Synthesis of the First Neutral Spiro Selenium(II) Complex Containing a True Square Planar Se(Se_4) Core – Preparation and Crystal Structure of Bis[*N*-(diphenylphosphanylselenoyl)-*P,P*-diphenylphosphanylselenoic amidato-*Se, Se′*]selenium(II)☆

Raymundo Cea-Olivares*[a], Graciela Canseco-Melchor[a], Verónica García-Montalvo[a], Simón Hernández-Ortega[a], and Josef Novosad[b]

Instituto de Química, Universidad Nacional Autónoma de México[a],
Circuito Exterior, Ciudad Universitaria, México 04510 D.F., México
Fax: (internat.) + 52-5/6162203
E-mail: cea@servidor.unam.mx

Inorganic Chemistry Department, Masaryk University[b],
61137 Brno, Czech Republik

Received March 23, 1998

Keywords: Selenium / Spiro compounds / Phosphazene heterocycles / Chelates

The Bis[*N*-(diphenylphosphanylselenoyl)-*P,P*-diphenylphosphanylselenoic amidato-*Se,Se′*]selenium(II) (**1**) was prepared by treating [K{N($SePPh_2$)$_2$}] with [Se{S_2P(O-*i*Pr)$_2$}$_2$] in THF. The title compound was characterized by means of IR and ^{31}P-NMR spectroscopy and positive-ion FAB mass spectrometry and elemental analysis. The molecular structure was determined using single-crystal X-ray diffraction. The Se(Se_4) core exhibited a quasi perfect square planar geometry. Two selenide ligands are coordinated symmetrically to the central atom forming a spiro complex.

Introduction

The extraordinary ability of the anions $[R_2P(X)NP(X)R_2]^-$ (R = Me, Ph; X = O, S, Se) to form very unusual carbon-free chelate complexes is well known. Some examples are the tetrahedral [M{N($SPMe_2$)$_2$-*S,S′*}$_2$] (M = Ni, Fe)[1], the six-coordinated lanthanide complexes [Ln{N($OPPh_2$)$_2$-*O,O′*}$_2$][2], the true square planar tellurium(II) complex [Te{N($SPPh_2$)$_2$-*S,S′*}$_2$][3] and recently the square planar tin(II) complex [Sn{N($SePPh_2$)$_2$-*Se,Se′*}$_2$][4] with the first example of such a geometry for Sn^{II}. The great flexibility of these chelate rings with wide variations in the ring angles (P−N−P, M−X−P, X−P−N) and large bites X···X enables the central atom to "reveal" its preference for a particular geometry, since there is no restrictions imposed by the presence of rigid organic rings, e. g. the β-diketonates, or small rings, with great stereochemical restrictions, like the dithiophosphates or dithiophosphinates.

Twenty years ago, Husebye et al. classified five types of geometries for divalent sulphur, selenium and tellurium complexes with bidentate dithio and related ligands[5]. Complexes of class I are trapezoid planar tetracoordinated with all intramolecular ligand bonds. Class-II compounds are also trapezoid planar, however two of the ligand bonds are intramolecular and the other two intermolecular. Class-III compounds are mainly represented by the bis(4-morpholinethiocarbonyl) trisulfide with a "zigzag" framework; *trans* square planar complexes with monodentate ligands correspond to class IV and bidentate square planar molecules to class V. In 1982, Husebye et al. used the imidotetraphenyldithiodiphosphinate anion as a chelating ligand with a very large bite, in order to synthesis true square planar complexes (class V) with Te^{II} and Se^{II}. They obtained [Te{N($SPPh_2$)$_2$-*S,S′*}$_2$][3] which was a true square planar Te^{II} compound (a class-V complex), while the structure of the selenium analogous compound, [Se{N($SPPh_2$)$_2$-*S,S′*}$_2$], was intermediate between class I and class II, yet much closer to a class-II complex[6].

