Anion pore structure through packing of molecular triangles

Ralf-Dieter Schnebeck, Eva Freisinger and Bernhard Lippert*

Fachbereich Chemie, Universität Dortmund, D-44221 Dortmund, Germany. E-mail: lippert@pop.uni-dortmund.de

Received (in Basel, Switzerland) 4th February 1999, Accepted 24th February 1999

A molecular triangle, generated from [(en)Pd(2,2′-bpz-N^1,$N^{1'}$)]$^{2+}$ and *trans*-$(NH_3)_2Pt^{II}$, encapsulates a ClO_4^- and aggregates in the solid state in such a way as to form long channels containing a string of anions.

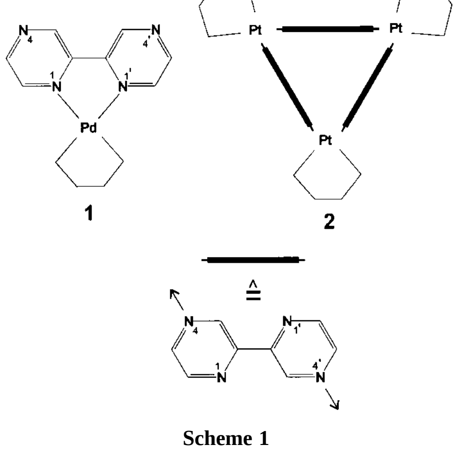
The thermodynamically preferred product of the reaction between $[(en)Pd(H_2O)_2]^{2+}$ and 2,2′-bipyrazine (2,2′-bpz) is the mononuclear chelate [(en)Pd(2,2′-bpz-N^1,$N^{1'}$)]$^{2+}$ **1**.[1] By contrast, $[(en)Pt(H_2O)_2]^{2+}$ forms the kinetic product, triangular [{(en)Pt(2,2′-bpz-N^4,$N^{4'}$)}$_3$]$^{6+}$ **2** (Scheme 1).[1] Both **1** and **2** bind additional metal electrophiles *via* the still available N^4 (**1**) and N^1 (**2**) sites, respectively, to give hexanuclear molecular cups [after reacting **1** with additional (en)Pd^{II} or **2** with (en)M^{II} (M = Pt or Pd)[2,3]], or a flat triangle upon reaction of **1** with *trans*-$(NH_3)_2Pt^{II}$, as demonstrated here.

The compound isolated† and structurally characterised‡ proved to be [{(en)Pd}$_{2.5}$(2,2′-bpz)$_3${$(NH_3)_2Pt$}$_3$]$(ClO_4)_6$-$(NO_3)_5\cdot 5H_2O$ **3** (Fig. 1), a molecular triangle of C_2 symmetry with one of the Pd corners [enPd(2)] having a 50% occupancy only.

Both the Pd_3 and Pt_3 triangles are close to equilateral, with Pd–Pd distances of 13.5 Å and Pt–Pt distances of 7.6–7.7 Å. As a consequence of the incompatibility of the bite angle at Pd (*ca.* 80°) and the 60° angles of the triangle, the Pt atoms are not centred on the sides of Pd_3 but lie outside the sides of these by *ca.* 0.5 Å, with Pt–Pd–Pt angles of *ca.* 69°. Triangle **3** differs from **2** in that the bpz ligands in **3** are, unlike in **2**, essentially coplanar with all metal ions. A single ClO_4^- anion is encapsulated in the centre of the cation, bearing some similarity with the situation in a recently described Co_8 compound.[4] Pairs of triangles approach each other *via* the half-occupied Pd(2) positions [ideally separated by 4.363(8) Å] and are propeller-twisted by *ca.* 50°.

The packing of the cations of **3** is such that they are approximately parallel oriented, yet by 180° rotation the triangles form a stair, which is inclined by *ca.* 60° and has treads separated by *ca.* 6.1 Å (Fig. 2). In the interior of this stair, a channel is formed (Fig. 3), which hosts one ClO_4^- per subunit. This situation is in a way reminiscent of self-assembling ion channels that generate pore structures,[5] however, there are also differences: the interaction between the layered triangles is neither *via* direct stacking, the NH_3 ligands of the three Pt^{II} ions are roughly perpendicular to the triangle plane, thereby preventing stacking of the bpz rings, nor by direct H bonding between the layers, as seen in nanotubes generated by cyclic peptides, for example.[6] Rather NO_3^- anions and water molecules, sandwiched between adjacent triangles, act as a ‘glue’ between the positively charged triangles, reinforced by ClO_4^- anions at the periphery of the triangles, all of which are involved in multiple H bonding interactions with NH_3 and en ligands.

