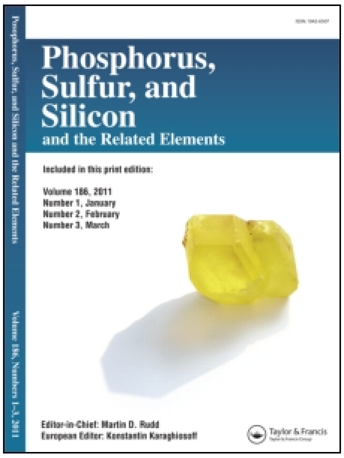

Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

Structural Diversity of [M{N(SePPh$_2$)$_2$-*Se, Se*'}2,3] [M(II) = Sn, Pb, Cd, Hg, Se ; M(III)= In, Sb, Bi].

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To cite this Article Cea-Olivares, Raymundo , Montalvo, Verónica García , Novosad, Josef , Kilian, Petr , Woollins, Derek J. , Slawin, Alexandra M. Z. , García, Patricia García y. , López-Cardoso, Marcela , Espinosa-Pérez, Georgina , Toscano, Rubén-Alfredo , Hernández, Simón , Canseco-Melchor, Graciela , Lima-Montaño, Leticia and Rodríguez-Nárvaez, Cristina(1997) 'Structural Diversity of [M{N(SePPh$_2$)$_2$-*Se, Se*'}2,3] [M(II) = Sn, Pb, Cd, Hg, Se ; M(III)= In, Sb, Bi].', Phosphorus, Sulfur, and Silicon and the Related Elements, 124: 1, 347 — 354

To link to this Article: DOI: 10.1080/10426509708545640

URL: http://dx.doi.org/10.1080/10426509708545640

Phosphorus, Sulfur, and Silicon, 1997, Vol. 124 & 125, pp. 347–354
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STRUCTURAL DIVERSITY OF [M{N(SePPh$_2$)$_2$-*Se, Se'*}$_{2,3}$] [M(II) = Sn, Pb, Cd, Hg, Se ; M(III)= In, Sb, Bi].

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The anion [N(SePPh$_2$)$_2$]$^-$ forms stable complexes with cations M(II, III); [M(II) = Sn, Se, Cd, Hg; M(III) = In, Sb, Bi], they exhibit a large diversity of structural arrangements around the metal centre. Tin(II) complex crystallizes dimorphically, as square planar and distorted tetragonal pyramidal, Pb(II) is also distorted tetragonal pyramidal, Cd(II) and Hg(II) are tetrahedral, but the Se(II) is square planar. The coordination geometry in the M(III) complexes can be described as a distorted octahedron. The structural situation around the Sb(III) and Bi(III) suggests a stereochemically non-active electron lone pair.

Keywords: Phosphazene metallacycles / Selenium ligands / Main group complexes / Sn(II) square planar.

INTRODUCTION

The anionic phosphazenic ligands $[R_2P(X)NP(X')R_2]^-$ (R = Ph, alkyl; X = X' = O, S, Se, or their combinations), are able to form inorganic (carbon free) chelate rings with many transition and main group cations. In function of the high flexibility of the PNP angle and the X•••X' large bite, such ligands are specially suitable for testing the presence of a stereochemically active lone pair, in main group complexes, or in general to test the cation "true preferences" for a special geometry. They produce very interesting complexes, as some tetrahedral Ni(II) and Fe(II) derivatives,[1] true square planar Se(II) and Te(II) complexes[2-3] or the quite unusual non-solvated six-coordinate lanthanide complexes[4].

The complexes with the anions $[Ph_2P(X)NP(X)Ph_2]^-$ (X = O, S) are well known, however, the corresponding diselenide ligand has been much less studied, may be the problem was the difficulties in the reported preparation for such ligand. Recently, some of us informed an easy synthetic method[5] .The soft character of the selenium donor atoms, its tendency to present Se•••Se interactions and of course the high degree of ring flexibility of the formed chelate ring, prompted us to test the possible structural diversity of the main group complexes with such exciting ligand.

In three different papers,[6-8] as well as in the 8th Inorganic Rings Systems Symposium (IRIS VIII) we presented some of our results.

RESULTS AND DISCUSSION

All complexes and starting materials were obtained as described in references [5-8], with the exception of [Se{N(SePPh$_2$)$_2$-*Se*,*Se*'}$_2$] which was obtained from the reaction between [Se{S$_2$P(O-*i*Pr$_2$)$_2$}$_2$] and [K{N(SePPh$_2$)$_2$]. The complexes are discrete molecules, the only compound with intermolecular interactions is the yellow isomer of [Sn{N(SePPh$_2$)$_2$-*Se*,*Se*'}$_2$].

