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Bis(diethoxyselenophosphinoyl) triselenide and bis(diisopropoxy-selenophosphinoyl) diselenide

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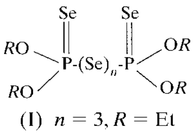
The title compounds, bis(diethoxyselenophosphinoyl) triselenide, $[P(OEt)_2Se]Se_3[P(OEt)_2Se]$, and bis(diisopropoxyselenophosphinoyl) diselenide, $[P(O^iPr)_2Se]Se_2[P(O^iPr)_2Se]$, comprise an Se_3 chain or an Se_2 chain bridging two $(RO)_2PSe$ groups.

Comment

As part of our investigation of selenometalate complexes, we have recently reported the preparation, structure and spectroscopy of $[Mo_3(\mu_3\text{-}S)(\mu_2\text{-}S_2)_3(Se_2P(OEt)_2)_3]Br$ (Béreau & Ibers, 2000). Although the H^+ (Jørgensen, 1962) and K^+ salts (Kudchadker *et al.*, 1968) of the $Se_2P(OEt)_2$ ligand have been known for some time, metal complexes of the ligand are rare; only three compounds containing $[Se_2P(OEt)_2]$ have been structurally characterized (Liu *et al.*, 1998, 1999; Béreau & Ibers, 2000). As an extension of these studies we reacted $K[Se_2P(OEt)_2]$ with VCl_3 in ethanol. Triselenide (I) was obtained as a by-product. This synthesis is very different from the literature preparation (Kudchadker *et al.*, 1968), which involves refluxing a stoichiometric mixture of P_2Se_5 and ethanol in cyclohexane for 4 h. Diselenide (II) was obtained according to this same procedure from P_2Se_5, 2-propanol and *n*-heptane.


$$(RO)_2P(=Se)\text{-}(Se)_n\text{-}P(=Se)(OR)_2$$

(I) $n = 3, R = \mathrm{Et}$
(II) $n = 2, R = {}^i\mathrm{Pr}$

Figs. 1 and 2 show the molecular structures of (I) and (II), respectively. Compound (II) has a crystallographically imposed center of symmetry, but it possesses non-crystallographic symmetry very close to $2/m$. The least-squares plane through atoms Se1, Se1^i, Se2, Se2^i, P1 and P1^i [symmetry code: (i) $1 - x, 1 - y, -z$] has the equation in crystal coordinates of $-2.830x + 5.713y + 5.419z = 1.441$. The coefficients do not have rational ratios and hence the molecular symmetry does not correspond to undetected crystallographic symmetry.

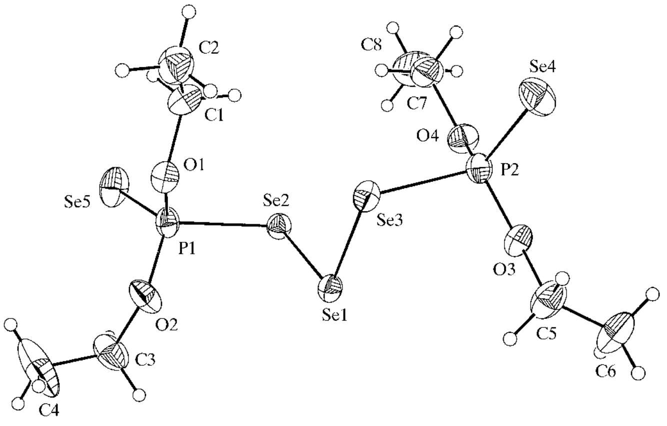


Figure 1
The molecular structure of (I). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of an arbitrary radius.

Within the Se_3 bridge of (I), the Se—Se bond distances are equivalent with Se1—Se2 = 2.3448 (6) and Se1—Se3 = 2.3439 (6) Å. In the Se_2 bridge of (II), the Se—Se bond distance is Se2—Se2 = 2.3951 (6) Å. These distances are normal for Se—Se single bonds (Tattershall *et al.*, 1997). The two P atoms have tetrahedral environments in both (I) and (II), being bonded to two Se atoms and two O atoms. The P—Se bond distances involving Se atoms of the Se_3 and Se_2 chains are 2.2412 (11) and 2.2378 (10) Å for (I), and 2.2223 (8) Å for (II); these correspond to single bonds. Those P—Se bonds involving terminal Se atoms, at 2.0652 (9) and 2.0721 (9) Å for (I), and 2.0733 (7) Å for (II), correspond to double bonds. The P—O bond distances range from 1.569 (2) to 1.581 (2) Å for (I) and are 1.567 (2) and 1.567 (2) Å for (II).

