

An octanuclear pyromellitimidato(2-) palladium complex: coordinative assembly of a molecular box

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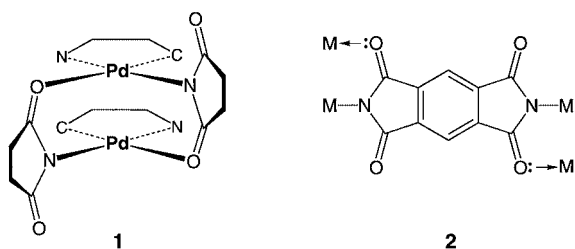
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Reaction of pyromellitimide with the binuclear palladium complex $[\text{Pd}_2(\mu\text{-Cl}_2)(1,2\text{-C}_6\text{H}_4\text{NMe}_2)_2]$ in the presence of base affords a box-like, pyromellitimidato(2-), octa-palladium complex exhibiting helical chirality, for which ^1H NMR and single crystal X-ray data are reported.

In the decade which has elapsed since the first metallamacrocyclic complexes were reported,¹ interest in the coordinative assembly of molecular fragments into nanoscale structures with potential for selective complexation and/or catalysis has increased dramatically.² This type of assembly is generally directed by the relative orientations of donor and acceptor orbitals associated with ligand and transition metal subunits so that, for example, a linearly-coordinating, bidentate donor ligand will generally assemble with a *cis*-constrained, square planar, acceptor unit to afford a square, tetranuclear complex.¹ Variations in the angles subtended by donor and acceptor orbitals can, in principle (and increasingly in practice), give rise to a wide variety of high-nuclearity polygonal and polyhedral structures.³

It has long been known that imidato(1-) ligands such as those obtained by deprotonation of succinimide or phthalimide are capable of bridging pairs of palladium atoms *via* N,O-coordination, giving rise to binuclear complexes such as **1**



(where $\overline{\text{N}}\overline{\text{C}}$ = orthometallated dimethylbenzylamine) in which the two imide-derived ligands are directed at right angles to one another.⁴ The existence of this type of structure suggested to us that the dianion obtained by N,N'-deprotonation of pyromellitimide⁵ might well act as a linearly-coordinating ligand (**2**), capable of bridging *two* pairs of metal atoms and thus perhaps able to generate octanuclear box-like structures. We now report the synthesis and structure of the first such complex—a novel octapalladium species exhibiting helical chirality.

Reaction of pyromellitimide (0.39 g) with an equimolar quantity of the binuclear, orthopalladated complex $[\text{Pd}_2(\mu\text{-Cl}_2)(1,2\text{-C}_6\text{H}_4\text{NMe}_2)_2]$ ⁶ in refluxing dichloromethane (30 cm³) for four hours, in the presence of a tenfold molar excess of triethylamine, led to formation of an orange solution. After washing with water to remove excess amine and amine hydrochloride this solution was dried over magnesium sulfate and evaporated to dryness. Two recrystallisations of the residue from dichloromethane-diethyl ether afforded a yellow crystalline compound (**3**) in *ca.* 30% yield (on the basis of a 1:1 reaction). The ^1H

