

A Planar, Four-coordinate Se(II) Compound.

The Preparation and Crystal Structure of Bis(imidotetraphenyldithiodiphosphino-*S,S'*)selenium(II)

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Bis(imidotetraphenyldithiodiphosphino-*S,S'*)selenium(II), $[\text{Se}\{\text{N}(\text{Ph}_2\text{PS})_2\}_2]$ has been prepared from $\text{NH}_4^+\text{N}(\text{Ph}_2\text{PS})_2^-$ and $[\text{Se}\{(\text{EtO})_2\text{PS}_2\}_2]$ in methanol. Its crystal structure has been determined by X-ray crystallographic methods. Unit cell dimensions are $a=10.703(1)$, $b=13.760(2)$, $c=17.499(3)$ Å, $\alpha=112.00(1)$, $\beta=90.81(1)$, $\gamma=91.31(1)^\circ$, $Z=2$.

Full matrix least squares refinement of 5064 observed reflections resulted in an R -value of 0.044. The triclinic crystals, space group $P\bar{1}$, are built up of four-coordinate Se(II) complexes. The SeS_4 coordination sphere is roughly trapezoid planar with selenium forming a long and a short bond to each bidentate ligand. Se–S bond lengths are Se–S1=2.264(1) Å, Se–S2=2.948(1) Å, Se–S3=2.270(1) Å and Se–S4=3.054(1) Å. For the intraligand S–Se–S angle, an average value of $84.0(2)^\circ$ was found.

It has previously been shown that divalent selenium and tellurium have a great tendency to form trapezoid planar complexes with bidentate dithio ligands having small bites. In such compounds the ligands are anisobidentate, *i.e.* each ligand forms one strong and one weak bond to either the same central atom (class I), or two separate central atoms (weakly bonded polymers, class II).¹ Recent structural work on bis(imidotetraphenyldithiodiphosphino-*S,S'*)tellurium(II) demonstrated that it was possible to form true square planar complexes of divalent tellurium with bidentate ligands with large bites (class V complexes).² The present investigation was undertaken to see if divalent selenium also could form square planar complexes with such ligands.

EXPERIMENTAL

Preparation of complex. The ammonium salt of the ligand, $\text{L}=\text{N}(\text{Ph}_2\text{PS})_2^-$, was prepared by published procedures.^{3,4} To 0.29 g (0.45 mmol) of bis(diethyldithiophosphato)selenium(II), $[\text{Se}\{(\text{EtO})_2\text{PS}_2\}_2]$ ⁵ dissolved in 40 ml methanol, was added 0.47 g (1.0 mmol) of ligand salt dissolved in 80 ml methanol. A yellow precipitate formed. It was filtered off and washed with cold ethanol and ether. Yield 90 % based on selenium compound added, m.p. 190–192 °C (decomp). Large, flat, light yellow prisms formed upon recrystallization from carbon disulfide.

Formation of Se_2S_6 upon decomposition of complex. The complex was very soluble in slightly polar solvents such as CH_2Cl_2 and CHCl_3 . Attempts at recrystallization from such solvents resulted in orange crystals of poor quality. A preliminary X-ray investigation of the crystals from CHCl_3 showed that they corresponded to the Se_2S_6 phase with the disordered structure previously found by Laitinen, Niinistö and Steudel.⁶

X-Ray data. All data were measured on an Enraf-Nonius CAD-4 diffractometer. The crystal used for data collection had approximate dimensions $0.16 \times 0.18 \times 0.32$ mm³. Unit cell parameters were found from least squares refinement of the setting angles of 25 high-angle reflections. They are $a=10.703(1)$, $b=13.760(2)$, $c=17.499(3)$ Å, $\alpha=112.00(1)$, $\beta=90.81(1)$, $\gamma=91.31(1)^\circ$, $Z=2$, $D_m=1.34$ gcm⁻³, $D_x=1.36$ gcm⁻³, $\mu(\text{MoK}\alpha)=11.8$ cm⁻¹. The space group is $P1$ (No. 1) or $P\bar{1}$ (No. 2).

