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Tetraphenylarsonium tetraiodothallate(III)

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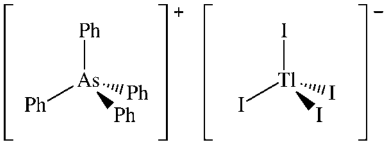
The As and Tl atoms in title compound, $(C_{24}H_{20}As)[TlI_4]$, sit on fourfold inversion centres, resulting in a $[TlI_4]^-$ anion with D_{2d} symmetry and a Tl—I bond length of 2.7691 (3) Å. The tetrahedral anion is tetragonally distorted, being flattened in the direction of the *c* axis of the tetragonal unit cell, so that the two unique I—Tl—I angles differ by about 9°. In contrast, the cation has S_4 symmetry and the tetrahedral coordination geometry of the As atom is very slightly stretched in the direction of the *c* axis.

Comment

11 different structures containing the tetraiodothallate(III) anion have been reported and of these only two have the anion on a site of high crystallographic symmetry. Often the nature of the cation keeps the space-group symmetry low (Drew *et al.*, 1970; Glaser *et al.*, 1982, 1983; Beno *et al.*, 1987; Geiser *et al.*, 1988, 1996; Riera *et al.*, 1989; Tebbe *et al.*, 1995; Ilyukhin *et al.*, 2000; Slavin *et al.*, 2000), but even $CsTlI_4$ crystallizes in space group $P2_1/c$ with the anion in a general position (Thiele *et al.*, 1986). In the salt with the Et_3S^+ cation (Svensson *et al.*, 2000), the $[TlI_4]^-$ anion sits on a fourfold inversion centre, but the cation is reported to be so highly disordered that the C atoms were not included in the model, thus detracting from the precision of the geometry of the anion. The only reported ordered structure with high symmetry is that of ammonium ammonia tetraiodothallate(III) bis(18-crown-6) clathrate (Domasevitch *et al.*, 1999), in which the $[TlI_4]^-$ anion has crystallographic T_d symmetry and the 18-crown-6 molecule has C_3 symmetry. We were interested in finding a simpler system in which the $[TlI_4]^-$ anion displays high crystallographic symmetry and chose $(Ph_4As)^+$ as the counter-ion because the size and symmetry of the cation should be compatible with the $[TlI_4]^-$ anion and favour crystallization of the salt in a high-symmetry space group. This cation is used frequently in organometallic syntheses, appears in over 530 structures in the Cambridge Structural Database (CSD, April 2002 Release; Allen & Kennard, 1993) and is often found to adopt high crystallographic site symmetry in structures with amenable anions.



(I)

The structure of the title salt, (I), does indeed present ions with high crystallographic site symmetry. The As and Tl atoms sit on fourfold inversion centres (Fig. 1) so that the cation and anion have S_4 and D_{2d} symmetry, respectively. The Tl—I bond length (Table 1) is in agreement with those found in other structures containing $[TlI_4]^-$ anions. For the eight such structures for which coordinates are present in the CSD, plus that of $CsTlI_4$, there were 31 hits for a unique Tl—I bond, with a range of bond lengths of 2.69–2.83 Å and a mean value of 2.758 (6) Å. Considering only structures with highly symmetrical $[TlI_4]^-$ anions, the unique Tl—I bond length in the Et_3S^+ salt is 2.757 (1) Å (Svensson *et al.*, 2000), while it is 2.766 (2) and 2.748 (2) Å (two independent anions) in the 18-crown-6 clathrate (Domasevitch *et al.*, 1999). The unique As—C bond length in the cation compares well with the mean value of 1.905 (1) Å for 1990 hits for this bond among 427 error-free structures in the CSD involving $[Ph_4As]^+$ cations for which coordinates are present. For these hits, the range of As—C bond lengths is 1.70–2.15 Å, although over 98% of the entries are in the narrower range of 1.82–1.98 Å.

Except for the perfectly tetrahedral $[TlI_4]^-$ anion in the 18-crown-6 clathrate (Domasevitch *et al.*, 1999), most other examples show a very small distortion from this geometry. The range of I—Tl—I angles across the eight structures in the CSD, plus $CsTlI_4$, is 100–117°. Normally, this variation is because each Tl—I bond in the anion is crystallographically independent, which allows a certain degree of flexibility that can be influenced by the surrounding environment. However, even for the title compound with its four symmetry-equivalent Tl—I bonds, the anion shows significant tetragonal distortion. The $[TlI_4]^-$ tetrahedron is flattened in the direction of the *c* axis of the tetragonal unit cell so that the two unique I—Tl—I angles in the anion differ by about 9° (Table 1). In contrast, for the Et_3S^+ salt, in which the anion also has $\bar{4}$ symmetry, the tetragonal distortion is negligible.

