(17), <O(1)–Pd–N(2) 170.34(17), <N(1)–Pd–N(2) 96.36(18), <O(1)–Pd–O(1a) 77.13(15), <Pd–O(1)–Pd(a) 102.88(16)°. The Pd–Pd(a) distance is 3.1511(6) Å. In contrast to the folded conformation of the protonated ligand $[LH_4]^{2+}$, the macrocycle in $[Pd_2(L)]^{2+}$ is highly planar, thus removing the possibility of intramolecular π–π interaction between phenyl rings.

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‡ Products have been characterised by elemental analyses, and by NMR, IR, electronic and FAB (fast atom bombardment) mass spectroscopy.

§ *Crystal data* for: $C_{24}H_{30}N_4O_2{}^{2+}2PF_6{}^{-}{\cdot}MeNO_2$, M = 757.35, monoclinic, space group $P2_1/c$, a = 14.4770(6), b = 11.2662(12), c = 20.0823(20) Å, β = 97.213(7)°, V = 3250 $Å^3$ [from 2θ values of 26 reflections measured at ±ω (2θ = 24–26°, $\bar{\lambda}$ = 0.71073 Å), T = 298 K], Z = 4, D_c = 1.548 g cm^{-3}, μ(Mo-Kα) = 0.235 mm^{-1}. A red block (0.36 × 0.28 × 0.24 mm) was mounted on a Stoë Stadi-4 four-circle diffractometer. Data collection using Mo-Kα X-radiation ($\bar{\lambda}$ = 0.71073 Å), ω–2θ scans and the learnt-profile method[9] gave 5313 reflections ($2\theta_{max}$ 45°), 4250 unique (R_{int} 0.074), of which 2833 with $F \geqslant 4\sigma(F)$ were used in all calculations. Following solution by automatic direct methods,[10] the structure was refined by full-matrix least-squares (on F), with anisotropic thermal parameters for all non-H atoms; methyl groups were treated as rigid entities, while other H atoms were included in fixed, calculated positions.[11] At final convergence, R = 0.0578, R_w = 0.0791, S = 1.337 for 455 parameters and the final ΔF synthesis showed no feature above 0.43 e $Å^{-3}$.

¶ *Crystal data* for $C_{24}H_{26}N_4O_2Pd_2{}^{2+}2BF_4{}^{-}{\cdot}2MeNO_2$, M = 911.03, triclinic, space group $P\bar{1}$, a = 7.545(4), b = 8.566(4), c = 13.057(7) Å, α = 101.30(4), β = 94.82(3), γ = 102.92(3)°, V = 799.2 $Å^3$ [from 2θ values of 26 reflections measured at ±ω (2θ = 24–28°, $\bar{\lambda}$ = 0.71073 Å), T = 150.0(1) K], Z = 1 (implying that each dication lies across a crystallographic inversion centre), D_c = 1.892 g cm^{-3}, μ(Mo-Kα) = 1.205 mm^{-1}. A brown tablet (0.23 × 0.19 × 0.12 mm) was mounted on a Stoë Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems low-temperature device.[12] Data collection using Mo-Kα X-radiation ($\bar{\lambda}$ = 0.71073 Å), ω–2θ scans and the learnt-profile method[9] gave 2700 reflections ($2\theta_{max}$ 45°), 2045 unique (R_{int} 0.024), of which 1950 with $F \geqslant 4\sigma(F)$ were used in all calculations. Following identification of the Pd position from a Patterson synthesis, iterative cycles of least-squares refinement and difference Fourier synthesis located the remaining non-H atoms. Slight disorder in the anion was modelled by refining two idealised $BF_4{}^{-}$ tetrahedra with a common B-atom (major occupancy 0.89, minor occupancy 0.11). The structure was refined by full-matrix least-squares (on F), with anisotropic thermal parameters for all non-H atoms except the F atoms with the minor occupancy; methyl H atoms were treated as part of rigid groups while other H atoms were included in calculated positions.[11] At final convergence, R = 0.0348, R_w = 0.0423, S = 1.131 for 238 parameters and the final ΔF synthesis showed no feature above 1.21 e $Å^{-3}$. Atomic coordinates, bond lengths and angles, and thermal parameters for both compounds have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

