Synthesis and Crystal Structure of a Salt containing the *trans*-Diphenyldi-μ-seleno-diselenodistannate(2−) Anion *

Sandrine Sportouch, Monique Tillard-Charbonnel and Claude Belin
Laboratoire des Agrégats Moléculaires et Matériaux Inorganiques, URA 79, Université de Montpellier II, Sciences et Techniques du Languedoc, 2, Place Eugène Bataillon, 34095 Montpellier Cédex 5, France

The salt $[PPh_4]_2[Sn_2Ph_2Se_4]$ was prepared by reduction of an alloy of nominal composition $Bi_2Sn_3Se_6$ by potassium in the presence of tetraphenylphosphonium bromide. Its structure has been determined by single-crystal X-ray diffraction. The anion $[Sn_2Ph_2Se_4]^{2-}$ contains a square-planar Sn_2Se_4 ring, *exo*-selenium atoms and the phenyl groups are attached, in a *trans* configuration, to tin atoms which are approximately tetrahedrally co-ordinated. The stability of the experimental *trans* geometry as well as that of the alternative *cis* configuration of the anion has been investigated by means of extended-Hückel molecular-orbital calculations.

The chemistry of organotin compounds has been considerably developed over the last 30 years as a result of their wide range of applications.[1] Tin–selenium compounds have been much less investigated than their sulfur analogues. The organotin sulfides, selenides or tellurides can be prepared by treating the corresponding organotin chlorides with sodium sulfide, selenide or telluride.[2] Insertion of sulfur, selenium or tellurium into a metal–metal bond for example Sn–Sn or Sn–Li is a well known chemical reaction. Triphenylstannyl lithium reacts with sulfur, selenium or tellurium to form SnLiX which is used with triphenyltin chloride to give the corresponding SnXSn compound.[3] The compound Sn_2Me_6 reacts directly with sulfur to form $(Me_3Sn)_2S$.[2] Many of these compounds exist in the solid state as polymeric species: di-*tert*-butyltin selenide is a dimer with a planar central ring Sn_2Se_2,[4] methyltin sesquisulfide has been isolated as a tetramer with an adamantane-like structure.[5]

Recently the compound $Sn_3Cl[Fe(CO)_2(\eta\text{-}C_5H_5)]_3Se_4$ was synthesized by treating the corresponding tin chloride with Na_2Se in tetrahydrofuran (thf); it contains a bicyclic Sn_3Se_4 framework.[6] Reaction of SnR_2Cl_2 [R = $Fe(CO)_2(\eta\text{-}C_5H_5)$ or $Mo(CO)_3(\eta\text{-}C_5H_5)$] with $Te(SiMe_3)_2$ yields $Sn_2R_4Te_2$ containing a planar Sn_2Te_2 ring, and $Sn_4R_4Te_6$ with an adamantane-like Sn_4Te_6 skeleton.[7] Numerous tin–selenium anionic frameworks are encountered in inorganic compounds: the three-dimensional polymeric $[Sn_2Se_5]^{2-}$ anion is found in $K_2[Sn_2Se_5]$ and $Rb_2[Sn_2Se_5]$,[8,9] and $Cs_2[Sn_3Se_7]$ contains polyselenostannate(IV) sheet anions $[Sn_3Se_7]^{2-}$.[10] The discrete polyselenostannate anions $[SnSe_4]^{4-}$,[11] $[Sn_2Se_3]^{2-}$,[12] $[Sn_2Se_6]^{4-}$,[13] $[Sn_2Se_7]^{6-}$ [14] and $[Sn_3Se_8]^{4-}$ [15] have also been isolated in the solid state. The geometry of $[Sn_2Ph_2Se_4]$ described herein is closely related to those of the selenodistannate anions cited above.

Experimental

The preparation of the present compound was performed in several steps. An alloy of nominal composition $Bi_2Sn_3Se_6$ was prepared by allowing the elements to react at 700 °C in an evacuated silica reactor. Ethylenediamine was dried on calcium hydride, then distilled under vacuum into a Pyrex flask containing small pieces of sodium, and thereafter distilled from it for utilization. Tetraphenylphosphonium bromide (synthesis grade) was used as received from Merck laboratories. Powdered $Bi_2Sn_3Se_6$ (4.21×10^{-4} mol) was allowed to react with potassium in molar ratio 1 : 1 in ethylenediamine (25 cm^3). The initially colourless solution was stirred for 2 d until it became yellow, then a slight excess of PPh_4Br was added and the solution stirred again for 3 d until the potassium was consumed. The light green solution was filtered to eliminate precipitated K_2Se and KBr as well as the unreacted alloy and, after slow evaporation, yellow crystals were deposited in *ca.* 13% yield. Qualitative electron microprobe analysis of a single crystal indicated the presence of P, Sn, Se in the approximate ratio 1.3 : 1.0 : 2.5; bismuth was not detected. Single crystals were checked by the Weissenberg X-ray diffraction technique and the most suitable one was selected for crystal structure determination.

