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5-Methyl-2,8-diselena-1,3,7-triphosphatricyclo[3.3.1.$0^{3,7}$]nonane 1-Selenide

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Abstract. $C_5H_9P_3Se_3$, $M_r = 398{\cdot}93$, monoclinic, $P2_1/c$, $a = 6{\cdot}643\,(2)$, $b = 14{\cdot}318\,(5)$, $c = 11{\cdot}636\,(7)$ Å, $\beta = 95{\cdot}40\,(9)°$, $V = 1102\,(2)$ Å^3, $Z = 4$, $D_x = 2{\cdot}405$ g cm^{-3}, λ(Mo $K\alpha$) = 0·70926 Å, $\mu = 102{\cdot}89$ cm^{-1}, $F(000) = 744$, $T = 295\,(2)$ K, final $R = 0{\cdot}061$ for 1551 unique reflections. The molecule consists of a tricyclic noradamantane cage. The basis of the cage is a five-membered $P_2Se_2P(Se)$ ring with an exocyclic Se atom. The organic group $CH_3C(CH_2)_3$ bridging the three P atoms forms a heteronoradamantane ring system. It has an enlarged cage structure with an expanded C—C(H_2)—P(=Se) bond angle of 121° at the methylene C atom. The mean value of the P—Se distances within the P_2Se_2P ring is 2·246 Å and the exocyclic P=Se length is 2·089 (2) Å. All other distances and angles are normal.

Introduction. Melting of 4-methyl-1,2,6-triphosphatricyclo[2.2.1.$0^{2,6}$]heptane [$CH_3C(CH_2P)_3$, P_3-nortricyclane] with selenium in the molar ratio of 1:3 results in the formation of the title compound $CH_3C(CH_2P)_3Se_3$ (Ellermann, Demuth & Bauer, 1986). From the composition it is comparable to $CH_3C(CH_2P)_3S_3$ (Zimmermann, Gomm, Ellermann & Köck, 1987) and $CH_3C(CH_2As)_3S_3$ (Ellermann, Lietz, Merbach, Thiele & Zoubek, 1979). Whereas the phosphorus–sulfur compound consists of a noradamantane cage with a five-membered P_2S_2P(=S) ring and an exocyclic P=S bond, the arsenic–sulfur derivative consists of an adamantane cage containing a six-membered As_3S_3 ring. In order to establish whether $CH_3C(CH_2P)_3Se_3$ is a noradamantane or an adamantane derivative, a crystal-structure analysis has been undertaken.

Experimental. Recrystallization of $C_5H_9P_3Se_3$ from tetrahydrofuran gave light-yellow crystals; spherical crystal with $r = 0{\cdot}11$ (1) mm used for X-ray analysis; Philips PW 1100 diffractometer (graphite monochromator, Mo $K\alpha$ radiation), ω–2θ scans with scan width $(0{\cdot}800 + 0{\cdot}345\tan\theta)°$; profile analysis with a modified Lehmann & Larsen (1974) procedure; lattice parameters refined by least-squares procedure *GIVER* (Krogmann, 1966) on the basis of 34 reflections with $22{\cdot}3 \leq 2\theta \leq 25{\cdot}1°$; spherical absorption-correction factor $A = 4{\cdot}723 \pm 0{\cdot}185$; index range $h \pm 7$, k 0/15, l 0/12; six standard reflections (intensity variation 0·7%); $(\sin\theta)_{\max}/\lambda = 0{\cdot}55$ Å^{-1}, 6198 reflections were measured, 266 reflections affected strongly by absorption were eliminated, after averaging symmetrical equivalents, 1551 reflections [40 unobserveds included, $I < 3\sigma(I)$] remained; $R_{\rm int} = 0{\cdot}032$. Structure solved by direct methods for Se and P, subsequent Fourier map revealed all non-H atoms, all H atoms were located from a difference Fourier map; the residual electron density (0·58 to −0·66 e Å^{-3}) prevents a precise refinement of the H coordinates. Blocked least-squares refinement based on F and weights $w = 1/\sigma^2(|F_o|)$, final cycles refined scale factor, coordinates, anisotropic temperature factor for non-H atoms; the isotropic temperature factor of some H atoms became negative and a fixed overall $U = 0{\cdot}0396$ Å^2 was employed; $R = 0{\cdot}061$, $wR = 0{\cdot}029$, $S = 2{\cdot}02$, max. $\Delta/\sigma = 0{\cdot}56$; scattering factors taken from *International Tables for X-ray Crystallography* (1974). The *CRYSTAN* system (Burzlaff, Gomm & Zimmermann, 1986) was used for all computations and diagrams were drawn with *ORTEP*II (Johnson, 1977).

