

Note

Role of O,C,O-ligand in a new coordination mode of organotin compounds to 2-mercapto-1-methylimidazol. Stabilization of its thione form

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Received 29 June 2006; received in revised form 25 August 2006; accepted 29 September 2006

Available online 5 October 2006

Abstract

The reaction of the organotin compound $[\text{Ph}_2\text{LSn}]^+ [\text{OTf}]^-$ (**1**), $(\text{L}(\text{O},\text{C},\text{O}) = 2,6-(t\text{-BuOCH}_2)_2\text{C}_6\text{H}_3)$, with the sodium salt $\text{Na}(\text{mimt})$, $\text{mimt} = 1\text{-methylimidazole-2-thiolate}$, resulted in the isolation of $\text{Ph}_2\text{LSn}(\text{mimt})$ (**2**), where the polar group (mimt) has been stabilized as the thione-tautomeric form by the triorganotin fragment Ph_2LSn . Product **2** was characterized by ^1H , ^{13}C and ^{119}Sn NMR and IR spectroscopy, ESI/MS, elemental analyses and X-ray diffraction.

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Keywords: Organotin; Pincer ligands; S-ligands; NMR; Crystal structure

Organotin compounds containing various mercapto groups are extensively studied for their biological activities, most importantly as antitumor agents and their *in vitro* potency against trypanozoma cultures was demonstrated as well [1]. These compounds containing covalent Sn–S bond are also studied for industrial use, namely as stabilizers for polyvinyl chlorides [2]. An interesting class of organotin mercapto derivatives comprises those of general formula $\text{R}_3\text{Sn}(\text{SR}')$, where R' contains a donor atom (D) capable of forming a secondary bond with tin atom [3]. The second donor atom (D) in mercapto groups is most commonly the nitrogen atom (N) and these ligands are known to possibly exist in two tautomeric thione and thiol forms (Scheme 1) [4]. While the thione form of the free ligand is more favorable and is preferred in solution based on ^1H NMR studies, where the presence of N–H instead of

S–H has been detected, the thiol form of these polar groups can be found in the chemistry of organotin compounds resulting in the presence of the Sn–S covalent bond.

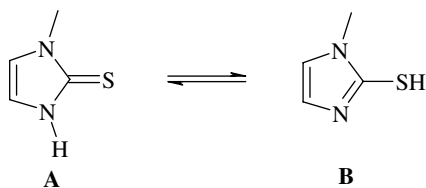
In connection with our previous studies that were focused on hypercoordinated organotin derivatives of Y,C,Y-pincer ligands containing covalent bond Sn–X, where X was a monodentate polar group that could not affect the geometry of the central tin atom [5], we decided to prepare a triorganotin compound containing 1-methylimidazole-2-thiol (Hmimt), which contains a nitrogen donor atom capable of forming an additional coordination bond $\text{Sn} \leftarrow \text{N}$. Here we report on the use of the triorganotin fragment Ph_2LSn containing pincer type ligand L ($\text{L}(\text{O},\text{C},\text{O}) = 2,6-(t\text{-BuOCH}_2)_2\text{C}_6\text{H}_3$) on the stabilization of thione-form in $\text{Ph}_2\text{LSn}(\text{mimt})$ (**2**) ($\text{mimt} = 1\text{-methylimidazole-2-thiolate}$).

The triorganotin compound $[\text{Ph}_2\text{LSn}]^+ [\text{OTf}]^-$ (**1**) has been prepared according to literature [5] and stirring a solution of **1** with sodium salt $\text{Na}(\text{mimt})$ in dry degassed tetrahydrofuran overnight yielded a solid powder (Scheme 2) [6].

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Scheme 1. Thione (A) and thiol (B) tautomeric forms of the mercapto ligands.

The analytical data show that the polar group (mimt) is stabilized in a thione form both in solution and solid state. The value of chemical shift C2 in ^{13}C NMR spectroscopy is the most informative for thiol–thione tautomeric form determination [7]. The ^{13}C NMR data revealed broad signal of C2 at 163.5 ppm for **2** that is comparable to the same signal of C2 in free ligand (Hmimt) ($\delta^{13}\text{C}(\text{C}2) = 160.2$ ppm) existing in the thione form in solution [7]. To the best of our knowledge, such a stabilization of the thione form of this ligand has been reported in several organotin cations ($\delta^{13}\text{C}(\text{C}2) = 157.0$ ppm), where free ligand (Hmimt) has been used as the S-donor ligand for organotin cations resulting in the Sn–S bond (Chart 1) [8].