The mixture of solutions of tin(II) chloride and [K{N(SePPh$_2$)$_2$]. produces a yellow precipitate, [Sn{N(SePPh$_2$)$_2$-*Se*,*Se*'}$_2$], however during the process of crystal growing we isolate two types of crystals, in higher proportion yellow ones, that corresponds to the first example of a spiro square-planar tin(II) compound and red crystals with a typical distorted pyramidal geometry. Figure 1.

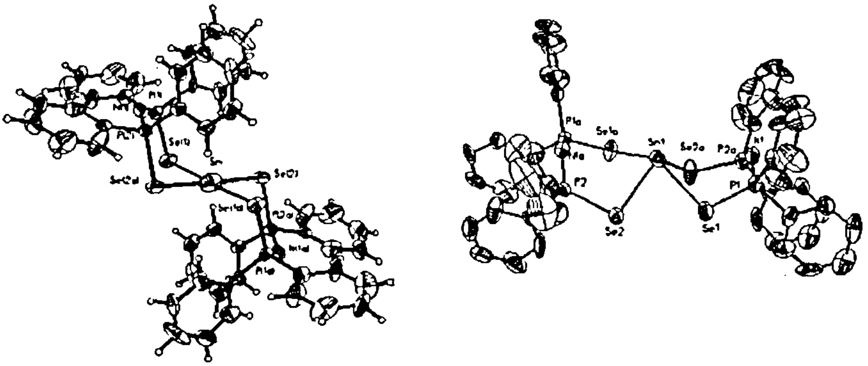

FIGURE 1. Molecular structure of the square planar and distorted tetragonal pyramidal isomers of [Sn{N(SePPh$_2$)$_2$-*Se*, *Se*'}$_2$].

The yellow isomer exhibit two crystallographically independent molecules, the main difference between these molecules lies in the Sn-Se-P angles, [97.0°, 96.8° for the first molecule and 96.4° and 88.5° for the second one], the P-N-P angles in both molecules are wider [136.2° and

138.7°] than in the free ligand [132.3°]. The conformation of the six membered ring is a distorted chair, like such found by Prof. Husebye in the square-planar selenium(II) and tellurium(II) complexes, [(Se)(Te){N(SPPh$_2$)$_2$-*S,S'*}$_2$][2-3]. The reasons for the stabilisation of such strange square planar geometry in the yellow isomer of [Sn{N(SePPh$_2$)$_2$-*Se,Se'*}$_2$] is related with the presence of tricentric orbitals, Se-Sn-Se, and intermolecular contacts between the selenium and hydrogen atoms from the two neighbouring and crystallographically different molecules. Of course all is supported by the flexibility and large bite of the di- selenium ligand. The structure of the red isomer of [Sn{N(SePPh$_2$)$_2$-*Se,Se'*}$_2$], is the expected one, trigonal bipyramid distorted towards a tetragonal pyramid. The structure of the lead(II) complex is practically identical with the Sn(II) red isomer, in both compounds the MSe$_2$P$_2$N chelate rings present a distored boat conformation. The geometry in the Cd(II) and Hg(II) derivatives is also quite normal, a distorted tetrahedral arrangement, with small deviations from the tetrahedral values. Figure 2 shows the structures of the Pb(II) and the Hg(II) complexes.

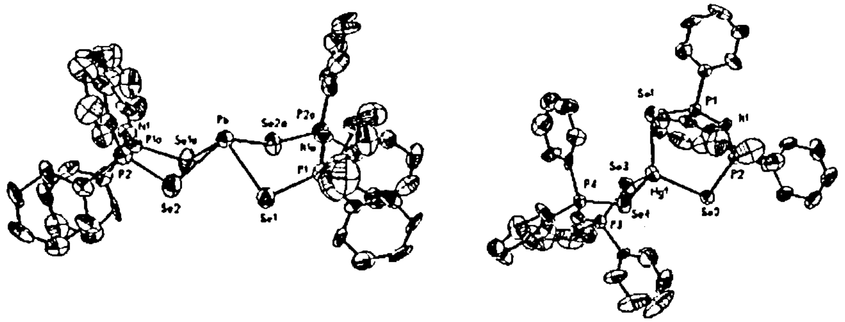

FIGURE 2. Molecular structure of [Pb{N(SePPh$_2$)$_2$-*Se, Se'*}$_2$] and [Hg{N(SePPh$_2$)$_2$-*Se, Se'*}$_2$].

