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A Selenium(II) Complex with an Unusual Type of Intermolecular Interaction. The Crystal Structure of Bis(diethyldithiophosphato)selenium(II)

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The crystal and molecular structure of the title compound have been determined from low-temperature diffractometer data by the heavy-atom method. The crystals are triclinic, space group $P\bar{1}$, with unit cell dimensions (−135 °C) $a=8.364(2)$, $b=10.755(1)$, $c=12.387(2)$ Å, $\alpha=63.28(1)$, $\beta=70.78(2)$, $\gamma=83.93(1)°$, $Z=2$. Full matrix least-squares refinement of 3623 reflections resulted in an R-value of 0.032. Each selenium atom is surrounded by four sulfur atoms. The SeS_4 coordination sphere is roughly trapezoid planar with the central selenium atom forming two short intramolecular Se–S bonds of average length 2.209 Å at an S–Se–S angle of 104.05°, and two weak intermolecular Se---S bonds of average length 3.432 Å at an S–Se–S angle of 92.92°. These latter bonds are to sulfur atoms already involved in strong S–Se bonds in neighbour molecules. Thus, only one of the two sulfur atoms in the potentially bidentate diethyldithiophosphate ligands is forming bonds to the central selenium atoms.

The present study is an extension of work done on divalent tellurium and selenium compounds with bidentate dithio ligands[1–4] having small bites. Previous structural work on bis(dialkyldithiophosphato)tellurium(II) complexes[5,6] reveals a great tendency to form trapezoid planar complexes. The X-ray structure determination of a dialkyldithiophosphato selenium(II) complex has not been done before, so for this reason and for the sake of comparison with corresponding tellurium complexes, the structure of the bis(diethyldithiophosphato)selenium(II) complex was solved.

EXPERIMENTAL

Preparation of complex. This was prepared according to an earlier description[7] and recrystallized from ethanol as yellow prisms.

IR spectrum. The IR spectrum in the region from 4 000–200 cm^{-1} was measured on a Perkin-Elmer 683 instrument by the CsI disc method for the solid state, while the spectrum in solution was obtained with CCl_4 as solvent.

X-Ray data. Intensity data and data for measurement of unit cell dimensions were obtained on an Enraf-Nonius CAD-4 diffractometer at −135 °C. The crystal used for data collection had approximate dimensions 0.14×0.24×0.30 mm^3. Unit cell parameters were determined from least-squares refinement of the setting angles of 25 reflections $(9<\theta<19°)$. The values are $a=8.364(2)$, $b=10.755(1)$, $c=12.378(2)$ Å, $\alpha=63.28(1)°$, $\beta=70.78(2)°$, $\gamma=83.93(1)°$, $Z=2$, $D_x(-135\ °C)=1.591$ g cm^{-3}, $D_m(22\ °C)=1.530$ g cm^{-3}, $\mu(MoK\alpha)=25.80$ cm^{-1}. The space group is either $P1$ or $P\bar{1}$. Reflection intensities were collected using omega-scans with scan width $(1.50+0.35\mathrm{tg}\theta)°$ and Mo$K\alpha$ radiation. The scan rate was 4.0°min^{-1} for all reflections. 4511 independent reflections with $2\theta\leq56°$ were measured and 3623 of these were considered observed $[I\geq2\sigma(I)]$. The intensities were corrected for absorption based on crystal faces and dimensions (transmission factor range 0.55 to 0.70). Data collection and computer programs used throughout this investigation belong to the

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Table 1. Positional Parameters and Their Estimated Standard Deviations.[a]