However, the stabilization of the anionic polar group (mimt) $^-$ in thione form in organotin compounds resulting in the presence of Sn–N bond is unknown so far. The structurally similar compound $\text{Ph}_3\text{Sn}(\text{mimt})$ contains the covalent bond Sn–S indicating the presence of thiol form of (mimt) $^-$ (compare $\delta^{13}\text{C}(\text{C}2) = 138.7$ ppm) [7]. The presence of thione form in **2** was also corroborated by IR spectroscopy where bands at 694 and 536 cm^{-1} assignable to $\sigma(\text{C}=\text{S})$ and $\pi(\text{C}=\text{S})$ were found [8].

Single crystals of **2** were obtained from a toluene solution at -5°C and the molecular structure is shown in Fig. 1 [9]. The selected bond lengths, and angles of **2** and related compound $\text{Ph}_3\text{Sn}(\text{mimt})$ are given in Table 1.

The shape of the coordination polyhedron of **2** can be described as a distorted trigonal bipyramid, with carbon atoms in equatorial positions. One axial position is occupied by the oxygen donor atom from ligand L, while the nitrogen atom from mercapto polar group (mimt) is in the second one (found bonding angle $\text{O}(1)\text{--}\text{Sn}(1)\text{--}\text{N}(1) = 168.07(8)^\circ$). The found bond length $\text{Sn}(1)\text{--}\text{O}(1)$ (2.7875(16) Å) indicates the presence of medium strong Sn–O intramolecular interaction in **2**. Bond length $\text{Sn}(1)\text{--}\text{N}(1)$ (2.1518(19) Å) is comparable to the $\Sigma_{\text{cov}}(\text{Sn}$,

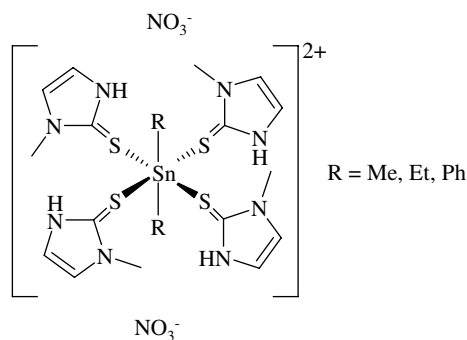


Chart 1.

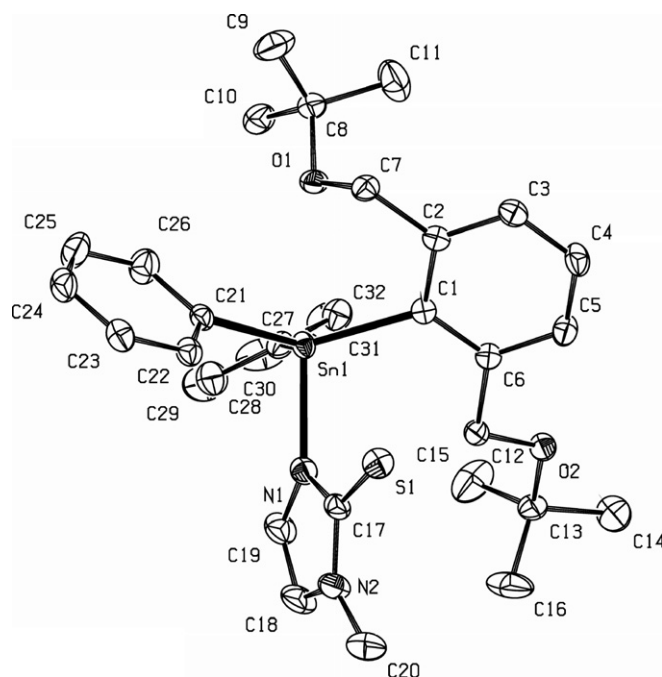
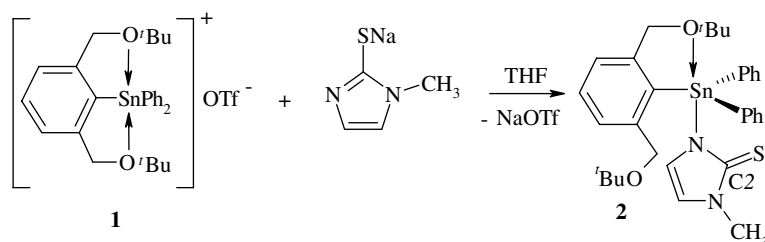


Fig. 1. General view (ORTEP) of a molecule showing 50% probability displacement ellipsoids and the atom-numbering scheme for **2**. The hydrogen atoms are omitted for clarity.

$\text{N}) = 2.154$ Å and clearly demonstrates the presence of covalent bond Sn–N in compound **2**. The presence of thione form of (mimt) is also corroborated by bond length $\text{C}(17)\text{--}\text{S}(1)$ (1.696(2) Å) that is comparable to those found in organotin cations containing Hmimt in its thione form [8] and both double bonds $\text{C}(17)\text{--}\text{S}(1)$ (1.696(2) Å) and



Scheme 2. Preparation and labeling of titled compound **2**.

