A true square-planar tin(II) spiro complex: molecular structure of bis(imidotetraphenyldiselenodiphosphino-*Se,Se′*)tin(II) and its distorted tetragonal-pyramidal isomer

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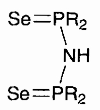
The yellow complex $[Sn\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$ is the first example of a true square-planar spiro tin(II) compound; the structure of the distorted tetragonal-pyramidal isomer is also described.

It is well known that tin(II) compounds are bent, pyramidal and mostly distorted, and there are few examples of tin(II) compounds where the lone pair is not stereochemically active.[1] We report here the synthesis and characterisation of the first example of a true square-planar tin(II) complex, the yellow $[Sn\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$.

Systematic structural studies upon the ligand behaviour of the anions $[R_2P(X)NP(X)R_2]^-$, (R = Me, Ph; X = O, S, Se), show that they are suitable for testing the presence of a stereochemically active lone pair in main group complexes[2,3] as well as the theories about the geometry of the main group metal complexes that result from the presence of a ligand with a large bite and a large degree of conformational freedom due to the variable M–X–P angle and PNP conjugated system.[4] Furthermore, these ligands have enabled the preparation of anhydrous lanthanide complexes from aqueous solutions.[5] They are also able to form complexes with unusual structures, *e.g.* the tetrahedral carbon-free chelate complexes $[M\{N(SPMe_2)_2\text{-}S,S'\}_2]$ (M = Ni, Fe[6]), $[Mn\{N(SePPh_2)_2\text{-}S,S'\}_2]$,[7] the true square-planar tellurium(II) complex $[Te\{N(SPPh_2)_2\text{-}S,S'\}_2]$,[4] the quasi-ideal *trans*-octahedral geometry found in the organometallic complexes $[Sn\{N(XPPh_2)_2\text{-}X,X'\}_2R_2]$ (R = Me, Bu^n, X = O, S, Se),[8] or the six-coordinate lanthanide complexes.[9]

In contrast to the large number of known complexes with the anions $[Ph_2P(X)NP(X)Ph_2]^-$ (X = O,S), the diselenide ligand (**1**) has not been studied as much and only in the case of transition metals.[10] Recently, some of us reported an easy preparation method for such a diselenide ligand.[11] As expected, the palladium(II) and platinum(II) complexes with **1** are square planar,[11] as in the nickel(II) complex.[12] This situation is quite interesting, because the related $[Ni\{N(SPPh_2)_2\text{-}S,S'\}_2]$ complex shows a distorted tetrahedral geometry.[11] The structure of $[Sn\{N(OPPh_2)_2\text{-}O,O'\}_2]$ in the solid state corresponds to a distorted Ψ-tbp and it is fluxional in solution.[13] The tendency of the flexible anions $[R_2P(X)NP(X)R_2]^-$ to generate metal complexes with unusual structures, and the observation of the square-planar character of the $[Ni\{N(SPPh_2)_2\text{-}S,S'\}_2]$ complex together with the absence of a stereochemically active lone pair in SnSe, prompted us to synthesise $[Sn\{N(SePPh_2)_2\text{-}Se,Se'\}_2]$, in the hope of obtaining the first example of a molecular spiro square-planar tin(II) complex.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The compound $[Sn\{N(SePPh_2)_2\text{-}Se,Se'\}_2$ **1** was very easily obtained, as a yellow powder,† from $SnCl_2$ and $K[N(SePPh_2)_2]$. During the process of crystal growth, we also grew a small quantity of red crystals (compound **2**). **1** is a square-planar complex and **2** is a highly distorted tetragonal-pyramidal isomer.

A single-crystal structural analysis of **1**‡ establishes that it consists of discrete molecules of two crystallographically independent molecules, 1 (Fig. 1) and 1′. The most important feature of the structure is the square-planar character of the Sn^{II} atom. The $SnSe_4$ system is coplanar [Σ(Se–Sn–Se) = 360°] with *trans* Se–Sn–Se angles of 180.0(0)°, the Sn–Se bond lengths are asymmetric. In each chelate ring there are two types of Sn–Se bonds, long ones [2.662(2) and 2.681(3)Å] and short ones [2.643(3) and 2.634(3)Å] for complexes 1 and 1′ respectively. This inequivalence is similar to that found in the palladium(II) and platinum(II) complexes with this diselenium ligand. The main difference between molecules 1 and 1′ lies in the Sn–Se–P angles: the values of such angles for 1 are equal,