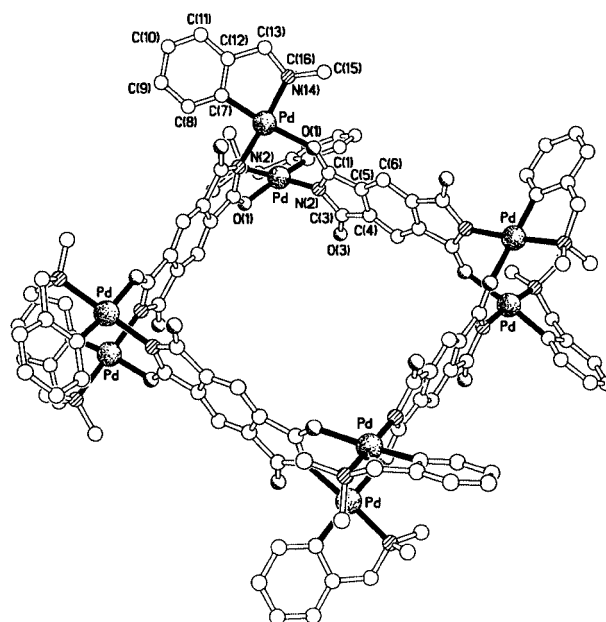


Fig. 1 X-Ray structure of compound **3** (hydrogen atoms and solvent molecules omitted). Selected bond lengths (Å) and angles (°): Pd–C(7) 1.961(7), Pd–N(2) 2.033(5), Pd–N(14) 2.079(5), Pd–O(1) 2.143(4); C(7)–Pd–N(2) 93.6(3), C(7)–Pd–N(14) 82.9(3), N(2)–Pd–N(14) 174.9(2), N(2)–Pd–O(1) 90.5(2), C(7)–Pd–N(14) 82.9(3), C(7)–Pd–O(1) 171.8(3), N(14)–Pd–O(1) 92.5(2).

NMR spectrum of this material showed a very narrow singlet at 7.88 ppm, assignable to equivalent protons of the pyromellitimidato(2-) ligand, together with singlet resonances at 2.01 and 2.95 ppm assigned to inequivalent N-methyl groups of orthometallated dimethylbenzylamine. Also present was an AB “quartet”, centred at 3.55 ppm and assigned to inequivalent *gem*-methylene protons. The ^1H NMR spectrum strongly suggested that a box-type structure might well have been formed, since inequivalent N-methyl and N-methylene protons in an orthometallated dimethylbenzylamine ligand are only found for binuclear complexes where the bridging ligands [generally imidato(1-) or carboxylato(1-)] enforce a “U-shaped” or “orthogonal” molecular geometry rather than the “coplanar” structure adopted in halide(1-)-bridged structures.⁴

Single crystals suitable for X-ray analysis were grown by vapour diffusion of diethyl ether into a dichloromethane-methanol solution of **3**.[†] The molecular structure of **3** is shown in Fig. 1. Eight palladium atoms are located at the corners of a slightly skewed square prism, and are linked in pairs by four tetradentate (N,N',O,O') pyromellitimidato(2-) ligands. In keeping with the NMR data, these ligands traverse the *diagonals* of the box, so that the two 1,4-related aromatic protons on each ligand are equivalent. Moreover, one of the two N-methyl groups associated with each orthometallated ligand

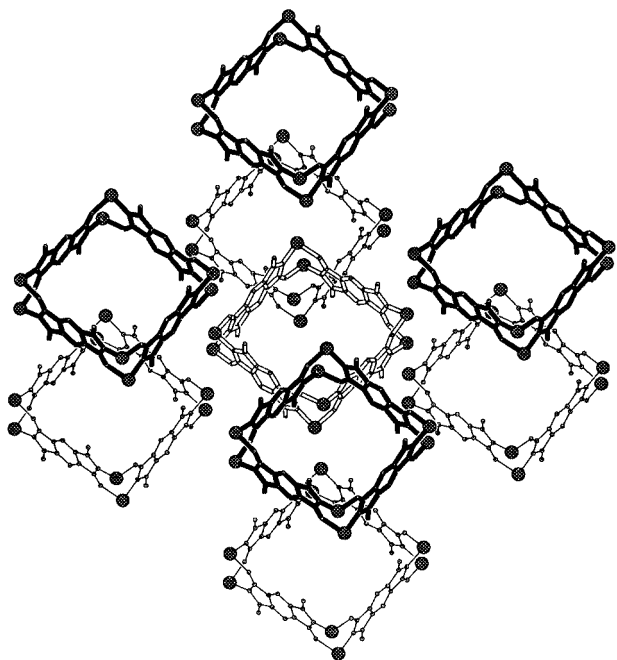


Fig. 2 Crystal packing of compound **3** (orthometallated ligands omitted) showing the corner-to-corner molecular stacking and the alternating chirality of molecules in adjacent layers.

