A New Class of Structure for Selenium(II) Dithiocomplexes. The Trigonal Molecular Structure of Bis(diethyldithiophosphinato)selenium(II), [Se(S₂PEt₂)₂]

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The crystal and molecular structure of bis(diethyldithiophosphinato)-selenium(II), [Se(S₂PEt₂)₂], has been determined by X-ray diffractometry. The coordination sphere displays a planar trigonal geometry around the central selenium atom, which is strongly bonded to two monodentate dithiophosphinate ligands and weakly to one sulfur atom from a neighboring molecule. The molecular association through this intermolecular Se···S interaction builds up a polymeric network. This SeS₃ arrangement has not been observed in analogous divalent sulfur, selenium or tellurium systems, and thus it may be classified as a new class of structures for related systems (class VI).

Husebye and his co-workers have extensively studied the chemistry of divalent sulfur, selenium and tellurium compounds with monodentate and bidentate sulfur-containing ligands.[1,2] Those works are especially noteworthy, and they are largely responsible for stimulating a number of later investigations.[3–6] According to the systematic structural studies of Husebye, the structures of these compounds can be divided into five classes.[1] Complexes of classes I and II are four-coordinated trapezoid planar. Class I consists of essentially monomeric molecules, where the central atom is bonded to four sulfur atoms in the molecule. In compounds of class II, the central atom is strongly bonded to two sulfur atoms in the molecule proper and weakly to two sulfur atoms belonging to different neighboring molecule. Class III is mainly represented by the bis(4-morpholinethio-carbonyl) trisulfide with a 'zigzag' framework.[7] Trans square planar complexes with monodentate ligands correspond to class IV and square planar molecules with bidentate ligands to class V.

We report here the crystal and molecular structure of bis(diethyldithiophosphinato)selenium(II), the structure of which does not belong to any of the classes described above. It displays a planar trigonal geometry around the selenium atom with two intramolecular and one weaker intermolecular selenium atom to ligand bonds. Therefore,

it may be regarded as the first example of a new class of compounds, i.e. Class VI.

Experimental

The FAB mass spectrum was measured on a 3-nitro-benzyl alcohol support in the positive ion mode on a Jeol JMS-SX102A instrument, the infrared spectrum (as KBr discs) on a Perkin Elmer 283B spectrometer. The ^{1}H, ^{13}C, ^{31}P and ^{77}Se NMR spectra were recorded in CDCl₃ on a Varian VXR 300s spectrometer using as an external reference Si(CH₃)₄, H₃PO₄ 85% and Ph₂Se, respectively. Galbraith Laboratories (Knoxville, TN) performed microanalyses.

Bis(diethyldithiophosphinato)selenium(II), [Se(S₂PEt₂)₂], was prepared by the method of Husebye.[8] Suitable crystals for X-ray diffraction were grown by allowing a layer of n-hexane to diffuse slowly into a solution of the complex in dichloromethane at room temperature. M.p. 122–123 °C (lit. 116–117 °C[8]). IR (KBr) cm^{-1}: $\tilde{v}$ = 572 [v_{as}(PS₂)]; 451 [v_s(PS₂)]. NMR (CDCl₃) ppm: ^{1}H: δ = 1.54 (dtd) [6 H, CH₃, ^3J(HH) = 3.29 Hz, ^3J(PH) = 7.49 Hz], 2.23 m [4 H, P–CH₂]; ^{13}C: δ = 6.53 (td) [CH₃, ^2J(PC) = 16.44 Hz], 27.7 (dd) [P–CH₂, ^1J(PC) = 22.45 Hz]; ^{31}P: δ = 89.03 (s); ^{77}Se: δ = 1033(s). MS (FAB⁺, CH₃Cl, for ^{80}Se) m/z: 386 [M^+], 153 [S₂PEt₂⁺],

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121 [SPEt$_2$$^+$]. C$_8H_{20}P_2S_4$Se: calc. C 24.93; H 5.19, S 33.23; found: C 24.7; H 5.3, S 33.2.

