

Bis(tetraphenylphosphonium) tris(oxalato-*O,O'*)germanate(IV)

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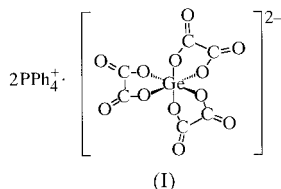
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The synthesis and structure of the title compound, $(C_{24}H_{20}P)_2[Ge(C_2O_4)_3]$, are reported. The PPh_4^+ cations in the structure form infinite zigzag chains in which the $P \cdots P$ distances alternate between 6.229 (1) and 7.118 (1) Å, and the $P \cdots P \cdots P$ angle is 131.4 (1)°. The shorter $P \cdots P$ distance is associated with a sixfold phenyl embrace. However, the longer $P \cdots P$ distance is associated with both phenyl–phenyl interactions and interactions between the cations and a twofold symmetric $[Ge(C_2O_4)_3]^{2-}$ anion. In the cation–anion interactions, the $P \cdots O$ distance is 4.444 (2) Å, the $O \cdots P - C_{\text{distal}}$ angle is 175.0 (1)° and the shortest $H \cdots O$ distances are 2.74 and 3.09 Å.

Comment

As part of a study of the packing of salts of phenylphosphonium cations (Dance & Scudder, 1995, 1996, 1998; Hasselgren *et al.*, 1997), we have characterized the new salt $(PPh_4)_2[Ge(C_2O_4)_3]$, (I). The structure consists of recognizable PPh_4^+ cations and $[Ge(C_2O_4)_3]^{2-}$ anions, the latter having crystallographic twofold symmetry (Fig. 1). The structure is almost isostructural with that of $(AsPh_4)_2[Tc(C_2O_4)_3]$ (Colman *et al.*, 1987).



The bond distances and angles within the anion (Fig. 1) can be compared with those found in $K_2[Ge(C_2O_4)_3] \cdot H_2O$, (II) (Jorgensen & Weakley, 1980). The s.u.'s found for (I) are smaller than those found for (II). In no case do the bond distances or ligand bite angles observed for the anion in (I)

differ significantly from those observed in (II). In addition, the $C - O_{\text{terminal}}$ distances of (I) do not differ significantly from each other, even though atom O1Ox1 appears to be involved in an anion–cation interaction, as discussed below.

The cations in (I) are linked into pairs [closest approach 6.229 (1) Å], by a sixfold phenyl embrace, or 6PE, which is an attractive interaction (Dance & Scudder, 1995, 1996, 1998). In addition, each cation is linked to a further cation at a distance of 7.118 (1) Å by a fourfold phenyl embrace, or 4PE (Dance & Scudder, 1998). This 4PE is unusual in that it is made up of two offset face-to-face interactions, with a twofold axis bisecting the $P \cdots P$ vector, instead of the more commonly found centre of inversion at its midpoint. The $P \cdots P \cdots P$ angle is 131.4 (1)°. In this way, infinite zigzag chains of alternating 6- and 4PEs are formed. However, the longer $P \cdots P$ distance is associated not only with the 4PE, but also with cation–anion interactions.

The single shortest $P \cdots O$ interaction at each P atom is 4.444 (2) Å. While this is longer than the sum of the van der Waals radii (3.35 Å; Bondi, 1964), the near-linearity of $O1Ox1$, P and the distal carbon [$O \cdots P - C_{\text{distal}}$ 175.0 (1)°] is reminiscent of the near-linearity of $P \cdots P - C_{\text{distal}}$ that characterizes the 6PE (Dance & Scudder, 1995, 1996). As in the 6PE, the

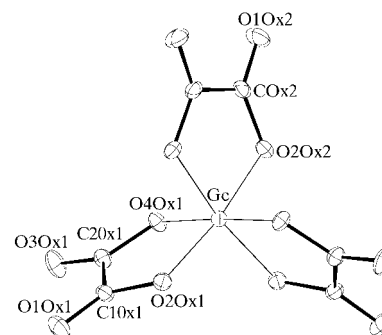


Figure 1

A view of the $[Ge(C_2O_4)_3]^{2-}$ anion in (I) showing the labelling of the atoms. Displacement ellipsoids are shown at the 10% probability level.

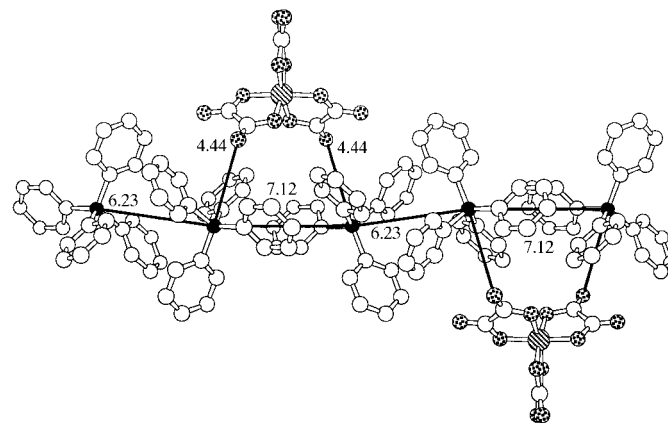


Figure 2

A view of the chain structure adopted by the cations and anions in (I); distances are in Å. One anion, with the twofold axis running through it, spans each fourfold phenyl embrace. The H atoms have been omitted for clarity.

