Isolation of $[Sn(PSe_5)_3]^{5-}$ and $[Sn_2Se_4(PSe_5)_2]^{6-}$; the first discrete complexes from molten alkali-metal polyselenophosphate fluxes

Konstantinos Chondroudis and Mercouri G. Kanatzidis*

Department of Chemistry, Michigan State University, East Lansing, Michigan 48824, USA

The use of basic polychalcophosphate fluxes yields the quaternary molecular compounds $[Sn(PSe_5)_3]^{5-}$ and $[Sn_2Se_4(PSe_5)_2]^{6-}$, the first examples of discrete complexes produced from molten fluxes.

Recently, we demonstrated that the polychalcophosphate fluxes are very useful for the synthesis of new ternary and quaternary solid state thiophosphate and selenophosphate compounds.[1] The formation of these fluxes takes place by *in situ* fusion of A_2E, P_2E_5, and E (E = S, Se), and yields $[P_yE_z]^{n-}$ ligands (E = S, Se) which, in the presence of metal ions, coordinate to build interesting new materials. The variation of the flux composition stabilizes different ligands such as $[P_2E_7]^{4-}$, $[PE_4]^{3-}$, $[P_2Se_6]^{4-}$, $[P_2Se_9]^{4-}$, *etc.*, which become the building blocks of various polymeric structures.[2-5] To access molecular compounds a high concentration of $[P_yE_z]^{n-}$ ligands is necessary which can be achieved by increasing the basicity of the flux. The compounds synthesized below came out of a very basic flux. Herein, we report the synthesis, structural characterization, optical and thermal properties of the first examples of molecular, selenophosphate, complexes found in the compounds $A_5Sn(PSe_5)_3$ (A = K, Rb) and $A_6Sn_2Se_4(PSe_5)_2$ (A = Rb, Cs). It is noteworthy that access to these molecular compounds is more convenient through the flux method than using 'wet' chemistry, because of the difficulty of stabilizing the highly charged $[P_yE_z]^{n-}$ species in solution. Furthermore, the complexes themselves are very highly charged (5− and 6−) and their stabilization through conventional synthesis would be troublesome.

Compounds $A_5Sn(PSe_5)_3$ (A = K, Rb) form in a polyselenophosphate flux.†‡ In the rubidium salt two different crystalline forms, α and β, were observed. The latter is formed at a reaction temperature 20 °C higher than the former. The molecular anion in $A_5Sn(PSe_5)_3$ contain the rare $[PSe_5]^{3-}$ ion as a chelating unit (Fig. 1). The $[PSe_5]^{3-}$ ligand can be derived from the tetrahedral $[PSe_4]^{3-}$ group[6] by substitution of an Se_2^{2-} ion for a monoselenide. The only other known example of a compound featuring this ligand is $[PPh_4]_2[Fe_2(CO)_4(PSe_5)_2]$[7] in which $[PSe_5]^{3-}$ acts as a tridentate ligand. In $A_5Sn(PSe_5)_3$, three such ligands chelate to a Sn^{IV} atom, each employing the diselenide 'arm' and one of the remaining monoselenides. In this way, three five-membered rings are formed [*e.g.* Sn–Se(1)–Se(2)–P(1)–Se(5)] with the tin in a slightly distorted octahedral environment. There are two sets of Sn–Se distances; the first set of long distances is between Sn and Se(5), Se(10), Se(11), Se(15) with an average distance of 2.76(2) Å and the second set of short distances is between Sn and Se(1) and Se(6) with an average distance of 2.66(1) Å. $[Sn(PSe_5)_3]^{5-}$ bears a resemblance to $[Sn(Se_4)_3]^{2-}$,[8] in which three Se_4^{2-} bidentate ligands, coordinate to a tin atom forming three five-membered rings, two of which adopt a puckered and one an envelope conformation. In $[Sn(PSe_5)_3]^{5-}$ two rings (both crystalline forms) have an envelope conformation, and one ring adopts the puckered conformation. The complex is expected to be optically active, but since every unit cell contains both Λ and Δ enantiomorphs, the compound is racemic (the Δ enantiomorph is shown in Fig. 1). The non-planarity of the rings introduces dissymmetry and the actual conformation of the complex is Δλλδ (or Λδδλ), similar to that of a-$[Pt(Se_4)_3]^{2-}$,[9] whereas $[Sn(Se_4)_3]^{2-}$[8] crystallizes as the Δλδδ conformer. The P–Se distances range from 2.157(6) to 2.299(5) Å, with the non-coordinated selenium atoms [*e.g.* Se(3), Se(4), *etc.*] displaying the shorter ones, and compare well with those found in PSe compounds.[1-7] There are two six-coordinate rubidium cations [Rb–Se(mean) 3.6(1) Å], one seven-coordinate [Rb–Se(mean) 3.6(1) Å], and two eight-coordinate [Rb-Se(mean) 3.6(1) Å].

