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Structure of Bis(tetraphenylphosphonium) Pentaselenide

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Abstract. $[P(C_6H_5)_4]_2[Se_5]$, $M_r = 1073·6$, monoclinic, $P2_1$ (C_2^2), $a = 9·573$ (7), $b = 16·945$ (12), $c = 13·563$ (10) Å, $\beta = 105·29$ (2)°, $V = 2122$ (3) Å^3, $Z = 2$, $D_x = 1·68$ g cm^{-3}, Mo $K\alpha$, $\lambda(K\alpha_1) = 0·7093$ Å, $\mu = 43·8$ cm^{-1}, $F(000) = 1054·6$ including anomalous dispersion, $T = 123$ K, $R(F^2) = 0·075$ for 3681 reflections. The Se_5^{2-} chain has a *trans* conformation with short terminal and long internal Se—Se bonds of average lengths 2·315 (2) and 2·361 (2) Å, respectively. The internal and the average terminal Se—Se—Se angles are 110·59 (7) and 108·93 (6)°, respectively. The Se(1) and Se(5) atoms are twisted out of the Se(2), Se(3), Se(4) plane by torsion angles of 77·32 (8) and 89·16 (7)°, respectively.

Introduction. Soluble salts of transition-metal selenium anions $[M_xSe_y]^{2-}$ are rare. We recently showed that selenation of ammonium metavanadate with bis(dimethyloctylsilyl) selenide produced the $V_2Se_{13}^{2-}$ ion (Chau, Wardle & Ibers, 1987). As a continuation of our efforts to discover new transition-metal selenium anions we have investigated the reaction of zirconium tetraethoxide with bis(dimethyloctylsilyl) selenide. In an attempt to crystallize the resulting product, we obtained the title compound, presumably as a result of air-oxidation of a zirconium selenide anion. Here, we report its molecular structure and compare it with that of other Se_5^{2-} anions.

Experimental. Dark-brown crystals of the title compound were obtained by slow diffusion of ether into a DMF solution of the product that resulted from the selenation of zirconium tetraethoxide by bis(dimethyloctylsilyl) selenide. The red powdery product was prepared by combining 0·1 g zirconium, 0·5 g zirconium tetraethoxide, 0·2 g selenium, and 0·9 g tetraphenylphosphonium chloride in 25 mL DMF with 1·5 g bis(dimethyloctylsilyl) selenide. After stirring overnight at room temperature the dark red-brown solution was filtered. Addition of ether caused the precipitation of the red powder; it was filtered, washed twice with ether, and suction dried. This material has an infrared absorption at 270 cm^{-1}. When the material was recrystallized to give the title compound this absorption peak disappeared, possibly because of decomposition. A very broad absorption at 460 cm^{-1} corresponding to that of a polyselenide (Teller, Krause & Haushalter, 1983) was observed instead.

A single crystal, approximately 0·26 × 0·25 × 0·05 mm, bounded by {100} and {011}, crystal volume 2·77 × 10^{-3} mm^3, was mounted on a glass fiber with the long dimension as the approximate axis of rotation. Unit-cell parameters were derived from a least-squares refinement of 25 reflections in the range $13 < \theta < 18°$, automatically centered on an Enraf–Nonius CAD-4 X-ray diffractometer. As opposed to the limitations of the usual CAD-4 software, we imposed the condition $\alpha = \gamma = 90°$. Intensity data were collected with the ω-scan technique; intensities of six standards monitored every 3 h throughout data collection showed a 10% decline in intensity that was corrected for during data reduction. A total of 3918 measured, 3681 unique, 2835 observed $[I \geq 3\sigma(I)]$ X-ray diffraction intensities, collected to $(\sin\theta)_{\max}/\lambda = 0·5958$ Å^{-1}, in the index range $0 \leq h \leq 11$, $0 \leq k \leq 20$, $-16 \leq l \leq 16$, were corrected for absorption with use of the analytical method (de Meulenaer & Tompa, 1965); min. and max. transmission factors were 0·45 and 0·79.

