

The Crystal Structure of Germanium(II,IV) Phosphinate, $\text{Ge}_2(\text{H}_2\text{PO}_2)_6$

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Summary: The crystals are trigonal-rhombohedral, space-group $R\bar{3}$, $a=11.86(1)$, $c=9.58(1)$ Å. Successive centres of symmetry along c are occupied alternately by Ge^{IV} and disordered Ge^{II} atoms, which are linked by triple Ge-O-P-O-Ge bridges (Ge^{IV} -O, 1.869; mean Ge^{II} -O, 2.32 Å).

Introduction

Following the determination [1] of the structures of $\text{Ge}(\text{H}_2\text{PO}_2)\text{Cl}$ and $\text{Sn}(\text{H}_2\text{PO}_2)\text{Cl}$, we attempted to prepare $3\text{Ge}(\text{H}_2\text{PO}_2)_2, \text{GeI}_2$. The method of Everest [2] in our hands usually afforded small, yellow, hexagonal or pseudo-hexagonal prisms whose diffraction photographs showed them to be poorly crystalline. The iodine-free title compound was obtained by chance on three occasions as colourless, well-diffracting, hexagonal plates, and we now report its structure.

Crystal Structure Determination

Crystal data. - $\text{Ge}_2(\text{H}_2\text{PO}_2)_6$, $M=535.2$. Trigonal, $R\bar{3}$, $a=11.86(1)$, $c=9.58(1)$ Å, $Z=3$, $D_m=2.18$ (floatation), $D_c=2.26$ g cm^{-3} ; $\text{Cu K}\alpha$ radiation, $\lambda=1.5418$ Å, $\mu=0.9$ cm^{-1} . The associated primitive rhombohedral cell has dimensions: $a=7.56(1)$ Å, $\alpha=103.4(2)^\circ$.

Equi-inclination multi-film Weissenberg photographs were recorded from a crystal mounted on the trigonal a axis (layers 0 to 7). Spot intensities were measured by use of a scanning microdensitometer (S.E.R.C. service, Daresbury Laboratory). Data reduction yielded 405

unique reflections. Absorption corrections were applied. The positions of the Ge and P atoms were obtained from a Patterson synthesis. It became apparent during refinement that Ge(2) was disordered, from its large thermal parameters and from the nearby residual peaks in difference syntheses. Various models were tried, with Ge(2) as fractional atoms on the three-fold axis at $0, 0, \frac{1}{2} \pm \delta$ or at general positions near $0, 0, \frac{1}{2}$, but a properly-converging refinement was only achieved when Ge(2) was fixed at the inversion centre. Ge(2) remained close to $0, 0, \frac{1}{2}$ when the structure was treated as non-centrosymmetric, space-group $R3$. Refinement in $R3$ terminated at $R=0.093$ (32 parameters), with anisotropic thermal parameters for all Ge, P, and O atoms and with H atoms included at calculated positions (P-H 1.40 Å). The SHELX-76 program [3] was used in all calculations. A table of structure factors is available from the author.

Discussion

Atomic positions and thermal parameters are given in Table 1, and bond lengths and angles in Table 2. The Ge atoms occupy crystal inversion cent-

Table 1. Atomic coordinates and anisotropic thermal parameters (all $\times 10^4$)

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ge(1)	0	0	0	106(11)	106(11)	51(14)	0	0	53(5)
Ge(2)	0	0	5000	569(21)	569(21)	402(26)	0	0	284(10)
P	332(3)	2120(3)	2110(3)	321(18)	144(16)	130(16)	-12(10)	-10(11)	128(13)
O(1)	-495(8)	985(8)	1094(8)	194(42)	236(43)	171(37)	-55(31)	-15(31)	116(34)
O(2)	465(11)	1753(9)	3557(8)	692(74)	267(47)	86(39)	-44(33)	-91(40)	227(49)

The temperature factor is in the form $T = \exp[-2\pi^2(h^2a^2U_{11} + \dots + 2klb^2c^2U_{23})]$.