The molecular anion in $A_6Sn_2Se_4(PSe_5)_2$ (A = Rb, Cs)§ is shown in Fig. 2. The structure consists of a centrosymmetric $[Sn(\mu\text{-}Se)(Se)]_2$ dimeric core in which two μ-Se^{2-} ions bridge two adjacent tin atoms. This core is further coordinated to two $(PSe_5)^{3-}$ ligands at either side. In this case, however, the ligand is monodentate and uses only the diselenide 'arm' to coordinate. This is a unique coordination mode and further illustrates the many different bonding modes that the $[P_yE_z]^{n-}$ ligands can exhibit. The coordination geometry around tin is tetrahedral and the Sn–Se distances range from 2.438(2) to 2.626(2) Å, in good agreement with $[Sn_2Se_6]^{4-}$,[10] in which tin features a tetrahedral coordination. The P–Se distances range from 2.162(4) to

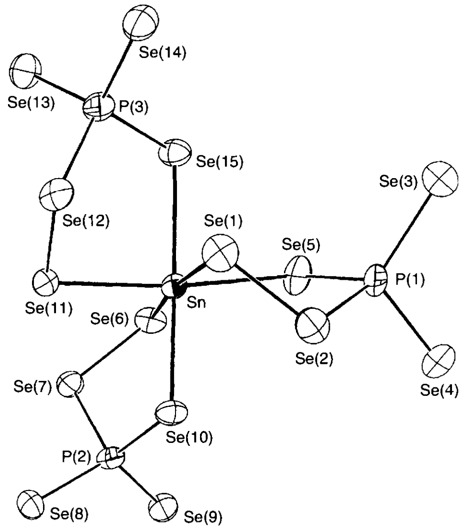

Fig. 1 ORTEP representation and labelling scheme of the structure of the $[Sn(PSe_5)_3]^{5-}$ anion (Δλλδ enantiomorph). Selected distances (Å) are as follows: Sn–Se(1) 2.653(2), Sn–Se(5) 2.782(3), Sn–Se(6) 2.673(2), Sn–Se(10) 2.736(2), Sn–Se(11) 2.743(2), Sn–Se(15) 2.781(3), Se(1)–Se(2) 2.338(3), Se(6)–Se(7) 2.319(3), Se(11)–Se(12) 2.354(3), Se(2)–P(1) 2.289(6), Se(3)–P(1) 2.160(6), Se(4)–P(1) 2.170(5), Se(5)–P(1) 2.233(4), Se(7)–P(2) 2.299(5), Se(8)–P(2) 2.157(6), Se(9)–P(2) 2.160(5), Se(10)–P(2) 2.237(5), Se(12)–P(3) 2.281(6), Se(13)–P(3) 2.166(5), Se(14)–P(3) 2.161(5), Se(15)–P(3) 2.235(5). Selected angles (°): Se(1)–Sn–Se(5) 90.72(7), Se(1)–Sn–Se(6) 171.49(8), Se(1)–Sn–Se(10) 86.48(7), Se(1)–Sn–Se(11) 98.75(7), Se(1)--Sn–Se(15) 89.10(7), Se(5)–Sn– Se(6) 81.55(7), Se(5)–Sn–Se(10) 97.83(7), Se(5)–Sn–Se(11) 167.13(7), Se(5)–Sn–Se(15) 84.94(8), Se(6)–Sn–Se(10) 91.06(7), Se(6)–Sn–Se(11) 89.45(7), Se(6)–Sn–Se(15) 93.71(7), Se(10)–Sn–Se(11) 91.48(8), Se(10)–Sn–Se(15) 174.80(7), Se(11)–Sn–Se(15) 86.50(7), Se(1)–Se(2)–P(1) 103.5(1), Se(6)–Se(7)–P(2) 102.0(2), Se(11)–Se(12)–P(3) 100.8(1). Torsion angles around Se–Se bonds (°): Sn–Se(1)–Se(2)–P(1) 63.0(1), Sn–Se(6)–Se(7)–P(2)–63.3(1), Sn–Se(11)–Se(12)–P(3) 67.8(1).