The number of compounds where the selenium atom is surrounded by four selenium atoms [Se(Se_4) core] are quite scarce. The bis(*N,N*-diethyldiselenocarbamate)Se^{II} is a class-I trapezoid planar complex[7]. The bis(diethyldiselenophosphinate)Se^{II} is a class-II complex[8]. The low-temperature ^{77}Se-NMR solution data of the analogous bis(diisobutildiselenocarbamate) of Se^{II} suggests a four-coordinated structure[9]. Another example with bidentate ligands corresponds to the dianionic complex [(Bu_4N)$_2${Se[Se_2C=C(CN)$_2$]$_2$}], with intrachelating Se−Se−Se angles of 75° and an $SeSe_4E_2$ (E = lone pair) distorted octahedral geometry[10]. Several examples of polyselenide derivatives containing the anion $[Se\{Se_5\}_2]^{-2}$ are known. This anion exhibits a geometry close to the square planar one[11]. The square planar Se_5 moiety with monodentate ligands was observed in tetrakis[*N*-methylbenzothiazole)-3*H*-selenone]selenium(II) tetrafluoroborate (class-IV complex)[12]. However, there are no examples of neutral true square planar neutral complexes containing the Se(Se_4) core and bidentate ligands (a class-V complexes) in the literature.

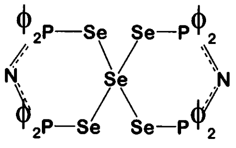
We decided to synthesise the compound [Se{N($SePPh_2$)$_2$-*Se,Se′*}$_2$] to determine whether it is a class-V complex, or

1434−1948/98/1010−1573 $ 17.50+.50/0

isotructural with $[Se\{N(SPPh_2)_2\text{-}S,S'\}_2]$ (a class-II compound).

Results and Discussion

Treatment of $[K\{N(SePPh_2)_2\}]$ with $[Se\{S_2P(O\text{-}i\text{Pr})_2\}_2]$ in THF at room temperature, yielded $[Se\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ (**1**). The compound was purified by thin layer chromatography. Attempts of purification by normal recrystallization methods were unsuccessful because the compound tends to decompose giving red selenium, free ligand, and other compounds. Derivative **1** was characterized on the basis of its elemental analysis and its ^{31}P-NMR, IR and positive-ion FAB MS data and by X-ray crystallography. It is a yellow-orange, air-stable solid, that tends to decompose in solution, soluble in polar organic solvents such as $CHCl_3$, yet insoluble in ethanol or hexane.



1

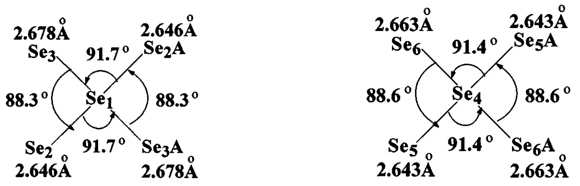
^{31}P-NMR spectra show that all phosphorus atoms are equivalent. As with other main-group complexes with this ligand, in the IR spectrum the assignments of the phosphazene bands were relatively easy, after identification of the usual phenyl group bands common to the $[(PPh_2X)_2N]^-$ ligands[13] . Individual assignments of the ν(PSe) bands is not fully possible because of the overlap with the corresponding PNP vibrations.

To date, few P−Se vibrations have been clearly assigned[14]. The FAB mass spectrum of the compound exhibits a low-intensity signal for the corresponding molecular ion, but rather intense peaks resulting from the expected first fragmentations. The most intense peak containing selenium corresponds to $[Se(PPh_2)_2N^+]$. Since the FAB mass spectrum was obtained in solution, it also shows some fragments due to a decomposition product, e.g. $[\{Ph_2P(Se)NP(Ph_2)\}_2O$; *m/z*: 944 and 864]. All the observed signals exhibit the expected isotopic pattern.

