

A new polymorph of dichlorido-triphenylantimony

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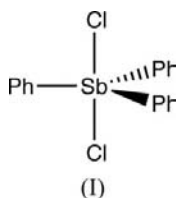
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In a new polymorphic form of dichloridotriphenylantimony, [Sb(C₆H₅)₃Cl₂], there are two crystallographically unique molecules in the asymmetric unit and it has been determined that this polymorph is one of two kinetically favoured phases of pure dichloridotriphenylantimony, both of which have $Z' > 1$. A third polymorph, corresponding to (C₆H₅)₃SbCl_{1.8}F_{0.2}, is also known and has $Z' = 2$. By contrast, the thermodynamically preferred polymorph of pure (C₆H₅)₃SbCl₂ has $Z' = 1$. A brief comparison of the known polymorphic forms of dichloridotriphenylantimony is presented.

Comment

Dichloridotriphenylantimony, (I), is a versatile commercially available compound. It is primarily used as a starting material in organostilbene chemistry (Alonzo *et al.*, 1996), including the preparation of polynuclear antimony complexes (Chandrasekhar & Thirumoorthi, 2009) and carboxylate-containing derivatives of antimony (Li *et al.*, 2001; Quan *et al.*, 2009). The latter are of particular interest since they may have anti-tumour activity (Li *et al.*, 2001). Condensation polymers of (I) with Lewis bases are potent antibacterial agents (Carragher *et al.*, 1983) and have been suggested as possible anticancer drugs (Siegmann-Louda *et al.*, 2001).



Three different polymorphic forms of (I) are currently known. Polymorph (Ia), the first to be structurally characterized, crystallizes in $P2_12_12_1$ (Polynova & Porai-Koshits, 1966) [Cambridge Structural Database (CSD; Allen, 2002) refcode

PCSTIB]. In the original report, the five-coordinate geometry of (I) was confirmed, with Cl atoms in apical positions of a trigonal bipyramid and phenyl groups occupying the equatorial sites. An improved structural determination of polymorph (Ia), with a reassignment of cell axes, has since been reported (Begley & Sowerby, 1993). In an attempt to isolate the mixed halide complex (C₆H₅)₃SbClF, Sowerby and co-workers found a second orthorhombic polymorph, (Ib), also in $P2_12_12_1$, but with two molecules in the asymmetric unit (CSD refcode PCSTIB01; Bone *et al.*, 1992). To be more accurate, the molecule isolated in (Ib) corresponds to (C₆H₅)₃SbCl_{1.8}F_{0.2}, which may account for the observed doubling of the unit-cell volume. A third polymorph, (Ic), with $Z' = 4$ in $Pbca$, has also been reported (CSD refcode PCSTIB03; Belyaev *et al.*, 2002). It was postulated that (Ic) was formed from the decomposition of a binuclear osmium complex of composition [Os₂^{IV}(μ-O)(μ-O₂CCH₃)₂Cl₄(SbPh₃)₂].

We now report the structure (with data collected at 150 K, Table 1) of a new polymorph, denoted (Id), recovered as a minority species from the flash distillation of an acetonitrile solution of (I). Because the data for the other polymorphs were collected at ambient temperature, a unit cell for (Id) was determined at room temperature confirming that it is not a low-temperature phase of (I). In order to further explore the