The inner cavity within **3**, across diagonal C(3)H proton sites, is 6.24–6.42 Å wide. The ClO_4^- is located in such a



Scheme 1

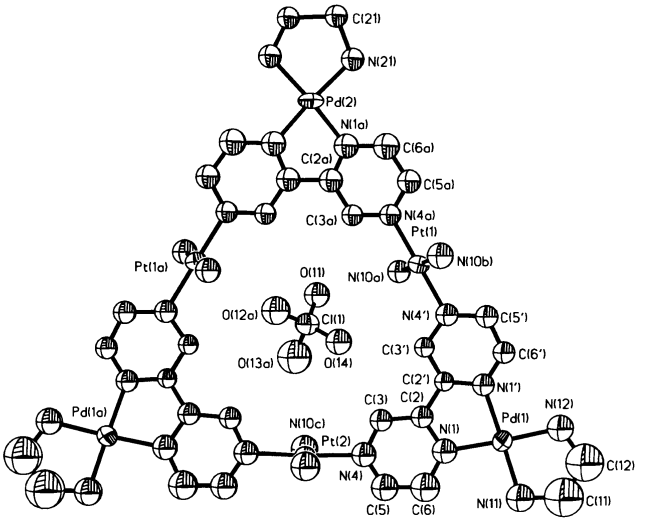


Fig. 1 Crystal structure of cation **3** with encapsulated ClO_4^-. Note that (en)Pd(2) has a 50% occupancy only. Relevant distances (Å) and angles (°): Pt(1)–N(4′) 1.97(2), Pt(1)–N(10b) 1.98(2), Pt(1)–N(10a) 2.00(2), Pt(1)–N(4a) 2.00(2), Pt(2)–N(10c) 2.02(2), Pt(2)–N(10c)#1 2.02(2), Pt(2)–N(4) 2.01(2), Pt(2)–N(4)#1 2.01(2), Pd(1)–N(1) 2.02(2), Pd(1)–N(1′) 2.03(2), Pd(2)–N(1a) 2.00(2), Pd(2)–N(1a)#1 2.00(2), N(10b)–Pt(1)–N(10a) 179.0(7), N(4′)–Pt(1)–N(4a) 178.7(6), N(10c)–Pt(2)–N(10c)#1 179.7(10), N(4)–Pt(2)–N(4)#1 177.1(11), N(1)–Pd(1)–N(1′) 80.5(7), N(1a)–Pd(2)–N(1a)#1 80.4(11).

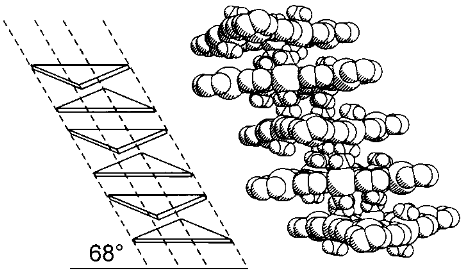


Fig. 2 Schematic representation and space filling of the layered triangles forming a ‘stair’. Two NO_3^- anions and two H_2O molecules are layered between adjacent triangles and form multiple H bonds between each other and the Pt-NH_3 groups (not shown). At the periphery ClO_4^- anions interact *via* H bonds with NH_2 groups of Pd(en) entities as well as Pt–NH_3 groups (not shown), thereby generating a very compact structure that resembles a pipe rather than a stair.

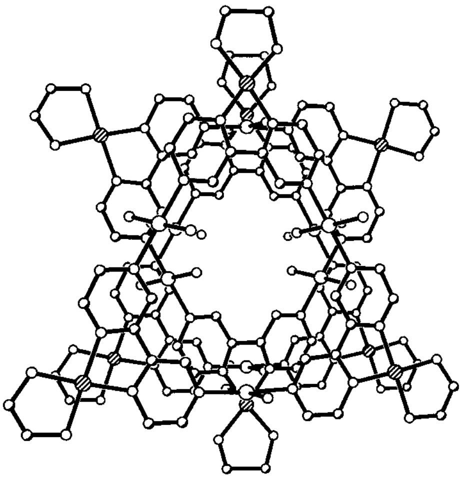


Fig. 3 View along the central channel formed by cations of **3** with ClO_4^- anions omitted. The molecular triangles are not perpendicular to the view but rather inclined by *ca.* 68°.

manner that Cl resides in the plane of the triangle, whereas the oxygen atoms lie pairwise above and below this plane and are clearly disordered. It appears that the oxygen atoms can weakly H bond to both the heterocyclic C(3)H protons [distances: $O_3ClO\cdots C(3)$ 3.02(4)–3.40(4) Å; angles: $O_3Cl–O\cdots H(3)$ 100.8(17)–128.4(19)°] and to the NH_3 protons of the Pt ions (distances: $O_3ClO\cdots H$ 2.6(1)–2.8(1) Å; angles: $O_3Cl–O\cdots H$ 168.8(21)–168.81(21)°], hence simultaneously to both hydrophobic and hydrophilic areas within the channel.