Intensity data were collected using an ω -scan with scan width $(1.00+0.35 \text{ tg } \theta)^\circ$, a graphite monochromator and MoK α radiation. The scan

Table 1. Atomic coordinates in fractions of cell edges with standard deviations.

Atom	x	y	z
Se	0.23853(4)	-0.00557(3)	0.24914(3)
S1	0.0568(1)	-0.06507(9)	0.28293(7)
S2	0.3304(1)	-0.21219(10)	0.23390(8)
S3	0.1682(1)	0.14549(9)	0.24251(7)
S4	0.4944(1)	0.08338(10)	0.22881(8)
P1	0.0035(1)	-0.17487(8)	0.16804(7)
P2	0.2476(1)	-0.27558(8)	0.12428(7)
P3	0.2332(1)	0.24814(9)	0.35698(7)
P4	0.4998(1)	0.18970(9)	0.34152(7)
N1	0.1036(3)	-0.2514(3)	0.1167(2)
N2	0.3726(3)	0.2427(3)	0.3807(2)
C111	-0.0651(4)	-0.1066(3)	0.1090(2)
C112	-0.1394(5)	-0.0205(4)	0.1453(3)
C113	-0.1993(5)	0.0253(4)	0.0975(3)
C114	-0.1857(5)	-0.0148(4)	0.0144(3)
C115	-0.1117(6)	-0.0981(4)	-0.0221(3)
C116	-0.0502(5)	-0.1444(3)	0.0249(3)
C121	-0.1199(4)	-0.2474(3)	0.1948(3)
C122	-0.2412(5)	-0.2176(4)	0.2041(4)
C123	-0.3314(5)	-0.2786(5)	0.2243(4)
C124	-0.2979(6)	-0.3685(5)	0.2315(4)
C125	-0.1780(7)	-0.3984(4)	0.2223(4)
C126	-0.0879(6)	-0.3386(4)	0.2048(3)
C211	0.3297(4)	-0.2431(3)	0.0469(3)
C212	0.2901(5)	-0.2917(4)	-0.0349(3)
C213	0.3546(7)	-0.2692(5)	-0.0943(3)
C214	0.4518(7)	-0.2020(5)	-0.0747(4)
C215	0.4894(6)	-0.1534(4)	0.0050(4)
C216	0.4310(5)	-0.1736(4)	0.0677(3)
C221	0.2574(4)	-0.4162(3)	0.0877(3)
C222	0.3718(5)	-0.4619(4)	0.0858(3)
C223	0.3792(5)	-0.5695(4)	0.0580(4)
C224	0.2756(5)	-0.6325(4)	0.0313(4)
C225	0.1627(6)	-0.5884(4)	0.0316(4)
C226	0.1540(5)	-0.4808(4)	0.0590(3)
C311	0.1351(4)	0.2554(3)	0.4317(2)
C312	0.0086(4)	0.2041(4)	0.4156(3)
C313	-0.0649(5)	0.1805(4)	0.4708(3)
C314	-0.0127(5)	0.1783(4)	0.5415(3)
C315	0.1121(5)	0.2019(4)	0.5595(3)
C316	0.1873(5)	0.2249(4)	0.5042(3)
C321	0.2008(4)	0.3729(3)	0.3513(3)
C322	0.1399(5)	0.4494(4)	0.4118(3)
C323	0.1243(6)	0.5473(4)	0.4084(4)
C324	0.1674(6)	0.5672(4)	0.3436(4)
C325	0.2252(8)	0.4930(4)	0.2824(4)
C326	0.2427(7)	0.3958(4)	0.2862(3)
C411	0.6062(4)	0.2974(3)	0.3489(3)
C412	0.7239(5)	0.2789(4)	0.3178(3)
C413	0.8072(5)	0.3621(5)	0.3257(3)
C414	0.7705(6)	0.4619(4)	0.3634(4)
C415	0.6552(7)	0.4798(4)	0.3931(5)
C416	0.5724(6)	0.4001(4)	0.3872(4)
C421	0.5649(4)	0.1393(3)	0.4153(3)
C422	0.5760(5)	0.2042(4)	0.4967(3)
C423	0.6229(6)	0.1656(5)	0.5533(3)
C424	0.6607(6)	0.0654(5)	0.5299(4)

Table 2. Interatomic distances (Å) with standard deviations.

