Coordination of $SnCl_2$ and $GeCl_2$ onto a One-dimensional Platinum Network: Synthesis and Structural Characterization of the $[PPh_4]_2[Pt_8(ECl_2)_4(CO)_{10}]$ (E = Sn, Ge) Complexes

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The preparation and molecular structures of two anions $[Pt_8(ECl_2)_4(CO)_{10}]^{2-}$ (E = Sn, Ge), obtained from the reaction of $[Pt_{15}(CO)_{30}]^{2-}$ with tin dichloride and germanium tetrachloride, are reported; X-ray analysis shows that the two isomorphous and isostructural anions exhibit an array of metal atoms formed by an edge-to-edge condensation of three tetrahedra generating a one-dimensional framework along the $\bar{4}$ axis with four ECl_2 groups capping four independent exposed butterfly surfaces.

Despite the wide range of characterized carbonyl clusters containing main group elements there are comparatively few carbonyl clusters incorporating the heavy group 14 elements.[1] The encapsulation of silicon, germanium and tin (but not lead) atoms in a transition metal cage is feasible provided that the cavity generated by the metal framework is large enough. Clusters in which either tin or germanium atoms, or fragments containing these atoms, interact with three or more metal atoms are quite common; nevertheless they are a source of current interest in view of the relevance of the Pt–E bond in some catalytic processes.[2]

Some years ago, the only examples of clusters containing interstitial germanium and tin atoms, *i.e.* $[Ni_{12}(CO)_{22}Ge]^{2-}$, $[Ni_{10}(CO)_{20}Ge]^{2-}$ and $[Ni_{12}(CO)_{22}Sn]^{2-}$, were reported.[3] These compounds were obtained by reacting $[Ni_6(CO)_{12}]^{2-}$ with $GeCl_4$ or $SnCl_2$ in THF solution, and the interstitial atoms were found to lodge in a pentagonal antiprismatic cavity of nickel atoms.

Although extensive studies on the thermal decomposition of anionic platinum carbonyl clusters leading to the isolation and characterization of several high-nuclearity carbonyl clusters, *viz.* $[Pt_{19}(CO)_{22}]^{4-}$,[4] $[Pt_{24}(CO)_{30}]^{2-}$,[5] and $[Pt_{26}(CO)_{32}]^{2-}$,[5] have been previously reported, to our knowledge there is only one report on the reactivity of platinum carbonyl clusters with main group elements. The $[\{Pt(PEt_3)_2\}_3(\mu_3\text{-}Te)_2]^{2+}$ dication was recently synthesized by reacting the $[Pt_3(CO)_6]_n{}^{2-}$ dianions (n = 3–5) with $TePEt_3$ in THF.[6]

Furthermore, there is no evidence of Pt forming clusters with interstitial main group atoms. This prompted our investigations to try and produce the Pt analogues of the above Ni clusters *via* reaction of $[Pt_3(CO)_6]_n{}^{2-}$ dianions (n = 3–5) with $GeCl_4$ and $SnCl_2$. In this paper we report the syntheses and the solid-state structures of the two clusters $[PPh_4]_2[Pt_8(ECl_2)_4(CO)_{10}]$ (E = Sn **1a**, Ge **2a**) which are the first examples of high nuclearity platinum carbonyl clusters containing coordinated $SnCl_2$ and $GeCl_2$ groups.

Compounds **1a** and **2a** were prepared by reacting $[PPh_4]_2[Pt_{15}(CO)_{30}]$ with $SnCl_2$ or $GeCl_4$. The Pt–Sn cluster was obtained by reacting $[PPh_4]_2[Pt_{15}(CO)_{30}]$ with $SnCl_2$ in a molar ratio 1 : 6. After 24 hours the solution contained mainly two products which were separated by their different solubilities in a THF–propan-2-ol mixture. The portion which comes out of solution first is compound **1a** while the second compound is presently uncharacterised. Crystals of $[PPh_4]_2[Pt_8(SnCl_2)_4(CO)_{10}]$ were obtained by layering propan-2-ol over a THF solution containing the cluster. In contrast, when the reaction between the pentadecanuclear platinum carbonyl cluster and $GeCl_4$ was performed under different conditions (*i.e.* by varying the molar ratio between the reactants, the nature of the solvents and the temperature) no reaction was observed, probably owing to the greater stability of the Ge–Cl bond with respect to the Sn–Cl bond. However, $[Pt_{15}(CO)_{30}]^{2-}$ reacts rapidly with $GeCl_4$ in the presence of a reducing agent such as $LiAlH_4$ giving $[Pt_8(GeCl_2)_4(CO)_{10}]^{2-}$ as the major product. Crystals of $[PPh_4]_2[Pt_8(GeCl_2)_4(CO)_{10}]$ were obtained by layering propan-2-ol over a THF solution containing the cluster. The characterisation of complexes **1a** and **2a** was initially based on spectroscopic and analytical data.[†] Neither compound reacted with hydrogen or carbon monoxide and no transformation was observed when a THF solution of **2a** was refluxed under nitrogen. A solution of **1a** proved unstable under the same conditions, affording two uncharacterized compounds presently under investigation.

