Inclusion Compounds

$[Pt@Pb_{12}]^{2-}$

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The icosahedron is a regular (platonic) polyhedron that contains 12 vertices, 20 triangular faces and has I_h point symmetry in the limiting case. Icosahedral clusters of atoms are relatively common[1] among organometallic complexes,[2–4] inorganic clusters,[5–8] boranes and carboranes,[9–11] intermetallics, and other solid-state materials.[12–14] However, homoleptic free-standing icosahedral clusters are not as common and those with I_h point symmetry (either crystallographically imposed or virtual symmetry) are in fact quite rare. $(B_{12}H_{12})^{2-}$ is the prototype[15] free-standing icosahedron, whereas $[Tl_{13}]^{11-}$ and $[Tl_{12}Cd]^{12-}$ are examples of centered, symmetrical homoleptic icosahedra found in solid-state compounds.[12,14,16] Other structurally characterized clusters with I_h point symmetry include dodecahedrane ($C_{20}H_{20}$),[17] C_{60} and its derivatives,[18,19] and $[As@Ni_{12}@As_{20}]^{3-}$.[20] We describe herein the free-standing naked icosahedral cluster, $[Pt@Pb_{12}]^{2-}$, that contains a Pt atom centered in a *closo*-$[Pb_{12}]^{2-}$ icosahedral Zintl ion with virtual I_h point symmetry.

The $[Pt@Pb_{12}]^{2-}$ ion was prepared from reactions between ethylenediamine (en) solutions that contain $[Pb_9]^{4-}$ ions and toluene solutions of $[Pt(PPh_3)_4]$ in the presence of 2,2,2-crypt. Despite the extensive fragmentation necessary for the growth of the Pb cluster from the parent Zintl anion (i.e. $[Pb_9] \rightarrow [Pb_{12}]$), the title complex crystallizes as a dark brown $[K(2,2,2\text{-crypt})]^+$ salt in good yield (60%). In contrast to related Pt-

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DOI: 10.1002/ange.200353287

Zintl ion chemistry,[21] oxidation of the $[Pb_9]^{4-}$ Zintl ion to form the title complex does not result in H_2 gas evolution. The crystalline salt is air-sensitive, forms stable dark greenish-brown solutions (dimethylformamide (dmf), dimethyl sulfoxide (dmso)) and has been characterized by energy-dispersive X-ray (EDX) analysis, ^{207}Pb and ^{195}Pt NMR spectroscopy and single crystal XRD.

The $[\{K(2,2,2\text{-crypt})\}_2][Pt@Pb_{12}]$ salt is trigonal, space group $P\bar{3}$, and is surprisingly devoid of disorder.[22] Both the $[Pt@Pb_{12}]^{2-}$ ion and the $[K(2,2,2\text{-crypt})]^+$ ions have crystallographically imposed threefold symmetry and reside on $\bar{3}$ inversion and threefold rotation axes, respectively. The $[Pt@Pb_{12}]^{2-}$ anion is defined by an icosahedron of 12 Pb atoms with a centered Pt atom and has near-perfect I_h point symmetry (Figure 1). The central atom refines equally well as either a Pb or Pt atom, however, EDX and NMR spectroscopy, and structural considerations unequivocally identify it as platinum.

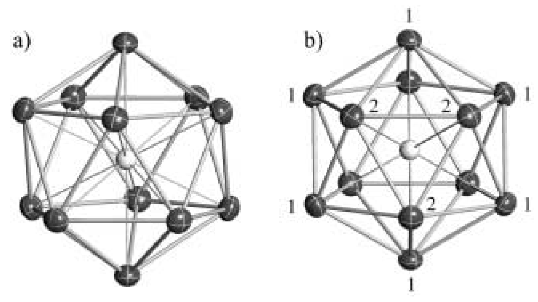

Figure 1. ORTEP drawings of the $[Pt@Pb_{12}]^{2-}$ ion showing a) the icosahedral structure and b) a view down the $\bar{3}$ axis. Pt is gray, Pb is black, thermal ellipsoids are set at the 50 % probability level.

The $[Pt@Pb_{12}]^{2-}$ cluster is a 12-vertex 26-electron polyhedron with a highly-regular *closo* icosahedral structure as expected from a Wade–Mingos type analysis. In this analysis, the Pb and Pt atoms donate two electrons and zero electrons to cluster bonding, respectively, that give a 26 electron, $2n+2$ cluster with a *closo* geometry when the -2 charge of the cluster is taken into consideration. The 30 Pb–Pb bonds and 12 Pt–Pb bonds are very symmetrical with average contacts of 3.216(12) Å and 3.058(2) Å, respectively. There is a slight elongation of the cluster along the $\bar{3}$ axis giving slightly longer Pb1–Pb2 contacts (3.223(10) Å) relative to the Pb1–Pb1 (3.206(2) Å) and Pb2–Pb2 (3.205(2) Å) distances. However, all of the Pb–Pb contacts are in the range found for the $[Pb_9]^{4-}$ and $[Pb_9]^{3-}$ ions.[23–25] The Pt–Pb bonds are equivalent within experimental error and similar Pt complexes for comparison do not exist to our knowledge.