Table 1
Selected bond length (Å) and angles (°) of **2** and related compound Ph₃Sn(mimt)

Compound	2	Ph ₃ Sn(mimt)
<i>Bond length (Å)</i>		
Sn(1)–N(1)	2.1518(19)	2.920(3)
Sn(1)–S(1)	3.5989(10)	2.437(1)
C(17)–S(1)	1.696(2)	1.746(4)
C(18)–C(19)	1.340(4)	1.321(9)
Sn(1)–O(1)	2.7875(16)	–
<i>Bond angle (°)</i>		
N(1)–C(17)–S(1)	127.34(17)	123.7(4)
O(1)–Sn(1)–N(1)	168.08(7)	–
O(1)–Sn(1)–S(1)	118.85(4)	–

C(18)–C(19) (1.340(4) Å) are well localized in **2**. There is no additional interaction between Sn and S as indicated by interatomic distance Sn(1)–S(1) (3.5989(10) Å). The comparison of **2** with related Ph₃Sn(mimt) (C(17)–S(1) = 1.746(4) Å, Sn(1)–N(1) = 2.920(3) Å and Sn(1)–S(1) = 2.437(1) Å) also demonstrates the different coordination mode of the mercapto group (mimt).

In summary we have reported on the preparation of Ph₂LSn(mimt) (**2**) containing polar group 1-methylimidazole-2-thiolate in the thione form, where the presence of covalent bond Sn–N was determined. Since the structurally related compound Ph₃Sn(mimt) contains this polar group in traditional thiol form (the presence of covalent bond Sn–S is usual for organotin compounds containing mercapto derivatives) the important role of O,C,O-chelating ligand in the new coordination mode of organotin fragments towards mercapto derivatives can be proposed and will be investigated in more detail.

Acknowledgements

The authors thank the Ministry of Education of the Czech Republic (Project Nos. VZ0021627501 and LC523) for financial support.

Appendix A. Supplementary data

CCDC 610595 contains the supplementary crystallographic data for **2**. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.jorganchem.2006.09.056](https://doi.org/10.1016/j.jorganchem.2006.09.056).

