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Crystal and molecular structure of bis(di-*n*-propylammonium) dioxalatodiphenylstannate, $[n\text{-Pr}_2\text{NH}_2]_2[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]$

Abstract: The title compound $[n\text{-Pr}_2\text{NH}_2]_2[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]$ (**1**) has been synthesized by allowing Ph_2SnCl_2 to react with $[n\text{-Pr}_2\text{NH}_2]_2\text{C}_2\text{O}_4$. In **1**, characterized using X-ray crystallography, the Sn atom is six-coordinated by two phenyl groups and four oxygen atoms belonging to two asymmetrically chelating oxalate ligands. The geometry is *cis* octahedral about tin. In the structure of **1**, there are two $[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]^{2-}$ moieties differentiated by their $\angle\text{C-Sn-C}$ angles [105.07° (15°) and 107.43° (16°)]. These similar, but distinct, anions are connected by $[n\text{-Pr}_2\text{NH}_2]^+$ cations through N-H...O hydrogen bonds leading to two infinite alternating chains (1) and (2), which loosely assemble *via* π - π stacking between phenyl groups of adjacent molecules to generate an overall layered structure.

Keywords: *cis*-coordinated diphenyltin; hydrogen bonds; monochelating oxalate; two alternating chains structure; X-ray.

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Introduction

Compounds containing SnPh_2 residue are known for their potential biological activity (Evans and Karpel, 1985). One of our groups has been interested in the coordination ability of oxy-anions and has previously reported several papers dealing with this topic (Gueye et al., 1993; Diop et al., 1999; Diassé-Sarr et al., 2004). As a continuation of this interest, we have initiated here a study of the interactions between $[n\text{-Pr}_2\text{NH}_2]_2\text{C}_2\text{O}_4$ and SnPh_2Cl_2 , which

have yielded crystals of $[n\text{-Pr}_2\text{NH}_2]_2[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]$ (**1**). The dioxalatodiphenyltin (IV) anion $[\text{SnPh}_2(\text{C}_2\text{O}_4)_2]^{2-}$ has previously been reported (Ng and Kumar-Das, 1993; Xu et al., 2003), with the supporting cation being either $[i\text{-Pr}_2\text{NH}_2]^+$ or $[\text{Cy}_2\text{NH}_2]^+$. In the search for new diorganotin-containing compounds, several papers have been reported (Alcock et al., 1992; Schranzer et al., 1993; Cruz-Huerta et al., 2008; Gueye et al., 2010).

An X-ray study of $(n\text{-Pr}_2\text{NH}_2)_2(\text{C}_2\text{O}_4)_2\text{SnPh}_2$ has now been carried out and is presented here, and data are compared with those of previous studies.

Results and discussion

The asymmetric unit of **1** is shown in Figure 1, whereas aspects of the lattice structure formed through hydrogen bonds are shown in Figure 2. There are two, essentially equivalent, molecules in the asymmetric unit. Only data for one of these are discussed as typical.

In **1**, the crystallographic study shows oxalate ligands chelating the tin center. The Sn atom is six-coordinated by the two phenyl groups [Sn(1)-C 2.141 (5) and 2.151 (7) Å] and four oxygen atoms derived from two asymmetrically chelating oxalate ligands. Each ligand contains two oxygen atoms coordinating the tin atom [Sn(1)-O(1) 2.181 (3) Å, Sn(1)-O(3) 2.138 (3) Å, Sn(1)-O(7) 2.202 (3) Å, and Sn(1)-O(5) 2.132 (3) Å], with two other oxygen atoms involved in the hydrogen bonds. The C-O bond distances [1.257 (5)–1.297 (5) Å] are significantly longer than the other C=O bond distance [1.212 (6)–1.236 (5) Å], and both are in the range of C-O and C=O bonds reported in similar compounds (Ng and Kumar-Das, 1993; Xu et al., 2003). The tin has a distorted octahedral environment with two phenyl groups in *cis* conformation [$\angle\text{C}(1)\text{-Sn}(1)\text{-C}(7)$ 105.07° (15°); $\angle\text{C}(23)\text{-Sn}(2)\text{-C}(17)$ 107.43° (16°)]. Compared with the data reported by Ng and Kumar-Das (1993), the Sn(1)-O distances in **1** are longer–2.138 (3) and 2.132 (3) Å—and shorter–2.181 (3) and 2.202 (3) Å (the same observations can also be made for Sn(2)); i.e., the chelation is more asymmetric for **1** than in the $[i\text{-Pr}_2\text{NH}_2]^+$ analogue.