Discussion. Atomic coordinates and equivalent isotropic temperature factors are reported in Table 1.

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Table 1. *Atom coordinates* ($\times 10^4$) *with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* ($Å^2 \times 10^2$)

$$U_{eq} = (1/6\pi^2)\textstyle\sum_i\sum_j\beta_{ij}(\mathbf{a}_i.\mathbf{a}_j).$$

	x	*y*	*z*	U_{eq}
Se(1)	2879 (1)	1940 (1)	6049 (1)	6·3
Se(2)	−1372 (1)	719 (1)	7045 (1)	5·1
Se(3)	3026 (1)	818 (1)	8865 (1)	5·4
P(1)	1967 (2)	796 (1)	6986 (1)	3·9
P(2)	−1260 (3)	−653 (1)	8010 (2)	4·6
P(3)	1645 (3)	−586 (1)	9218 (2)	4·8
C(1)	2775 (9)	−327 (4)	6438 (5)	4·0
C(2)	−92 (9)	−1384 (4)	6940 (6)	4·7
C(3)	3004 (8)	−1333 (4)	8233 (6)	4·4
C(4)	2208 (9)	−1257 (4)	6980 (6)	4·2
C(5)	3158 (11)	−2010 (5)	6262 (7)	6·9

Table 2. *Bond lengths* (Å), *intermolecular distances* (Å) *and bond angles* (°)

E.s.d.'s are given in parentheses.

P(1)—Se(1)	2·089 (2)	P(3)—Se(3)	2·262 (2)
P(1)—Se(2)	2·229 (2)	P(3)—C(3)	1·862 (7)
P(1)—Se(3)	2·233 (2)	C(1)—C(4)	1·536 (9)
P(1)—C(1)	1·828 (6)	C(2)—C(4)	1·535 (8)
P(2)—Se(2)	2·260 (2)	C(3)—C(4)	1·508 (9)
P(2)—P(3)	2·280 (2)	C(4)—C(5)	1·536 (10)
P(2)—C(2)	1·852 (7)	C—H	0·84–1·19 (6)
H(31)···H(53^{i})	2·53 (8)	P(2)···Se(1^{iii})	3·802 (2)
Se(1)···H(21^{ii})	2·81 (6)	Se(3)···P(2^{ii})	3·932 (2)
P(3)···P(3^{ii})	3·414 (3)	Se(3)···P(3^{ii})	4·017 (2)
P(3)···P(2^{ii})	3·711 (3)	Se(1)···Se(3^{i})	4·102 (1)
Se(1)—P(1)—Se(2)	113·16 (7)	Se(3)—P(3)—P(2)	105·07 (7)
Se(1)—P(1)—Se(3)	114·85 (8)	Se(3)—P(3)—C(3)	99·8 (1)
Se(2)—P(1)—Se(3)	101·14 (6)	P(2)—P(3)—C(3)	91·6 (1)
Se(1)—P(1)—C(1)	113·5 (2)	P(1)—C(1)—C(4)	121·9 (5)
Se(2)—P(1)—C(1)	107·0 (2)	P(2)—C(2)—C(4)	113·0 (4)
Se(3)—P(1)—C(1)	106·1 (2)	P(3)—C(3)—C(4)	114·0 (4)
P(1)—Se(2)—P(2)	94·14 (5)	C(1)—C(4)—C(2)	111·9 (5)
P(1)—Se(3)—P(3)	93·99 (5)	C(1)—C(4)—C(3)	112·5 (5)
Se(2)—P(2)—P(3)	104·83 (7)	C(2)—C(4)—C(3)	106·2 (4)
Se(2)—P(2)—C(2)	98·8 (1)	C(1)—C(4)—C(5)	104·8 (4)
P(3)—P(2)—C(2)	93·1 (1)	C(2)—C(4)—C(5)	111·0 (5)
		C(3)—C(4)—C(5)	110·5 (5)