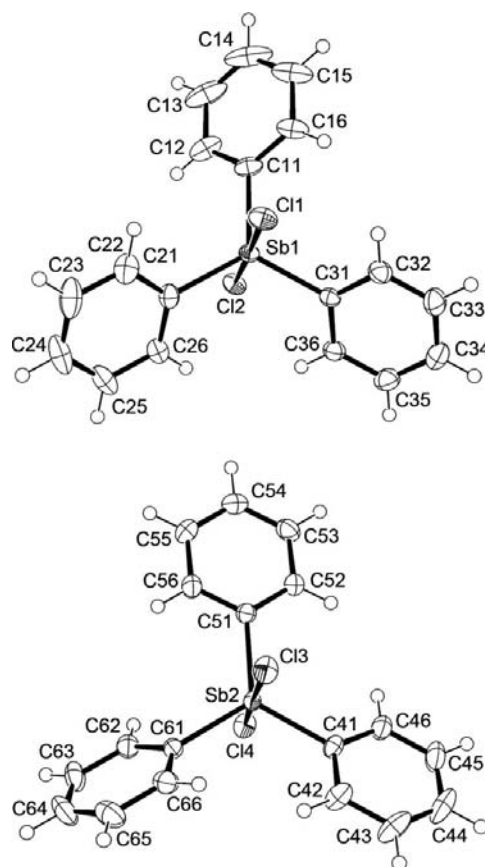


Figure 1

The two crystallographically unique molecules of polymorph (Id); they are not shown in their relative positions in the structure. All displacement ellipsoids are drawn at the 50% probability level.

nature of these various polymorphs, a few simple crystal growth trials were performed and the unit cells were determined for representative samples of each observed crystal habit in the resulting solids. We have found that crystals grown by slow evaporation of either a methylene chloride or an acetonitrile solution of (I) produce polymorph (Ia) exclusively. By contrast, crystals grown by flash distillation of the solvent from an acetonitrile solution of (I) result in the formation of colourless crystals of three different habits, *viz.* needles, rods and plates. By visual inspection, the majority of the sample appears to be the colourless needles, identified as phase (Ia); however, there are also colourless rods corresponding to (Ic) and colourless plates of the title compound, (Id). We believe this indicates that (Ia) is the thermodynamically preferred polymorph, while (Ic) and (Id) are both kinetically favoured. This is consistent with the simple packing motif of phase (Ia) and the absence of very large or very small torsion angles in phenyl-ring positions relative to the equatorial plane of the molecule (*vide infra*).

In all four polymorphs, (I) has the same trigonal-bipyramidal coordination geometry (Fig. 1). There is very little deviation in the Cl–Sb–Cl bond angle [ranging from 175.55 (8) to 178.716 (19)°], but differences in the orientation of the phenyl rings are observed. In particular, there is significant variation among the angles observed between the mean plane of the phenyl rings (as defined by the six C atoms) and the mean equatorial plane of the molecules (as defined by the Sb atom and the three coordinating C atoms of the phenyl rings). These angles illustrate the extent to which the phenyl rings are rotated out of the equatorial plane of the molecule. Most of these angles have values of approximately 35° [24.96 (11)–41.4 (6)°, average 35.0°] or approximately 55° [47.01 (11)–66.2 (9)°, average 54.8°]. There are several exceptions, however, wherein a phenyl ring lies approximately perpendicular to the equatorial plane of the molecule [86.6 (9)°] or lies approximately in the equatorial plane of the molecule [6.51 (11), 10.9 (7) and 13.3 (7)°]. A complete list of these angles can be found in Table 2. Another indicator of strained or unusual molecular geometry is the angle made by the Sb atom, the coordinating C atom of a phenyl ring and the C atom in the *para* position of the same phenyl ring. This parameter illustrates the extent to which a phenyl ring is bent out of the equatorial plane of the molecule. There is little deviation from the ideal 180° in any of these polymorphs; the values range from 174.9 (3) to 179.9 (4)°.

Polymorph (Ia), wherein $Z' = 1$, is the simplest structure. The phenyl groups form a ‘propeller’-type arrangement, with all three rings tilted in the same direction. Thus, only one enantiomer exists in the crystal. The disordered Cl/F polymorph (Ib) has two crystallographically unique molecules in the asymmetric unit. One of these molecules exhibits the simple ‘propeller’ conformation seen in (Ia), while the other has one phenyl ring lying roughly perpendicular to the equatorial plane. Polymorph (Ic), wherein $Z' = 4$, is more complex still. All four crystallographically unique molecules deviate from a simple ‘propeller’ arrangement of phenyl groups. In two of the four molecules (containing Sb1 and Sb4), the mean