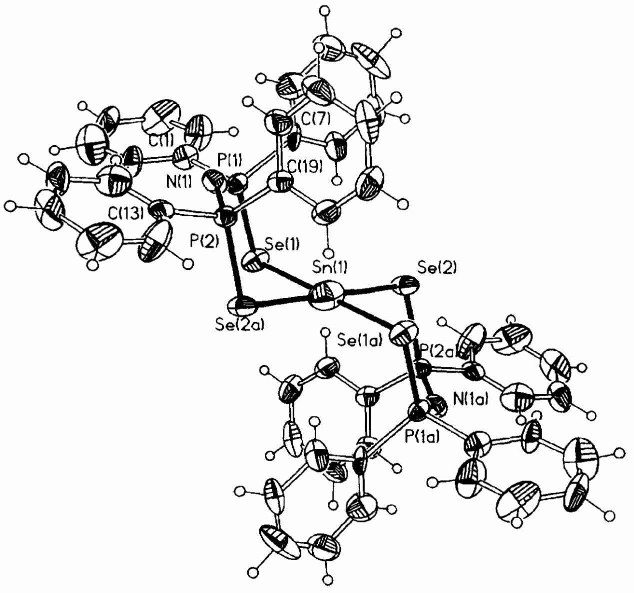

Fig. 1 Selected bond distances (Å) and angles (°) for complex **1**. Sn(1)–Se(1) 2.643(3), Sn(1)–Se(2) 2.662(2), Sn(1)–Se(1a) 2.643(3), Sn(1)–Se(2a) 2.662(2), Se(1)–P(1) 2.173(6), Se(2)–P(2a) 2.177(6), Se(1)–Sn(1)–Se(2) 91.6(1), Se(1)–Sn(1)–Se(1a) 180.0(1), Se(2)–Sn(1)–Se(1a) 88.4(1), Se(1)–Sn(1)–Se(2a) 88.4(1), Se(2)–Sn(1)–Se(2a) 180.0(1), Se(1a)–Sn(1)–Se(2a) 91.6(1), P(1)–N(1)–P(2) 136.2(13).

[97.0(2), 96.8(2)°], whereas in 1′ they are very different [96.4(2) and 88.5(2)°], this second value is also very short in comparison with the 100 and 108° for the homologous compounds with palladium(II) and platinum(II). As usual in this type of compound, the P–Se distances in 1 and 1′ are longer than in the free ligand, whilst the P–N bond lengths are shorter.

The values of the P–N–P angles [136.2(1) and 138.7(12)°] for 1 and 1′ respectively are extraordinary large, wider than in the free ligand [132.3(2)°], and are indicative of the high flexibility of the phosphazene system, since it is expected that the coordination of the selenium atoms should contract the angle, as happens in the compounds with Pd and Pt. However, these large P–N–P angles are not related to a corresponding unusually large value of the Se···Se bite. The bite values of 3.697(4) and 3.692(4) Å for 1 and 1′ respectively, are not very far from the values of 3.667(4) and 3.771(3) Å found in Te[{N(SPPh$_2$)$_2$-*S,S′*}$_2$]. The endocyclic Se–Sn–Se angles [88.4(1), 88.0(1)°] are lower than the corresponding exocyclic ones [91.6(1) and 92.0(1)°]. It is possible to say that from the structural point of view, the high flexibility of the P–N–P angle in conjunction with the soft character of the selenium donor atoms are responsible of this unusual tin(II) structure. The bonding in the linear Se–Sn–Se systems is probably of the three-centre four-electron type, which would be satisfactory given the highly polarizable character of the selenium atoms. The possibility of the presence of a hydride compound of the type [Sn{N(SePPh$_2$)$_2$-*Se,Se′*}$_2$H$_2$] was discarded in the solid state, because we did not find any electron density above and below the Sn^{II} atom and there are no especially short intermolecular contacts involving the metal atom. The only contacts between the molecules correspond to short distances between selenium atoms and hydrogens of the phenyl rings. In solution, ^{1}H NMR spectroscopy shows no hydride protons, and the ^{119}Sn NMR spectrum was unchanged with or without proton decoupling. We thus consider that **1** is a true square-planar compound.

The single crystal structure determination of the red crystals of compound **2**§ showed that it corresponds to a distorted tetragonal-pyramidal molecule (Fig. 2) with the possible stereochemical presence of the lone pair. The chelate rings present two types of Sn–Se bonds, long ones of 2.943(2) Å and short ones of 2.803(2) Å, both values being larger than the Sn–Se bond lengths in **1**. The P–N–P angle of 129.3(10)° is smaller than that in the free ligand.

Further studies on the conversion of the square-planar compound into the tetragonal-pyramidal isomer as well as new main group and transition-metal complexes with this imido-tetraphenyldiselenodiphosphino ligand are in progress in our laboratories.

