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Triphenylselenonium iodide

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Abstract

The title compound, Ph_3SeI or $C_{18}H_{15}Se^+ \cdot I^-$, forms an ionic solid comprised of centrosymmetric dimers, in which two Ph_3Se^+ ions are bridged by two I^- ions. The coordination about the Se^{IV} centers can be described as either a twofold capped trigonal pyramid or a distorted pseudo-octahedron, with the selenium lone pair occupying the sixth position. Selected structural parameters are: Se—C 1.926 (4), 1.929 (4) and 1.944 (4) Å, Se···I 3.722 (1) and 4.153 (1) Å, C—Se—C 100.21 (15), 102.51 (15) and 98.62 (16)°, and C—Se···I 84.4 (1), 166.5 (1), 92.7 (1), 94.3 (1), 86.2 (1) and 161.4 (1)°.

Comment

In our study of ligand-exchange reactions of group 16 elements, we attempted the synthesis of triorgano-selenonium iodides from triorganoselenonium chlorides by the exchange of Cl for I *via* NaI. In contrast to NaI, NaCl does not dissolve in acetonitrile, and its precipitation is the driving force of the reaction. The ^{77}Se NMR shifts of Ph_3SeCl and Ph_3SeI in CD_3CN

do not differ substantially (504.8 and 499.4 p.p.m., respectively), which suggests dissociation into Ph_3Se^+ and X^-. We were thus curious to see whether Ph_3SeI is also a more or less ionic solid.

The molecular structure of the triphenylselenonium iodide centrosymmetric dimer in the solid state is shown in Fig. 1 and selected structural parameters are given in Table 1. The dimer, (I), consists of two Ph_3Se^+ ions bridged by two I^- ions. One Se···I distance is slightly shorter and the other longer than the sum of the van der Waals radii (3.88 Å; Bondi, 1964); Ph_3SeI is thus predominantly ionic in the solid state.

(I)
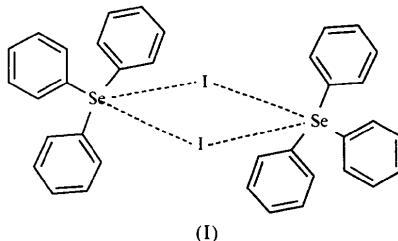
This view is confirmed by the angles at selenium. The three C—Se—C angles are of similar size and are thus more like those in a trigonal pyramid than in a pseudo-trigonal bipyramid. Furthermore, four out of six C—Se···I angles and the I—Se···I angle are close to 90°, the remaining two C—Se···I angles being close to 180°. The trigonal pyramid is thus capped by two I^- ions to give a distorted pseudo-octahedral geometry about the Se atom, with the lone pair of the Se atom occupying the sixth position. The sum of the C—Se—C angles in Ph_3SeI is 301.34° and is thus similar to those in other Ar_3SeX compounds, *e.g.* 302.4° in Ph_3SeNCS (Ash *et al.*, 1977), 300.2° in (*p*-Tol)$_3$SeCl·H$_2$O, 302.6° in (*p*-Tol)$_3$SeBr·H$_2$O (Bel'skii *et al.*, 1982) and 301.2° in $Ph_3SeCl·2H_2O$ (Lee & Titus, 1976), and 15–20° larger than in the corresponding
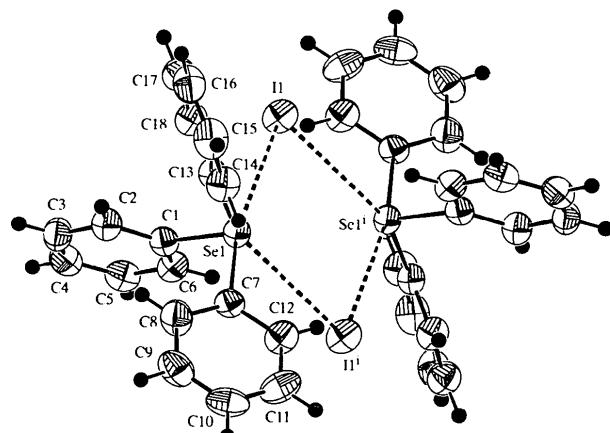

Fig. 1. *ORTEP*II plot (Johnson, 1976) of Ph_3SeI with 50% probability displacement ellipsoids. The radius of the H atoms is arbitrary. [Symmetry code: (i) $1 - x$, $1 - y$, $1 - z$.]