Se-S1	2.264(1)	P3-C311	1.799(4)
Se-S2	2.948(1)	P3-C321	1.798(4)
Se-S3	2.270(1)	P4-C411	1.813(5)
Se-S4	3.054(1)	P4-C421	1.816(5)
S1-P1	2.074(2)	S1-S2	3.529(2)
S2-P2	1.972(2)	S3-S4	3.604(2)
S3-P3	2.071(2)	S1-S3	3.423(2)
S4-P4	1.966(2)	S2-S4	4.425(2)
P1-N1	1.561(3)	P1-P2	2.960(1)
P2-N1	1.598(3)	P3-P4	2.971(2)
P3-N2	1.554(3)	S1-P2	3.831(2)
P4-N2	1.598(3)	S2-P1	3.775(2)
P1-C111	1.796(4)	S3-P4	3.862(2)
P1-C121	1.808(4)	S4-P3	3.827(2)
P2-C211	1.811(5)	Se-N1	3.564(3)
P2-C221	1.803(4)	Se-N2	3.581(3)

rate varied between 6.7 and 1.5° min⁻¹. Out of a total of 8392 unique reflections with $2\theta \leq 50^\circ$, 5064 had $I \geq 2\sigma(I)$ and were treated as observed. The intensities were corrected for absorption (transmission factor range 0.81–0.87). More details about data collection and computer programs

used in this investigation can be found in a previous paper.⁷

IR spectrum. An IR spectrum of the crystals was obtained, using a Perkin-Elmer 683 instrument and the CsI disc technique.

Table 3. Bond angles (°) with standard deviations.

S1-Se-S2	84.14(4)	S3-P3-C311	106.30(14)
S1-Se-S3	98.06(5)	S3-P3-C321	101.53(15)
S1-Se-S4	172.01(4)	N2-P3-C311	109.35(20)
S2-Se-S3	172.47(4)	N2-P3-C321	111.24(20)
S2-Se-S4	94.99(4)	C311-P3-C321	110.09(20)
S3-Se-S4	83.83(5)	S4-P4-C411	110.53(16)
Se-S1-P1	99.16(5)	S4-P4-C421	111.93(17)
Se-S2-P2	89.75(5)	N2-P4-C411	105.60(20)
Se-S3-P3	98.50(5)	N2-P4-C421	105.14(20)
Se-S4-P4	93.52(5)	C411-P4-C421	103.71(20)
S1-P1-N1	118.22(13)	P1-C111-C112	121.5(4)
S2-P2-N1	117.59(14)	P1-C111-C116	119.2(3)
S3-P3-N2	117.93(14)	P1-C121-C122	123.6(4)
S4-P4-N2	118.69(14)	P1-C121-C126	117.1(4)
P1-N1-P2	139.13(22)	P2-C211-C212	118.4(4)
P3-N2-P4	140.98(23)	P2-C211-C216	121.2(4)
S1-P1-C111	108.10(14)	P2-C221-C222	120.3(4)
S1-P1-C121	101.38(14)	P2-C221-C226	121.6(3)
N1-P1-C111	110.27(19)	P3-C311-C312	120.5(3)
N1-P1-C121	110.10(20)	P3-C311-C316	119.9(3)
C111-P1-C121	108.09(19)	P3-C321-C322	122.6(4)
S2-P2-C211	112.07(18)	P3-C321-C326	119.7(4)
S2-P2-C221	109.41(15)	P4-C411-C412	120.8(4)
N1-P2-C211	107.11(20)	P4-C411-C416	121.2(4)
N1-P2-C221	106.55(19)	P4-C421-C422	119.2(4)
C211-P2-C221	102.98(20)	P4-C421-C426	120.7(4)

STRUCTURE DETERMINATION

The structure was solved by means of conventional heavy atom techniques and refined by least-squares full-matrix methods. 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 and a constant temperature factor ($B=8.0 \text{ \AA}^2$); the value is the average found in the initial refinements with H included. The final $R=0.044$, while R_w with $p=0.02$ was 0.042. The error in an observation of unit weight was 1.235. A difference map showed no peaks above 0.4 e/\AA^3 . Tables of thermal parameters and observed and calculated structure factors are available from the authors upon request. Final atomic coordinates are shown in Table 1.