X-Ray diffraction studies. A yellow prismatic crystal having dimensions of 0.48 × 0.40 × 0.38 mm was mounted on a glass fiber and used for this study. Unit cell parameters are close to those determined by Husebye.[8] Data collection was performed at room temperature on a Siemens P4 four-circle diffractometer by using graphite-monochromated Mo-K$_\alpha$ radiation ($\lambda = 71\,073$ Å). Table 1 compiles the data for the structure determination. A total of 5124 ($3 < 2\theta < 60°$) reflections were measured, from which 2295 [$F > 4.0\sigma(F)$] were used for calculations. A face-indexed numerical absorption correction was applied. The structure was solved by direct methods, using the Siemens SHELXTL-PLUS program (PC version)[9] and refined by full-matrix least-square calculations. The numbers of refined parameters were 137. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were calculated as a riding model with fixed isotropic $U = 0.08$ Å^2.

Results and discussion

The structure of the title compound consists of [Se(S$_2$PEt$_2$)$_2$] molecules, which are associated through only one intermolecular Se$\cdots$S interaction, building up a polymeric network. Selected bond lengths and bond angles, with their estimated standard deviations, are

Table 1. Crystallographic and structure solution data for the [Se(S$_2$PEt$_2$)$_2$] complex.

Empirical formula	C$_8$H$_{20}$P$_2$S$_4$Se
Formula weight	385.4
Color, habit	Yellow, prism
Space group	$P2_1/c$ (No. 14)
Crystal system	Monoclinic
a/Å	12.127(1)
b/Å	12.627(1)
c/Å	12.298(2)
β/°	116.40(1)
V/Å^3	1686.8(5)
Z	4
ρ_{calcd}/mg cm^{-3}	1.518
F(000)	784
Scan type	ω
2θ range/°	3.0–60.0
Scan speed/° min^{-1}	4.00–60.00
Reflections collected	5124
Independent reflections	4917 ($R_{int} = 3.37\%$)
Observed reflections	2295 [$F > 4.0\sigma(F)$]
μ/mm^{-1}	2.884
Absorption correction	Face-indexed
Min./max. transmission	0.2512/0.4146
Weighting scheme	$w^{-1} = \sigma^2(F) + 0.0008F^2$
Parameters refined	137
R (F_o) (%)	5.57
Rw (F_o) (%)	6.11
Data-to-parameter ratio	16.8 : 1
Largest difference peak/e Å^{-3}	0.55
Largest difference hole/e Å^{-3}	−0.63
Goodness-of-fit	1.17

Table 2. Selected bond lengths (in Å) and angles (in °) for [Se(S$_2$PEt$_2$)$_2$].

Se–S$_1$	2.207(2)	P$_1$–C$_3$	1.799(6)
Se–S$_3$	2.193(2)	P$_2$–S$_3$	2.114(3)
Se$\cdots$S$_{2'}$	3.342(2)	P$_2$–S$_4$	1.939(3)
P$_1$–S$_1$	2.111(3)	P$_2$–C$_5$	1.799(7)
P$_1$–S$_2$	1.947(3)	P$_2$–C$_7$	1.807(8)
P$_1$–C$_1$	1.799(9)		
S$_1$–Se–S$_3$	104.0(1)	S$_2$–P$_1$–C$_1$	115.1(3)
S$_1$–Se$\cdots$S$_{2'}$	127.8(3)	S$_2$–P$_1$–C$_3$	116.7(3)
S$_3$–Se$\cdots$S$_{2'}$	128.3(2)	S$_3$–P$_2$–C$_5$	107.7(3)
Se–S$_1$–P$_1$	105.9(1)	S$_3$–P$_2$–C$_7$	107.0(3)
Se–S$_3$–P$_2$	106.9(1)	S$_4$–P$_2$–C$_5$	116.9(3)
S$_1$–P$_1$–S$_2$	103.5(1)	S$_4$–P$_2$–C$_7$	116.3(3)
S$_1$–P$_1$–C$_1$	107.6(3)	C$_1$–P$_1$–C$_3$	105.0(3)
S$_1$–P$_1$–C$_3$	108.2(3)	C$_5$–P$_2$–C$_7$	104.8(3)

listed in Table 2. The molecular structure is shown in Fig. 1 and includes the Se$\cdots$S bond. The central selenium atom is strongly bonded to two sulfur atoms from two ligands and weakly to one sulfur atom from a neighboring molecule. Thus a planar trigonal geometry is observed around the selenium atom. This new arrangement may be classified into an additional class of structures for related systems (class VI).