References

- (a) A.G. Davis, *Organotin Chemistry*, VCH, Weinheim, 1997;
- (b) P. Smith, *Chemistry of Tin*, Blackie Academic & Professional an imprint of Thompson Science, London, 1998;
- (c) W.T. Piver, *Environ. Health Perspect.* 4 (1973) 61;
- (d) G.J.M. van de Klerk, J.J. Zuckerman (Eds.), *Organotin Compounds*, American Chemical Society, Washington, DC, 1976, p. 1;
- (e) P. Yang, M. Guo, *Coord. Chem. Rev.* 185/86 (1999) 189;
- (f) M. Gielen, *Coord. Chem. Rev.* 151 (1996) 41;
- (g) M. Gielen, M. Biesemans, R. Willem, *Appl. Organomet. Chem.* 19 (2005) 440;
- (h) M. Gielen, *J. Braz. Chem. Soc.* 14 (2003) 870;
- (i) M. Gielen, M. Biesemans, R. Willem, E.R.T. Tiekink, *Eur. J. Inorg. Chem.* 3 (2004) 445;
- (j) M. Gielen, *Appl. Organomet. Chem.* 16 (2002) 481.
- (a) C.J. Evans, S. Karpel, *Organotin Compounds in Modern Technology*, Elsevier, Amsterdam, 1985, p. 23;
- (b) C.J. Evans, *Spect. Chem.* 11 (1991) 152.
- (a) C.V. Rodarte de Moura, A.P.G. Sousa, R.M. Silva, A. Abras, M. Horner, A.J. Bortoluzzi, C.A.L. Filgueiras, J.L. Wardell, *Polyhedron* 18 (1999) 2961, and reference therein;
- (b) M.V. Castano, A. Macías, A. Castineiras, A.S. González, E.G. Martínez, J.S. Casas, J. Sordo, *J. Chem. Soc., Dalton Trans.* 1001 (1990).
- (a) J. Susperregui, M. Bayle, J.M. Léger, G. Délérís, *J. Organomet. Chem.* 556 (1998) 105;
- (b) A.S. González, E.G. Martínez, J.S. Casas, J. Sordo, U. Casellato, R. Graziani, U. Russo, *J. Organomet. Chem.* 463 (1993) 91;
- (c) M.D. Couce, G. Faraglia, U. Russo, L. Sindellari, V. Valle, *J. Organomet. Chem.* 513 (1996) 77.
- (a) B. Kašná, R. Jambor, L. Dostál, A. Růžička, I. Císařová, J. Holeček, *Organometallics* 23 (2004) 5300;
- (b) B. Kašná, R. Jambor, L. Dostál, L. Kolářová, I. Císařová, J. Holeček, *Organometallics* 25 (2006) 148.
- THF solution of Na(mimt) (42 mg; 0.31 mmol) was added to 20 ml of THF solution of **1** (206 mg; 0.31 mmol) and stirred overnight. Hexan/CH₂Cl₂ (15 ml, 2:1) mixture was added after the evaporation of THF, the suspension was filtrated off and organic solvents evaporated to give the white powder identified as **2**. Yield: 121 mg of **2** (59%). Characterization: MW = 635.4 g/mol, m.p. 175–178 °C; Elemental Anal.: Calc. (Found), C 61.03 (61.33); H 6.52 (6.77); ESI/MS: *m/z* 113, 15% [mimt][−], *m/z* 523, 60% [M–mimt]⁺, *m/z* 632 [M+H]⁺, *m/z* 563, 30% [M+H–*t*BuOH]⁺, *m/z* 411, 80% [M–mimt–2butane]⁺, ¹H NMR δ (ppm): 0.88 (18H, s, O-*t*Bu), 3.45 (3H, s, NCH₃ (mimt)), 4.53 (4H, s, CH₂O), 6.59 (1H, bs, mimt), 6.63 (1H, bs, mimt), 7.4 (9H, m, Ar–H), 7.8 (4H, m, Ar–H), ¹³C NMR δ (ppm): 27.4 (OCCH₃), 34.8 (NCH₃), 65.7 (CH₂O), 75.1 (OC(CH₃)₃), 120.3 (C–mimt), 121.5 (C–mimt), 126.4 (C(3,5)), 128.5 (C(3',5')), 129.5 (C(4)), 129.6 (C(4')), 135.9 (C(1)), (¹J(¹¹⁹Sn,¹³C) = 713 Hz), 137.2 (C(2',6')), 141.5 (C(1')), (¹J(¹¹⁹Sn,¹³C) = 715 Hz), 147.3 (C(2,6)), 163.5 (SC2), δ (¹¹⁹Sn) ppm = −173.53.
- (a) J.S. Casas, A. Castineiras, E.G. Martínez, A.S. González, A. Sánchez, J. Sordo, *Polyhedron* 16 (1997) 795;
- (b) J. Bravo, M.B. Cordero, J.S. Casas, A. Sánchez, J. Sordo, E.E. Castellano, S. Zukermann, *J. Organomet. Chem.* 482 (1994) 147;
- (c) E. Bunzel, A.R. Norris, S.E. Taylor, W.J. Racz, *Can. J. Chem.* 60 (1982) 3033.
- (a) E.G. Martínez, A.S. González, J.S. Casas, J. Sordo, U. Casellato, R. Graziani, *Inorg. Chim. Acta* 191 (1992) 75;
- (b) J.S. Casas, E.G. Martínez, A.S. González, J. Sordo, U. Casellato, R. Graziani, U. Russo, *J. Organomet. Chem.* 493 (1995) 107;
- (c) J.S. Casas, A. Castineiras, E.G. Martínez, A.S. González, J. Sordo, E.M.V. Lopez, *Polyhedron* 15 (1996) 891.
- Colorless crystals of **2** were obtained from toluene solution at −5 °C. The intensity data were collected on a KUMA KM-4 CCD kappax diffractometer using a graphite monochromatized Mo Kα radiation C₃₂H₄₀N₂O₂SSn, *M* = 635.42, triclinic, space group *P*1, *a* = 10.256(2) Å, *b* = 10.471(2) Å, *c* = 14.351(3) Å, α = 86.78(3)°, β = 83.94(3)°, γ = 87.24(3)°, *U* = 1528.7(5) Å³, *Z* = 4, ρ = 1.383 g cm^{−3}, μ = 0.934 mm^{−1}, 14,411 reflections collected, of which

6106 were independent [$R_{\text{int}} = 0.0278$]. Final R indices [$I > 2\sigma(I)$]: $R_1 = 0.027$, $wR_2 = 0.069$. The structure was solved by direct methods (G.M. Sheldrick: SHELX-97 [10] program package, University of Goettingen, 1997; G.M. Sheldrick: SHELXTL V 5.1 [11], Bruker AXS GmbH.) Non-hydrogen atoms were refined anisotropically while

hydrogen atoms were inserted in calculated positions and isotropically refined assuming a ride-on model.

[10] G.M. Sheldrick: SHELX-97 program package, University of Goettingen, 1997.

[11] G.M. Sheldrick: SHELXTL V 5.10, Bruker AXS Inc., Madison, WI, 1997.