RESULTS

Interatomic distances and angles are listed in Tables 2 and 3. Molecular planes and interplanar angles are shown in Table 4. Fig. 1 shows the bis(imidotetraphenyldithiodiphosphino-*S,S'*)-selenium(II) molecule (SeL_2) seen roughly along the normal to the SeS_4 coordination plane (a), and also at approximately right angles to the above normal, (b). In Fig. 2, the SeS_4 coordination sphere is shown. For comparison, the TeS_4 group of the corresponding tellurium(II) complex and the SeS_4 groups of $[\text{Se}(\text{CH}_3\text{OCS}_2)_2]^1$ and $\text{Se}(\text{Et}_2\text{NCS}_2)_2$ is included in the figure. The packing of the molecules is indicated in Fig. 3. From the figures, it is seen that the structure is built up of separate SeL_2 molecules. Each selenium atom is coordinated to all four sulfur atoms of the molecule in a trapezoid planar configuration with greatly asymmetric Se-S bonds.

DISCUSSION

The SeS_4 group. The SeS_4 molecular core is roughly planar, with all atoms within 0.19 \AA of its least squares plane. There are two short Se-S bonds, $\text{Se-S1}=2.264(1)$ and $\text{Se-S3}=2.270(1) \text{ \AA}$. *Trans* to these, at an average angle of $172.24(33)^\circ$ there are two long, weak bonds, $\text{Se-S2}=2.948(1)$ and $\text{Se-S4}=3.054(1) \text{ \AA}$. The *intra*-ligand S-Se-S angles are both close to 84° , while the *inter*-ligand

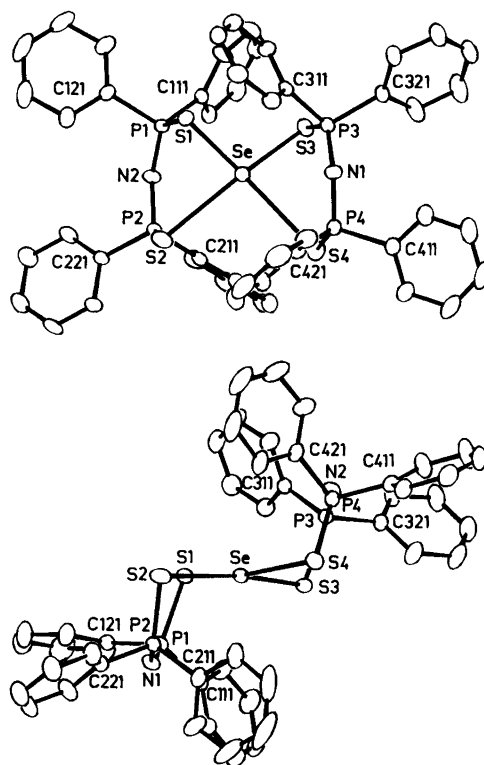


Fig. 1. a. The bis(imidotetraphenyldithiodiphosphino-*S,S'*)selenium(II) molecule as seen along the normal to the SeS_4 coordination plane. b. The complex molecule seen at right angles to the normal in 1a along a line approximately bisecting angle S1-Se-S3 .

angles, S1-Se-S3 and S2-Se-S4 are close to 98 and 95° , respectively.

Since there are no intermolecular secondary bonds, this compound is best classified as a class I complex. From Fig. 2, it can clearly be seen that SeL_2 with respect to Se-S bond lengths is intermediate between a class I and a class II complex and that it is much closer to a class II complex with respect to Se-S bond angles. The average Se-S bond length is 2.634 \AA as compared to 2.54 \AA , the normal value for a class I complex⁸ and 2.21 \AA , the sum of Paulings covalent radii. From Fig. 2, the difference in the MS_4 groups ($\text{M}=\text{Te,Se}$) of SeL_2 and TeL_2 are clearly seen. While M-S bond angles are similar, there is only a slight asymmetry in the Te-S bonds ($\Delta=0.02 \text{ \AA}$) as compared to the great asymmetry in the Se-S bonds ($\Delta=0.73 \text{ \AA}$). In both complexes, the