There appears to be no literature on the metal coordination chemistry of compounds (I) and (II). Yet, given the extensive literature on chalcogen ligands, we believe that (I) and (II) could act as potential ligands, exhibiting an *Se*,*Se*-chelation mode through the two terminal Se atoms to form an eight-

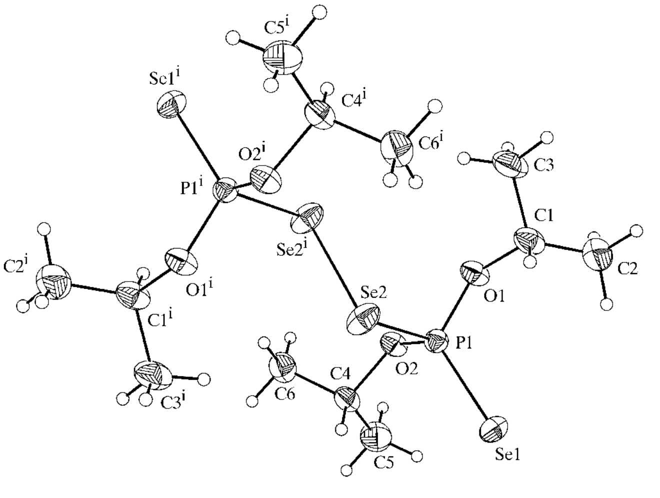


Figure 2
The molecular structure of (II). Displacement ellipsoids are drawn at the 50% probability level and H atoms are drawn as spheres of an arbitrary radius [symmetry code: (i) $1 - x, 1 - y, -z$].

membered ring for (I) and a seven-membered ring for (II). For (I), the μ_2-Se ligand could act as an additional coordination site and the ligand could exhibit η^3-coordination through the two terminal Se atoms and the bridging Se atom.

Experimental

Compound (I) was prepared from a mixture of VCl_3 (50 mg, 0.3 mmol) and $K[Se_2P(OEt)_2]$ (280 mg, 0.9 mmol) in previously degassed absolute ethanol (10 ml). The deep purple solution was stirred at room temperature for 2 h. The solvent was removed under vacuum. The residue was disolved in diethyl ether (10 ml) and the resulting solution was stored at 277 K. Yellow crystals grew in 35% yield over two weeks. Spectroscopic analysis, ^{1}H NMR (CD_3OD, p.p.m.): 4.16 (*m*, CH_2), 1.80 (*t*, CH_3); ^{31}P NMR (CD_3OD, p.p.m., $^1J_{PSe}$ in Hz): 69.5 (901, 570). Some pink crystals of unknown composition were also obtained. Compound (II) was prepared according to the synthesis reported by Kudchadker *et al.* (1968). Orange crystals were grown directly from the reaction mixture in 55% yield. Spectroscopic analysis, ^{1}H NMR (CD_3OD, p.p.m.): 5.11 (*m*, CH), 1.56 (*d*, CH_3); ^{31}P NMR (CD_3OD, p.p.m., $^1J_{PSe}$ in Hz): 63.3 (884, 532).

Compound (I)

Crystal data

$C_8H_{20}O_4P_2Se_5$
$M_r = 636.98$
Triclinic, $P\overline{1}$
$a = 8.320\ (2)$ Å
$b = 11.222\ (3)$ Å
$c = 12.409\ (3)$ Å
$\alpha = 115.317\ (4)^\circ$
$\beta = 107.351\ (4)^\circ$
$\gamma = 92.688\ (4)^\circ$
$V = 979.0\ (5)$ Å^3

$Z = 2$
$D_x = 2.161$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.05$–25.00°
$\mu = 9.521$ mm^{-1}
$T = 153\ (2)$ K
Needle, yellow
0.31 × 0.07 × 0.03 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face-indexed (*SHELXTL*; Sheldrick, 1997)
$T_{min} = 0.434$, $T_{max} = 0.921$
6938 measured reflections

3398 independent reflections
2893 reflections with $I > 2\sigma(I)$
$R_{int} = 0.017$
$\theta_{max} = 25^\circ$
$h = -9 \rightarrow 9$
$k = -13 \rightarrow 13$
$l = -14 \rightarrow 14$
Intensity decay: <2%

Table 1

Selected geometric parameters (Å, °) for (I).