Description of the Structure

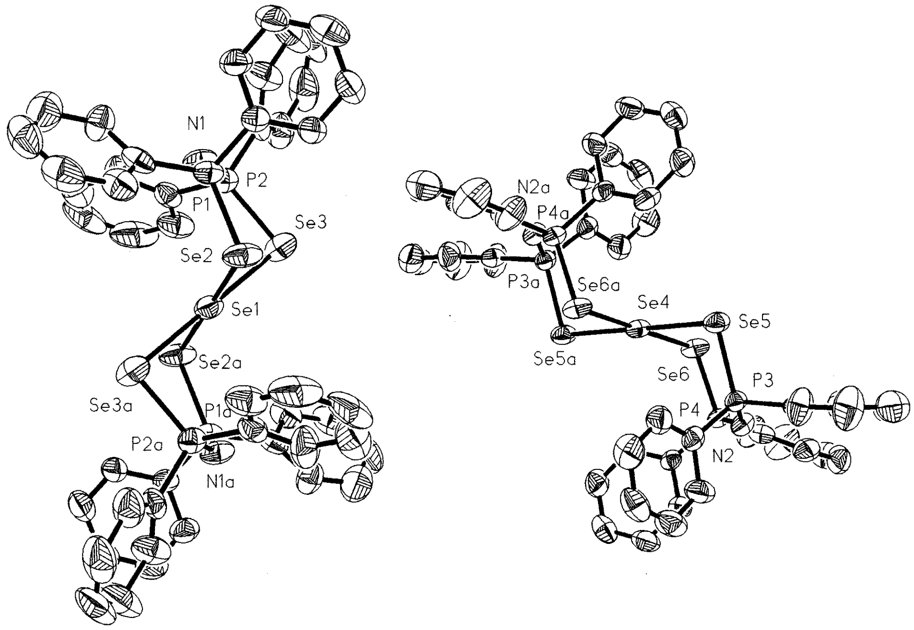
The structure is built of discrete neutral $[Se\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ molecules, the central selenium atom is coordinated to four other selenium atoms, forming two six-membered carbon-free chelate rings, in a typical spiro arrangement. There are two crystallographically independent molecules in the cell (**1a** and **1b**). According to the cell parameters, **1** is isomorphic with the yellow $[Sn\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ [a = 10.124(5), b = 13.085(4), c = 18.260 Å, α = 89.42(2), β = 82.75(2) , γ = 77.62(2)°] [4] and $[Te\{N(SPPh_2)_2\text{-}S,S'\}_2]$ [a = 10.187(1), b = 12.929(5), c = 18.282(3) Å, α = 89.04(2) , β = 82.98(1) , γ = 77.40(2)°][3]. Figure 1 presents the inner coordination sphere, with angles and distances for molecules **1a** and **1b**, whereas Figure 2

Figure 1. The inner coordination sphere in **1a** and **1b**



1a **1b**

Figure 2. ORTEP plot of **1a** and **1b**, independent molecules of $[Se\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$



1a **1b**

shows the molecular structures and atomic labelling scheme of compound **1**.

The most remarkable feature of the structure is the square planar character of the selenium coordination sphere. The $SeSe_4$ core is coplanar [Σ{Se−Se−Se} = 360°] with *trans*-Se−Se−Se angles of 180.0(1)°. There is a slight asymmetry in the Se−Se bond lengths in both molecules [long ones of 2.678(1) and 2.663(1) Å and short ones of 2.646(1) and 2.643(1) for **1a** and **1b**, respectively]. These values are similar with those found in polyselenide anions[14]. The Se···Se bite of 3.708(2) Å is intermediate between the values of 3.667(4) and 3.771(3) Å found in [Te{N($SPPh_2$)$_2$-*S,S′*}$_2$]. As in [Sn{N($SePPh_2$)$_2$-*Se,Se′*}$_2$], the main difference between molecules **1a** and **1b** lies in the Se−Se−P angle [96.3(1) and 88.7(1)° for **1a**, and 97.1(1) and 96.9(1)° for **1b**]. The values of the P−N−P angles for **1a** and **1b**, [139.5(5) and 136.4(5)°] are also extraordinary large − larger than that found in the free ligand [132.3(2)°][14]. Since it is expected that the coordination of the donor atoms should contract the angle, the opening is indicative of the high flexibility of the P−N−P system and explains the ability of this ligand to form unusual structures. The endocyclic Se−Se−Se angles [88.31(4) and 88.67(3)°] are smaller than the corresponding exocyciclic ones [91.69(4) and 90.46(3)°].

The existence of this new neutral square planar structure for a Se^{II} compounds, demonstrates the ability of the [$Ph_2P(Se)NP(Se)Ph_2$]$^-$ anion to fulfill the preferences imposed by the central atom, in function of the great flexibility of the phosphazenic system and the soft character of the donor atoms.