Ar$_3$TeX analogs, e.g. 282.2° in Ph$_3$TeCl·CHCl$_3$ (Collins et al., 1988), 286.0° in Ph$_3$TeNCS (Lee et al., 1977) and 286.8° in Ph$_3$TeNCO·CHCl$_3$ (Titus et al., 1976).

The crystal structure of Ph$_3$SeI is distinctly different from that of Me$_3$SeI, which forms infinite planar –Se— I—Se—I– chains rather than dimers; it is, however, similar to that of triphenyltelluronium chloride, Ph$_3$TeCl (Ziolo & Extine, 1980), although the latter does not exhibit inversion symmetry.

The Te···Cl interactions are stronger than their Se···I counterparts, as can be judged from the Se···I and Te···Cl distances compared with the van der Waals radii (Se 1.90, Te 2.06, Cl 1.75 and I 1.90 Å; Bondi, 1964). The two Se···I distances are 96 and 107%, while the Te···Cl distances (3.142–3.234 Å) are between 82 and 85% of the sum of the corresponding van der Waals radii.

Experimental

Ph$_3$SeI was prepared by adding a solution of NaI (0.85 g, 5.7 mmol) in acetonitrile (10 ml) to an ice-cooled and stirred solution of Ph$_3$SeCl (1.64 g, 4.7 mmol) in acetonitrile (10 ml). A precipitate formed and the solution became orange. After approximately 1 h, the mixture was allowed to warm to room temperature, when the color changed to red. The solution was filtered and concentrated. From the filtrate, at 278 K, yellow crystals of Ph$_3$SeI formed within a few days. Elemental analysis (C$_{18}$H$_{15}$ISe, M_r = 437.16) calculated: C 49.45, H 3.46%; found: C 49.54, H 3.37%. NMR (293 K, CDCl$_3$, TMS for ^{1}H and ^{13}C, SeMe$_2$ for ^{77}Se, p.p.m.): ^{1}H 7.70 (m, 6H, H$_{ortho}$), 7.645 (tt, 3H, H$_{para}$), 7.564 (tt, 6H, H$_{meta}$); ^{13}C 133.2, 131.5, 131.3, 126.7; ^{77}Se 485.1.

Crystal data

C$_{18}$H$_{15}$Se$^+$·I$^-$
M_r = 437.16
Monoclinic
$P2_1/n$
a = 13.327 (3) Å
b = 8.672 (2) Å
c = 14.382 (3) Å
β = 98.23 (1)°
V = 1645.0 (6) Å^3
Z = 4
D_x = 1.765 Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 25–28°
μ = 4.147 mm^{-1}
T = 298 (2) K
Plate
0.60 × 0.42 × 0.15 mm
Yellow

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: Gaussian (Coppens et al., 1965)
T_{min} = 0.20, T_{max} = 0.53
4969 measured reflections
4784 independent reflections

3289 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
θ_{max} = 29.95°
h = 0 → 18
k = 0 → 12
l = –20 → 19
3 standard reflections frequency: 60 min intensity decay: 8%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.041
$wR(F^2)$ = 0.105
S = 0.999
4784 reflections
181 parameters
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.957 e Å^{-3}
$\Delta\rho_{min}$ = –1.033 e Å^{-3}
Extinction correction: none
Scattering factors from International Tables for Crystallography (Vol. C)

Table 1. Selected geometric parameters (Å, °)

Se1—Cl	1.926 (4)	Se1···I1	3.722 (1)
Se1—C7	1.929 (4)	Se1···I1^i	4.153 (1)
Se1—C13	1.944 (4)		
Cl—Se1—C7	100.21 (15)	C7—Se1···I1	166.53 (11)
Cl—Se1—C13	102.51 (15)	C7—Se1···I1^i	86.20 (10)
C7—Se1—C13	98.62 (16)	C13—Se1···I1	92.66 (11)
Cl—Se1···I1	84.40 (10)	C13—Se1···I1^i	161.36 (11)
Cl—Se1···I1^i	94.26 (12)	I1···Se1···I1^i	80.81 (8)

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

Data collection: CAD-4 Software (Enraf–Nonius, 1989). Cell refinement: CAD-4 Software. Data reduction: CORINC (Dräger & Gattow, 1971). Program(s) used to solve structure: SIR92 (Altomare et al., 1994). Program(s) used to refine structure: SHELXL97 (Sheldrick, 1997). Molecular graphics: ORTEPII (Johnson, 1976).

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