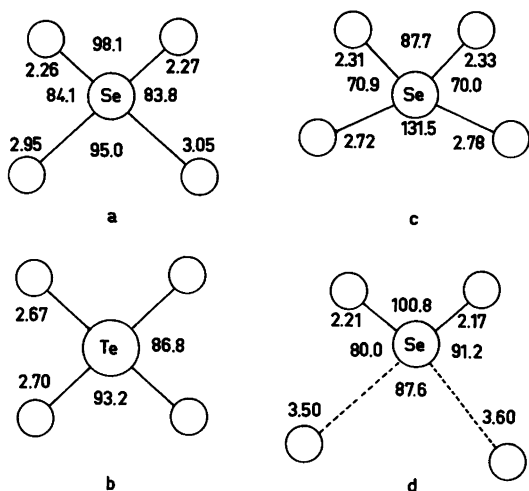


Fig. 2. Examples of planar four-coordinate selenium and tellurium complexes. a. $[\text{SeL}_2]$; b. $[\text{TeL}_2]$; $\text{L}=\text{N}(\text{Ph}_2\text{PS})_2$; c. $[\text{Se}(\text{Et}_2\text{NCS}_2)_2]^{18}$ and d. $[\text{Se}(\text{MeOCS}_2)_2]^{10}$. The MS_4 coordination spheres are seen along the normals to their least squares planes. Unlabelled spheres represent sulfur atoms. Bond lengths and angles (average values in b) are in ångströms and degrees. Intermolecular, secondary bonds are dashed.

bonding in the MS_4 group is probably essentially of the 3-center, 4-electron type.⁹ Why then are their coordination spheres so different? It has been found earlier that $\text{Te}(\text{II})$ is a better acceptor of ligand electron density than $\text{Se}(\text{II})$ so that only with very strong donor ligands like dithiocarbamates do they both form complexes with relatively short average Te-S and Se-S bonds (2.68 and 2.54 Å, respectively).^{1,9} Since the imidotetraphenyldithiodiphosphinate ion is a weaker donor, the overall Se-S bonding becomes weaker than the corresponding Te-S bonding. An even greater difference is found for ML'_2 , where $\text{M}=\text{Se}(\text{II})$ and $\text{Te}(\text{II})$ and $\text{L}'=\text{methylxanthate}$.^{1,10}

Ligand structure and molecular form. Average P-S and P-N bond lengths in the ligands are 2.021 and 1.578 Å, respectively, in good agreement with earlier investigations.² However, due to the asymmetry in the Se-S bond lengths, there is a pronounced tendency in the six-membered ligand-selenium rings of alternate short and long bonds. The short Se-S bond, average length 2.267(4) Å, is followed by a long S-P bond of average length 2.073(2) Å. This is joined to a short P-N bond, average length 1.558(5) Å which is connected to a long N-P bond, average length 1.598(0) Å. Completing the ring is a short P-S bond, average length 1.969(4) Å and a long S-Se

Table 4. Molecular planes.^a

No. of plane	Atoms included	Interplanar angles (°)			
1	Se, S1, S2, S3, S4	1-2	74.7	6-7	7.2
2	S1, P1, S2, P2	1-3	71.6	6-8	8.0
3	S3, P3, S4, P4	1-6	6.0	6-9	11.4
4	P1N1P1	1-7	6.4	7-8	10.2
5	P3N2P4	1-8	3.8	7-9	7.8
6	S1SeS2	1-9	5.7	8-9	7.5
7	S1SeS3	2-3	9.8		
8	S2SeS4	2-4	6.8		
9	S3SeS4	2-10	95.1		
10	C111P1C121	2-11	91.2		
11	C211P2C221	3-5	7.9		
12	C311P3C321	3-12	91.4		
13	C411P4C421	3-13	88.8		

^a Atomic displacement from planes 1-3 (Å).