The two intramolecular Se–S bonds are 2.207(2) Å [Se–S$_1$] and 2.193(2) Å [Se–S$_3$]. Those may be compared to 2.21 Å, the sum of the respective covalent radii[10] and the corresponding bond lengths found in analogous selenium derivatives like [Se{S$_2$P(OEt)$_2$}$_2$] (class II),[11] [Se(S$_2$COMe)$_2$] (class II),[12] (NBu$_4$)[Se{S$_2$C=C(CN)$_2$}$_2$] (class I)[4] and [Se{(SPPh$_2$)$_2$N}$_2$] (class V).[13] The weak intermolecular Se$\cdots$S bond is 3.342(2) Å, which is longer than a covalent Se–S bond, but significantly shorter than the sum of the van der Waals radii, ca. 3.7 Å.[14] The value is also in the range of the reported Se$\cdots$S distances to date.[6,11–13] The S$_3$–Se–S$_1$ angle is 104.0(1)°, which is nearly identical to those of 104.05(2),
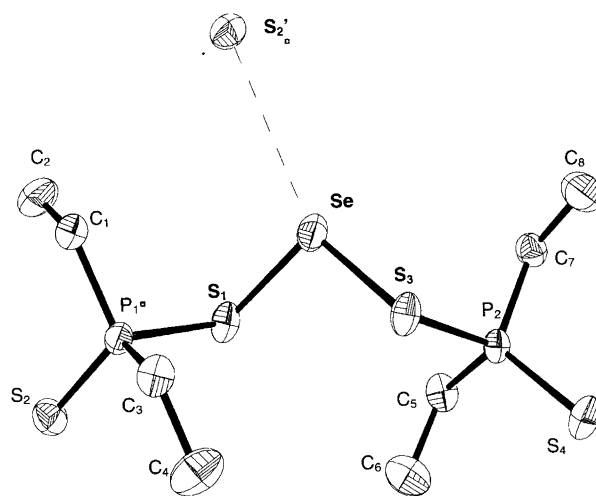

Fig. 1. ORTEP view of [Se(S$_2$PEt$_2$)$_2$] (hydrogen atoms are omitted for clarity) and the coordination around the central atom.
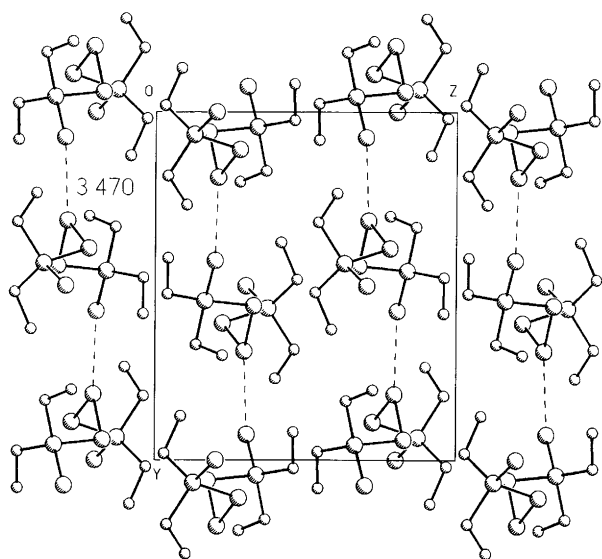
Fig. 2. View of the unit cell (*YZ*-plane).

103.9(2) and 104.6(1)° found for the corresponding angle in trapezoid complexes of $[Se\{S_2P(OEt)_2\}_2]$.[11] $[Se\{Se_2PEt_2\}_2]$[15] and in the angular $[S\{S_2CNC_4H_8O\}_2]$,[7] respectively. The two remaining bond angles at the selenium central atom are 128.3(2)° (S_3–Se$\cdots$$S_{2'}$) and 127.8(3)° ($S_1$–Se$\cdots$$S_{2'}$).