The molecular structure of the anion $[Pt_8(SnCl_2)_4(CO)_{10}]^{2-}$ **1**,[‡] is shown in Fig. 1, together with the labelling scheme. The same Figure may also represent the isostructural germanium derivative **2**,[‡] by replacement of the Sn with Ge. Selected structural parameters for **1** and **2** are reported in Table 1.

The crystallographic symmetry of the whole anion is D_{2d} ($\bar{4}2m$). The Pt_8 metal core consists of three stacked edge-sharing tetrahedra of platinum atoms which generate four concave

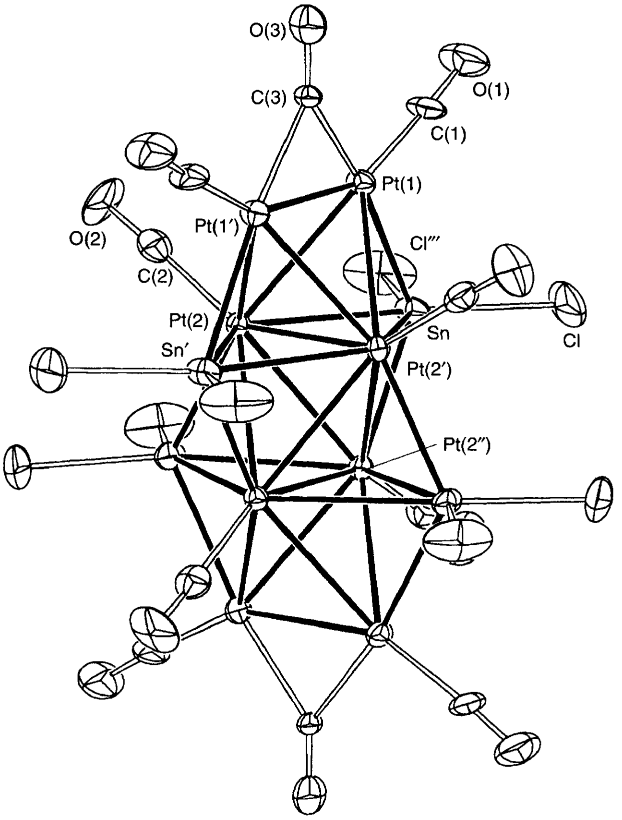

Fig. 1 ORTEP diagram of the anion $[Pt_8(SnCl_2)_4(CO)_{10}]^{2-}$ **1**. Primed, doubly primed and triply primed atoms are related to unprimed ones by the symmetry operations: $1 - x$, $1 - y$, z; x, $1 - y$, $2 - z$; and y, x, z, respectively.

butterfly surfaces, each of which is coordinated by one $SnCl_2$ group. The whole Pt_8Sn_4 metal framework can be thought of as deriving from the layering of two outer, symmetry-related Pt(1)–Pt(1) edges and two inner, symmetry related Pt(2)–Sn–Pt(2)–Sn planar rhombuses. The chlorine atoms are essentially coplanar with the Pt_2Sn_2 rhombuses. Of the ten carbonyl ligands, eight are terminally bonded to the eight Pt atoms, and two are double-bridging the outer Pt(1)–Pt(1) edges. The platinum tetrahedra are significantly elongated along the $\bar{4}$ axis, average Pt–Pt bonds being 2.665 (intralayer) and 2.925 Å (interlayer). The intralayer Pt–Sn distance, 2.950(1) Å, is much longer than the average interlayer one, 2.604 Å, so that the coordination around the tin atoms is best described as distorted tetrahedral [Pt(1)–Sn–Pt(2″) 120.1(1), Cl–Sn–Cl‴ 98.1(3)°]. The stereochemical features of the germanium derivative are quite similar, with obvious shortenings of the Pt–E (interlayer) and E–Cl bond lengths (*ca.* 0.17 and 0.15 Å, respectively, see Table 1), and also a remarkable shortening of the average Pt–Pt interlayer distance, 2.839 in **2** *vs.* 2.925 Å in **1**, which probably derives from the presence of the aforementioned shorter Pt–Ge interlayer bonds. The metal disposition in **1** and in **2** can be viewed as a monodimensional structure, as already seen in the platinum oligomers of general formula $[Pt_3(CO)_6]_n{}^{2-}$ (n = 2–6).[7] In the present case the monodimensional growth of the platinum skeleton is supported by $SnCl_2$ or $GeCl_2$ ligands while in the platinum oligomers the Pt_3 triangles are held together only by metal–metal bonds. This kind of growth can generate an infinite chain of metal atoms in a cluster having general formula $[Pt_{6+2n}(ECl_2)_{2+2n}(CO)_{8+2n}]^{2-}$. An analogous monodimensional growth of metal atoms supported by post-transition elements has been recently found in the $[Bi_4Co_9(CO)_{16}]^{2-}$ and $[Bi_8Co_{14}(CO)_{20}]^{2-}$ anions.[8] In these clusters the concave bow-tie surfaces generated by vertex-sharing octahedra are capped by bismuth atoms.