Recently, in order to compare with the sulphur analogue, we obtained the per-selenated compound, $[Se\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$, such compound presents a very interesting $SeSe_4$ core in a square planar arrangement. Figure 3. The cell exhibit two crystallographically independent molecules, almost identical. The co-ordination of the ligand in this Se(II) complex is practically isobidentate, the values of the *trans* bond angles Se-Se-Se are 180.0(1)°, the *intra*-ligand Se-Se-Se angles of 88.3(1)° and 88.6(1)°, while the *inter*-ligand angles, are 91.7(1)° and 91.4(1)° ,respectively for both molecules. The situation is much more symmetrical than in $[Se\{N(SPPh_2)_2\text{-}S,S'\}_2]$, in such compound the SeS_4 molecular core presents an anisobidentate behaviour, with two short, and two long, weak Se-S bonds. The *trans* angles S-Se-S have an average value of 172.24(33)°[2].

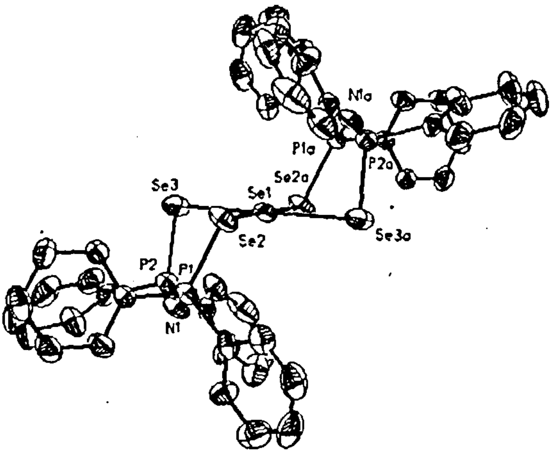

FIGURE 3. Molecular structure of $[Se\{N(SePPh_2)_2\text{-}Se, Se'\}_2]$.

The octahedral co-ordination mode of the $[M(III)\{N(SePPh_2)_2\text{-}Se,Se'\}_3]$ complexes (M = In, Sb, Bi) is much more symmetrical in the case of the In(III) complex than in the Sb(III) and Bi(III) ones, in these last two compounds the co-ordination mode is asymmetrical chelating, with two distinct sets of M-Se bond lengths, but in the In(III) derivative all the In-Se bonds are approximately equal. Figure 4 presents the structure of the indium and antimony complexes. In the three M(III) compounds, the conformation of the six membered chelate rings corresponds to a distorted boat, all distances Se---Se are longer than the sum of the van der Waals radii. The geometry of the $[\mathrm{Bi}\{\mathrm{N(SePPh_2)_2}\text{-}Se,Se'\}_3]$ and $[\mathrm{Sb}\{\mathrm{N(SePPh_2)_2}\text{-}Se,Se'\}_3]$ suggests that the lone pair is stereochemically inactive, in agreement with the Wynne theory about the geometry of the compounds $[\mathrm{MX_6E}]$[9].

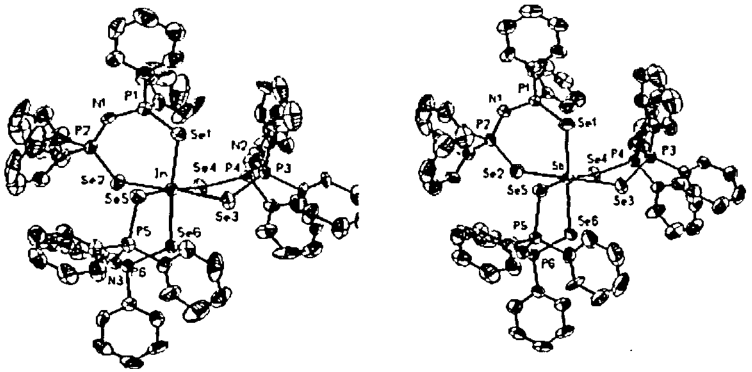

FIGURE 4. Molecular structure of $[\mathrm{In}\{\mathrm{N(SePPh_2)_2}\text{-}Se, Se'\}_3]$ and $[\mathrm{Sb}\{\mathrm{N(SePPh_2)_2}\text{-}Se, Se'\}_3]$.

CONCLUSIONS

The structural diversity of the main group complexes with the selenated anionic ligand, $[\mathrm{N(SePPh_2)_2}]^-$ is very high, going for the M(II) cations, from almost perfect square planar [Sn(II) yellow isomer, Se(II)] to tetrahedral [Cd(II), Hg(II)], passing through the distorted tetragonal pyramidal geometry [Sn(II) red isomer, Pb(II)]. For the M(III) complexes, we made a comparison between two cations of the Group 15, Sb and Bi, with the possible presence of a lone pair stereochemically active, that is a MX$_6$E systems, and the corresponding In(III) complex, that is, a cation without lone pair. The structural evidences are that in [M{N(SePPh$_2$)$_2$-*Se,Se'*}$_3$] [M = Sb, Bi] the lone pair is not stereochemically active.

Acknowledgments

We are grateful to the Mexican National Council of Science and Technology for financial support through a grant (0109PE) and fellowships to some of the participants.

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