plane of one phenyl ring is roughly in the equatorial plane of the molecule. In three of the four molecules (containing Sb1, Sb2 and Sb3), the phenyl rings are not all tilted in the same direction. The new polymorph (Id) has two crystallographically unique molecules in the asymmetric unit. Again, neither molecule can be described as having a ‘propeller’ arrangement of phenyl rings. In one of the molecules, the mean plane of one phenyl ring is roughly in the equatorial plane of the molecule, and in both molecules the phenyl rings that are rotated out of the equatorial plane are not all tilted in the same direction.

Fig. 2 shows comparable diagrams of the packing of (Ia), (Ic) and (Id), viewed approximately down the Cl–Sb–Cl

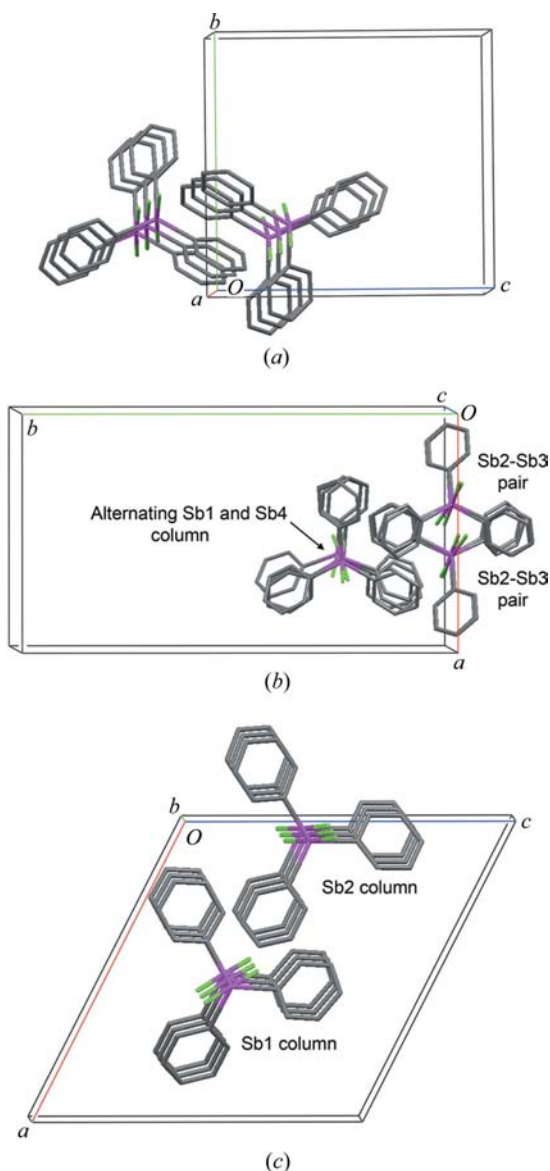


Figure 2

Illustrations of the crystal packing in polymorphs (Ia), (Ic) and (Id), showing selected molecules in the unit cells for clarity. (a) In polymorph (Ia), the molecules are viewed down the *a* axis. (b) In polymorph (Ic), the view is down the *c* axis, showing how the pairs of Sb complexes pack in two different styles. (c) In polymorph (Id), the respective columns of Sb1 and Sb2 are shown packing along the *b* axis.

