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High-nuclearity icosahedral carbonylphosphineplatinum clusters: synthesis and crystal structure of $Pt_{17}(\mu_2\text{-}CO)_4(CO)_8(PEt_3)_8$

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Abstract

A new high-nuclearity cluster $Pt_{17}(\mu_2\text{-}CO)_4(CO)_8(PEt_3)_8$ has been prepared from pentanuclear $Pt_5(CO)_6(PEt_3)_4$ by thermolysis in decane. An X-ray diffraction study (−120 °C, λ(Mo), 4416 reflections, $R = 0.063$) revealed the 17-vertex centrosymmetric cluster to be a distorted centred icosahedron with four additional Pt caps.

Large transition metal clusters, studied by use of X-ray diffraction, usually display close packing of metal atoms in the cluster core [1]. One of the possible packing types, having five-fold symmetry (i.e. pentagonal or icosahedral packing) cannot exist in an infinite crystal lattice, but is typical, according to calculations, in naked atomic aggregates [2]. Large clusters with five-fold symmetry packing were found mainly in gold derivatives [3,4], though centred, pentagonal polyhedra are also known in $[Rh_{15}(C)_2(CO)_{28}]^-$ and $[Pt_{19}(CO)_{22}]^{4-}$ [1]. However, the large carbonyl phosphine clusters we investigated previously [5,6] do not possess pentagonal metal polyhedra.

In continuation of our investigation of large clusters (e.g. ref. 6) we have synthesized and structurally characterized the first high-nuclearity carbonylphospine cluster of platinum with metal atom packing of five-fold symmetry, viz. $Pt_{17}(\mu_2\text{-}CO)_4(CO)_8(PEt_3)_8$ (I), bearing in mind that neutral clusters free of distortions due to charge, are of interest as good examples of a metal surface covered by chemisorbed ligands [1].

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The most common synthetic route to carbonylphosphine clusters is the addition of phosphines, PR_3, to an oligomeric "platinum dicarbonyl" $[Pt(CO)_2]_n$ in solution [7,8]. As this method allows clusters with nuclearities of 5 or less to be prepared, it has been combined with the standard cluster enlargement routine, viz. thermolysis under an inert atmosphere [1].

In the synthesis of I, 0.184 g of the cluster $Pt_5(CO)_6(PEt_3)_4$ prepared by a published procedure [8a], was dissolved in 3 ml of decane heated in a water bath under argon. The solution was then heated in a n-hexan-1-ol bath at 153–155 °C for 30 min; the color of the solution changed from bright red to dark brown. The reaction mixture was slowly cooled during 36 h to room temperature, and the resulting black crystalline precipitate was filtered off and dried in vacuo, yield 0.021 g (14%). Found: Pt, 73.36, P, 5.73. $C_{60}H_{120}O_{12}P_8Pt_{17}$ calcd.: Pt, 72.13; P, 5.39%. IR spectrum (Nujol, ν(CO) cm^{-1}): 1970sh, 1963s., 1944s., 1920w., 1728s., 1720sh.

An X-ray diffraction study on crystals of I was carried out with a Syntex $P2_1$ automated diffractometer at -60 °C (λMo-K_α, $\theta/2\theta$ scan, $2\theta < 48°$, 4599 measured, 4416 observed ($I > 2\sigma$) reflections, $R = 0.063$). Crystals are monoclinic, a 13.742(5), b 24.488(7), c 14.070(7) Å, β 105.48(4)°, space group $P2_1/a$, $Z = 2$. The structure was solved by direct methods and refined by block-diagonal least squares with anisotropic thermal parameters for Pt and P atoms and isotropic ones for other non-hydrogen atoms. Absorption corrections were applied by use of the DIFABS procedure [9]. The table of atomic coordinates and the full list of bond lengths and angles in I have been deposited at the Cambridge Crystal Structure Database *.

The centrosymmetric molecule, I, is shown in Fig. 1. The Pt_{17} cluster of approximate non-crystallographic D_{2h} symmetry consists of a distorted centred icosahedron with four caps, linked pairwise by Pt–Pt bonds. The capping atoms Pt(7) and Pt(8) (as well as Pt(7′) and Pt(8′) related to them by inversion) may also be regarded as a part of the heptanuclear pentagonal bipyramidal moieties, involving also Pt(0), Pt(1), Pt(2), Pt(5) and Pt(6) atoms and symmetry-related counterparts. The five-fold axes of these bipyramids are parallel to each other, but do not coincide with any of the corresponding axes in the core icosahedron. Thus the structure of I is the first step in the enveloping of the Pt_{13} icosahedron by the second atomic shell of metal.