Intensity statistics favored the absence of a center of symmetry. The initial positions for the five Se atoms in space group $P2_1$ were determined by direct methods by the use of *MULTAN*80 (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1980). Positions for the P and C atoms were obtained from subsequent electron density syntheses; full-matrix least-squares refinement on F; phenyl H atoms were derived with the assumption of idealized geometries; all non-C and non-H atoms refined anisotropically; scattering factors and anomalous-dispersion terms were taken from the usual sources (Cromer & Waber, 1974; Cromer, 1974). All calculations were performed on a Harris 1000 computer with methods and programs standard for this laboratory (Waters & Ibers, 1977). Determination of the polar direction for the chosen crystal was made from a full refinement of both possibilities based on F with reflections having $F_o^2 \geq 3\sigma(F_o^2)$. The final refinement on F_o^2, based on 255 variables and 3681 observations, resulted in an R index on F^2 of 0·075 with Δ/σ not exceeding 0·53. Other residuals are $wR(F^2) = 0·084$; $w = 1/\sigma^2(F^2)$; $S(F^2) = 1·12$; $R(F) = 0·044$ for

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Table 1. *Positional parameters and isotropic thermal parameters for* $[PPh_4]_2[Se_5]$

$$B_{eq} = (8\pi^2/3)\textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}(Å^2)
Se(1)	0·60659 (13)	0·411272 (91)	0·450413 (82)	1·74 (3)
Se(2)	0·43943 (12)	0·382996 (89)	0·297003 (80)	1·36 (3)
Se(3)	0·36864 (12)	$\frac{1}{4}$	0·298417 (81)	1·43 (3)
Se(4)	0·54947 (12)	0·165590 (88)	0·267693 (81)	1·55 (3)
Se(5)	0·50680 (13)	0·146136 (91)	0·093416 (82)	1·89 (3)
P(1)	−0·06676 (33)	−0·30789 (17)	0·43667 (21)	1·15 (8)
P(2)	0·05358 (33)	−0·19976 (18)	0·03189 (21)	1·16 (8)
C(1)	−0·0789 (11)	−0·35169 (62)	0·55462 (73)	1·2 (2)
C(2)	0·0400 (11)	−0·34227 (67)	0·64004 (79)	1·7 (2)
C(3)	0·0323 (12)	−0·37019 (65)	0·73485 (83)	1·8 (2)
C(4)	−0·0880 (13)	−0·40705 (68)	0·74469 (89)	2·1 (2)
C(5)	−0·2055 (12)	−0·41772 (65)	0·66170 (84)	1·7 (2)
C(6)	−0·2004 (12)	−0·38987 (63)	0·56528 (80)	1·4 (2)
C(7)	−0·2093 (11)	−0·34348 (63)	0·33403 (73)	1·2 (2)
C(8)	−0·2897 (12)	−0·28987 (63)	0·26112 (83)	1·5 (2)
C(9)	−0·3927 (13)	−0·31819 (65)	0·17921 (85)	1·9 (2)
C(10)	−0·4226 (13)	−0·39861 (65)	0·16782 (87)	1·8 (2)
C(11)	−0·3473 (13)	−0·45125 (69)	0·23857 (86)	2·0 (2)
C(12)	−0·2391 (13)	−0·42389 (66)	0·32346 (86)	1·8 (2)
C(13)	−0·0915 (12)	−0·20324 (64)	0·44399 (82)	1·6 (2)