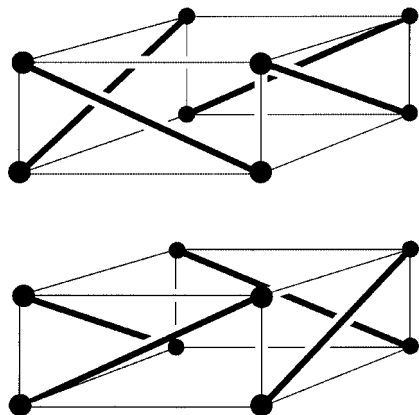


Fig. 3 The two enantiomers of compound **3** [bold lines represent the N...N axes of pyromellitimido(2-) ligands].

is directed towards the face of an aromatic (dimethylbenzylamine) ring bound to the adjacent palladium, thus accounting for the large upfield shift ($\Delta\delta = 0.94$ ppm) relative to that of its adjoining N-methyl substituent.

The complex has crystallographic D_4 symmetry and, as a consequence, contains only one unique palladium centre in the asymmetric unit. The geometry at palladium is slightly distorted square planar with *cis*-angles in the range 82.9–93.6(3)°, the most acute angle being associated with the orthometallated ligand. The transannular separation of parallel pyromellitimido(2-) planes is 10.98 Å, and adjacent palladium coordination planes are mutually inclined by some 47°, with a non-bonded Pd...Pd separation of 3.32 Å.

The crystal is very heavily solvated, with “chains” of disordered diethyl ether molecules filling the “internal” channels and molecules of dichloromethane occupying the “external” channels, formed by corner-to-corner stacking of the boxes (Fig. 2). The diagonal orientation of the four pyromellitimido(2-) ligands gives the molecule as a whole helical chirality (Fig. 3),⁷ though the crystal is in fact racemic, with alternate layers of molecules having opposite chirality as shown in Fig. 2. Such chirality is also retained in solution, since addition of the aromatic chiral shift reagent (*S*)-(+)-trifluoro-1-(9-anthryl)ethanol (1 molar equivalent) to a solution of **3** in

CD₂Cl₂ results in a splitting of the pyromellitimide singlet resonance into two peaks of equal intensity ($\Delta\delta = 0.03$ ppm). Resonances associated with the orthometallated ligand are however unaffected by the chiral shift reagent, suggesting that it must hydrogen-bond to complex **3** in a regiospecific as well as a diastereoselective fashion, presumably *via* one of the non-coordinated imidato carbonyl groups.

It should be noted that, prior to recrystallisation, the crude reaction product shows a number of additional resonances in the ¹H NMR spectrum, in particular a series of nine weak lines in the range 7.6–8.0 ppm, several of which are split into very narrow doublets ($J < 1$ Hz). An analysis of possible isomers of compound **3** suggests that these additional resonances may be assigned to other octapalladium species in which either two or four pyromellitimido(2-) ligands traverse the *edges*, rather than the diagonals of the box. This would give rise to inequivalence of the 1,4-related pyromellitimide protons and hence to five-bond ¹H–¹H coupling between them, so providing a possible explanation for the observed series of doublets. Work aimed at isolating and identifying these additional species is currently in progress. Also, given the known ability of pyromellitimide and its derivatives to form charge-transfer complexes with electron-rich aromatic molecules,⁸ the ability of **3** to encapsulate such species in solution and in the solid state is under investigation.

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Notes and references

† Crystal data for **3**: C₁₁₂H₁₀₄N₁₆O₁₆Pd₈·8C₄H₁₀O·4CH₂Cl₂, $M = 3713.98$, tetragonal, space group *P4/nnc*, $a = 22.069(1)$, $c = 17.491(2)$ Å, $V = 8518.3(9)$ Å³, $T = 183$ K, $Z = 2$, $D_c = 1.488$ g cm⁻³, $\mu(\text{Cu-K}\alpha) = 83.35$ cm⁻¹, $F(000) = 3776$. $R_1 = 0.0501$, $wR_2 = 0.1080$ for 2107 independent observed reflections [$2\theta \leq 120^\circ$, $F_o > 4\sigma(F_o)$].

Data were measured on a Siemens P4/RA diffractometer with graphite-monochromated Cu-K α radiation using ω -scans. The data were corrected for Lorentz and polarisation effects, and a semi-empirical absorption correction (from ψ -scans) was applied. The structure was solved by the heavy-atom method and non-hydrogen atoms were refined anisotropically using F^2 data and the SHELXTL program package version 5.03. CCDC reference number 186/1550. See <http://www.rsc.org/suppdata/dt/1999/2651/> for crystallographic files in .cif format.

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