Atom	*x*	*y*	*z*	*B*(A2)
Se	0.24631(3)	0.04735(2)	0.00100(2)	1.571(5)
S1	0.41139(8)	0.12931(6)	0.06410(5)	1.59(1)
S2	0.02272(8)	0.17640(6)	0.00790(5)	1.63(1)
S3	0.47733(9)	0.04809(7)	0.32999(6)	2.69(2)
S4	−0.10936(9)	0.44624(7)	−0.18670(6)	2.48(2)
P1	0.32268(8)	0.01050(6)	0.26263(6)	1.67(1)
P2	0.09232(8)	0.34571(6)	−0.17348(5)	1.53(1)
O11	0.2872(2)	−0.1438(2)	0.2935(2)	2.13(4)
O12	0.1306(2)	0.0453(2)	0.3061(2)	1.86(4)
O21	0.2529(2)	0.4232(2)	−0.1877(1)	1.80(4)
O22	0.1846(2)	0.2917(2)	−0.2753(1)	1.65(4)
C1	0.4106(4)	−0.2499(3)	0.3086(3)	3.38(8)
C2	0.3318(5)	−0.3824(3)	0.4118(3)	3.97(9)
C3	0.0858(4)	0.1853(3)	0.2937(2)	2.14(6)
C4	−0.1029(4)	0.1809(3)	0.3516(3)	3.06(8)
C5	0.2423(4)	0.4953(3)	−0.1101(2)	2.22(6)
C6	0.4146(4)	0.5586(3)	−0.1490(3)	3.55(7)
C7	0.0963(4)	0.2010(3)	−0.2993(2)	2.26(6)
C8	0.1645(4)	0.2340(3)	−0.4361(2)	3.23(7)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: (4/3) [a2B(1,1)+b2B(2,2)+c2B(3,3)+ab(cos gamma) B(1,2)+ac(cos beta) B(1,3)+bc(cos alpha) B(2,3)].

Enraf-Nonius Structure Determination Pack, SDP-Plus 1982. More details about the programs used can be found in an earlier paper.[8]

STRUCTURE DETERMINATION

The structure was solved by means of conventional heavy atom techniques, and refined by least-squares full-matrix methods assuming the centrosymmetric space group $P\bar{1}$. The choice of $P\bar{1}$ as the proper space group was supported by the subsequent successful refinement. Anisotropic temperature factors were used for all atoms except hydrogen. The hydrogen positions were calculated and the hydrogen atoms included in the final refinement cycles with fixed positions (all C−H bonds equal to 0.95 Å) and a constant temperature factor B=3.5 Å^2. This value is the average found in previous least-squares iterations with hydrogen atom parameters included as variables. The function minimized is $\Sigma w(\Delta F)^2$, the attributed weights correspond to the counting statistics plus 2 % of the net intensity for each reflection (fudge factor p=0.02).[8] The final conventional R factor was 0.032, while R_w was 0.028 and S, $[\Sigma w\Delta F^2/(m-n)]^{\frac{1}{2}}$, was 1.3706. A difference map showed no peaks above 0.5 e/Å^3. Refined atomic coordinates are shown in Table 1. The interatomic distances and angles as well as molecular planes and interplanar angles are listed in Tables 2 and 3, respectively. Tables of thermal parameters and observed and calculated structure factors are available from the author K.M.M. upon request.

RESULTS AND DISCUSSION

The structure of the bis(diethyldithiophosphato)selenium(II) molecule is shown in Fig. 1. Included in this figure are two weak intermolecular Se---S bonds, one from each of two different neighbour molecules. These two bonds complete a roughly planar four-coordination around the central selenium atom. The molecular structure is typical for a class II complex.[1,5,6,9,10] Unlike most class II complexes, the intermolecular Se---S bonds are to ligand sulfur atoms already bonded to a central selenium atom in neighbour molecules. Recently, another example of such intermolecular bonding has been found in the analogous Te(II) complex,[6] but only for one out of six such bonds.

Se−S bond lengths. The two intramolecular

Table 2. Interatomic distances (Å) and angles (°) with standard deviations.

Bond		Angle	
Se−S1	2.209(1)	S1−Se−S2	104.05(2)
Se−S2	2.210(1)	S1′−Se−S2′	92.92(1)
Se−S1′[a]	3.342(1)	S1−Se−S1′	82.04(2)
Se−S2′	3.523(1)	S1−Se−S2′	161.77(2)
S1−P1	2.097(1)	S2−Se−S2′	83.74(2)
S2−P2	2.094(1)	S2−Se−S1′	169.65(2)
P1−S3	1.912(1)	Se−S1−P1	102.01(3)
P1−O11	1.565(2)	Se−S2−P2	102.98(3)
P1−O12	1.580(2)	S1−P1−S3	107.06(4)
P2−S4	1.918(1)	O11−P1−O12	96.07(3)
P2−O21	1.574(2)	S1−P1−O11	108.91(7)
P2−O22	1.564(2)	S1−P1−O12	105.72(7)
O11−C1	1.445(3)	S3−P1−O11	118.93(7)
O12−C3	1.463(3)	S3−P1−O12	119.10(7)
O21−C5	1.460(3)	S2−P2−S4	105.69(4)
O22−C7	1.464(3)	O21−P2−O22	96.25(8)
C1−C2	1.451(4)	S2−P2−O21	107.55(7)
C3−C4	1.499(4)	S2−P2−O22	109.21(7)
C5−C6	1.493(4)	S4−P2−O21	118.74(7)
C7−C8	1.479(3)	S4−P2−O22	118.78(7)
Se−O11	3.380(2)	P1−O11−C1	124.8(2)
Se−O22	3.415(2)	P1−O12−C3	120.3(2)
S1−S2	3.483(1)	P2−O21−C5	121.1(2)
S1−S3	3.226(1)	P2−O22−C7	121.5(1)
S2−S4	3.199(1)	O11−C1−C2	110.3(2)
		O12−C3−C4	107.0(2)
		O21−C5−C6	107.2(2)
		O22−C7−C8	108.8(2)
		Se−S1−Se′	97.36(2)
		Se−S2−Se″	96.29(2)