Triethylphosphine ligands are bonded to four capping Pt atoms and four Pt vertices in the equatorial part of the cluster core. In accord with the IR data, the ligand shell also includes eight terminal and four μ_2-bridging CO ligands.

The intrapolyhedral Pt(0) atom in I has a closed 18e configuration similar to the interstitial Au atom in icosahedral $[Au_{13}(PMe_2Ph)_{10}Cl_2]^{3+}$ [3,10]. The average peripheral Pt–Pt bond length in the icosahedral framework of I (2.837 Å) is 1.052 times larger than the average internal Pt(0)–Pt distance (2.698 Å). The intermediate average $Pt_{icos.}$–Pt_{cap} distance (2.780 Å) coincides with the shortest interatomic distance in Pt metal (2.775 Å [11]). The corresponding calculated ratio for centred-icosahedral Lennard–Jones' aggregate is 1.052 [2], and the observed value for the icosahedral gold cluster is 1.048 [3]. It is noteworthy that in the $Pd_{23}(CO)_{22}(PEt_3)_{12}$ four-capped ν_2-octahedron, the internal (2.847 Å) and peripheral (2.849 Å) mean

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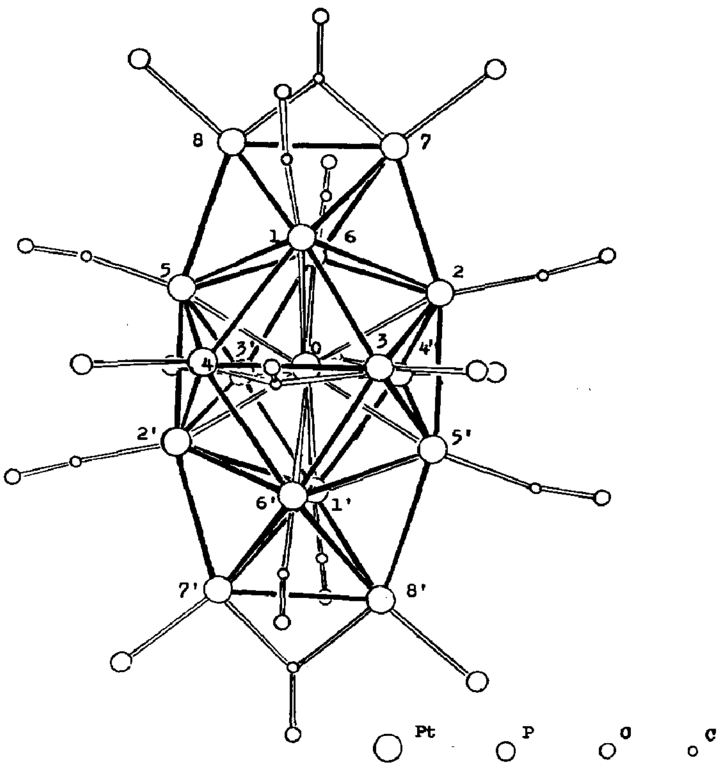

Fig. 1. Structure of $Pt(\mu_2\text{-}CO)_4(CO)_8(PEt_3)_8$ (Et substituents not shown). Primed numbers correspond to atoms, related to the independent part of the molecule by inversion. Bond distances Pt–Pt, Å,: 2.706 (0–1), 2.678 (0–2), 2.717 (0–3), 2.703 (0–7 (0–4), 2.689 (0–5), 2.697 (0–6), 2.891 (1–2), 2.814 (1–3), 2.795 (1–4), 2.849 (1–5), 2.945 (1–6), 2.745 (1–7), 2.729 (1–2′), 2.829 (2–3), 2.850 (2–4), 2.851 (2–5′), 2.829 (2–6), 2.830 (2–7), 2.858 (3–4), 2.835 (3–5′), 2.803 (3–6′), 2.831 (4–5), 2.802 (4–6′), 2.845 (5–6), 2.801 (5–8), 2.787 (6–7), 2.785 (6–8), 2.860 (7–8); Pt–P 2.20–2.26; Pt–C(μ_2) 1.94–2.13, Pt–$C_{term.}$ 1.64–1.83, C–O 1.10–1.32 Å. E.s.d.'s, Å: Pt–Pt 0.002–0.003, Pt–P 0.01, Pt–C 0.04–0.07, C–O 0.05–0.08.

metal–metal distances in the cubo-octahedral closest environment of the interstitial Pd atom, are equal and ca. 0.10 Å longer than the shortest interatomic distance in Pd metal [11].

The mean number of electron donated by the ligands per metal atom surface in I is 2.5. This value is typical for large clusters in the nickel subgroup, reflecting the fulfillment of Chini's condition [1], that all bonding zones in the metal polyhedron must be occupied by electrons (see ref. 12).

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