Crystallography.—Crystal data. $[PPh_4]_2[Sn_2Ph_2Se_4]$, M_r = 1385.8, monoclinic, space group $P2_1$, a = 11.980(5), b = 13.722(2), c = 17.664(3) Å, β = 109.21(2)°, U = 2742(1) Å^3 (by least-squares refinement on diffractometer angles for 25 automatically centred reflections, graphite-monochromated Mo-Kα, λ = 0.710 69 Å), Z = 2, $F(000)$ = 1352, D_c = 1.68 g cm^{-3}, dimensions 0.20 × 0.20 × 0.15 mm, μ(Mo-Kα) = 38.4 cm^{-1}.

Data collection and processing. Intensity data were collected by the ω–θ technique, with ω scan width = 1 + 0.35 tan θ on a Nonius CAD-4 diffractometer in the range $4 \leqslant 2\theta \leqslant 50°$ within the octants $h\ k\ l$ and $h\ k\ -l$. 4755 Reflections were recorded of which 1642 with $I > 3\sigma(I)$ were used in the refinement. The data were corrected for background and Lorentz-polarization, and numerical absorption corrections were applied using the program SHELX 76.[16]

Structure analysis and refinement. In a first step, the structure was solved by direct methods in the centrosymmetric space group $P2_1/c$. Although the structure refined, overall, fairly well, the phenyl groups were found slightly disordered with respect to the inversion centre. This problem was overcome by lowering the symmetry to that of the non-centrosymmetric subgroup $P2_1$. Full-matrix least-squares refinements were carried out using SHELX 76 to a final $R(F)$ of 0.030 (R' = 0.038), using the weighting scheme $w = 1/[\sigma^2(F) + 0.0032\,F^2]$ with anisotropic thermal parameters for selenium, tin and phosphorus, and

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* *Supplementary data available* (No. SUP 57101, 5 pp.): ^{31}P NMR and IR spectra, X-ray powder diffraction patterns. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI unit employed: eV ≈ 1.60×10^{-19} J.

isotropic ones for light atoms. The carbon atom positions in each phenyl group were refined using the regular hexagon-fitting procedure of the SHELX 76 program with free individual isotropic thermal parameters. Hydrogen atoms were included as fixed atoms in idealized positions with fixed thermal parameters (U_{iso} = 0.050 Å^2). Since the crystal is non-centrosymmetric and Sn as well as Se atoms provide enough anomalous dispersion, the absolute configuration of the structure was established by inversion of the atomic coordinates. The parameters in Table 1 give a 0.7% reduction in both *R* and *R'*.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

The molecular structure of $[Sn_2Ph_2Se_4]^{2-}$ is depicted in Fig. 1 atomic coordinates are given in Table 1, and the main bond distances and angles in Table 2.

The arrangement around the tin atoms deviates from ideal tetrahedral geometry. The Sn–C bond lengths of 2.18(2) and 2.15(1) Å are similar to those observed in other phenyltin complexes,[17] and the bond angles around the tin range from 94.0 to 120.4°. Owing to its pseudosymmetry, the intramolecular Sn_2Se_2 ring is planar with Sn–Se–Sn angles of 86.3 and 85.7°, which are nearly 2° smaller than those observed in the planar ring in *trans*-$[Sn\{C_6H_2[CH(SiMe_3)_2]\text{-}2,4,6\}(C_6H_2Me_3\text{-}2,4,6)Se]_2$.[18] The Sn–Se–Sn angles are also very similar to those observed in the $[Sn_2Se_6]^{4-}$ anion in $Cs_4[Sn_2Se_6]$.[12] The exocyclic terminal Sn–Se bonds are considerably shorter [2.405(2) and 2.412(3) Å] than the endocyclic ones which range from 2.556(3) to 2.591(2) Å; in $[Sn_2Se_6]^{4-}$ the exo- and endocyclic bond lengths are 2.45 and 2.59 Å, respectively.

