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# Two tetrahydrofuran solvates of $HN(SePPh_2)_2$

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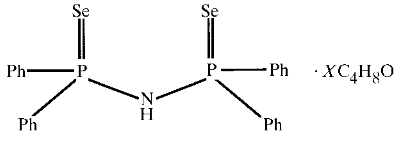
The X-ray crystal structures of *P*,*P*′-iminobis(diphenylselenophosphine) tetrahydrofuran solvate, $C_{24}H_{21}NP_2Se_2{\cdot}C_4H_8O$, (I), and bis(tetrahydrofuran) solvate, $C_{24}H_{21}NP_2Se_2{\cdot}2C_4H_8O$, (II), have been determined; (I) has twofold crystallographic symmetry. In each compound, the O atom of one molecule of tetrahydrofuran is hydrogen bonded to the amide-H atom of $HN(SePPh_2)_2$. The conformation of the Se—P—N—P—Se chains in (I), (II), and the crystal structure of the unsolvated $HN(SePPh_2)_2$ are different.

## Comment

As part of our work on soluble rare-earth chalcogenide species (Pernin & Ibers, 1997, 1999*a*, *b*) we have investigated rare-earth complexes of the imidodiphosphinochalcogenido ligand $[N(QPPh_2)_2]^-$ ($Q$ = S, Se) (Pernin & Ibers, 1999*b*). In addition to $\eta^2$-coordination through the two chalcogen atoms, the ligand adopts $\eta^3$-coordination through the two chalcogen atoms and the N atom to the rare-earth atoms. This is in contrast to the previously reported transition- and main group-metal complexes containing the ligand (Bhattacharyya, Slawin *et al.*, 1995; García-Montalvo *et al.*, 1997) where it typically adopts $\eta^2$-coordination. In this paper we show that the conformation of the Se—P—N—P—Se chain is sensitive to solvation.



(I) $X = 1$
(II) $X = 2$

Figs. 1 and 2 show displacement ellipsoid diagrams with the atom numbering of compounds (I) and (II). The molecules in (I) have an imposed crystallographic twofold axis. Tables 1, 2 and 3 contain selected bond distances and angles. In (I) and (II), P—Se [2.094 (1) for (I); 2.097 (1) and 2.099 (1) Å for (II)] and P—N [1.676 (1) for (I); 1.690 (2) and 1.680 (2) Å for (II)] bonding distances are similar to each other and to the P—Se distances of 2.085 (1) and 2.101 (1) Å and the P—N distances of 1.678 (4) and 1.686 (3) Å in unsolvated $HN(SePPh_2)_2$. The conformations of the Se—P—N—P—Se chains in the three compounds differ markedly, the Se—P···P—Se 'torsion angles' being 81.75 (3), 179.19 (3) and 154°, respectively. Both (II) and the unsolvated species are approximately *anti* with respect to that torsion angle whereas (I) is approximately *gauche*. The S—P···P—S 'torsion angle' is 156° in the unsolvated sulfur analogue, $HN(SPPh_2)_2$ (Husebye & Maartmann, 1983).

In the structure of the unsolvated species, $HN(SePPh_2)_2$ molecules are linked by N—H···Se hydrogen bonds to form dimer pairs. In the structure of $HN(SPPh_2)_2$ there are similar dimers. In each of the present structures, the $HN(SePPh_2)_2$ molecule is linked to a THF (tetrahydrofuran) molecule through an N1—H1*A*···O1 hydrogen bond (Table 2). The N1···O1 distances [2.771 (3) for (I) and 2.815 (3) Å for (II)] are similar to the distances in other THF-amide hydrogen-bonded interactions (Etter *et al.*, 1990; Bonamico *et al.*, 1991). The dihedral angle between the hydrogen-bonded THF molecules and the P—N—P plane is 79.3 (1) in (I) and 25.3 (3)° in (II). Some atoms of the THF molecules show large displacement ellipsoids for data collected at 153 K. This may be due to conformational changes between the twist and envelope forms of the five-membered rings (Cremer & Pople, 1975; Luo *et al.*, 1990; Westerhausen *et al.*, 1998). Nonetheless, C—O and C—C bonds are normal in (I) and exhibit some unreasonable distances in (II) [for example C25—C26 = 1.330 (6) Å, see Tables 1 and 3 for additional distances and angles]. This apparent disorder in the hydrogen-bonded THF molecule in (II) could not be modeled adequately with the superposition of more than one molecule of THF of differing conformation.