res on three-fold axes, and each is linked to its two nearest neighbours by Ge-O-P-O-Ge bridges (Fig. 1.). Thus, parallel chains extend in the c direction. There are no short contacts between atoms in adjacent chains. The composition derived from the structure analysis is $\text{Ge}(\text{H}_2\text{PO}_2)_3$, or $\text{Ge}^{\text{II}}\text{Ge}^{\text{IV}}(\text{H}_2\text{PO}_2)_6$. Atom Ge(1) is identified as Ge^{IV} . It has near-octahedral coordination, with a Ge-O bond length similar to that in, e.g., the $\text{Ge}(\text{C}_2\text{O}_4)_3^{2-}$ anion [4]. The Ge^{II} atom, Ge(2), is also in near-octahedral coordination, but the Ge-O distance of 2.32 Å is much longer than the Ge^{IV} -O bond lengths in, e.g., $\text{Ge}(\text{H}_2\text{PO}_2)\text{Cl}$ or $\text{Ge}(\text{acac})\text{I}$ (1.91 to 1.95

Å) [1,5]. Moreover the Ge atoms in the two latter compounds, as in $(\text{Me}_4\text{N})(\text{GeCl}_3)_3$, [6] are in trigonal-pyramidal coordination (sterically-active lone pair electrons) and form long secondary bonds. In the low-temperature rhombohedral form of CsGeCl_3 [7] the Ge atom forms three short and three long Ge-Cl bonds but in the cubic modification at higher temperatures the Ge atoms, which are presumably disordered about mean positions, appear to form six identical bonds of intermediate length. The latter situation is analogous to that for Ge(2), although the disorder could not be satisfactorily modelled during refinement. It would account for the considerable anisotropy and larger mean U of

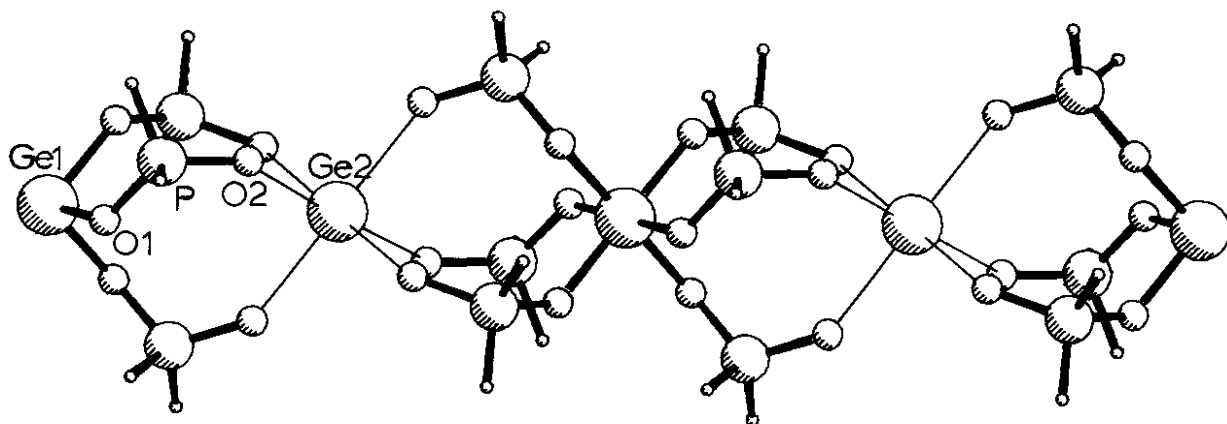


Fig. 1. Two repeating units of the $\text{Ge}_2(\text{H}_2\text{PO}_2)_6$ chain along the c axis.

Table 2. Bond lengths and inter-bond angles.

Ge(1)-O(1)	1.869(8) Å	P-O(1)	1.549(8) Å
Ge(2)-O(2)	2.322(9)	P-O(2)	1.485(8)
O(1)-Ge(1)-O(1 ⁱ)	91.6(3)°	O(1)-P-O(2)	116.4(5)°
O(1)-Ge(1)-O(1 ⁱⁱ)	88.4(3)	P-O(1)-Ge(1)	129.5(5)
O(2)-Ge(2)-O(2 ⁱ)	88.2(3)	P-O(2)-Ge(2)	143.7(5)
O(2)-Ge(2)-O(2 ⁱⁱⁱ)	91.8(3)		

Symmetry code: (i) $-y, x-y, z$; (ii) $y, y-x, -z$; (iii) $y, y-x, 1-z$.

O(2) compared with O(1); and also for the fact that the P-O(2) bond is just significantly shorter than P-O(1) (since less of the bonding capacity of O(2) is, on average, used in bonding to Ge).

References

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