[a] S1′, S2′, Se′ and Se″ belong to molecules whose transformations from the original one are, $1-x, \bar{y}, \bar{z}$; $\bar{x}, \bar{y}, \bar{z}$, $1-x, \bar{y}, \bar{z}$ and $\bar{x}, \bar{y}, \bar{z}$, respectively.

Table 3. Molecular planes and interplanar angles (°).[a]

No. of plane	Atoms included	Interplanar angles(°)	
1	Se, S1, S2, S1′, S2′	1−2	12.6
2	Se, S1, S2	1−3	5.9
3	Se, S1′, S2′	2−3	18.4
4	Se, S1, P1	1−4	95.7
5	Se, S2, P2	1−5	78.0
		4−5	76.0

[a] Atomic displacements from the first plane (Å) with their standard deviations: Se, 0.072(0); S1, −0.386(1); S2, 0.325(1); S1′, 0.239(1); S2′, −0.250(1).

Se−S bonds, Se−S1 and Se−S2 are 2.209(1) and 2.210(1) Å, respectively. This may be compared to 2.21 Å, the sum of the respective covalent radii[11] and 2.205(6) and 2.170(9) Å, the corresponding bond lengths found in [Se$(MeOCS_2)_2$]. In the analogous tellurium complex, the intramolecular Te−S bonds are a little longer than a covalent bond. For the weak intermolecular

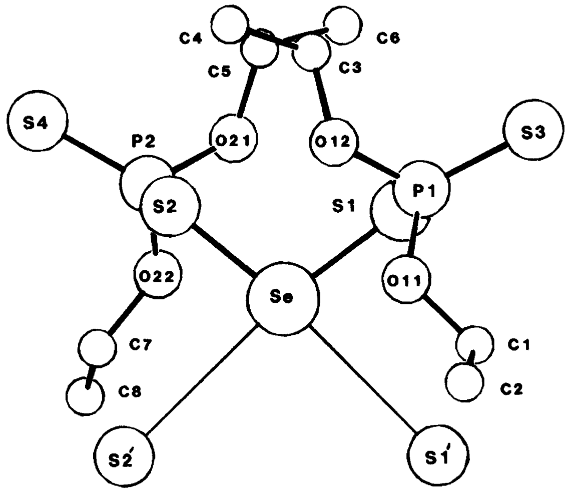

Fig. 1. The molecule as seen along the normal to the Se S1 S2 plane. Thin lines indicate weak intermolecular bonds. Hydrogen atoms are omitted for the sake of clarity.

bonds, Se---S1′ and Se---S2′, the bond lengths are 3.342(1) and 3.523(1) Å respectively. They are both significantly shorter than a van der Waals contact which is 3.70Å.[12] The average Se---S bond is thus 0.27Å shorter than a van der Waals contact as compared to 0.50Å for the average Te---S bond in the analogous tellurium complex, $[\mathrm{Te}\{(\mathrm{EtO})_2\mathrm{PS}_2\}_2]$.[6] According to the above, selenium is a poorer acceptor than tellurium in such complexes.