P—C bond distances for (I) [1.814 (2) and 1.815 (2) Å] and (II) [1.815 (3), 1.820 (2), 1.812 (3) and 1.818 (2) Å] are normal as are the average C—C distances, 1.381 (9) and 1.386 (8) Å.

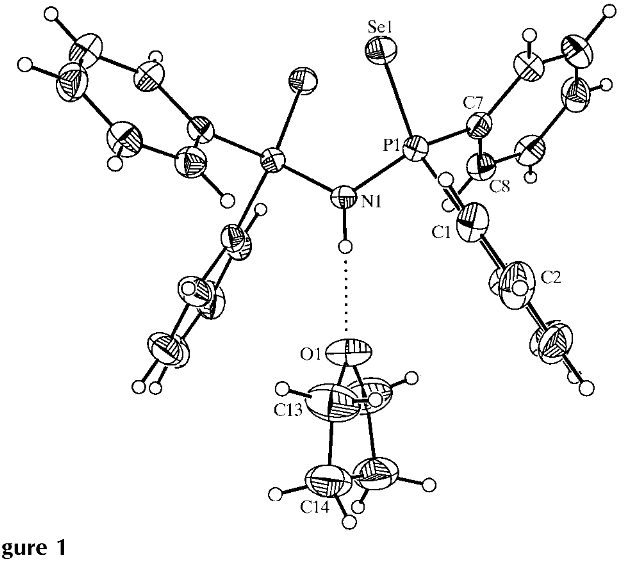


**Figure 1**
The structure of (I) showing 50% probability displacement ellipsoids and H atoms, in idealized positions, as small circles.

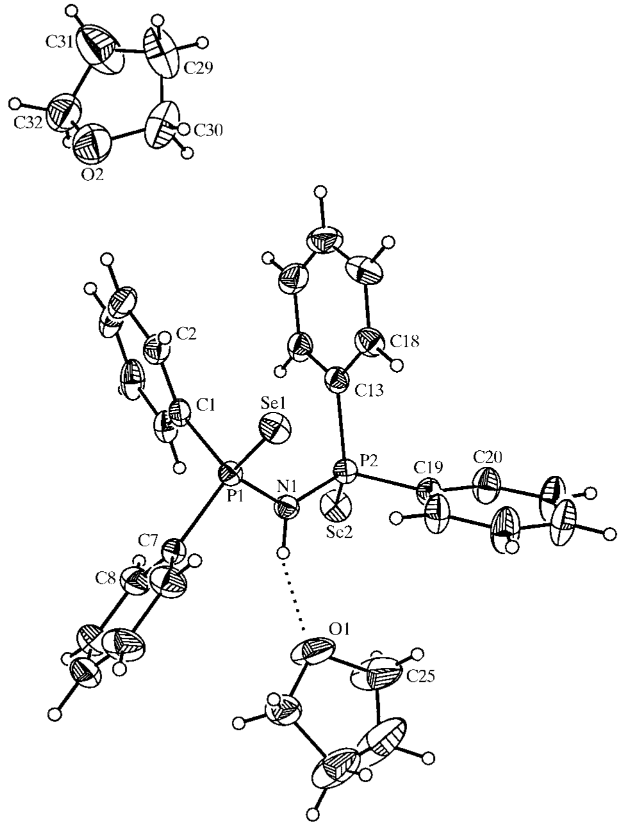


**Figure 2**
The structure of (II) showing 50% probability displacement ellipsoids and H atoms, in idealized positions, as small circles.

## Experimental

Unsolvated $HN(SePPh_2)_2$ was prepared by a literature method (Bhattacharya, Novosad *et al.*, 1995). The reaction of more than one equivalent of $HN(SePPh_2)_2$ with $Cp_3Y$ (Cp = cyclopentadienyl) in THF produces $Cp_2Y[N(SePPh_2)_2]$ in addition to leaving unreacted $HN(SePPh_2)_2$ in solution (Pernin & Ibers, 1999*b*). Upon dilution of the THF solution with pentane, crystals of $HN(SePPh_2)_2$ containing one, (I), and two, (II), molecules of THF were crystallized at 258 K.