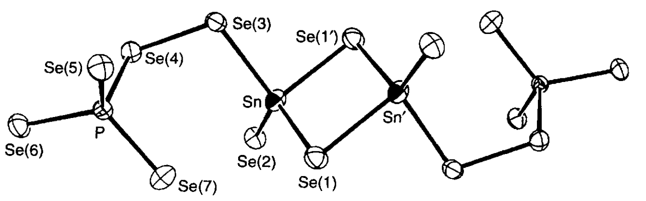

Fig. 2 ORTEP representation and labelling scheme of the structure of the $[Sn_2Se_4(PSe_5)_2]^{6-}$ anion. Selected distances (Å): Sn–Se(1) 2.550(2), Sn–Se(1′) 2.626(2), Sn–Se(2) 2.438(2), Sn–Se(3) 2.575(2), Se(3)–Se(4) 2.340(2), Se(4)–P 2.291(4), Se(5)–P 2.162(4), Se(6)–P 2.183(4), Se(7)–P 2.179(4), Sn–Sn 3.543(2). Selected angles (°): Se(1)–Sn–Se(1′) 93.62(6), Se(1)–Sn–Se(2) 119.18(6), Se(1′)–Sn–Se(2) 114.30(6), Se(1)–Sn–Se(3) 117.92(6), Se(1′)–Sn–Se(3) 89.17(5), Se(2)–Sn–Se(3) 115.44(6), Sn–Se(1)–Sn′ 86.38(6), Sn–Se(3)–Se(4) 103.80(6), Se(3)–Se(4)–P 103.1(1). Torsion angle around the Se(3)–Se(4) bond is 74.8(1)°.

2.291(4) Å, and in this case every $(PSe_5)^{3-}$ group displays three shorter distances since it is monodentate. There are two eight-coordinate caesium cations [Cs–Se(mean) 3.77(7) Å], and one six-coordinate [Cs–Se(mean) 3.76(9) Å].

Both compounds are insoluble in dmf and acetonitrile, but very soluble in a solution of crown ether, 18-crown-6, in dmf. They are also soluble, to a lesser degree, in a solution of the same crown ether in acetonitrile. The solutions are dark-green, and they are stable, according to UV–VIS, for up to 3–4 days. The dmf and MeCN/complexant solution gave similar UV–VIS spectra. For $Rb_5Sn(PSe_5)_3$ one strong absorption at *ca.* 340 nm (3.65 eV) (dmf), *ca.* 333 nm (3.72 eV) (MeCN), and for $Cs_3Sn(PSe_5)Se_2$ one strong absorption at *ca.* 398 nm (3.12 eV) (dmf), *ca.* 390 nm (3.18 eV) (MeCN). The solid-state UV–VIS diffuse reflectance spectra of both compounds show sharp optical gaps, where for $Rb_5Sn(PSe_5)_3$, E_g is 1.61 eV, while for $Cs_3Sn(PSe_5)Se_2$ this is 2.09 eV. The solid-state IR and Raman spectra of both compounds show peaks that are characteristic of both the nature and bonding mode of the $[PSe_5]^{3-}$ ligand.¶ Differential thermal analysis (DTA) shows that $Rb_5Sn(PSe_5)_3$ and $Cs_6Sn_2Se_4(PSe_5)_2$ melt congruently at 406 and 456 °C respectively.

The first molecular selenophosphate tin compounds with the unusual $[PSe_5]^{3-}$ ligand have been prepared in molten polyselenophosphate $A_x[P_ySe_z]$ fluxes. One of them, $Rb_5Sn(PSe_5)_3$, crystallizes in two forms, and access to each form can be very easily achieved by slight adjustment of the synthesis temperature. In addition, these compounds may be useful as starting materials or building blocks for further solution or solid-state chemistry.

Financial support from the National Science Foundation DMR-9527347 is gratefully acknowledged. This work made use of the SEM and TEM facilities of the Center for Electron Optics at Michigan State University.

Footnotes

† $A_5Sn(PSe_5)_3$ (A = K, Rb) were synthesized from a mixture of Sn (0.3 mmol), P_2Se_5(0.6 mmol), A_2Se (0.90 mmol), and Se (3 mmol) sealed under vacuum in a Pyrex tube and heated to 440 °C for 4 d followed by cooling to 150 °C at 4 °C h^{-1}. The excess $A_xP_ySe_z$ flux was removed with dmf to reveal black platelike crystals (80% yield based on Sn). The crystals are air- and water-sensitive.

Crystal data for $Rb_5Sn(PSe_5)_3$ at 26 °C: triclinic, space group $P\bar{1}$ (no. 2), $a = 11.745(3)$, $b = 19.230(5)$, $c = 7.278(3)$ Å, $\alpha = 99.97(3)$, $\beta = 107.03(2)$, $\gamma = 87.16(2)$ °, $U = 1548.1(9)$ Å^3, $Z = 2$, $D_c = 3.932$ g cm^{-3}, μ(Mo-Kα) = 261.85 cm^{-1} , $2\theta_{max} = 45$ °, total data collected, 4271; unique data, 4028; data with $F_0^2 > 3\sigma(F_0^2)$, 2853. Number of variables: 217. An empirical absorption correction based on ψ scans was applied to the data, followed by a DIFABS correction to the isotropically refined data. Final R,R_w = 0.041, 0.052.