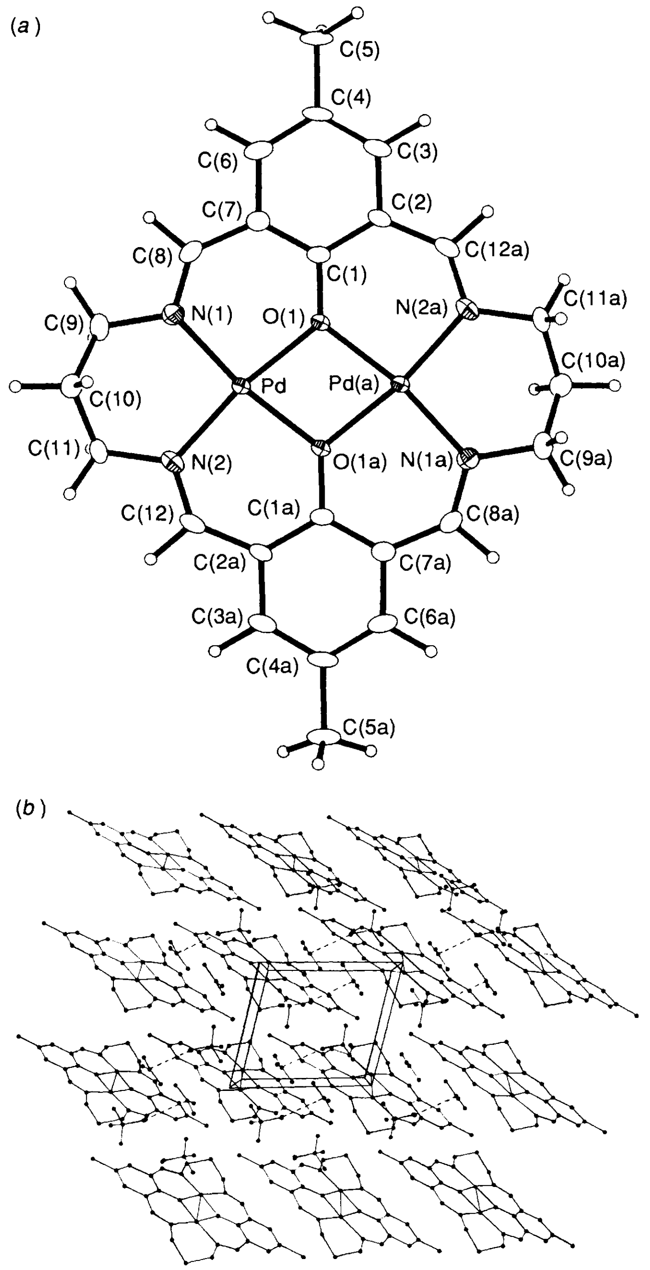

Fig. 2 (*a*) Structure of $[Pd_2(L)]^{2+}$ with numbering scheme adopted. (*b*) Packing diagram of $[Pd_2(L)](BF_4)_2{\cdot}2MeNO_2$.

However, intermolecular stacking of the phenyl rings occurs in the solid state to give a staggered array of cations [Fig. 2(b)].

The salt $[LH_4](Br_3)_2$ is not as useful a starting material for the preparation of these complexes as the PF_6^- or BF_4^- salts owing to its relative insolubility and competition reactions with Br^- ion during metal insertion reactions. However, direct condensation of 1,3-diaminopropane with 2,6-diformyl-4-methylphenol in thf (tetrahydrofuran) affords a yellow product containing the free binucleating ligand $[LH_2]$. However, some free aldehydic and free amine containing impurities are usually observed in these readily hydrolysed materials. Current work is aimed at an investigation of the redox properties of the binuclear complexes of L.

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