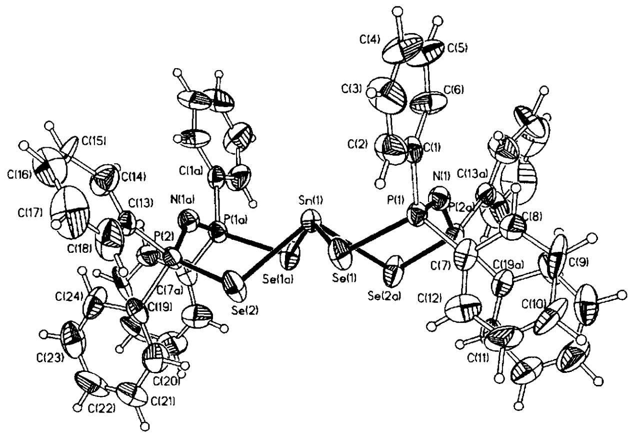

Fig. 2 Selected bond distances (Å) and angles (°) for complex **2**. Sn(1)–Se(1) 2.943(2), Sn(1)–Se(2) 2.803(2), Sn(1)–Se(1a) 2.943(2), Sn(1)–Se(2a) 2.803(2), Se(1)–P(1) 2.161(5), Se(2)–P(2) 2.188(5), Se(1)–Sn(1)–Se(2) 71.4(1), Se(1)–Sn(1)–Se(1a) 143.6(1), Se(2)–Sn(1)–Se(1a) 88.5(1), Se(1)–Sn(1)–Se(2a) 88.5(1), Se(2)–Sn(1)–Se(2a) 112.7(1), Se(1a)–Sn(1)–Se(2a) 71.44(1). P(1)–N(1)–P(2a) 129.3(10).

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Footnotes

† *Synthesis of* [Sn{N(SePPh$_2$)$_2$-*Se,Se′*}$_2$]. Anhydrous SnCl$_2$ (50 mg, 0.264 mmol) was dissolved in MeOH (5 ml), and added slowly by stirring into a methanolic solution of K[N(SePPh$_2$)$_2$] (307 mg, 0.528 mmol). A solid precipitated almost immediately, but the stirring was continued for 30 min. The bright yellow solid was filtered off from the methanolic solution and washed with methanol and diethyl ether. Yield 270 mg, 85% (Found: C, 47.82; H, 3.34. Calc. for $C_{48}H_{40}N_2P_4Se_2Sn$: C, 47.91; H, 3.35%).

Selected spectroscopic data: NMR (CDCl$_3$): ^{31}P{^{1}H}, δ 31.7; ^{119}Sn, δ −179.1 [qnt, $^2J(^{119}\text{Sn}–^{31}\text{P})$ 95 Hz]; ^{77}Se (ext. ref. Ph$_2$Se), δ 9.8 [d, $^1J(^{77}\text{Se}–^{31}\text{P})$ 560.7 Hz]. FAB-MS *m/z* 1206 ($C_{48}H_{40}N_2P_4{}^{80}Se_2{}^{118}Sn$), 544 (free anion). IR (KBr, cm^{-1}): ν(P$_2$N) 1172m, 800m; ν(P=Se) 535.

X-Ray quality yellow crystals of **1** were obtained by solvent diffusion from CHCl$_3$–*n*-hexane. It was observed that during the growing process some red crystals of **2** were also formed.

‡ *Crystal data* for **1**: $C_{48}H_{40}N_2P_4Se_4Sn$, *M* = 1203.2. Colour, habit: yellow, prism. Triclinic, space group $P\bar{1}$, *a* = 10.124(5), *b* = 13.085(4), *c* = 18.260(4) Å, α = 89.42(2), β = 82.75(2), γ = 77.62(2)°, *U* = 2234.3(17) Å^3, *Z* = 2, D_c = 1.705 g cm^{-3}, μ(Mo-Kα) = 3.824 nm^{-1}. Crystal dimensions: 0.36 × 0.28 × 0.18 mm. Data were measured at 293 K on a Siemens P4 automatic diffractometer with a highly oriented graphite crystal-monochromated Mo-Kα radiation using ω scans. The structure was solved by direct methods and refined using absorption corrected (ψ-scans) data to give R_1 = 0.0854 for 8145 independent observed reflections [$F > 4.0\sigma(F)$] and 536 parameters. The crystal structure determination was also made on another crystal using a Rigaku AFC7S diffractometer, with Cu-Kα radiation, the results and the R_1 value (0.085) were the same as with the Mo-Kα radiation.

§ *Crystal data* for **2**: $C_{48}H_{40}N_2P_4Se_4Sn$, *M* = 1203.2. Colour, habit: red, octahedron. Tetragonal, space group $P4_32_12$, *a* = 10.250(2), *c* = 43.882(6) Å, *U* = 4610.8(14) Å^3, *Z* = 2, D_c = 1.733 g cm^{-3}, μ(Mo-Kα) = 3.887 nm^{-1}. Crystal dimensions: 0.48 × 0.32 × 0.28 mm. Data were measured as with **1**, to give R_1 = 0.0779 for 6498 independent observed reflections [$F > 4.0\sigma(F)$] and 267 parameters. For both crystals, atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

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