The ^{207}Pb NMR spectrum (Figure 2a) shows a singlet at 1780 ppm flanked by Pt satellites ($^1J_{^{207}Pb\text{-}^{195}Pt} \approx 3440$ Hz, 34 % relative intensity), which indicates coupling to a single Pt atom. The measured T_1 value for this resonance is quite short at 1.5 msec and is over an order of magnitude shorter than the 39.8 msec T_1 value for $[Pb_9]^{4-}$ under the same conditions (dmf solvent, 11 °C, 104.6 MHz). The ^{195}Pt spectrum (Figure 2b) contains a single resonance at $\delta = -4527$ ppm with a satellite pattern consistent with coupling to 12 equivalent Pb atoms ($^1J_{^{207}Pb\text{-}^{195}Pt} \approx 3440$ Hz, see inset of Figure 2b for simulated intensities). Both spectra are consistent with the nuclearity of the cluster and its solid-state structure.

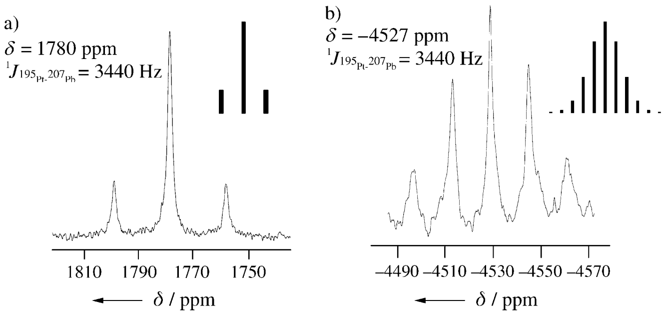

Figure 2. a) ^{207}Pb NMR spectrum of the $[Pt@Pb_{12}]^{2-}$ ion recorded in dmf at 11 °C and 83.7 MHz. b) ^{195}Pt NMR spectrum of the $[Pt@Pb_{12}]^{2-}$ ion recorded in dmf at 11 °C and 107.5 MHz. The insets show the simulated patterns based on isotopic abundances.

Rudolph and co-workers first described the reaction between $[Pt(PPh_3)_4]$ and $[Pb_9]^{4-}$ in the absence of 2,2,2-crypt in which a $[(Ph_3P)_xPt{-}Pb_9]^{4-}$ complex was identified by NMR studies.[26] Based on subsequent NMR studies,[27] we believe that their complex is the Pb analogue of our recently reported 10-vertex C_{3v} $[Sn_9Pt_2(PPh_3)]^{2-}$ ion.[21] In the presence of 2,2,2-crypt, the $[Pb_9Pt_2(PPh_3)]^{2-}$ complex is apparently converted to the icosahedral $[Pt@Pb_{12}]^{2-}$ ion.

An important ramification of the I_h point symmetry of the$[Pt@Pb_{12}]^{2-}$ ion is that the centered Pt atom experiences a cubic ligand field which renders the 5 d orbitals degenerate. The qualitative molecular-orbital diagram (Figure 3) shows the interaction of the valence $Pb_{12}{}^{2-}$ orbitals with the Pt-based s, p, and d orbitals, which transform under the a_{1g}, t_{1u}, and h_g irreducible representations, respectively. The primary interactions between the Pt atom and $\{Pb_{12}\}$ cage involve the Pt s (a_{1g}) and p (t_{1u}) atomic orbitals, therefore, the interactions

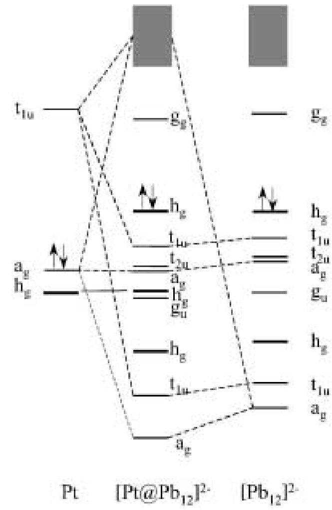

Figure 3. Qualitative MO diagram for the $[Pt@Pb_{12}]^{2-}$ ion constructed from the Pt atom and $[Pb_{12}]^{2-}$ fragments with the aid of extended Hückel molecular-orbital calculations. The highest occupied h_g levels of the $[Pt@Pb_{12}]^{2-}$ complex and $[Pb_{12}]^{2-}$ fragment were normalized for comparison.