- Se, 0.005(1); S1, -0.194(1); S2, 0.147(1); S3, 0.188(1); S4, -0.147(1);
- S1, 0.085(1); P1, -0.102(1); S2, -0.089(1); P2, 0.106(1); Se, 1.851(1); N1, -0.051(4); C111, 1.132(4); C121, -1.727(5); C211, 1.682(5); C221, -1.110(4)
- S3, -0.011(1); P3, 0.013(1); S4, 0.011; P4, -0.014(1); Se, -1.837(1); N2, -0.072(4); C311, -1.361(4); C321, 1.574(5); C411, 1.446(5); C421, -1.406(5)

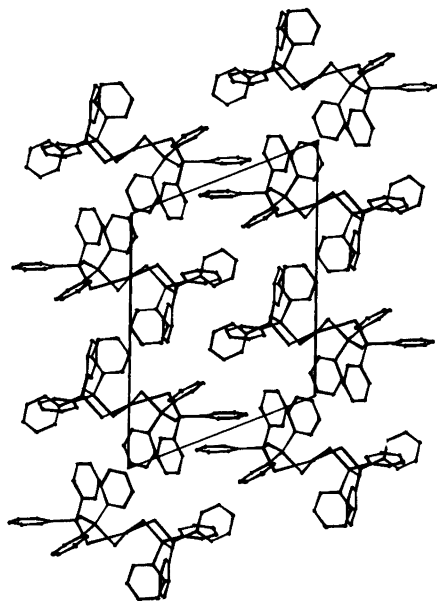


Fig. 3. The molecular packing as seen in the projection along *a*.

bond, average length 3.00(5) Å. Except for the Se–S bonds which are intermediate between a covalent bond and a van der Waals contact, the bond lengths are intermediate between single and double bonds, with the P–S bonds being close to both extremes. The average ring angles are similar to those in the tellurium analog.² As can be seen from Fig. 1b and Table 4, ligand ring 1 (S1,S2) has a tendency to chair form while ring 2 (S3,S4) has a tendency to boat form. The conformation of the whole molecule (minus the phenyl groups) approaches chair form, just like the tellurium analog. The average bond lengths and angles in the phenyl groups are 1.370(16) Å and 120.00(1.08)°, respectively.

Molecular packing. The packing of the molecules in the unit cell is shown in Fig. 3. There are no especially short contacts between the molecules, but there are more short van der Waals contacts than in the tellurium analog,² the shortest C–C contact being 3.48 Å.

Infrared spectra. The infrared spectrum of SeL₂ is very similar to that of TeL₂,² especially at frequencies above 650 cm⁻¹. Tentative assignments based on spectra of metal complexes with the imidotetraphenyldithiodiphosphinate ligand

and TeL₂² are (*v* in cm⁻¹): *v*_{as}(PNP), 1175 ms; *v*(PC), 709 s and 690 vs. The absorptions occur at nearly the same frequencies in TeL₂. However *v*_s(PS) is found at 600 cm⁻¹ as compared to 580 cm⁻¹ for TeL₂ while *v*_{as}(PS) is found at 545 cm⁻¹, as compared to 559 cm⁻¹ for TeL₂. These changes in the PS absorptions probably reflect the increased asymmetry in P–S bond strength in SeL₂ as compared to TeL₂. The PS absorptions may be compared to those found near 570–590 and near 450–470 cm⁻¹ and assigned to *v*(P=S) and *v*(P–S) for selenium and tellurium diethyldithiophosphinates.^{9,11} Similarly *δ*(PNP) found at 527 cm⁻¹(w) in TeL₂ has disappeared and may have merged with the absorption at 512–513 cm⁻¹ found in both compounds. Finally *δ*(NPS) is found at 438 (w) as compared to 430 in the tellurium analog. The differences in *δ*(PNP) and *δ*(NPS) for the two compounds SeL₂ and TeL₂ are probably due to the greater asymmetry in P–N and P–S bonding in the selenium compound. A medium strong absorption at 318 cm⁻¹ may be due to Se–S stretching. This is supported by the observation of Eysel *et al.* that a normal Se–S bond absorbs at 360 cm⁻¹.¹² The strong Se–S bonds observed in the present work are 0.06 Å longer than a covalent Se–S bond and should thus be expected to absorb at a lower frequency.

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