C(14)	−0·0039 (13)	−0·14984 (65)	0·40831 (85)	1·7 (2)
C(15)	−0·0385 (12)	−0·06838 (60)	0·40927 (82)	1·4 (2)
C(16)	−0·1544 (13)	−0·04565 (67)	0·44486 (86)	2·0 (2)
C(17)	−0·2390 (12)	−0·09857 (61)	0·47950 (78)	1·4 (2)
C(18)	−0·2075 (13)	−0·17640 (63)	0·48092 (79)	1·5 (2)
C(19)	0·1038 (11)	−0·33279 (61)	0·41345 (73)	1·1 (2)
C(20)	0·1119 (12)	−0·39547 (64)	0·34646 (82)	1·6 (2)
C(21)	0·2439 (13)	−0·42022 (67)	0·33540 (88)	2·1 (2)
C(22)	0·3702 (13)	−0·38554 (67)	0·39136 (87)	2·1 (2)
C(23)	0·3630 (12)	−0·32240 (64)	0·45542 (82)	1·8 (2)
C(24)	0·2323 (12)	−0·29692 (62)	0·46771 (81)	1·3 (2)
C(25)	0·0520 (12)	−0·30537 (64)	0·04497 (82)	1·5 (2)
C(26)	0·1667 (12)	−0·34874 (71)	0·02705 (82)	2·1 (2)
C(27)	0·1686 (14)	−0·42991 (75)	0·03896 (97)	2·7 (3)
C(28)	0·0588 (14)	−0·46746 (72)	0·06635 (93)	2·5 (2)
C(29)	−0·0561 (13)	−0·42433 (69)	0·08485 (89)	2·2 (2)
C(30)	−0·0620 (12)	−0·34196 (72)	0·07336 (83)	2·1 (2)
C(31)	0·2031 (12)	−0·15804 (60)	0·12436 (78)	1·1 (2)
C(32)	0·2480 (12)	−0·08274 (64)	0·11065 (76)	1·3 (2)
C(33)	0·3559 (12)	−0·04536 (62)	0·18456 (82)	1·5 (2)
C(34)	0·4175 (13)	−0·08671 (70)	0·27202 (85)	1·9 (2)
C(35)	0·3781 (13)	−0·16047 (64)	0·28818 (85)	1·8 (2)
C(36)	0·2676 (13)	−0·19810 (67)	0·21603 (84)	1·8 (2)
C(37)	−0·1107 (12)	−0·15890 (61)	0·04996 (82)	1·4 (2)
C(38)	−0·1069 (12)	−0·10286 (62)	0·12605 (77)	1·5 (2)
C(39)	−0·2343 (14)	−0·06926 (70)	0·13530 (92)	2·2 (2)
C(40)	−0·3635 (13)	−0·09093 (76)	0·07071 (91)	2·6 (2)
C(41)	−0·3691 (13)	−0·14593 (69)	−0·00445 (89)	2·2 (2)
C(42)	−0·2432 (14)	−0·18281 (70)	−0·01347 (85)	2·0 (2)
C(43)	0·0768 (12)	−0·17454 (61)	−0·09179 (78)	1·4 (2)
C(44)	−0·0408 (12)	−0·14863 (62)	−0·17073 (82)	1·5 (2)
C(45)	−0·0178 (12)	−0·12932 (67)	−0·26577 (82)	1·8 (2)
C(46)	0·1168 (12)	−0·13811 (63)	−0·28275 (80)	1·7 (2)
C(47)	0·2305 (12)	−0·16471 (62)	−0·20525 (83)	1·6 (2)
C(48)	0·2137 (13)	−0·18382 (64)	−0·10935 (77)	1·5 (2)

Table 2. *Selected bond distances* (Å) *and angles* (°) *for* $[PPh_4]_2[Se_5]$

Se(1)–Se(2)	2·316 (2)	Se(1)–Se(2)–Se(3)	108·83 (6)
Se(2)–Se(3)	2·355 (2)	Se(2)–Se(3)–Se(4)	110·59 (7)
Se(3)–Se(4)	2·366 (2)	Se(3)–Se(4)–Se(5)	109·02 (6)
Se(4)–Se(5)	2·314 (2)	C(1)–P(1)–C(7)	110·0 (5)
P(1)–C(1)	1·795 (10)	C(1)–P(1)–C(13)	108·5 (5)
P(1)–C(7)	1·778 (11)	C(1)–P(1)–C(19)	109·6 (5)
P(1)–C(13)	1·795 (11)	C(7)–P(1)–C(13)	107·0 (5)
P(1)–C(19)	1·793 (10)	C(7)–P(1)–C(19)	109·2 (5)
P(2)–C(25)	1·799 (11)	C(13)–P(1)–C(19)	112·5 (5)
P(2)–C(31)	1·782 (11)	C–C–C*	120 (1)
P(2)–C(37)	1·793 (11)		
P(2)–C(43)	1·801 (10)		
C–C*	1·39 (2)		