involving the d orbitals have been omitted from Figure 3 for clarity. The general electronic structure is quite similar to that of related centered icosahedra, such as $[Tl_{12}Cd^{12}]^{-}$.[12] The HOMO and LUMO frontier orbitals are primarily lead-based states and are presumably associated with the lowest-energy electronic "intraligand" charge-transfer transition that is responsible for the intense color of the compound. The presence of fivefold degenerate d states in a Pt complex is unusual and is reminiscent of the electronic structures of gas-phase atoms and endohedral complexes. The endohedral fullerenes (e.g. $[La@C_{60}]$) have received significant attention due to their unusual physical, electronic, and spectroscopic properties[28–31] and the centered Zintl clusters should prove to be equally interesting.[32]

During the review process of this manuscript, we learned of the theoretical studies of Schleyer, King, Lievens, and coworkers regarding the aromatic nature of the closely related icosahedral $[Si_{12}]^{2-}$ cluster,[33] its anomalous paratropic chemical shift,[33] and the identification of the isoelectronic $[Al@Pb_{12}]^{+}$ ion by mass spectroscopy.[34] A comparison of the chemical bonding and spectroscopic properties of related aromatic clusters (e.g., $[Ni@Pb_{10}]^{2-}$ and $[Al@Pb_{10}]^{+}$)[27,34] will hopefully shed light on the unusual properties of this growing class of highly symmetric aromatic inorganic structures.

Experimental Section

Preparation of $[K(2,2,2\text{-crypt})]_2[PtPb_{12}]$: In a drybox, $[K_4Pb_9]$ (80 mg, 0.039 mmol) and 2,2,2-crypt (59.6 mg, 0.156 mmol) were dissolved in en (ca. 2 mL) in vial 1 and stirred for about 5 min to yield a dark green solution. In vial 2, $[Pt(PPh_3)_4]$ (49 mg, 0.039 mmol) was dissolved in toluene (ca. 1 mL) to yield a pale yellow solution. The solution from vial 2 was added drop wise to vial 1 and the resulting mixture was stirred for about 2 h to yield a reddish-brown solution. The solution was then filtered through tightly packed glass wool. After 24 h, large dark brown crystals of $[\{K(2,2,2\text{-crypt})\}_2][PtPb_{12}]$ precipitated. Yield: ≈48 mg (≈60%). EDX analysis on crystals showed presence of Pb, K, Pt atoms. ^{207}Pb NMR (dmf, 11 °C): $\delta = 1780$ ppm (vs 1.0 M $Pb(NO_3)_2$, $\delta = -2961$), $\Delta\nu_{1/2} = 190$ Hz, $^{1}J_{Pt-Pb} = 3430(\pm 20)$ Hz. ^{195}Pt NMR (dmf, 11 °C): $\delta = -4527$ ppm (vs H_2PtCl_6, $\delta = 0$), $\Delta\nu_{1/2} = 165$ Hz, $^{1}J_{Pt-Pb} = 3440(\pm 15)$ Hz. Errors in coupling constants were estimated from the experimental digital resolution and line width of the corresponding spectral lines. The average coupling constant is reported in the text.

Received: November 10, 2003 [Z53287]

Keywords: aromaticity · cluster compounds · inclusion compounds · lead · platinum

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[22] X-ray structure for $[K(2,2,2\text{-crypt})]_2[Pt@Pb_{12}]$: A small dark brown crystal $0.15 \times 0.09 \times 0.07$ mm^3 was analyzed using a Bruker SMART1000 single crystal CCD-diffractometer operating at 173 K. Data were corrected for absorption (SADABS) and Lorentz and polarization effects and the structure solved and refined (against F^2) by using the SHELXTL program. Crystal Data: Trigonal, space group $P\bar{3}$, $a = 13.041(6)$, $c = 11.672(11)$ Å; $V = 1718.1(19)$ Å^3, $\rho_{calcd} = 3.393$ g cm^{-1}, $3.48° < 2\theta < 49.86°$, $Mo_{K\alpha}$ radiation, $\mu(Mo_{K\alpha}) = 31.44$ mm^{-1}, 2022 unique reflns for 103 parameters. GOF (F^2) = 1.055, $R1 = 0.0352$, $wR2 = 0.0825$ for $I > 2\sigma(I)$ and $R1 = 0.0703$, $wR2 = 0.0959$ for all data. CCDC 223732 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB21EZ, UK; fax: (+44)1223-336-033; or deposit@ccdc.cam.ac.uk).

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