axes. Polymorph (*Ib*) is not shown since the packing is haphazard due to the Cl/F disorder and this polymorph has not been observed for a pure sample of (*I*). Polymorph (*Ia*) arises from columnar packing of molecules along [100]. The molecules within a column are spaced by one unit-cell length along the *a* axis [10.882 (4) Å], thus there are no close contacts between molecules in a column. Molecules in neighbouring columns are staggered by half of the unit-cell length. Polymorph (*Id*) shows a similar columnar packing scheme along [010], with separate columns of molecules containing Sb1 only and containing Sb2 only, and spacing of one cell length [10.0348 (3) Å] between molecules within a column. The molecules in neighbouring Sb1 columns and Sb2 columns are also staggered along the stacking direction. In contrast, polymorph (*Ic*) has quasi-columnar arrays, but the packing is significantly more complex. Molecules containing the Sb1 and Sb4 atoms alternate, respectively, in columns along [001] at positions *z*, *z* + $\frac{1}{2}$, *z* + 1, etc. [*c* axis = 43.823 (8) Å]. As a crude measure of the spacing between neighbouring molecules, we can look at the distance between the Sb atoms. The distance between an Sb1 atom and the next Sb4 atom within a column alternates between 10.775 (3) and 11.143 (3) Å. As viewed down [001], the Sb2- and Sb3-containing molecules pack in mixed pairs rather than columns. The distance between the Sb2 atom and Sb3 atom within a pair is 10.813 (3) Å. Polymorphs (*Ia*) and (*Id*) are in noncentrosymmetric space groups, consistent with the regular columnar packing. In Fig. 2(*a*), the packing of (*Ia*) shows a head-to-tail arrangement between the phenyl rings of adjacent columns, whereas in Fig. 2(*c*), (*Id*) shows a head-to-head configuration. Polymorph (*Ic*) shows a mixed arrangement including a change of direction mid-cell that is consistent with the centrosymmetric space group.

Polymorphism is of interest to the pharmaceutical industry and, as such, is growing in general importance (Blagden & Davey, 2003). Recent studies suggest that polymorphism is relatively common for molecular organic species (Stahly, 2007) and perhaps more so for organometallic species (Braga & Grepioni, 2000). Dichloridotriphenylantimony provides an interesting example of an organometallic species that exists in several polymorphic forms and exhibits some degree of conformational polymorphism due to the positions adopted by the phenyl rings. Evidence suggests that the thermodynamically preferred form is both the simplest packing motif and the simplest conformational structure, having one molecule per asymmetric unit and a propeller-like arrangement of the phenyl rings. The kinetically favoured forms have multiple molecules in the asymmetric unit and include phenyl-ring conformations that cannot be described as a simple propeller-like arrangement.

Experimental

Dichloridotriphenylantimony was purchased from Aldrich and used as received. The methylene chloride and acetonitrile solvents used in the crystallization trials were purchased from Caledon as HPLC grade and used as received.

Crystal data

| | |
|--|---------------------------------------|
| [Sb(C ₆ H ₅) ₃ Cl ₂] | <i>V</i> = 1665.33 (9) Å ³ |
| <i>M_r</i> = 423.95 | <i>Z</i> = 4 |
| Monoclinic, <i>Pc</i> | Mo <i>K</i> α radiation |
| <i>a</i> = 13.8005 (5) Å | <i>μ</i> = 1.97 mm ⁻¹ |
| <i>b</i> = 10.0348 (3) Å | <i>T</i> = 150 K |
| <i>c</i> = 13.4973 (4) Å | 0.11 × 0.10 × 0.06 mm |
| <i>β</i> = 117.008 (1)° | |

Data collection

| | |
|--|---|
| Bruker APEXII CCD diffractometer | 27243 measured reflections |
| Absorption correction: multi-scan (SADABS; Sheldrick, 2003) | 7897 independent reflections |
| <i>T_{min}</i> = 0.813, <i>T_{max}</i> = 0.891 | 7687 reflections with <i>I</i> > 2σ(<i>I</i>) |
| | <i>R_{int}</i> = 0.018 |

Refinement

| | |
|---|---|
| <i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)] = 0.016 | H-atom parameters constrained |
| <i>wR</i> (<i>F</i> ²) = 0.037 | Δρ _{max} = 0.65 e Å ⁻³ |
| <i>S</i> = 1.06 | Δρ _{min} = -0.27 e Å ⁻³ |
| 7897 reflections | Absolute structure: Flack (1983), |
| 307 parameters | with 3739 Friedel pairs |
| 2 restraints | Flack parameter: -0.005 (9) |

Table 1

Selected crystallographic and experimental parameters (Å, °) for polymorphs (*Ia*)–(*Id*).