Complexes **1** and **2** are the first examples of acid-base adducts between post-transition element halides and high-nuclearity platinum carbonyl clusters. Insertion of the $SnCl_2$ group into a metal–metal bond has been found previously in the planar cluster $Os_3SnCl_2(CO)_{11}(\mu\text{-}CH_2)$,[9] while to our knowledge a coordinated $GeCl_2$ group has only been found previously in the five-membered Co–Ge–Fe–Ge–Co heterocycle $\{(\pi\text{-}C_5H_5)Co(CO)\}_2(GeCl_2)_2Fe(CO)_4$.[10]

Moreover, **1** and **2** may serve as precursors to solid-state metal phases containing main group and transition-metal elements[11] and can be thought as good models either for studying the electronic effects when alloying a semiconductor with a conductor element[12] or for generating homogeneous catalyst precursors based on Pt–Sn or Pt–Ge systems.[13]

Table 1 Selected distances within the anions $[Pt_8(ECl_2)_4(CO)_{10}]^{2-}$ (E = Sn, Ge)

	d/Å	
	Sn	Ge
Pt(1)–Pt(1′)	2.674(1)	2.690(1)
Pt(1)–Pt(2)	2.899(1)	2.840(1)
Pt(2)–Pt(2′)	2.656(1)	2.717(1)
Pt(2)–Pt(2″)	2.977(1)	2.837(1)
Pt(1)–E	2.613(1)	2.447(2)
Pt(2)–E	2.950(1)	2.918(2)
Pt(2″)–E	2.595(1)	2.412(2)
E–Cl	2.356(4)	2.203(5)

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Footnotes

† *Spectroscopic data* for **1a**: yield 15% (based on Pt); ν_{CO}/cm^{-1} (THF solution) 2044s, 1848m; δ_{Pt} {[$^2H_8$]THF, from room temp. down to 203 K the spectra are temperature independent} two signals at δ −4065 and −5382 in the ratio 1 : 1 with unresolved coupling to ^{117}Sn, ^{119}Sn and ^{195}Pt; FABMS (negative ion, nitrobenzyl alcohol mull) unresolved peak at *m/z* 2600. For **2a**: yield 48.5% (based on Pt) ν_{CO}/cm^{-1} (THF solution) 2044s, 1844m; δ_{Pt} {[$^2H_8$]THF, from room temp. down to 198 K the spectra are temperature independent} two signals at δ −4010 and −5355 in the ratio 1 : 1 with unresolved coupling to ^{195}Pt.

‡ *Crystal data* for $[PPh_4]_2[Pt_8(SnCl_2)_4(CO)_{10}]$ **1a**; $C_{58}H_{40}Cl_8O_{10}P_2Pt_8Sn_4$, M = 3278.0, tetragonal, space group $I\bar{4}2m$ (no. 121), a = 14.550(3), c = 18.220(4) Å, U = 3857(2) Å^3, Z = 2, D_c = 2.822 g cm^{-3}, μ = 162.4 cm^{-1}, $F(000)$ = 2916. Reflections measured = 2341, unique = 857 with $I \geqslant 3\sigma(I)$. Empirical absorption correction (T_{min} = 0.58, T_{max} = 1). Final R = 0.024 and R_w = 0.032 for 87 parameters.

Crystal data for $[PPh_4]_2[Pt_8(GeCl_2)_4(CO)_{10}]$ **2a**; $C_{58}H_{40}Cl_8Ge_4O_{10}P_2Pt_8$, M = 3093.6, tetragonal, space group $I\bar{4}2m$ (no. 121), a = 14.417(4), c = 17.972(4) Å, U = 3736(2) Å^3. D_c = 2.750 g cm^{-3}, Z = 2, μ = 170.2 cm^{-1}, $F(000)$ = 2772. Reflections measured = 1189, unique = 825 with $I \geqslant 3\sigma(I)$. Empirical absorption correction (T_{min} = 0.62, T_{max} = 1). Refinement converged at R = 0.030 and R_w = 0.034 for 87 parameters.

Details common to the two structures are: ENRAF-NONIUS CAD4 diffractometer, Mo-Kα radiation, λ = 0.71073 Å, ω scan mode, scan limit $2\theta_{min}$ = 6°, $2\theta_{max}$ = 54°. The structures were solved by direct methods and refined by full-matrix least squares. Hydrogen atoms were placed in calculated positions. Program used was SDP 1.0 version. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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