The phenyl ligands originate from the cleavage of a phosphorus–carbon bond of the tetraphenylphosphonium salt. Such carbanions can be obtained by thermal decomposition of phosphonium hydroxides which are produced by well known nucleophilic reactions of phosphonium salts at the phosphorus atom. This requires the participation of two OH^- in the reaction pathway. It was not obvious how the cleavage of a phosphorus–carbon bond of the tetraphenylphosphonium cation could occur until the infrared spectrum of our commercial tetraphenylphosphonium bromide salt was exam-

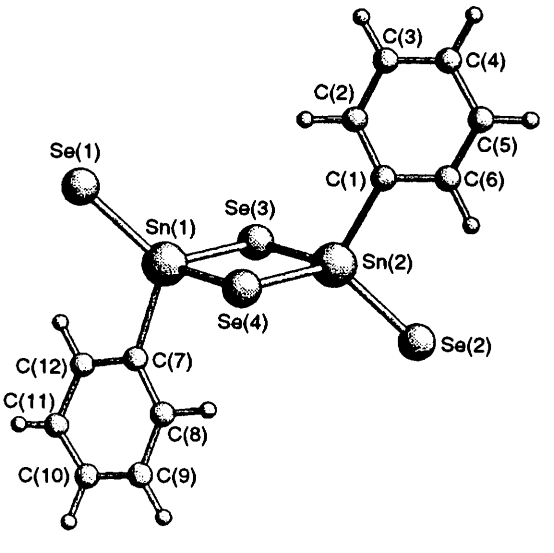


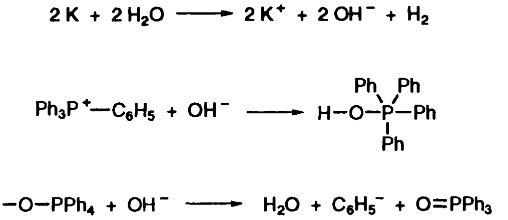
Fig. 1 Molecular structure of the $[Sn_2Ph_2Se_4]^{2-}$ anion

