

## Chloro(phosphinato)germanium(II) and Chloro(phosphinato)tin(II)

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**Abstract.** [GeCl(H<sub>2</sub>PO<sub>2</sub>)], *Pnam*,  $a = 8.178$  (4),  $b = 9.595$  (5),  $c = 5.299$  (5) Å,  $Z = 4$ ,  $D_x = 2.764$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 17.9$  mm<sup>-1</sup>. [SnCl(H<sub>2</sub>PO<sub>2</sub>)], *Pnam*,  $a = 8.045$  (8),  $b = 9.915$  (9),  $c = 5.517$  (6) Å,  $Z = 4$ ,  $D_x = 3.308$  Mg m<sup>-3</sup>,  $\mu(\text{Cu } K\alpha) = 52.6$  mm<sup>-1</sup>. The compounds are isostructural. The Ge and Sn atoms lie at the apices of trigonal pyramids. Each is bonded to one Cl atom and to two O atoms of different H<sub>2</sub>PO<sub>2</sub><sup>-</sup> groups so that chains extend parallel to *c*. Weak secondary bonds cross-link the chains.

**Introduction.** While studying the structural role of the phosphinate ('hypophosphite') anion, H<sub>2</sub>PO<sub>2</sub><sup>-</sup>, in crystals (Weakley, 1978*a,b*, 1979) we noted that although [GeCl(H<sub>2</sub>PO<sub>2</sub>)] and [SnCl(H<sub>2</sub>PO<sub>2</sub>)] were first prepared in the 1950's (Everest, 1951, 1952) their structures had not been reported. Although the structural chemistry of Sn<sup>II</sup> is extensive (Zubieta & Zuckerman, 1978) there has been far less work on Ge<sup>II</sup>. The procedures of Everest (1951, 1952) gave satisfactory crystals which were mounted on glass fibres and protected by a light coating of epoxy cement. Equi-inclination Weissenberg photographs (Cu radiation,  $\lambda = 1.5418$  Å) of levels *h0-5l* and *hk0-3* for [GeCl(H<sub>2</sub>PO<sub>2</sub>)] and *0-4kl* and *hk0-5* for [SnCl(H<sub>2</sub>PO<sub>2</sub>)] were scanned by the SRC Microdensitometer Service, Daresbury. The data reduction for both compounds was repeated with inclusion of an absorption correction when it had become clear that these formulae were correct. The structures were solved by the heavy-atom

Table 1. Atomic coordinates ( $\times 10^4$ ) for [GeCl(H<sub>2</sub>PO<sub>2</sub>)] and [SnCl(H<sub>2</sub>PO<sub>2</sub>)]

	<i>x</i>	<i>y</i>	<i>z</i>
[GeCl(H <sub>2</sub> PO <sub>2</sub> )]			
Ge	810 (2)	1643 (2)	2500
Cl	-1657 (5)	385 (4)	2500
P	783 (5)	3415 (4)	7500
O	-40 (9)	2899 (8)	5086 (14)
[SnCl(H <sub>2</sub> PO <sub>2</sub> )]			
Sn	1089 (1)	1599 (1)	2500
Cl	-1668 (5)	294 (5)	2500
P	667 (7)	3474 (4)	7500
O	-52 (14)	2899 (10)	5164 (12)

Table 2. Bond lengths (Å) and angles (°)

Ge—Cl	2.351 (4)	Sn—Cl	2.568 (4)
Ge—O	1.953 (7)	Sn—O	2.160 (9)
P—O	1.528 (8)	P—O	1.423 (8)
Ge...Cl <sup>i</sup>	3.36 (1)	Sn...Cl <sup>i</sup>	3.37 (1)
Ge...Cl <sup>ii</sup>	3.53 (1)	Sn...Cl <sup>ii</sup>	3.57 (1)
Ge...O <sup>ii</sup>	3.69 (1)	Sn...O <sup>ii</sup>	3.47 (1)
O—Ge—O <sup>iii</sup>	89.1 (4)	O—Sn—O <sup>iii</sup>	85.8 (4)
O—Ge—Cl	90.7 (2)	O—Sn—Cl	86.2 (3)
O—P—O <sup>iv</sup>	113.7 (6)	O—P—O <sup>iv</sup>	115.6 (8)
P—O—Ge	129.1 (5)	P—O—Ge	129.6 (7)

Symmetry code: (i)  $-x, -y, -z$ ; (ii)  $\frac{1}{2} + x, \frac{1}{2} - y, z$ ; (iii)  $x, y, \frac{1}{2} - z$ ; (iv)  $x, y, \frac{1}{2} - z$ .

method. H atoms, which could not be clearly located from difference syntheses, were included at calculated positions ( $d_{\text{P-H}} 1.40$  Å) in the last cycles of full-matrix least-squares refinement. Two low-angle reflections judged to be affected by extinction were omitted from the data set for [SnCl(H<sub>2</sub>PO<sub>2</sub>)]. Refinement in *Pnam*, with anisotropic thermal parameters for non-hydrogen atoms, converged at  $R 0.077$  for [GeCl(H<sub>2</sub>PO<sub>2</sub>)] (355 unique reflections above background, 28 parameters, unit weights) and at  $R 0.079$  for [SnCl(H<sub>2</sub>PO<sub>2</sub>)] (410 unique reflections, 28 parameters, weighting factor  $w = 1/(1 + 0.021F^2)$ ). *SHELX 76* (Sheldrick, 1976) was used in all calculations. The final coordinates are given in Table 1, and derived dimensions in Table 2.\* Attempts to refine the structures in the alternative *Pna2<sub>1</sub>* (45 parameters) lowered  $R$  significantly only for [GeCl(H<sub>2</sub>PO<sub>2</sub>)] (to 0.069) and for both compounds indicated improbable differences between the P—O lengths {1.43 and 1.63 Å in [GeCl(H<sub>2</sub>PO<sub>2</sub>)]}.