Temp = temperature and RT = room temperature.

| Polymorph and CSD refcode | Unit-cell parameters (Å, °) | Volume (Å ³) | Space group | Temp | <i>R</i> value | Solvent |
|---------------------------|---|--------------------------|--|-------|----------------|---------------------------------|
| (<i>Ia</i>) PCSTIB | <i>a</i> = 13.170 (3), <i>b</i> = 11.080 (3), <i>c</i> = 12.390 (3) | 1807.99 | <i>P</i> 2 ₁ 2 ₁ | RT | 17.0 | CHCl ₃ |
| (<i>Ia</i>) PCSTIB02 | <i>a</i> = 10.882 (4), <i>b</i> = 12.127 (4), <i>c</i> = 12.986 (4) | 1713.71 | <i>P</i> 2 ₁ 2 ₁ | RT | 5.80 | CHCl ₃ |
| (<i>Ib</i>) PCSTIB01 | <i>a</i> = 9.104 (4), <i>b</i> = 17.048 (7), <i>c</i> = 22.121 (9) | 3433.29 | <i>P</i> 2 ₁ 2 ₁ | RT | 2.72 | CH ₂ Cl ₂ |
| (<i>Ic</i>) PCSTIB03 | <i>a</i> = 13.122 (2), <i>b</i> = 23.885 (3), <i>c</i> = 43.823 (8) | 13735 | <i>Pbca</i> | RT | 3.53 | Glacial acetic acid |
| (<i>Id</i>) | <i>a</i> = 13.8005 (5), <i>b</i> = 10.0348 (3), <i>c</i> = 13.4973 (4), <i>β</i> = 117.008 (1) | 1665.33 | <i>Pc</i> | 150 K | 1.56 | CH ₃ CN |

H atoms were positioned geometrically and refined using a riding model, with C–H = 0.95 Å and *U*_{iso}(H) = 1.2*U*_{eq}(C).

Data collection: APEX2 (Bruker–Nonius, 2008); cell refinement: APEX2 and SAINT (Bruker–Nonius, 2008); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 2008); program(s) used to refine structure: SHELXL97 (Sheldrick, 2008); molecular graphics: XP in SHELXTL (Sheldrick, 2008) and PLATON (Spek, 2009); software used to prepare material for publication: XP in SHELXTL and PLATON.

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Table 2

Angle (°) between the mean plane of the phenyl ring and the mean equatorial plane for molecules in polymorphs (Ia)–(Id); unusual values are marked in bold.

| | (Ia), PCSTIB02 | (Ib), PCSTIB01 | (Ic), PCSTIB03 | (Id) |
|-----|----------------|-----------------|-----------------|------------------|
| Sb1 | 40.0 (4) | 34.3 (9) | 52.3 (6) | 39.68 (11) |
| | 33.1 (4) | 54.7 (9) | 13.3 (6) | 47.01 (11) |
| Sb2 | 60.0 (4) | 86.6 (9) | 26.6 (6) | 49.01 (11) |
| | | 66.2 (9) | 52.4 (6) | 24.96 (11) |
| Sb3 | | 51.2 (9) | 54.6 (6) | 6.51 (11) |
| | | 32.0 (9) | 38.1 (6) | 51.40 (11) |
| | | | 52.4 (6) | |
| Sb4 | | | 66.0 (6) | |
| | | | 41.4 (6) | |
| | | | 59.5 (6) | |
| | | | 10.9 (6) | |
| | | 37.9 (6) | | |

Note: the mean plane of the phenyl ring is defined by the six C atoms; the mean molecular equatorial plane is defined by the Sb atom and the three coordinating C atoms.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG3167). Services for accessing these data are described at the back of the journal.

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