Table 1 Atomic coordinates for $[PPh_4]_2[Sn_2Ph_2Se_4]$

Atom	*x*	*y*	*z*
Sn(1)	0.122 3(1)	0.070 69(0)	0.302 60(9)
Sn(2)	−0.123 9(1)	−0.070 7(1)	−0.803 13(8)
Se(1)	0.326 8(2)	0.078 0(2)	0.309 9(2)
Se(2)	−0.328 0(2)	−0.079 5(2)	−0.811 2(1)
Se(3)	0.959 4(2)	0.092 6(2)	0.167 3(1)
Se(4)	−0.958 8(2)	−0.095 0(1)	−0.668 1(1)
C(1)	0.105(1)	0.328(1)	−0.109 3(9)
C(2)	−0.004(1)	0.284(1)	−0.122(1)
C(3)	−0.019(1)	0.217(2)	−0.066(1)
C(4)	0.078(2)	0.190(1)	−0.001(1)
C(5)	0.189(1)	0.229(1)	0.009(1)
C(6)	0.203(1)	0.297(1)	−0.046(1)
C(7)	−0.067(1)	−0.323(1)	−0.375 3(8)
C(8)	0.042(1)	−0.276(1)	−0.350 4(9)
C(9)	0.073(1)	−0.205(1)	−0.396(1)
C(10)	−0.012(1)	−0.178(1)	−0.468(1)
C(11)	−0.125(1)	−0.220(1)	−0.495 2(9)
C(12)	−0.150(1)	−0.291(1)	−0.446 7(9)
P(1)	0.639 8(5)	0.485 8(4)	0.117 9(4)
C(11)	0.697(2)	0.477(1)	0.034(1)
C(12)	0.816(2)	0.442(1)	0.051(1)
C(13)	0.856(2)	0.430(1)	−0.006(1)
C(14)	0.800(2)	0.456(1)	−0.086(1)
C(15)	0.681(2)	0.495(2)	−0.105(2)
C(16)	0.623(2)	0.500(2)	−0.044(1)
C(21)	0.484(2)	0.066(1)	−0.095(1)
C(22)	0.591(2)	0.029(1)	−0.042(1)
C(23)	0.689(2)	0.082(1)	−0.012(1)
C(24)	0.687(2)	0.178(2)	−0.038(1)
C(25)	0.582(2)	0.216(2)	−0.091(2)
C(26)	0.471(2)	0.165(2)	−0.120(1)
C(31)	0.258(1)	0.037(1)	−0.207(1)
C(32)	0.181(2)	0.116(1)	−0.198(1)
C(33)	0.115(2)	0.156(1)	−0.267(1)
C(34)	0.114(2)	0.125(1)	−0.342(1)
C(35)	0.182(2)	0.040(2)	−0.347(1)
C(36)	0.253(2)	−0.001(1)	−0.280(1)
C(41)	0.400(2)	0.866(2)	−0.141(1)
C(42)	0.506(2)	0.856(1)	−0.156(1)
C(43)	0.535(2)	0.764(2)	−0.181(1)
C(44)	0.440(2)	0.684(2)	−0.193(1)
C(45)	0.363(2)	0.697(2)	−0.164(1)
C(46)	0.339(2)	0.788(1)	−0.134(1)
P(2)	−0.640 7(5)	−0.482 5(3)	−0.618 2(3)
C(51)	−0.703(2)	−0.472(1)	−0.542(1)
C(52)	−0.818(2)	−0.447(2)	−0.551(1)
C(53)	−0.858(2)	−0.450(2)	−0.480(2)
C(54)	−0.772(2)	−0.460(1)	−0.407(1)
C(55)	−0.660(2)	−0.479(1)	−0.397(1)
C(56)	−0.631(2)	−0.490(1)	−0.464(1)
C(61)	−0.485(2)	−0.061(1)	−0.418(1)
C(62)	−0.593(2)	−0.034(2)	−0.464(1)
C(63)	−0.689(2)	−0.110(2)	−0.484(1)
C(64)	−0.662(2)	−0.204(2)	−0.458(1)
C(65)	−0.561(2)	−0.224(2)	−0.417(1)
C(66)	−0.470(2)	−0.157(1)	−0.395(1)
C(71)	−0.244(2)	−0.034(1)	−0.296(1)
C(72)	−0.159(2)	−0.095(1)	−0.302(1)
C(73)	−0.083(2)	−0.144(1)	−0.238(1)
C(74)	−0.104(2)	−0.138(1)	−0.168(1)
C(75)	−0.183(2)	−0.072(1)	−0.151(1)
C(76)	−0.256(2)	−0.021(1)	−0.221(1)
C(81)	−0.405(2)	−0.867(1)	−0.354(1)
C(82)	−0.497(2)	−0.857(2)	−0.321(1)
C(83)	−0.517(2)	−0.768(2)	−0.293(1)
C(84)	−0.467(2)	−0.691(2)	−0.302(1)
C(85)	−0.351(2)	−0.698(2)	−0.319(1)
C(86)	−0.316(2)	−0.786(1)	−0.340(1)

Table 2 Main bond distances (Å) and angles (°) in the anion $[Sn_2Ph_2Se_4]^{2-}$

Sn(1)–C(7)	2.18(1)	Sn(2)–C(1)	2.15(1)
Sn(1)–Se(1)	2.412(3)	Sn(2)–Se(2)	2.405(2)
Sn(1)–Se(3)	2.556(3)	Sn(2)–Se(4)	2.569(3)
Sn(1)–Se(4)	2.591(2)	Sn(2)–Se(3)	2.576(3)
Se(1)–Sn(1)–Se(3)	119.6(1)	Se(3)–Sn(2)–C(1)	106.1(4)
Se(1)–Sn(1)–Se(4)	117.83(8)	Se(4)–Sn(2)–C(1)	110.7(4)
Se(1)–Sn(1)–C(7)	115.9(4)	Sn(1)–Se(3)–Sn(2)	86.31(8)
Se(3)–Sn(1)–Se(4)	93.95(8)	Sn(1)–Se(4)–Sn(2)	85.74(8)
Se(3)–Sn(1)–C(7)	100.8(4)	Sn(2)–C(1)–C(2)	118(1)
Se(4)–Sn(1)–C(7)	105.3(4)	Sn(2)–C(1)–C(6)	121(1)
Se(2)–Sn(2)–Se(3)	119.0(1)	C(2)–C(1)–C(6)	119(1)
Se(2)–Sn(2)–Se(4)	120.4(1)	Sn(1)–C(7)–C(8)	123(1)
Se(2)–Sn(2)–C(1)	105.7(4)	Sn(1)–C(7)–C(12)	118(1)
Se(3)–Sn(2)–Se(4)	94.00(8)	C(8)–C(7)–C(12)	117(1)



$$2K + 2H_2O \longrightarrow 2K^+ + 2OH^- + H_2$$

$$Ph_3P^+{-}C_6H_5 + OH^- \longrightarrow H{-}O{-}\overset{Ph\ \ Ph}{\underset{Ph}{P}}{-}Ph$$

$$H{-}O{-}PPh_4 + OH^- \longrightarrow H_2O + C_6H_5^- + O{=}PPh_3$$

Scheme 1

ined and indicated the presence of some non-negligible hydration. The formation of the $C_6H_5^-$ carbanion can be then summarized as in Scheme 1.