**Discussion.** The compounds have very similar structures (Fig. 1) in which all atoms other than O lie on crystal mirror planes. They are polymers with chains

\* Lists of structure factors and anisotropic thermal parameters for both compounds have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34762 (7 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

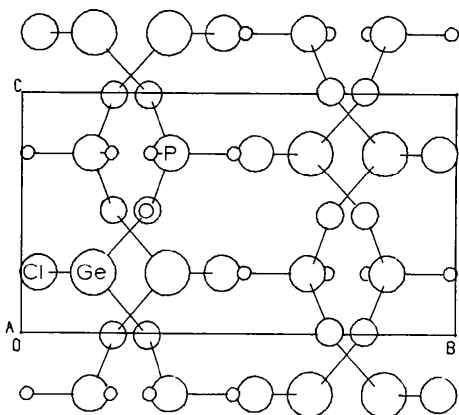


Fig. 1. [GeCl(H<sub>2</sub>PO<sub>2</sub>)]: *a*-axis projection.

(*M*—O—P—O—)<sub>∞</sub> (*M* = Ge or Sn) extending parallel to *c*. Long bridges of the type *M*—O—P—O—*M* are present in other phosphinates (Weakley, 1978*a,b*, 1979). The nearest neighbours of each *M* atom (two O atoms and one Cl) define the base of a trigonal pyramid. The bond angles (Table 2) are close to 90° at Ge and 86° at Sn. The bond lengths and angles at Sn are within the ranges found for other compounds with pyramidal Sn<sup>II</sup>Cl<sub>3</sub> or Sn<sup>II</sup>O<sub>3</sub> groups (Zubieta & Zuckerman, 1978). The bond-length differences (Sn—O) — (Ge—O) and (Sn—Cl) — (Ge—Cl) are both *ca* 0.21 Å, and imply a covalent radius for Ge<sup>II</sup> of about 1.32 Å, compared with 1.22 Å for Ge<sup>IV</sup> (Alcock, 1972). The Ge—Cl length of 2.35 Å is to be compared with 2.25, 2.54 Å in pyramidal [GeCl<sub>2</sub>(Ph<sub>3</sub>P)] (Bokii, Struchkov, Kolesnikov, Rogazhin & Nefedov, 1975) and with 2.32 Å for pyramidal GeCl<sub>3</sub><sup>-</sup> in the rhombohedral form of Cs[GeCl<sub>3</sub>] (Christensen & Rasmussen, 1965). In [Ge(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)Cl<sub>2</sub>] (Kulishov, Bokii, Struchkov, Nefedov, Kolesnikov & Perl'mutter, 1970) the Ge—Cl bonds are shorter (2.25, 2.28 Å) but in

compensation the Ge—O bonds are rather long (2.41, 2.48 Å).

Each *M* atom in [*M*Cl(H<sub>2</sub>PO<sub>2</sub>)] makes several contacts with atoms in neighbouring chains, on the side remote from the ligand atoms, at distances less than the van der Waals radii sum though much greater than normal covalent bond lengths. Alcock (1972), reviewing secondary bonding, gives van der Waals radii as: O, 1.52; Cl, 1.75; Ge, 1.95; Sn, 2.10 Å. On the basis of these values, the Ge...Cl, Sn...Cl, and Sn...O contacts listed in Table 2 (but not the Ge...O contact) indicate weak bonds which serve to cross-link the chains. For comparison, the Ge...Cl weak contacts in Cs[GeCl<sub>3</sub>] and [Ge(C<sub>4</sub>H<sub>8</sub>O<sub>2</sub>)Cl<sub>2</sub>] are 3.13 and 3.51 Å respectively. As in Cs[GeCl<sub>3</sub>], the overall coordination (3 + 3) in [GeCl(H<sub>2</sub>PO<sub>2</sub>)] is distorted octahedral.

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## The Structure of Trisodium Hydrogensilicate Dihydrate

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**Abstract.** Na<sub>3</sub>HSiO<sub>4</sub>·2H<sub>2</sub>O, orthorhombic, *Pbca*, *a* = 10.470 (4), *b* = 18.704 (12), *c* = 6.059 (3) Å, *Z* = 8, *D*<sub>c</sub> = 2.218 Mg m<sup>-3</sup>, *V* = 1186.5 Å<sup>3</sup>, λ(Mo *K*α) = 0.7107 Å. The structure consists of [HSiO<sub>4</sub>]<sup>3-</sup> tetrahedra, linearly arranged along the *a* axis and connected by Si—O...H—O—Si hydrogen bonds. These chains

are linked to each other by the Na atoms, and by hydrogen bonds from the water molecules. The Na atoms show irregular coordination with five or six oxygens within the first coordination sphere. The two crystallographically independent water molecules are chemically different. One H<sub>2</sub>O forms two hydrogen

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