The tetragonal distortion of the tetrahedral coordination geometry about the As atom in the $[Ph_4As]^+$ cation is less severe, with only a 2.5° difference between the unique C—As—C angles. The distortion is also in the opposite direction to that in the anion, so that the cation is slightly stretched in the direction of the *c* axis of the unit cell. For the 427 error-free structures in the CSD, the C—As—C angle for 3140 hits ranges from 97.5 to 119.3°, although over 96% of the entries are in the narrower range of 105–114°.

Compound (I) is not isostructural with any other known related structure. There are no entries in the CSD for any $[Ph_4As]^+$ salts which crystallize in space group $I4_1/a$, nor are there entries for any halothallate(III) salts having this space group. No related $[Ph_4P]^+$ salts are recorded either. Cotton *et*

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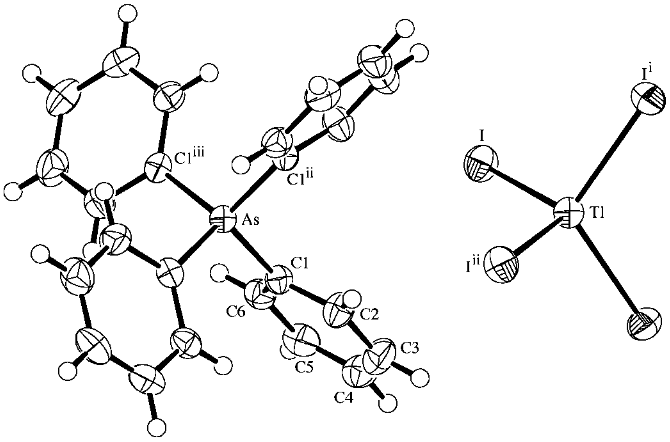

Figure 1
View of the structure of the title compound drawn with the *c* axis of the unit cell running horizontally from left to right and showing the atom-labelling scheme. Displacement ellipsoids are drawn at the 50% probability level. The symmetry codes are as in Table 1.

al. (1965) reported that powder diffraction measurements on $(Ph_4As)[TlCl_4]$ showed that it is isostructural with $(Ph_4As)[FeCl_4]$ (Zaslow & Rundle, 1957; Cotton & Murillo, 1975), but these compounds crystallize in the space group $I\bar{4}$.

Experimental

The title compound was prepared exactly as described by Cotton *et al.* (1965), and its melting point (413 K) and microanalytical data were identical to the reference values. Suitable crystals were grown by slow evaporation of a solution of (I) in acetone.

Crystal data

$(C_{24}H_{20}As)[TlI_4]$
$M_r = 1095.26$
Tetragonal, $I4_1/a$
$a = 14.7686$ (3) Å
$c = 13.1319$ (3) Å
$V = 2864.22$ (11) Å^3
$Z = 4$
$D_x = 2.540$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 21 361 reflections
$\theta = 2.0$–$30.0°$
$\mu = 11.10$ mm^{-1}
$T = 160$ (1) K
Prism, red
0.20 × 0.12 × 0.08 mm

Data collection

Nonius KappaCCD diffractometer
φ and ω scans with κ offsets
Absorption correction: numerical (Coppens *et al.*, 1965)
$T_{min} = 0.243$, $T_{max} = 0.458$
22 651 measured reflections
2100 independent reflections
1748 reflections with $I > 2\sigma(I)$
$R_{int} = 0.076$
$\theta_{max} = 30.0°$
$h = -20 \rightarrow 20$
$k = -20 \rightarrow 19$
$l = -18 \rightarrow 16$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.078$
$S = 1.06$
2099 reflections
69 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0288P)^2 + 7.2222P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.13$ e Å^{-3}
$\Delta\rho_{min} = -1.77$ e Å^{-3}
Extinction correction: *SHELXL*97
Extinction coefficient: 0.00031 (7)

The largest peak of residual electron density was 1.73 Å from atom H3. All H atoms were placed in geometrically idealized positions (C—H = 0.95 Å) and constrained to ride on their parent atoms, with $U_{iso}(H) = 1.2U_{eq}(C)$. One reflection was omitted from the final refinement because its lower than expected observed intensity was probably a result of being partially obscured by the beam stop.

Table 1
Selected geometric parameters (Å, °).

Tl—I	2.7691 (3)	As—C1	1.904 (4)
I—Tl—I^{i}	106.469 (6)	C1—As—C1^{ii}	107.8 (2)
I—Tl—I^{ii}	115.660 (13)	C1—As—C1^{iii}	110.31 (11)

Symmetry codes: (i) $\frac{5}{4}-y, \frac{1}{4}+x, \frac{5}{4}-z$; (ii) $1-x, \frac{3}{2}-y, z$; (iii) $\frac{5}{4}-y, \frac{1}{4}+x, \frac{1}{4}-z$.

Data collection: *COLLECT* (Nonius, 1999); cell refinement: *DENZO–SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO–SMN* and *SCALEPACK* (Otwinowski & Minor, 1997); structure solution: *SHELXS*97 (Sheldrick, 1997); structure refinement: *SHELXL*97; molecular graphics: *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97 and *PLATON* (Spek, 2002).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1564). Services for accessing these data are described at the back of the journal.

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