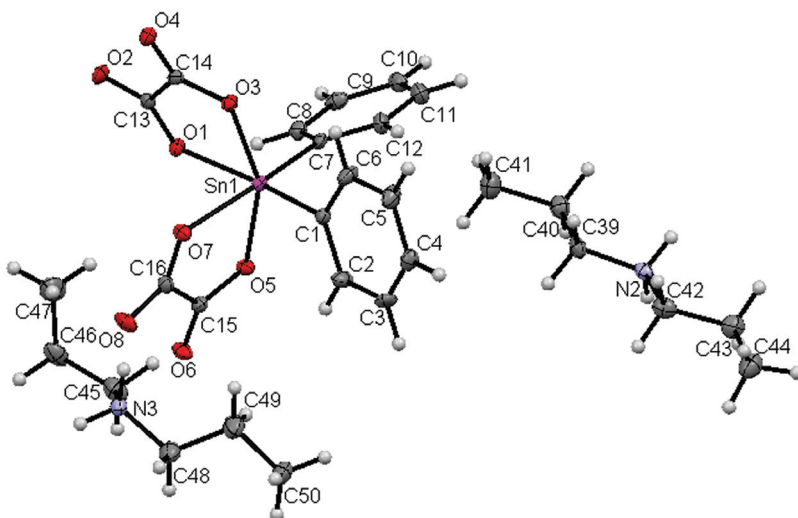


Figure 1 One formula unit of **1**, showing the atom numbering scheme.

Thermal ellipsoids are drawn at 50% probability level. Hydrogen atoms are represented by sphere of arbitrary size.

The C-Sn-C angle value of 106.0° (2°) reported by Ng and Kumar-Das (1993) is intermediate between the two C-Sn-C angles in **1**. The oxygen atoms noncoordinated to the tin center are involved in the N-H \cdots O hydrogen bond network, which links neighboring $[\text{SnPh}_2(\text{C}_2\text{O}_4)_2]^{2-}$ anions.

Selected bonds (\AA)

Sn(1)-C(1) 2.141 (5); Sn(1)-C(7) 2.151 (4); Sn(1)-O(1) 2.181 (3); Sn(1)-O(3) 2.138 (3); Sn(1)-O(5) 2.132 (3); Sn(1)-O(7) 2.202 (3); Sn(2)-C(17) 2.151 (5); Sn(2)-C(23) 2.150 (5); Sn(2)-O(9)

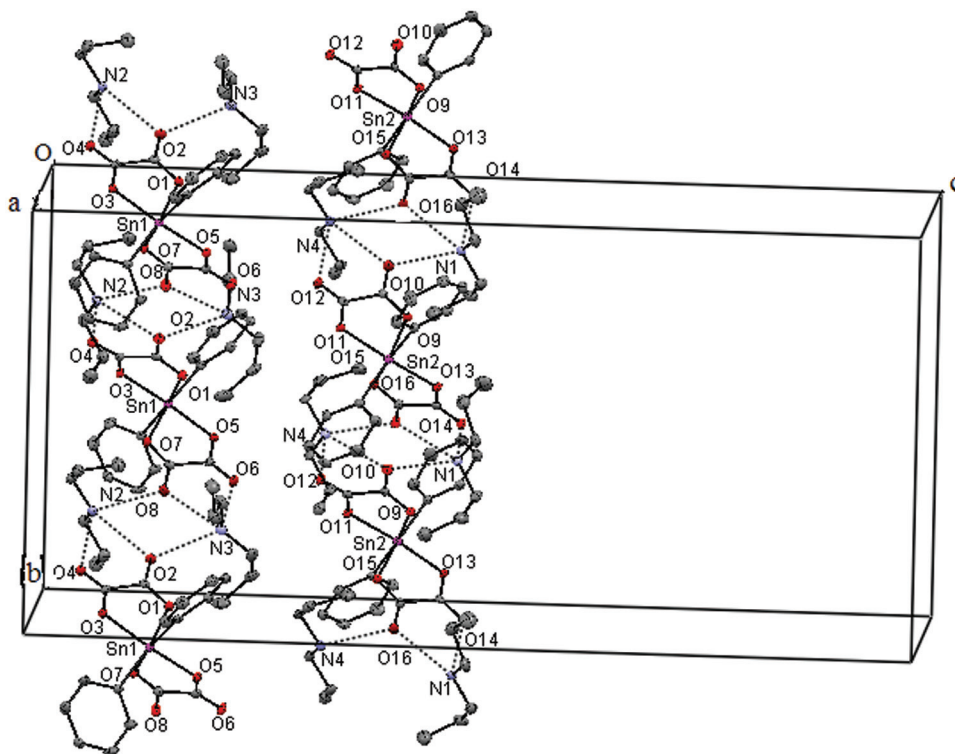


Figure 2 The lattice structure of **1** showing two different chains with the pattern of hydrogen bonds.