We thank the *Mexican National Council of Science and Technology*, CONACYT (Grant 109P-E) for financial support and Prof. Dr. *Husebye* for his comments and suggestions.

Experimental Section

The experiments were carried out with the exclusion of air and moisture, under argon.The solvents were purified and dried by the usual methods. Se{$S_2P(OiPr)_2$}$_2$][17] and bis[*N*-diphenylphosphanylselenoyl)-*P,P*-diphenylphosphanylselenoyl)amide[15] were prepared by literature methods. The latter was converted to its potassium salt by the reaction with KO*t*Bu according to a previously described procedure[16]. − ^{31}P NMR: Varian VXS 300S (121 MHz, external standard 85% H_3PO_4). − FAB MS (3-nitrobenzyl alcohol support): Jeol JMS-SX102A, positive-ion mode. − IR (KBr): Perkin-Elmer 283B. − Elemental analysis : Galbraith Laboratories.

Bis(imidotetraphenyldiselenodiphosphanyl-Se,Se′)selenium(II) (**1**): A solution of 3.0 g (5.1 mmol) of [K{N($SePPh_2$)$_2$}], in 50 ml of THF was added to a stirred solution of bis(diisopropyldithiophosphato)selenium(II) (1.30 g, 2.5 mmol) in 50 ml of THF. An orange solution was formed, the solvent was evaporated at low pressure and the obtained solid was washed with ethanol and filtered. 10% of the solid was subjected to a thin layer chromatographic separation using hexane/ethyl acetate as eluent (90:10). The less polar layer was separated and extracted with CH_2Cl_2 to obtain the desired compound (m. p. 210°C). Yield 62% (based on of the chromatographic separated portion). Crystals suitable for X-ray crystallography were obtained by solvent diffusion in a chloroform/*n*-hexane mixture at room temperature. − ^{31}P NMR ($CDCl_3$): δ = 34.35 (s). − IR (KBr): $\tilde{\nu}$ = 3053 cm^{-1} w [νCH)], 1211 s [νP−N)], 1177 s [ν(P−N)/δ(CH)], 744 m [ν(P−N)], 689 vs [ϕ(CC), Ph], 532 vs [γ(PNP)/ν(P−Se)]. − MS (FAB$^+$, $CHCl_3$, for ^{80}Se); *m/z*: 1164 [M$^+$], 1087 [M − Ph$^+$], 622 [Se{N($SePPh_2$)$_2$}$^+$], 544 [($SePPh_2$)$_2$-N $^+$], 464 [Se(PPh_2)$_2$N$^+$], 384 [(PPh_2)$_2$N$^+$], 307 [(Ph_2PNPPh^+]. − $C_{48}H_{40}N_2P_4Se_5$ (1163.5): calcd. C 49.55, H 3.46; found C 49.11, H 3.36. − Mol. mass 1164 (FAB MS; CH_3Cl for ^{80}Se).

Crystal-Structure Analysis: Data collection was performed at room temperature with a Siemens P4 four-circle diffractometer by using graphite-monochromated Mo-K_α radiation ((= 0.71073 Å). Crystal Data: $C_{48}H_{40}N_2P_4Se_5$, M = 1163.5, orange prisms, 0.24 × 0.20 × 0.12 mm; triclinic, space group $P\bar{1}$ (No. 2), a = 10.158(2), b = 13.090(2), c = 18.239(5) Å, α = 89.42(2), β = 82.56(2), γ = 77.72(2)°, V = 2349.4(1) Å^3, Z = 2, D_x = 1.645 Mg m^{-3}, μ(Mo-K_α) = 4.070 mm^{-1}, T = 293 K, F(000) = 1144, number of reflections: 8742 (8231 independent, R_{int} = 0.048), $R(F)$ = 0.041, $wR(F)$ = 0.034 (536 parameters). Structure Solution and Refinement: The structure was solved by direct methods and refined by full-matrix least-squares calculations using the program system SHELXTL-Plus (PC-version)[18]. Absorption effects were corrected by face-index numerical methods. H atoms were refined using a riding model (U = 0.06), while non-hydrogen atoms were refined anisotropically. The crystal structure data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101279. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int code + 44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

☆ Dedicated to Professor *Heinrich Nöth* on the ocassion of his 70th birthday.