* This is the standard deviation of a single observation on the assumption that the values averaged are from the same population. The fact that the value is the same as that estimated for a single observation from the inverse matrix indicates that the standard deviations so estimated are reliable.

2835 reflections with $F^2 \geq 3\sigma(F^2)$. The final difference electron density map showed max. and min. heights of 0·9 (1) and −0·6 (2) e Å^{-3}.

Table 1 lists fractional coordinates and isotropic thermal parameters. A list of selected bond distances and angles may be found in Table 2.* A perspective view of the Se_5^{2-} ion is given in Fig. 1.

Discussion. The Se_5^{2-} chain has approximate twofold symmetry with the direction of this twofold axis bisecting the Se(2)–Se(3)–Se(4) angle. No unusual bond lengths were found for the Se_5^{2-} chain. The unliganded Se_5^{2-} chains have *trans* conformations. Table 3 presents bond lengths and angles for representative Se_5^{2-} units having both chain and ring geometries. The

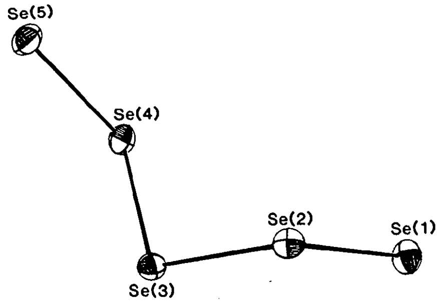

Fig. 1. Perspective view of the Se_5^{2-} ion in $[PPh_4]_2[Se_5]$ (50% probability thermal ellipsoids) along with the atom-numbering scheme.

Table 3. Se–Se *bond distances* (Å) *and angles* (°) *for representative pentaselenides*

	Chains			
	[Cs(18-crown-6)]$_2$-[Se$_5$]^a	Cs_2Se_5^{b}	Rb_2Se_5^{c}	$[PPh_4]_2[Se_5]$
Se(1)–Se(2)	2·316 (3)	2·33 (1)	2·31 (2)	2·316 (2)
Se(2)–Se(3)	2·343 (3)	2·38 (1)	2·36 (1)	2·355 (2)
Se(3)–Se(4)	2·343 (3)	2·34 (1)	2·37 (2)	2·366 (2)
Se(4)–Se(5)	2·316 (3)	2·29 (1)	2·33 (1)	2·314 (2)
Se(1)–Se(2)–Se(3)	109·6 (1)	107·2 (4)	109·1 (5)	108·83 (6)
Se(2)–Se(3)–Se(4)	106·6 (2)	104·6 (4)	104·5 (6)	110·59 (7)
Se(3)–Se(4)–Se(5)	109·6 (1)	110·8 (4)	108·0 (5)	109·02 (6)

	Rings	
	$Fe_2Se_2(Se_5)_2^{2-}$ ^{d}	$V_2Se_{13}^{2-}$ ^{e}
Se(1)–Se(2)	2·345 (2)	2·425 (3)
Se(2)–Se(3)	2·318 (2)	2·360 (3)
Se(3)–Se(4)	2·337 (2)	2·339 (3)
Se(4)–Se(5)	2·347 (2)	2·431 (3)
Se(1)–Se(2)–Se(3)	104·05 (6)	107·4 (1)
Se(2)–Se(3)–Se(4)	103·35 (7)	103·4 (1)
Se(3)–Se(4)–Se(5)	104·27 (7)	107·3 (1)

References: (*a*) Brese, Randall & Ibers (1987); (*b*) Kretschmann & Böttcher (1985); (*c*) Böttcher (1979); (*d*) Strasdeit, Krebs & Henkel (1984); (*e*) Chau, Wardle & Ibers (1987).