The presence of the triphenylphosphonium oxide molecule was checked by ^{31}P NMR and infrared spectroscopies.* It is characterized by its strong NMR peak at δ 27.0 and its infrared stretching mode at 1188 cm^{-1}. In this strongly reducing medium, $C_6H_5^-$ cannot be oxidized into C_6H_6, and H_2O is readily reduced to OH^- and is then able to react with another phosphonium cation. Interestingly, the use of dried tetraphenylphosphonium bromide in the reaction did not allow the formation of the tin selenium compound.

During the reaction, the alloy $Bi_2Sn_3Se_6$ is also reduced. The structure of this alloy is not reported in the literature but we think it is closely related to that of the isoelectronic $Bi_2Pb_3S_6$[19] compound since they have identical X-ray powder patterns. In the latter Bi and Pb are octahedrally co-ordinated to the chalcogen elements; this type of co-ordination is also observed in the $Bi_2Ge_3Te_6$[20] alloy. In $Bi_2Pb_3S_6$ (Fig. 2), the octahedral sites are occupied indiscriminately by Bi and Pb atoms which have respectively +3 and +2 formal oxidation states.

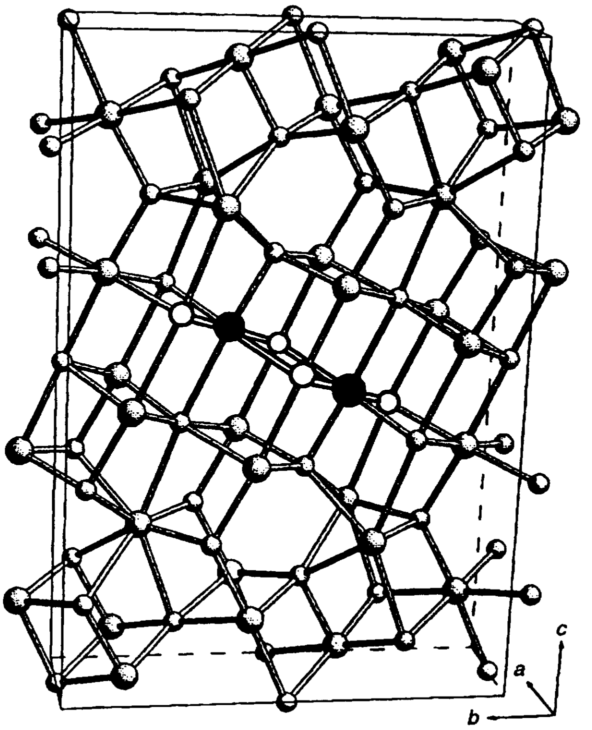
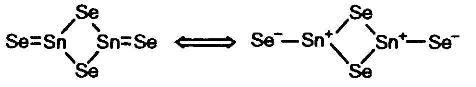


Fig. 2 Crystal structure of the $Bi_2Pb_3S_6$ phase displaying a Pb_2S_4 unit (black and white circles). Small spheres, S; large spheres, Pb or Bi atoms



Scheme 2

$$2Bi^{III}{}_2Sn^{II}{}_3Se_6 \longrightarrow 3Sn^{IV}{}_2Se_4 + 4Bi^0 \qquad (1)$$

Attack of $Bi_2Sn_3Se_6$ by strong reducing agents such as alkal metal solutions leads to the cleavage of metal–chalcogen bonds. Bismuth, which is more electronegative than tin, is reduced to Bi^0 while tin is oxidized to Sn^{IV} to give the intermediate fragment Sn_2Se_4 [equation (1)]. The geometry of Sn_2Se_4, a square-planar ring (Sn_2Se_2) with two exocyclic Sn–Se bonds, is indeed reminiscent of the $Bi_2Pb_3S_6$-type framework (Fig. 2). This planar configuration can be described with two double-bonded exocyclic selenium atoms or, owing to the electronegativities of the elements, with single bonds and formal charges (Scheme 2).