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

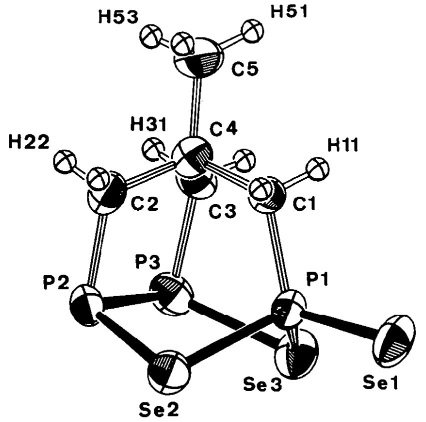

Fig. 1. The molecular conformation of $CH_3C(CH_2P)_3Se_2(Se)$, showing atom numbering. The thermal ellipsoids correspond to 50% probability.

Selected bond lengths and bond angles are listed in Table 2.* Fig. 1 shows the molecular numbering scheme.

The molecule consists of a five-membered P_2Se_2P ring with one exocyclic Se atom at P(1). This ring forms an envelope conformation with the four atoms Se(2), Se(3), P(2) and P(3) in a plane, with the fifth atom P(1) displaced by 1·27 Å. The five-membered ring is capped by the organic group $CH_3C(CH_2)_3$, which bonds to the three P atoms. In some respects the title compound shows similarity with the homologous sulfur compound $CH_3C(CH_2P)_3S_2(S)$: the P(2)—P(3) distance of 2·280 (2) Å corresponds within the limits of error to the value 2·281 (1) Å found for $C_5H_9P_3S_3$ (Zimmermann *et al.*, 1987). The P—C and C—C distances are slightly longer than in the sulfur compound.

The exocyclic P=Se bond length of 2·089 (2) Å is in the range of distances which are found *e.g.* in 2-methoxy-5,5-dimethyl-2-seleno-1,3,2-dioxaphosphorinane 2·055 (2) Å (Grand, Martin, Robert & Tordjman, 1975) or tetraphosphorous pentaselenide 2·123 (13) Å (Penney & Sheldrick, 1971). Also the P—Se bonds in the ring agree with the sum of covalent radii (2·27 Å; Pauling, 1973); comparable P—Se compounds, such as P_4Se_5 [2·26 Å (mean)] (Penney & Sheldrick, 1971) and P_4Se_3 [2·24 Å (mean)] (Keulen & Vos, 1959) show similar distances.

The angles in the hydrocarbon skeleton of the molecule are in accordance with the values in $C_5H_9P_3S_3$. However, the C—C—P angles at the methylene groups are somewhat larger in $C_5H_9P_3Se_3$ than in $C_5H_9P_3S_3$ because of expansion of the cage due to the Se atoms. As in the homologous sulfur compound and in the comparable noradamantane $CH_3C(CH_2)_3As_3Se_2$

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* Lists of structure factors, anisotropic thermal parameters and H coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44505 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

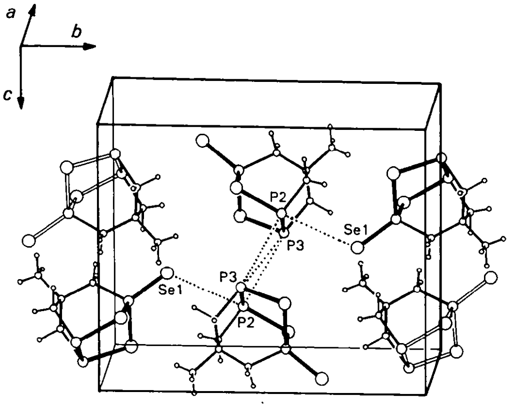

Fig. 2. Arrangement of the molecules in the crystal. Dotted lines show important intermolecular distances.