Bonding in the diethyldithiophosphate ligands. There is a P−S and P=S bond in each ligand. For the P−S bond lengths, the values are P1−S1=2.097(1) and P2−S2=2.094(1)Å. This is a normal single bond.[6] The P−S double bond lengths found are P1−S3=1.912(1) and P2−S4=1.918(1) Å. None of these two sulfur atoms are involved in S---Se bonding. The two bonds are significantly shorter than the corresponding bonds found in the analogous tellurium complex where the doubly bonded sulfur atoms do form S---Te bonds. Thus such intermolecular bonds tend to weaken the P=S bonds *trans* to themselves, but the effect is small. The P=S stretch in $[\mathrm{Se}\{(\mathrm{EtO})_2\mathrm{PS}_2\}_2]$ is found to be practically the same in solid CsI and in CCl_4 solution,

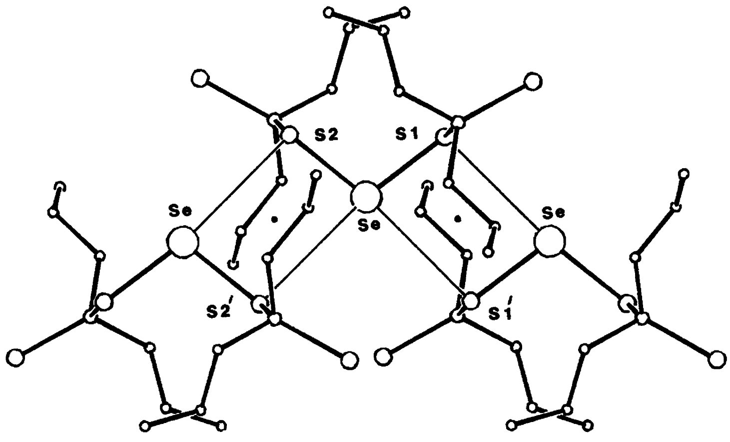

Fig. 2. Intermolecular interaction between one molecule and its two nearest neighbours.

being 650 and 649 cm^{-1}. In the analogous tellurium complex the P=S---Te interactions disappear in solution and the spectrum changes accordingly when going from the solid state to solution; $\nu_{P=S}$ (CCl$_4$) had the same value as found in the present investigation. The average P–O, C–O and C–C bond lengths are 1.571(8), 1.458(9) and 1.4821(21) Å, respectively. These are close to the corresponding values found in [Te{(EtO)$_2$PS$_2$}$_2$] and must be regarded as normal.[6]

Other structural aspects. The P–S–Se–S–P chain has the *trans* form with the phosphorus atoms on opposite sides of the central SeS$_2$ plane. The plane through each PS$_2$ group is almost perpendicular to the central plane, as is usual in class II complexes. Normal torsional angles of 170.9 and 170.0° are found for the Se–S1–P1–S3 and Se–S2–P2–S4 groups, respectively.[6] The molecule has a pseudo twofold symmetry axis through the central selenium atom. A twofold axis has been found in a related selenium compound.[10] In the SeS$_4$ coordination sphere, the maximum deviation of any atom from the best plane through the five atoms, is 0.386 Å. Thus the coordination sphere is only approximately planar. This is also seen from Table 3 where the SeS1S2/SeS$_4$ angle is 12.6°. Even if the deviation from planarity is greater than in other class II complexes, it is still best termed a trapezoid planar complex of Se(II). The S1–Se–S2 angle is 104.05(2)°, thus nearly identical to 103.9(2)° found for the corresponding angle in Se(Et$_2$PSe$_2$)$_2$[10]. The two asymmetric three-center systems S1–Se---S2 and S2–Se---S1 deviate *ca.* 18 and 10° from linearity, but the bonding in these may still be considered to be of the three-center four-electron type, although the asymmetry is so great that it almost represents an extreme of such bonding: a covalent bond *trans* to no bond.[13]

It may also be of interest to note that the Se–S---Se angles are close to 90° indicating that the sulfur atom bridging two selenium central atoms employs essentially *p* orbitals in its bonding. Angles centered on the phosphorus atoms are nearly the same as those found in the tellurium(II) dialkyldithiophosphates.[5,6]

Packing of the molecules. Each central selenium atom is weakly bonded to two sulfur atoms in two neighbouring molecules. Fig. 2 shows how one molecule is connected to two others by weak intermolecular Se---S bonds. In the tellurium complex, [Te{(EtO)$_2$PS$_2$}$_2$][6] the molecules are connected by weak intermolecular bonds into a three-dimensional network. Here the outer molecules in Fig. 2 are weakly bonded to other molecules, one on each side of the trimolecular system. Thus the molecules are connected together in infinite zigzag chains.

There are no other short intermolecular distances except for S4–C3 (in a molecule at $\bar{x}$, 1-y, $\bar{z}$) being 3.574(2) Å.

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