Se1—Se3	2.3439 (6)	P2—O4	1.578 (2)
Se1—Se2	2.3448 (6)	O1—C1	1.465 (4)
Se2—P1	2.2412 (11)	O2—C3	1.454 (4)
Se3—P2	2.2378 (10)	O3—C5	1.461 (4)
Se4—P2	2.0721 (9)	O4—C7	1.460 (4)
Se5—P1	2.0652 (9)	C1—C2	1.495 (5)
P1—O2	1.569 (2)	C3—C4	1.442 (5)
P1—O1	1.581 (2)	C5—C6	1.462 (5)
P2—O3	1.569 (2)	C7—C8	1.477 (5)
Se3—Se1—Se2	105.44 (3)	Se5—P1—Se2	107.83 (4)
P1—Se2—Se1	98.43 (3)	O3—P2—O4	96.42 (11)
P2—Se3—Se1	101.07 (2)	O3—P2—Se4	118.67 (9)
O2—P1—O1	96.40 (12)	O4—P2—Se4	118.52 (9)
O2—P1—Se5	118.86 (9)	O3—P2—Se3	109.68 (9)
O1—P1—Se5	118.51 (9)	O4—P2—Se3	107.83 (9)
O2—P1—Se2	108.76 (10)	Se4—P2—Se3	105.24 (4)
O1—P1—Se2	105.30 (8)		
P1—Se2—Se1—Se3	−87.84 (3)	Se2—Se1—Se3—P2	−87.75 (3)

Refinement

Refinement on F^2
$R(F) = 0.021$
$wR(F^2) = 0.054$
$S = 0.902$
3398 reflections
172 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.54$ e Å^{-3}
$\Delta\rho_{min} = -0.46$ e Å^{-3}

Compound (II)

Crystal data

$C_{12}H_{28}O_4P_2Se_4$
$M_r = 614.12$
Triclinic, $P\overline{1}$
$a = 8.3796\ (10)$ Å
$b = 8.5314\ (10)$ Å
$c = 8.5577\ (10)$ Å
$\alpha = 98.668\ (2)^\circ$
$\beta = 111.851\ (2)^\circ$
$\gamma = 93.459\ (2)^\circ$
$V = 556.81\ (11)$ Å^3

$Z = 1$
$D_x = 1.831$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.43$–24.99°
$\mu = 6.743$ mm^{-1}
$T = 153\ (2)$ K
Block, orange
0.13 × 0.09 × 0.04 mm

Data collection

Bruker SMART 1000 CCD diffractometer
ω scans
Absorption correction: numerical face-indexed (*SHELXTL*; Sheldrick, 1997)
$T_{min} = 0.425$, $T_{max} = 0.877$
4701 measured reflections

1933 independent reflections
1745 reflections with $I > 2\sigma(I)$
$R_{int} = 0.018$
$\theta_{max} = 24.99^\circ$
$h = -9 \rightarrow 9$
$k = -10 \rightarrow 10$
$l = -10 \rightarrow 10$
Intensity decay: <2%

Refinement

Refinement on F^2
$R(F) = 0.026$
$wR(F^2) = 0.071$
$S = 1.330$
1933 reflections
100 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 1.16$ e Å^{-3}
$\Delta\rho_{min} = -0.45$ e Å^{-3}

Table 2

Selected geometric parameters (Å, °) for (II).

P1—O2	1.567 (2)	O2—C4	1.484 (3)
P1—O1	1.567 (2)	C1—C2	1.505 (5)
P1—Se1	2.0733 (7)	C1—C3	1.516 (4)
P1—Se2	2.2223 (8)	C4—C5	1.505 (4)
Se2—Se2^i	2.3951 (6)	C4—C6	1.510 (4)
O1—C1	1.475 (3)		
O2—P1—O1	96.46 (10)	O1—P1—Se2	108.40 (8)
O2—P1—Se1	119.29 (8)	Se1—P1—Se2	104.04 (3)
O1—P1—Se1	119.34 (8)	P1—Se2—Se2^i	98.35 (2)
O2—P1—Se2	108.85 (8)		
P1—Se2—Se2^i—P1^i	180.0		

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

H atoms were generated in calculated positions and constrained with the use of a riding model. The isotropic displacement parameter for each H atom was set 20% larger than that of the parent atom.

For both compounds, data collection: *SMART* (Bruker, 1999); cell refinement: *SMART* (Bruker, 1999); data reduction: *SAINT-Plus* (Bruker, 1999); program(s) used to solve structure: *SHELXS* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 1997); software used to prepare material for publication: *SHELXTL*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: DA1125). Services for accessing these data are described at the back of the journal.

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