The Structure of a Platinum–Tin Cluster

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AN unusual platinum–tin metal atom cluster was postulated recently[1] as the basic unit of some platinum–tin complexes. We have established the molecular configuration of this metal atom cluster unit by an *X*-ray diffraction study of $(C_8H_{12})_3Pt_3(SnCl_3)_2$, where C_8H_{12} is cyclo-octa-1,5-diene. This represents the first characterization of a molecular complex with a trigonal bipyramidal metal atom cluster as well as the first characterization of a platinum–tin cluster.

Red, polyhedral-shaped crystals of $(C_8H_{12})_3Pt_3$-$(SnCl_3)_2$, supplied by Dr. R. V. Lindsey, jun., of this laboratory, belong to the monoclinic space group $P2_1/a$ with $a = 17{\cdot}97 \pm 0{\cdot}03$, $b = 18{\cdot}16 \pm 0{\cdot}03$, $c = 10{\cdot}23 \pm 0{\cdot}02$ Å, and $\beta = 111{\cdot}4 \pm 0{\cdot}2°$. The calculated and observed densities for $Z = 4$ are 2·90 g./cm.[3] A four-circle diffractometer was used to measure 2800 independent reflections using the θ–2θ scan technique. The data were corrected for absorption. The structure was solved by Patterson super position techniques. The full-matrix least-squares refinement gave a conventional R of 0·05; the refinement excludes hydrogen atoms and is based on isotropic thermal parameters for the carbon atoms and anisotropic thermal parameters for all other atoms.

The structure shown in the Figure consists of a triangle of Pt atoms each co-ordinated to a cyclo-octa-1,5-diene ring and capped above and below by $SnCl_3$ groups. All atoms shown are crystallographically independent. The actual point symmetry is essentially equal to the idealized C_3 and not C_{3v} because the $SnCl_3$ groups are staggered by about 15°. The average distances are 2·58(0·01) Å for three Pt–Pt distances, 2·80(0·01) Å for six Pt–Sn distances, and 2·39(0·02) Å for six Sn–Cl distances. The Sn atoms are 2·37 Å from the plane of the Pt atoms. Angles related by the idealized C_3 axis were found to be nearly equal with averages of 60·0° for Pt–Pt–Pt, 54·9° for Pt–Sn–Pt, and 62·5° for Pt–Pt–Sn.

The Pt atoms are co-ordinated to the double bonds of the cyclo-octa-1,5-diene rings in a fashion similar to that found[2] for $Ir(SnCl_3)(C_8H_{12})_2$. The double bonds of the C_8H_{12} groups are centred about the plane of the Pt atoms and nearly perpendicular to this plane with the distance from the Pt atoms to the centre of the double bonds being 2·15 Å. The average carbon–carbon distances within the cyclo-octa-1,5-diene rings are normal. The bonding within the metal atom cluster presumably consists of Pt–Pt single bonds with $SnCl_3$ groups each donating electrons to orbitals delocalized over the cluster.

Some preliminary crystal structure results have been reported[3] for another platinum–tin complex, $[Ph_3PCH_3]_3[Pt(SnCl_3)_5]$. This structure is not based on a metal atom cluster but on a trigonal bipyramidal arrangement of $SnCl_3$ groups bonded to a central Pt atom. The Pt–Sn distance found here was 2·54 Å; this structure has not been refined because of disorder problems.

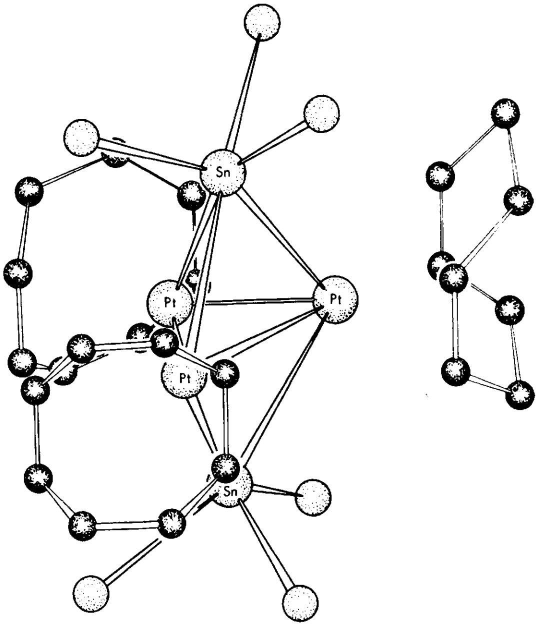

FIGURE. *The molecular configuration of* $(C_8H_{12})_3Pt_3(SnCl_3)_2$.

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