linearity is presumably indicative of an attractive interaction. A study of $(\text{MePh}_3\text{P})_2[\text{Cr}_2\text{O}_7]$ shows that such attraction occurs *via* C—H \cdots O hydrogen bonding (Lorenzo *et al.*, 1999). In the present case, the shortest H \cdots O distances are 2.74 and 3.09 Å, compared with values of 2.39–3.15 Å in $(\text{MePh}_3\text{P})_2[\text{Cr}_2\text{O}_7]$. The twofold axis referred to above leads to two identical P \cdots O interactions emanating from a single anion spanning each 4PE (Fig. 2). Similarly modified zigzag chains occur in $(\text{AsPh}_4)_2[\text{Tc}(\text{C}_2\text{O}_4)_3]$, where the As \cdots As distances are 6.27 and 7.23 Å, the As \cdots O distance is 4.35 Å and the O \cdots As—C angle is 174.3°. Related chains also occur in $(\text{AsPh}_4)_2[\text{Zn}(\text{S}_2\text{C}_2\text{O}_2)_2]$ (Golič *et al.*, 1986). There are two chains in this Zn salt, one with As \cdots As distances of 6.48 and 7.26 Å, the other with distances of 6.06 and 8.06 Å. Each chain is associated with one end of the anion to form two different O \cdots As contacts of 4.49 and 5.16 Å, the corresponding O \cdots As—C_{distal} angles being 163.6 and 167.5°.

In summary, the structure of (I) has allowed the recognition of an unusual chain structure of the cations occurring here and in some other EPh_4^+ salts of oxygen-bearing anions.

Experimental

A solution of $\text{K}_2[\text{Ge}(\text{C}_2\text{O}_4)_3]\cdot\text{H}_2\text{O}$ (0.440 g, 1.02 mmol) in warm water (*ca* 15 ml) and a solution of Ph_4PBr (0.853 g, 2.03 mmol) in methanol (*ca* 15 ml) were mixed, producing a white precipitate. The solid white product was separated by filtration, washed with water–methanol (1:1, *v/v*), dried and dissolved in boiling methanol. X-ray quality crystals of (I) were obtained as part of the second batch of crystals formed when the methanolic solution was allowed to cool to room temperature.

Crystal data

$(\text{C}_{24}\text{H}_{20}\text{P})_2[\text{Ge}(\text{C}_2\text{O}_4)_3]$
 $M_r = 1015.4$
 Monoclinic, $C2/c$
 $a = 22.759$ (5) Å
 $b = 13.618$ (2) Å
 $c = 15.813$ (3) Å
 $\beta = 104.34$ (1)°
 $V = 4748$ (2) Å³
 $Z = 4$

$D_x = 1.42$ Mg m⁻³
 Cu $K\alpha$ radiation
 Cell parameters from 10 reflections
 $\theta = 25$ – 27°
 $\mu = 2.04$ mm⁻¹
 $T = 294$ K
 Plate, colourless
 $0.15 \times 0.13 \times 0.06$ mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 $\omega/2\theta$ scans
 Absorption correction: analytical (de Meulenaer & Tompa, 1965)
 $T_{\min} = 0.64$, $T_{\max} = 0.90$
 4616 measured reflections
 4439 independent reflections
 3646 reflections with $I > 3\sigma(I)$

$R_{\text{int}} = 0.017$
 $\theta_{\text{max}} = 70^\circ$
 $h = -27 \rightarrow 27$
 $k = -16 \rightarrow 0$
 $l = 0 \rightarrow 19$
 1 standard reflection frequency: 30 min
 intensity decay: none

Refinement

Refinement on F
 $R = 0.034$
 $wR = 0.050$
 $S = 1.78$
 3646 reflections
 174 parameters

H-atom parameters not refined
 $w = 1/[\sigma^2(F) + 0.0016F^2]$
 $(\Delta/\sigma)_{\text{max}} = 0.013$
 $\Delta\rho_{\text{max}} = 0.38$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.40$ e Å⁻³

The asymmetric unit of (I) consists of one cation and half of one anion. A single ring was used to model all four phenyl rings, with their location and orientation as variables. H atoms were included in calculated positions and were not refined. The thermal motion of each phenyl ring was described by a 12-parameter **TL** model (where **T** is the translation tensor and **L** is the libration tensor).

Data collection: *CAD-4 Operations Manual* (Enraf–Nonius, 1977); cell refinement: *CAD-4 Operations Manual*; data reduction: local programs; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1994); program(s) used to refine structure: *RAELS* (Rae, 1989); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: local programs.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1190). Services for accessing these data are described at the back of the journal.

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