2.182 (3); Sn(2)-O(11) 2.139 (3); Sn(2)-O(13) 2.130 (3); Sn(2)-O(15) 2.190 (3); O(1)-C(13) 1.286 (5); O(2)-C(13) 1.236 (5); O(3)-C(14) 1.297 (5); O(4)-C(14) 1.229 (6); O(5)-C(15) 1.293 (5); O(6)-C(15) 1.212 (6); O(7)-C(16) 1.257 (5); O(8)-C(16) 1.236 (5); O(9)-C(29) 1.277 (5); O(10)-C(29) 1.235 (5); O(11)-C(30) 1.286 (5); O(12)-C(30) 1.226 (5); O(13)-C(31) 1.273 (5); O(14)-C(31) 1.233 (6); O(15)-C(32) 1.271 (5); O(16)-C(32) 1.234 (5); N(1)-C(33) 1.486 (6); N(1)-C(36) 1.526 (7); N(2)-C(39) 1.493 (6); N(2)-C(42) 1.496 (6); N(3)-C(45) 1.464 (6); N(3)-C(48) 1.511 (6); N(4)-C(54) 1.494 (6); N(4)-C(51) 1.511 (6).

Selected angles (degrees)

O(5)-Sn(1)-O(3) 154.77 (11); O(5)-Sn(1)-C(1) 101.26 (15); O(3)-Sn(1)-C(1) 93.52 (15); O(5)-Sn(1)-C(7) 92.77 (15); O(3)-Sn(1)-C(7) 103.07 (15); C(1)-Sn(1)-C(7) 105.07 (15); O(5)-Sn(1)-O(1) 84.80 (12); O(3)-Sn(1)-O(1) 76.05 (12); C(1)-Sn(1)-O(1) 164.10 (15); C(7)-Sn(1)-O(1) 89.15 (15); O(5)-Sn(1)-O(7) 76.06 (11); O(3)-Sn(1)-O(7) 84.14 (12); C(1)-Sn(1)-O(7) 88.29 (15); C(7)-Sn(1)-O(7) 164.19 (16); O(1)-Sn(1)-O(7) 78.85 (11); O(13)-Sn(2)-O(11) 153.81 (10); O(13)-Sn(2)-C(23) 95.13 (15); O(11)-Sn(2)-C(23) 101.49 (15); O(13)-Sn(2)-C(17) 100.24 (15); O(11)-Sn(2)-C(17) 93.95 (15); C(23)-Sn(2)-C(17) 107.43 (16); O(13)-Sn(2)-O(9) 84.63 (12); O(11)-Sn(2)-O(9) 76.34 (11); C(23)-Sn(2)-O(9) 86.75 (15); C(17)-Sn(2)-O(9) 164.35 (15); O(13)-Sn(2)-O(15) 76.39 (11); O(11)-Sn(2)-O(15) 82.31 (11); C(23)-Sn(2)-O(15) 163.75 (15); C(17)-Sn(2)-O(15) 87.89 (15); O(9)-Sn(2)-O(15) 78.75 (11).

For the anion based on Sn(1), the four hydrogens of the two associated cations bridge *via* hydrogen bonds such that each NH₂ group links oxalate groups of adjacent molecules; i.e., H(2A) and H(2B) link oxalate groups based on O(4) and O(8), while H(3A) and H(3B) span O(2) and O(16). An analogous situation pertains for the chain based on Sn(2) (Table 1). This pattern of hydrogen bonds is identical

Table 1 Bond lengths (Å) and angles (°) related to the hydrogen bonding for $[n\text{-Pr}_2\text{NH}_2]_2[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]$ (**1**).