### Compound (I)

*Crystal data*

$C_{24}H_{21}NP_2Se_2{\cdot}C_4H_8O$
$M_r = 615.38$
Tetragonal, $P4_12_12$
$a = 10.121$ (3) Å
$c = 26.118$ (10) Å
$V = 2675.5$ (14) Å$^3$
$Z = 4$
$D_x = 1.528$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 8192 reflections
$\theta = 2.16$–28.5°
$\mu = 2.905$ mm$^{-1}$
$T = 153$ (2) K
Block, colorless
0.30 × 0.20 × 0.10 mm

*Data collection*

Bruker Smart 1000 CCD diffractometer
$\omega$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.580$, $T_{max} = 0.748$
17047 measured reflections
2043 independent reflections (plus 1194 Friedel-related reflections)
2891 reflections with $I > 2\sigma(I)$
$R_{int} = 0.035$
$\theta_{max} = 28.53°$
$h = -13 \rightarrow 6$
$k = -12 \rightarrow 12$
$l = -31 \rightarrow 33$
Intensity decay: <2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.022$
$wR(F^2) = 0.059$
$S = 0.97$
3237 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.003$
$\Delta\rho_{max} = 0.25$ e Å$^{-3}$
$\Delta\rho_{min} = -0.25$ e Å$^{-3}$
Absolute structure: Flack (1983)
Flack parameter = −0.022 (8)

**Table 1**
Selected geometric parameters (Å, °) for (I).

| | | | |
|---|---|---|---|
| Se1—P1 | 2.0942 (7) | N1—O1 | 2.771 (3) |
| P1—N1 | 1.6757 (12) | C13—O1 | 1.424 (3) |
| P1—C1 | 1.814 (2) | C13—C14 | 1.477 (4) |
| P1—C7 | 1.815 (2) | C14—C14$^i$ | 1.490 (6) |
| N1—P1$^i$ | 1.6757 (12) | O1—C13$^i$ | 1.424 (3) |
| | | | |
| N1—P1—C1 | 102.38 (10) | C7—P1—Se1 | 113.54 (7) |
| N1—P1—C7 | 107.50 (7) | P1$^i$—N1—P1 | 125.15 (14) |
| C1—P1—C7 | 103.69 (9) | O1—C13—C14 | 107.1 (2) |
| N1—P1—Se1 | 114.54 (6) | C13—C14—C14$^i$ | 103.61 (17) |
| C1—P1—Se1 | 114.03 (7) | C13$^i$—O1—C13 | 108.9 (3) |
| | | | |
| C1—P1—N1—P1$^i$ | 169.78 (7) | Se1—P1—N1—P1$^i$ | 45.83 (3) |
| C7—P1—N1—P1$^i$ | −81.36 (7) | Se1—P1—P1$^i$—Se1$^i$ | 81.75 (3) |

Symmetry code: (i) $1 + y, x - 1, 2 - z$.

**Table 2**
Hydrogen-bonding geometry (Å, °).

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| (I) | | | | |
| N1—H1*A*···O1 | 0.88 | 1.89 | 2.771 (3) | 180 |
| (II) | | | | |
| N1—H1*A*···O1 | 0.88 | 1.99 | 2.815 (3) | 157 |

### Compound (II)

*Crystal data*

$C_{24}H_{21}NP_2Se_2{\cdot}2C_4H_8O$
$M_r = 687.49$
Triclinic, $P\overline{1}$
$a = 8.796$ (2) Å
$b = 13.248$ (3) Å
$c = 13.864$ (3) Å
$\alpha = 97.832$ (4)°
$\beta = 102.673$ (4)°
$\gamma = 94.545$ (4)°
$V = 1551.6$ (6) Å$^3$
$Z = 2$
$D_x = 1.471$ Mg m$^{-3}$
Mo $K\alpha$ radiation
Cell parameters from 7641 reflections
$\theta = 1.52$–28.3°
$\mu = 2.516$ mm$^{-1}$
$T = 153$ (2) K
Block, colorless
0.40 × 0.20 × 0.10 mm