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* Lists of structure amplitudes, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44685 (19 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shortening of the terminal bonds by some 0·04 Å might be explained by a localization of electronic charge at the two ends of the Se_5^{2-} chain. The covalent radii of Se and Br differ by about this, and Se^- is isoelectronic with Br. Our results do not conflict with this interpretation. Whereas the two terminal angles, Se(1)—Se(2)—Se(3) and Se(3)—Se(4)—Se(5), in $[PPh_4]_2[Se_5]$ are very similar to those found in the other Se_5^{2-} units (Table 3), the internal Se(2)—Se(3)—Se(4) angle, 110·59 (7)°, is at least 4° larger than that found in Rb_2Se_5, 104·5 (6) (Böttcher, 1979), Cs_2Se_5, 104·6 (4) (Kretschmann & Böttcher, 1985), $[Cs(18\text{-crown-}6)]_2[Se_5]$, 106·6 (2) (Brese, Randall & Ibers, 1987), $Fe_2Se_2(Se_5)_2^{2-}$, 103·35 (7) (Strasdeit, Krebs & Henkel, 1984), and $V_2Se_{13}^{2-}$, 103·4 (1)° (Chau, Wardle & Ibers, 1987). The torsional angles in the present Se_5^{2-} chain are 77·32 (8) and 89·16 (7)°. These are different from those of 75·0 and 67·1° found in Rb_2Se_5 (Böttcher, 1979).

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trans-2-Dimethylamino-3-*p*-nitrophenyl-1,4-diphenyl-3,4-dihydro-1-azetium Perchlorate

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Abstract. $C_{23}H_{22}N_3O_2^+.ClO_4^-$, $M_r = 471·4$, triclinic, $P\bar{1}$, $a = 8·168$ (6), $b = 8·644$ (6), $c = 16·609$ (12) Å, $\alpha = 100·03$ (4), $\beta = 92·58$ (3), $\gamma = 101·40$ (3)°, $U = 1128$ (1) Å^3, $Z = 2$, $D_x = 1·388$ Mg m^{-3}, Mo $K\alpha$ radiation, $\lambda = 0·70926$ Å, $\mu = 0·170$ mm^{-1}, $F(000) = 492$, $T = 293$ (1) K, $R(F) = 0·083$ for 3903 significant reflections. Within the planar four-membered ring the bond lengths are N(1)—C(2) 1·329 (7), C(2)—C(3) 1·508 (15), C(3)—C(4) 1·507 (8) and C(4)—N(1) 1·463 (14) Å. The exocyclic C—N linkage, 1·302 (11) Å, has considerable double-bond character; the H atoms at C(3) and C(4) have a *trans* configuration.

Introduction. 1-Substituted 2-dialkylamino-1-azetium salts are produced from α-chloroenamines and Schiff's bases (De Poortere, Marchand-Brynaert & Ghosez, 1974). We have found that, in a related reaction, the action of phosphorus oxychloride on a mixture of the dimethylamide (I) of an arylacetic acid or phenoxyacetic acid and a Schiff's base (II) in refluxing chloroform results in the formation of 1-azetium salts, which were isolated as perchlorates (III). Only one of the two possible geometrical isomers was obtained in each of the eleven reactions carried out. The products showed $C=N^+$ absorptions at 1710 cm^{-1}. In the ^{1}H NMR spectra the signals of the protons of the dimethylamino groups appeared as two singlets, which indicates substantial double-bond character of the exocyclic C—N linkage [*cf.* (III*A*)]. The protons attached to C(3) and C(4) resonated as doublets with coupling constants of 1·0 Hz or less, but assignment of *cis* or *trans* geometry was uncertain because the Karplus equation (Sternhell, 1969) does not hold for strained molecules. One of the salts, the perchlorate (III*a*), was therefore submitted to X-ray analysis, which

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