D-H...A	H...A	D...A	<DH...A
N ₁ -H ₁ A...O ₁₀	1.888	2.786	164.54
N ₁ -H ₁ B...O ₁₄	1.972	2.886	172.46
N ₂ -H ₂ A...O ₄	2.065	2.977	171.04
N ₂ -H ₂ B...O ₈	1.897	2.766	156.70
N ₂ -H ₂ B...O ₂	2.497	2.963	111.68
N ₃ -H ₃ A...O ₆	1.970	2.838	156.67
N ₃ -H ₃ A...O ₈	2.315	2.847	116.51
N ₃ -H ₃ B...O ₂	1.915	2.811	163.76
N ₄ -H ₄ A...O ₁₂	2.008	2.928	178.26
N ₄ -H ₄ B...O ₁₆	1.931	2.820	161.70

to that in the analogue involving $[i\text{-Pr}_2\text{NH}_2]^+$ cations (Xu et al., 2003). Finally, weak π - π stacking between phenyl groups of adjacent molecules generates an overall layered structure.

Conclusion

$[n\text{-Pr}_2\text{NH}_2]_2[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]$ has a structure consisting of alternating infinite chains of organotin units differentiated by their $\angle\text{C-Sn-C}$ angles. The chains comprise $[(\text{C}_2\text{O}_4)_2\text{SnPh}_2]^{2-}$ moieties connected by NH...O hydrogen bonds, which further generate a layered structure *via* weak π - π stacking between phenyl rings.

Experimental

The infrared spectra were recorded at the 'Instituto de Quimica' (UNAM), Mexico, by means of a BX FT-IR spectrometer type. Elemental analyses were performed at the Instituto de Quimica (UNAM), Mexico, and Mössbauer spectra were obtained as described previously (De Sousa et al., 2006). Infrared data are given in cm⁻¹ (IR abbreviations: vs, very strong; s, strong; m, medium; w, weak; vw, very weak). Mössbauer parameters are given in mm/s (Mössbauer abbreviations: QS, quadrupole splitting; IS, isomer shift; Γ , full width at half-height).

Synthesis

All chemicals were purchased from Aldrich (Germany) and used without any further purification. $[n\text{-Pr}_2\text{NH}_2]_2\text{C}_2\text{O}_4$ was prepared by completely neutralizing oxalic acid with Pr₂NH in water. The white powder collected after slow evaporation is $[n\text{-Pr}_2\text{NH}_2]_2\text{C}_2\text{O}_4$. Analytical data were as follows: % calculated (% found): C 57.50 (57.39), H 11.03 (10.95), N 9.59 (9.45).

When $[n\text{-Pr}_2\text{NH}_2]_2\text{C}_2\text{O}_4$ was mixed with SnPh₂Cl₂ in a 2:1 ratio, in ethanol, a colorless solution was obtained, which gave, after a slow solvent evaporation, crystals of **1** suitable for X-ray diffraction (yield 71%, m.p.=210°). Analytical data were as follows: % calculated for C₂₈H₄₂N₂O₈Sn (found), C 48.69 (48.84); H 6.67 (6.38); N 4.05 (4.09). Infrared (cm⁻¹) and Mossbauer data (mm/s) for **1** were as follows: $\nu_{\text{as}}(\text{C}=\text{O})$: 1670 vs, 1652 s; $\nu_{\text{s}}(\text{C}=\text{O})$: 1230 vs; δCOO : 795 s; QS=2.04, IS=1.05, Γ =0.95.

Crystal structure determination

A crystal of approximate dimensions 0.35×0.30×0.15 mm was used for data collection. Intensity data were collected at 150 K on a Nonius Kappa CCD diffractometer (Enraf-Nonius B.V., Rotterdam, The Netherlands) equipped with an Oxford cryostream (Oxford Cryosystems, Oxford, UK) using graphite monochromated MoK α radiation at $\lambda=0.71073$ Å. Data were processed using the Nonius Software (Otwinowski and Minor, 1997). A symmetry-related (multiscan)

absorption correction was applied. Structure solution, followed by full-matrix least-squares refinement, was performed using the WinGX-1.80 software (Farrugia, 1999) suite of programs throughout. In the final cycles of least-squares refinement, all nonhydrogen atoms were refined anisotropically. Hydrogen atoms were placed on calculated positions using a riding model. Both H atoms attached to the N of the cations have been located in the difference Fourier map and were freely refined. The program used to solve and refine the structure was SHELXS97 (Sheldrick, 2008). Crystal data and structure refinement: empirical formula. $C_{28}H_{42}N_2O_8Sn$, formula weight: 653.33; crystal system: orthorhombic; space group: Pbc2₁; a (Å): 11.95490 (10); b (Å): 15.70510 (10); c (Å): 32.6221 (3); V (Å³): 6124.89 (9); Z=8; ρ_{calc} (mgm⁻³): 1.417; F(000): 2704; reflections collected: 70,741; independent reflections: [R(int)] 13,902 [0.0966]; reflections observed: (>2 sigma) 10,322; data completeness: 0.994; maximum, minimum transmission:

0.8790, 0.7476; refinement method: full-matrix least squares on F². Data/restraints/parameters: 3902/1/711; goodness of fit on F²: 1.012; final R indices: [I>2σ(I)] 0.0416, 0.0838; R indices (all data): 0.0729, 0.0950; Flack parameter: -0.057 (16); largest difference peak and hole (ρ, eÅ⁻³): 1.482 and -0.768. Deposition number (CCDC): 840656.