The ^1H NMR spectrum of **3** in D_2O, (pH* = 3.3) confirms the presence of more than a single species in solution. Spectra recorded within 2 h after dissolving crystals of **3** are dominated by three intense resonances in the aromatic region, namely at δ 10.62 (s, H3,H3′), 9.70 (s, w = 14 Hz, H5,H5′), and 8.99 (d, ^3J 3.7 Hz, H6,H6′) which are assigned to the Pd_3Pt_3 species. In addition, there is a large number (> 15) of minor resonances. For the Pd_2Pt_3 species nine sets of aromatic proton resonances are to be expected, each having an intensity of one third of the intensity of the resonances of Pd_3Pt_3. The ^{195}Pt NMR spectrum confirms also the presence of at least two species with PtN_4 coordination (δ −2449 and −2500, *ca.* 3 : 1). The larger number of observable resonances and also the time-dependent changes in the spectrum (resonances due to Pd_3Pt_3 decrease with time) strongly point toward the existence of more species than just Pd_3Pt_3 and Pd_2Pt_3 in solution, possibly $PdPt_3$ is present. There are two ways to simplify the spectrum: first, addition of $[(en)Pd(D_2O)_2]^{2+}$ to a solution of **3** leads to an increase in the intensities of the three resonances assigned to Pd_3Pt_3 with some of the minor resonances, however, still detectable. The relative intensities of the ^{195}Pt NMR resonances are now *ca.* 10 : 1. Second, addition of excess NaCl to an aqueous solution of **3** causes rapid precipitation of yellow $(en)PdCl_2$ and formation of a new major species with three intense sets of resonances at δ 10.20 (s), 9.28 (d, ^3J 3.2 Hz) and 9.18 (br, d), with some additional minor resonances still observable. The major component is tentatively assigned as a Pt_3 species. We have been as yet unable to isolate this compound and to prepare it directly from 2,2′-bpz and *trans*-$(NH_3)_2Pt^{II}$.

In summary, compound **3** is unique in that it (i) combines structural features of ‘molecular triangles’ which commonly have metal entities either at the corners[1,9] or at the centres of the sides[10] and in addition (ii) crystallises in a fashion that is reminiscent of an anion channel comprised of identical subunits.

This work was supported by the Fonds der Chemischen Industrie.

Notes and references

† $[\{(en)Pd\}_{2.5}(2,2'\text{-}bpz)_3\{(NH_3)_2Pt\}_3](ClO_4)_6(NO_3)_5\cdot 5H_2O$ **3** was obtained in two steps. (a) *trans*-$(NH_3)_2PtCl_2$ (57.5 mg, 0.192 mmol) was suspended in water (10 ml), $AgNO_3$ (63.4 mg, 0.373 mmol) added, and the mixture stirred for three days at 45 °C. The mixture was cooled and AgCl removed by filtration. (b) $[(en)Pd(2,2'\text{-}bpz)](ClO_4)_2$ (100 mg, 0.191 mmol) was added to the filtrate and the reaction mixture stirred for three days at 45 °C. Red–yellow **3** was obtained in 35% yield after 7 days at 4 °C. Satisfactory elemental analysis for $C_{29}H_{66}O_{44}N_{28}Cl_6Pd_{2.5}Pt_3$: Anal. Calc. for **3**: C = 13.5, H = 2.8, N = 15.2. Found C = 13.6, H = 2.5, N = 14.9%.

‡ *Crystal data* for **3**: M = 1287.53, orthorhombic, space group *Ccca*, a = 31.616(6), b = 35.691(7), c = 13.355(3) Å, U = 15069.9(53) Å^3, Z = 16, D_c = 2.270 g cm^{-3}, μ = 6.462 mm^{-1} (Mo-Kα, λ = 0.71069 Å), $F(000)$ = 9912, T = 293(2) K. Enraf-Nonius-CAD4 diffractometer, crystal size 0.38 × 0.06 × 0.06 mm, 20205 reflections measured, 5555 unique (R_{int} = 0.1895), 2086 observed reflections with $F_0 > 4\sigma(F_0)$, R_1 = 0.0613, wR_2 = 0.1308 (observed data), S = 1.177. The structure was solved by the Patterson method[7] and refined using least-squares.[8] The crystals were of poor quality but showed no decay during measurements. Some of the anions and water molecules are disordered, *e.g.* one perchlorate and two nitrate anions in the crystallographic unit are only half occupied, respectively. Only a few atoms are refined anisotropically, because of the poor data to parameter ratio. CCDC 182/1179. See http://www.rsc.org/suppdata/cc/1999/675 for crystallographic files in .cif format.

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Communication 9/00964G