The P_1–S_1–Se–S_3–P_2 chain has the *trans* form, with the phosphorus atoms on the opposite sides of the central SeS_2 plane. Normal torsional angles of 177.9 and 179.8° are found for the Se–S_1–P_1–S_2 and Se–S_3–P_2–S_4 sequences. The same *trans* arrangement has been observed in some structures of complexes ($[Se\{S_2P(OEt)_2\}_2]$,[11] $[Se\{Se_2PEt_2\}_2]$[15] and $[Te\{Se_2PEt_2\}_2]$[16]), which are trapezoid class II compounds, or in the S_3–S–S_1–C moiety of the angular class III trisulfide derivative.[7]

In each dithiophosphinate group there is a short and a long P–S bond. The lengths correspond within the error limits to double and single bonds[10] and agree well with the dimensions found for corresponding bonds in previous structure determinations. On the phosphorus atom the angles vary between 103.9(1) and 116.9(3)°. The average is 109.39° and corresponds to tetrahedral hybridization. The two S–P–C angles are the largest ones [116.9(3), 116.3(3), 116.7(3) and 115.1(3)°], while the other angles on phosphorus are below 107.7(3)°. This may be accounted for by repulsion between the P=S

double bond and the ethyl substituents on the phosphorus atom.

A comparison of the structure described here with those of the known selenium analogs and some related complexes reveals plenty of similarities, as is illustrated above. However, the most remarkable feature is that the arrangement at the central atom in our structure is trigonal planar, while that of the analogous structures belongs to some of the classes described by Husebye. The closest related examples, $[Se\{S_2P(OEt)_2\}_2]$[11] and $[Se\{Se_2PEt_2\}_2]$,[15] are trapezoid planar complexes with two intermolecular bonds (class II). Crystal packing essentially consists of molecular chains of associated $[Se(S_2PEt_2)_2]$ units, which run parallel to the *Y*-axis (Fig. 2).

References

1. Brøndmo, N. J., Esperås, S. and Husebye, S. *Acta Chem. Scand., Ser. A 29* (1975) 93.
2. Bjørnevåg, S., Husebye, S. and Maartmann-Moe, K. *Acta Chem. Scand., Ser. A 36* (1982) 195.
3. Mazaki, Y. and Kobayashi, K. *Tetrahedron Lett. 30* (1989) 2813.
4. Hummel, H.- U., Fischer, T. and Wolski, A. *Z. Anorg. Allg. Chem. 620* (1994) 1483.
5. Brese, N. E., Randall, C. R., Ibers, I. A. *Inorg. Chem. 27* (1988) 940.
6. Cea-Olivares, R., Canseco-Melchor, G.; García-Montalvo, V., Hernández-Ortega, S. and Novosad, J. *Eur. J. Inorg. Chem.* (1998) 1573.
7. Husebye, S. *Acta Chem. Scand. 27* (1973) 756.
8. Husebye, S. *Acta Chem. Scand. 19* (1965) 1045.
9. *SHELXTL PLUS, Release 4.0 for Siemens R3 Crystallographic*, Siemens Analytical Instruments, Madison, WI 1989.
10. Haiduc, I. *Coord. Chem. Rev. 158* (1997) 325.
11. Refaat, L. S., Maartmann-Moe, K. and Husebye, S. *Acta Chem. Scand., Ser. A 38* (1982) 303.
12. Gould, R. O., Jones, C. L., Savage, J. and Stephenson, A. *J. Chem. Soc., Dalton Trans.* (1976) 908.
13. Husebye, S. and Maartmann-Moe, K. *Acta Chem. Scand., Ser. A 37* (1983) 219.
14. Bondi, A. *J. Phys. Chem. 68* (1964) 441.
15. Husebye, S. and Helland-Madsen, G. *Acta Chem. Scand. 23* (1969) 1398.
16. Husebye, S. *Acta Chem. Scand. 23* (1969) 1389.