(Thiele, Rotter, Lietz & Ellermann, 1984) the P(1)—C(1)—C(4) angle is enlarged, and here has a value of 121·9 (5)°, whereas P(2)—C(2)—C(4) and P(3)—C(3)—C(4) are only 113·0 (4) and 114·0 (4)°, respectively.

The molecular arrangement in the crystal is shown in Fig. 2. There are close intermolecular P···P interactions [P(3)···P(3) 3·414 (3), P(2)···P(3) 3·711 (3) Å] across the inversion centres (000, $0\frac{1}{2}\frac{1}{2}$). These 'dimers' are stabilized in three dimensions by P···Se and Se···Se intermolecular contacts listed in Table 2.

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Diaquadiiodozinc(II)–18-Crown-6 Ether* Monohydrate

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Abstract. $[ZnI_2(H_2O)_2].C_{12}H_{24}O_6.H_2O$, $M_r = 637·6$, monoclinic, $P2_1/c$, $a = 9·386$ (1), $b = 13·612$ (2), $c = 20·058$ (2) Å, $\beta = 115·76$ (5)°, $V = 2308·0$ (5) Å^3, $Z = 4$, $D_x = 1·835$ (1) Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 3·770$ (1) mm^{-1}, $F(000) = 1240$, $T = 295$ K, $R = 0·037$, $wR = 0·040$ for 1732 reflexions [$I > 3\sigma(I)$] and 220 variables. The structure is built up of stacks of crown ethers which are linked by weak hydrogen bonds, O···O = 2·79 (1) to 2·86 (1) Å, to a water molecule and to the $ZnI_2(H_2O)_2$ tetrahedra. The mean Zn—I and Zn—O distances are 2·543 (1) and 2·004 (5) Å, the I—Zn—I angle is 122·2 (5)°.

Introduction. The crystal structures have been determined for several 18-crown-6 ether complexes with cadmium or mercury halides (Paige & Richardson, 1984; Pears, Stoddart, Crosby, Allwood & Williams, 1986; Hazell, 1988). In these the metal atom is at the centre of the crown and is eight-coordinated. The attempted preparation of the corresponding zinc compound yielded the title compound in which the crown ethers are not coordinated to zinc but are weakly hydrogen-bonded to $ZnI_2(H_2O)_2$ tetrahedra and to a water molecule.

Experimental. The compound was prepared by dissolving equimolar amounts of ZnI_2 and 18-crown-6 ether in acetonitrile from which it was recrystallized. A crystal was mounted on a Huber four-circle diffractometer. The cell dimensions were determined from the setting angles of 60 reflexions with $18 \leq 2\theta \leq 26°$. Intensities were measured out to $2\theta_{max} = 50°$ using an ω–2θ scan with Nb-filtered Mo $K\alpha$ radiation, the scan width was $(1·0 + 0·692\tan\theta)°$ which was divided into 50 steps, the counting time was 1 s step^{-1}. Reflexions with $-10 \leq h \leq 11$, $-16 \leq k \leq 0$, $-23 \leq l \leq 0$ were measured giving 3946 independent reflexions of which 1732 had $I > 3\sigma(I)$. Reflexions 080 and 400 were monitored every 100 reflexions, the overall fall off in intensity was 0·3%. Reflexions were integrated using the Nelmes (1975) method, the data were corrected for

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* 18-Crown-6 ether is 1,4,7,10,13,16-hexaoxacyclooctadecane.