‡ *Crystal data* for β-$Rb_5Sn(PSe_5)_3$ at 23 °C: triclinic, space group $P\bar{1}$ (no. 2), $a = 13.566(3)$, $b = 16.244(4)$, $c = 7.303(2)$ Å, $\alpha = 102.04(2)$, $\beta = 94.22(2)$, $\gamma = 76.91(2)$ °, $U = 1532.6(6)$ Å^3, $Z = 2$, $D_c = 3.951$ g cm^{-3}; the crystals are also black, platelike and air-sensitive. Data were also collected in this unit cell. The solution of the structure illustrated that in this unit cell the same molecular unit is present. Both crystalline forms have the same IR spectra and DTA response.

§ $A_6Sn_2Se_4(PSe_5)_2$ (A = Rb, Cs) were synthesized from a mixture of Sn (0.3 mmol), P_2Se_5(0.45 mmol), A_2Se (1.20 mmol) and Se (3 mmol) by heating at 495 °C for 4 d and isolated as above to reveal orange rodlike crystals (89% yield based on Sn). The crystals are air- and water-sensitive.

Crystal data for $Cs_6Sn_2Se_4(PSe_5)_2$ at 25 °C: triclinic, space group $P\bar{1}$ (no. 2), $a = 9.899(1)$, $b = 12.416(2)$, $c = 7.497(1)$ Å, $\alpha = 91.62(1)$, $\beta = 110.19(1)$, $\gamma = 79.94(1)$ °, $U = 851.0(2)$ Å^3, $Z = 1$, $D_c = 4.297$ g cm^{-3}, μ(Mo-Kα) = 226.73 cm^{-1} , $2\theta_{max} = 50$ °, total data collected, 3171; unique data, 2979; data with $F_0^2 > 3\sigma(F_0^2)$, 2033. Number of variables: 110. Corrections were applied as above. The complete anisotropic refinement resulted in a final R,R_w = 0.032, 0.041. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/84.

¶ The IR spectrum of $[Sn(PSe_5)_3]^{5-}$ displays absorptions at *ca.* 490, 477, 436, 402, 212 and 177 cm^{-1}, while $[Sn_2Se_4(PSe_5)_2]^{6-}$ displays absorptions at *ca.* 550, 475, 379, 350, 267, 240, 198, 183 and 142 cm^{-1}. The absorptions at 267, and 240 cm^{-1} are attributed to Se–Se stretching vibrations,[8] those at 198, 183, 177, 142 cm^{-1} to Sn–Se vibrations,[8] and those at higher energies are due to P–Se vibrations.[1,5] The Raman spectra of $[Sn(PSe_5)_3]^{5-}$ displays absorptions at *ca.* 480, 437, 387, 282, 264, 224 and 160 cm^{-1}, while $[Sn_2Se_4(PSe_5)_2]^{6-}$ displays absorptions at *ca.* 473, 379, 354, 263, 227, 195, 159 and 143 cm^{-1}.

References

1 T. J. McCarthy and M. G. Kanatzidis, *Inorg. Chem.*, **34**, 1257.
2 T. J. McCarthy, T. Hogan, C. R. Kannewurf and M. G. Kanatzidis, *Chem. Mater.*, 1994, **6**, 1072.
3 T. J. McCarthy and M. G. Kanatzidis, *J. Chem. Soc., Chem. Commun.*, 1994, 1089.
4 T. J. McCarthy and M. G. Kanatzidis, *Chem. Mater.*, 1993, **5**, 1061.
5 K. Chondroudis and M. G. Kanatzidis, *Inorg. Chem.*, 1995, **34**, 5401.
6 K. Chondroudis, T. J. McCarthy and M. G. Kanatzidis, *Inorg. Chem.*, 1996, **35**, 841.
7 J. Zhao, W. T. Pennington and J. W. Kolis, *J. Chem. Soc., Chem. Commun.*, 1992, 265.
8 S. P. Huang, S. Dhingra and M. G. Kanatzidis, *Polyhedron*, 1990, **9**, 1389.
9 J. M. McConnachie, M. A. Ansari and J. A. Ibers, *Inorg. Chem.*, 1993, **32**, 3250.
10 W. S. Sheldrick and H. G. Braunbeck, *Z. Naturforsch., Teil B.*, 1989, **44**, 851.

Received, 16th April 1996; Com. 6/02653B