*Data collection*

Bruker Smart 1000 CCD diffractometer
$\omega$ scans
Absorption correction: empirical (*SADABS*; Sheldrick, 1996)
$T_{min} = 0.576$, $T_{max} = 0.778$
14636 measured reflections
7046 independent reflections
5578 reflections with $I > 2\sigma(I)$
$R_{int} = 0.024$
$\theta_{max} = 28.27°$
$h = -11 \rightarrow 11$
$k = -17 \rightarrow 17$
$l = -18 \rightarrow 17$
Intensity decay: <2%

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)] = 0.035$
$wR(F^2) = 0.089$
$S = 1.242$
7046 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.04F_o^2)^2]$
$(\Delta/\sigma)_{max} = 0.010$
$\Delta\rho_{max} = 1.11$ e Å$^{-3}$
$\Delta\rho_{min} = -1.17$ e Å$^{-3}$

**Table 3**
Selected geometric parameters (Å, °) for (II).

| | | | |
|---|---|---|---|
| Se1—P1 | 2.0967 (7) | C25—O1 | 1.451 (4) |
| Se2—P2 | 2.0990 (7) | C26—C27 | 1.515 (4) |
| P1—N1 | 1.6896 (19) | C27—C28 | 1.494 (4) |
| P1—C1 | 1.815 (3) | C28—O1 | 1.410 (3) |
| P1—C7 | 1.820 (2) | C29—C30 | 1.500 (6) |
| P2—N1 | 1.6804 (19) | C29—C31 | 1.511 (6) |
| P2—C19 | 1.812 (3) | C30—O2 | 1.426 (4) |
| P2—C13 | 1.818 (2) | C31—C32 | 1.489 (5) |
| N1—O1 | 2.815 (3) | C32—O2 | 1.422 (4) |
| C25—C26 | 1.330 (6) | | |
| N1—P1—C1 | 104.00 (10) | P2—N1—O1 | 106.87 (10) |
| N1—P1—C7 | 100.91 (10) | P1—N1—O1 | 118.72 (10) |
| C1—P1—C7 | 107.79 (11) | C26—C25—O1 | 109.3 (3) |
| N1—P1—Se1 | 117.36 (7) | C25—C26—C27 | 106.3 (4) |
| C1—P1—Se1 | 113.05 (8) | C28—C27—C26 | 102.7 (3) |
| C7—P1—Se1 | 112.56 (8) | O1—C28—C27 | 105.9 (2) |
| N1—P2—C19 | 105.26 (11) | C30—C29—C31 | 103.6 (3) |
| N1—P2—C13 | 107.57 (10) | O2—C30—C29 | 105.0 (3) |
| C19—P2—C13 | 105.86 (11) | C32—C31—C29 | 104.5 (4) |
| N1—P2—Se2 | 111.96 (7) | O2—C32—C31 | 107.7 (3) |
| C19—P2—Se2 | 112.39 (8) | C28—O1—C25 | 108.2 (2) |
| C13—P2—Se2 | 113.26 (8) | C32—O2—C30 | 104.8 (3) |
| P2—N1—P1 | 132.67 (12) | | |
| C19—P2—N1—P1 | 104.35 (18) | Se2—P2—N1—O1 | 62.51 (11) |
| C13—P2—N1—P1 | −8.2 (2) | C1—P1—N1—P2 | 58.93 (18) |
| Se2—P2—N1—P1 | −133.26 (14) | C7—P1—N1—P2 | 170.57 (17) |
| C19—P2—N1—O1 | −59.89 (13) | Se1—P1—N1—P2 | −66.77 (18) |
| C13—P2—N1—O1 | −172.44 (12) | Se1—P1—P2—Se2 | 179.19 (3) |

H atoms were placed at calculated positions (0.88 Å for amide protons, 0.95 Å for aliphatic protons and 0.99 Å for aromatic protons) and refined with a riding model. The $U_{\rm iso}$ value for a given H atom was assigned as 1.2 times the $U_{\rm iso}$ of the atom to which it is attached.

For both compounds, data collection: *SMART* (Bruker, 1999*a*); cell refinement: *SMART*; data reduction: *SAINT-Plus* (Bruker, 1999*b*); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1990); program(s) used to refine structure: *SHELXTL*97 (Sheldrick, 1997); molecular graphics: *SHELXTL*; 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: BK1508). Services for accessing these data are described at the back of the journal.

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