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References

- Alcock, N. W.; Culver, J.; Roe, S. M. J. Bis(acetate-O,O')-diphenyltin(IV). *J. Chem. Soc. Dalton Trans.* **1992**, *9*, 1477–1484.
- Cruz-Huerta, J.; Carillo-Morales, M.; Santacruz-Juarez, E.; Hernandez-Ahuaczi, I. F.; Escalante-García, J.; Godoy-Alcázar, C.; Guerrero-Alvarez, J. A.; Hopfi, H.; Morales-Rojas, H.; Sanchez, M. Bis(μ₂-4-(Benzyl(carbodithioato)amino)butanoato)-tetraphenyl-di-tin(IV). *Inorg. Chem.* **2008**, *47*, 9874–9885.
- De Sousa, G. F.; Defflon, V. M.; Gambardella, M. T.; Do, P.; Francisco, R. H. P.; Ardisson, J. D.; Niquet, E. X-ray crystallographic and Mossbauer spectroscopic applications in dependence of partial quadrupole splitting, [R], on the C-Sn-C angle seven-coordinated diorganotin(IV) complexes. *Inorg. Chem.* **2006**, *45*, 4518–4525.
- Diassé-Sarr, A.; Barry, A. H.; Jouini, T.; Diop, L.; Mahieu, B.; Mahon, M. F.; Molloy, K. C. Synthesis, spectroscopic studies and crystal structure of (Et₄N)(SnMe₃)₇(HAsO₄)₄·2H₂O. *J. Organomet. Chem.* **2004**, *689*, 2087–2091.
- Diop, C. A. K.; Qamar, H.; Cissé, I.; Diop, L.; Russo, U. (R₄N)₂AO₄[SnPh₃X]_m (R=Me, Et; A=Mo, Cr, S, C₂; m=2, 3; X=Cl, Br): synthesis and spectroscopic studies. *Main Group Met. Chem.* **1999**, *22*, 41–44.
- Evans, C. J.; Karpel, S. Organotin compounds in modern technology. *J. Organomet. Chem.* **1985**, Library, 16, Elsevier, Amsterdam.
- Farrugia, L. J. Suite for single crystal small molecule crystallography. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
- Gueye, O.; Qamar, H.; Diop, L.; Diop, C. A. K. A new synthetic route for mono- and poly- Tin(IV) oxalate adducts: IR and Mossbauer study. *Polyhedron.* **1993**, *12*, 1245–1249.
- Gueye, N. D.; Diop, L.; Molloy, K. C.; Kociok-Köhn, G. Bis(dicyclohexylammonium)μ-oxalato-κ⁴O¹O²:O¹,O²-[aqua(oxalato-κ²O¹,O²)diphenylstannate(IV)]. *Acta Crystallogr.* **2010**, *E66*, m1645–m1646.
- Ng, S. W.; Kumar Das, V. G. Structural studies on organostannates. Crystal structure of the diorganostannate, bis(dicyclohexylammonium)bisoalatodiphenylstannate. *Main Group Met. Chem.* **1993**, *16*, 87–93.
- Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data Collection in Oscillation Mode. In *Methods in Enzymology, Vol. 276, Macromolecular Crystallography, Part A*. Carter, C. W. Jr; Sweet, R. M., Eds. Academic Press: New York, **1997**; p. 1307.
- Schranzer, G. N.; Chadha, M.; Zhang, C.; Reddy, H. K. Octa-, hexa-, and tetracoordination in Tin(IV) derivatives of cis-β-(methylthio)stilbene-α-thiol. *Chem. Ber.* **1993**, *126*, 2367–2371.
- Sheldrick, G. M. A short history of SHELX. *Acta Crystallogr.* **2008**, *A64*, 112–122.
- Xu, T.; Yang, S. Y.; Xie, Z. X.; Ng, S. W. Bis(diisopropylammonium) diphenyl dioxalo stannate(IV). *Acta Crystallogr.* **2003**, *E59*, m873–m875.