The $C_6H_5^-$ carbanion can attach itself to the electrophilic site at the tin atoms. The stability of the anion has been investigated by means of extended-Hückel molecular orbital calculations.[21] We can envisage the formation of the anion through the interaction of fragments Sn_2Se_4 and $C_6H_5^-$. The neutral Sn_2Se_4 intermediate, with a central Sn_2Se_2 planar ring, may have planar, *cis* or *trans* configurations depending on the orientation of the Sn–Se *exo* bonds. Calculations show that the bonding energy levels practically do not shift from one model to another, but the lowest unoccupied molecular orbital (LUMO) is raised in energy by nearly 1 eV for the planar configuration.

In order better to understand the orbital interactions, a diagram has been constructed using the FMOs (fragment molecular orbitals) of the Sn_2Se_4 fragment in its *trans* configuration. Stabilization of the anion $[Sn_2Ph_2Se_4]^{2-}$ is largely due to the interaction of the highest occupied molecular orbital (HOMO) of $C_6H_5^-$ with the LUMO of Sn_2Se_4; the latter is slightly antibonding along the Sn–Se *exo* bonds and essentially non-bonding at the Sn atoms. The resulting molecular frontier-orbital energy-level diagram of $[Sn_2Ph_2Se_4]^{2-}$ (Fig. 3) indicates that with 92 valence electrons the anion is rather stable with a HOMO–LUMO separation of 2 eV. On the other hand, the HOMO and the five orbitals lying just below have non-bonding character and correspond to filled lone pairs on the selenium atoms. The LUMO of the C_6H_5

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* The ^{31}P NMR measurements were made on a Bruker WP200SY FT-NMR spectrometer at 81.02 MHz with ^1H decoupling and 85% H_3PO_4 as external reference. The spectrum of the mother-liquor displayed four singlets at δ 8.9, 23.0 (PPh_4Br), 27.0 and 35.6. The high-intensity peak at δ 27.0 was unambiguously assigned to $O{=}PPh_3$ since addition of extra triphenylphosphine oxide to the solution increased its intensity. The peaks at δ 8.9 and 35.6 with smaller intensities have not yet been attributed. The infrared spectrum of the mother-liquor was recorded on a BOMEM DA8 FT-IR spectrometer. By comparison with the spectra of pure tetraphenylphosphonium bromide and triphenylphosphine oxide, the strong band at 1188 cm^{-1} was attributed to the P=O stretching mode of the triphenylphosphine oxide.

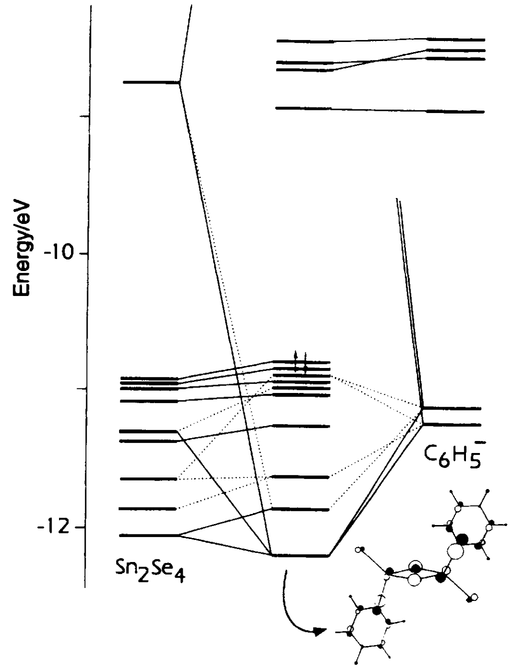

Fig. 3 Molecular orbital derivation of the frontier orbitals of the $[Sn_2Ph_2Se_4]^{2-}$ anion

fragments does not interact and becomes the LUMO of the $[Sn_2Ph_2Se_4]^{2-}$ anion. Overlap-population analysis (mean values of 0.72 and 0.56 for *exo*- and *endo*-Sn–Se bonds) is in agreement with a partial double-bond character for the short exocyclic bonds [2.405(2) and 2.412(3) Å]. This anion appears less stable than the homologue $[Sn_2Se_6]^{4-}$ [13] which has a HOMO–LUMO separation of 7.3 eV. Calculations were also performed in the case of the hypothetical *cis* configuration of $[Sn_2Ph_2Se_4]^{2-}$ (with facing phenyl groups to minimize steric hindrance). This geometry is found to be a bit less stable with a decrease in the HOMO–LUMO gap of 0.1 eV and an increase in the sum of one-electron energies by 1 eV.

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