[1] M. R. Churchill, J. Wormald, *Inorg. Chem.* **1971**, *10*, 1778. − M.R. Churchill, J. Cooke, J.P. Fennessey, J. Wormald, *Inorg. Chem.* **1971**, *10*, 1031.

[2] I. Rodríguez, C. Alvarez, J. Gómez-Lara, R. Cea-Olivares, *Lanthanide Actinide Res.* **1985-6**, *1*, 253. − N. Platzer, H. Rudler, C. Alvarez, L. Barkaoui, B. Denise, N. Goasdoué, M. N. Rager, J. Vaissermann, J. C. Daran, *Bull. Soc. Chim. Fr.* **1995**, *132*, 95.

[3] S. Bjørnevåg, S. Husebye, K. Maartmann-Moe, *Acta Chem. Scand. A* **1982**, *36*, 195.

[4] R. Cea-Olivares, J. Novosad, J. D Woollins, A. M. Z. Slawin, V. García-Montalvo, G. Espinosa Pérez , P. García y García. *J. Chem. Soc., Chem. Comm.* **1996**, 519. − V. García-Montalvo, J. Novosad, P. Kilian, J. D. Woollins, A. M. Z. Slawin, P. García y García, M. López-Cardoso, G. Espinosa-Pérez, R. Cea-Olivares, *J. Chem. Soc., Dalton Trans.* **1997**, 1025.

[5] N. J. Brøndmo, J. Esperås, S. Husebye, *Acta Chem. Scand. A* **1975**, *29*, 93. − H. Graver, S. Husebye, *Acta Chem. Scand. A* **1975**, *29*, 14.

[6] S. Husebye, K. Maartmann-Moe, *Acta Chem. Scand. A* **1983**, *37*, 219.

[7] R. O. Gould, C. L. Jones, E. J. Savage, T. A. Stephenson, *J. Chem. Soc., Dalton Trans.* **1976**, 908.

[8] S. Husebye, G. Helland-Madsen, *Acta Chem. Scand. A* **1969**, *23*, 1398.

[9] Y. Masaki, K. Kobayashi, *Tetrahedron Lett.* **1989**, *30*, 2813.

[10] H. U. Hummel, E. Fischer, T. Fischer, D. Gruss, A. Franke, W. Dietzsch, *Chem. Ber.* **1992**, *125*, 1565.

[11] M. G. Kanatzidis, S. P. Huang, *Coord. Chem. Rev.* **1994**, *130*, 509.

[12] C. Adamo, F. Demartin, P. Deplano, F. A. Devillanova, F. Isaia, F. Lelj, V. Lippolis, P. Lukes, M. L. Mercuri, *J. Chem. Soc., Chem. Comm.* **1996**, 873.

[13] R. Cea-Olivares, V. García-Montyalvo, J. Novosad, J. D. Woolllins, R. A. Toscano, G. Espinosa-Pérez,. *Chem. Ber.* **1996**, *129*, 919, and references cited therein.

[14] V. Krishnan, R. A. Zingaro, *Inorg. Chem.* **1969**, *8*, 2337. – J. Ellermann, A. A. M. Demuth, W. Bauer, *Z. Naturforsch., B* **1986**, *41*, 863. – J. Ellermann, J. Sutler, F. A. Knoch, M. Moll, *Chem. Ber.* **1994**, *127*, 1015.

[15] P. Bhattacharyya, J. Novosad, J. Phillip, A. M. Z. Slawin, D. J. Williams, J. D. Woollins, *J. Chem. Soc., Dalton Trans.* **1995**, 1607.

[16] A. Schmidpeter, H. Groeger, *Z. Anorg. Allg. Chem.* **1966**, *345*, 106.

[17] S. Husebye, *Acta Chem. Scand. A* **1965**, *19*, 1045.

[18] Siemens, *SHELXTL PLUS, Release 4.0*, for Siemens R3 Crystallographic, Madiso, WI, **1998**.

[98074]