Yaya Sow, Libasse Diop*, Kieran C. Molloy, Gabriele Kociok-Köhn and José D. Ardisson

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

**Abstract:** The title compound [\textit{n}-\textit{Pr}_2\textit{NH}_2]_2[(\textit{C}_2\textit{O}_4)_2\textit{SnPh}_2] (1) has been synthesized by allowing \textit{Ph}_2\textit{SnCl}_2 to react with [\textit{n}-\textit{Pr}_2\textit{NH}_2]_2\textit{C}_2\textit{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 \textit{cis} octahedral about tin. In the structure of 1, there are two [(\textit{C}_2\textit{O}_4)_2\textit{SnPh}_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 [\textit{i}-\textit{Pr}_2\textit{NH}_2]^+ cations through N-H···O hydrogen bonds leading to two infinite alternating chains (1) and (2), which loosely assemble via \( \pi \)-\( \pi \) stacking between phenyl groups of adjacent molecules to generate an overall layered structure.

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

*Corresponding author: Libasse Diop, Laboratoire de Chimie Minérale et Analytique (LACHIMIA), Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal, e-mail: dlibasse@gmail.com

**Yaya Sow:** Laboratoire de Chimie Minérale et Analytique (LACHIMIA), Département de Chimie, Faculté des Sciences et Techniques, Université Cheikh Anta Diop, Dakar, Sénégal

**Kieran C. Molloy and Gabriele Kociok-Köhn:** Department of Chemistry, University of Bath, Bath BA2 7AY, UK

**José D. Ardisson:** Laboratorio de Física Aplicada, CDTN/CNEN, Belo Horizonte M.G., 31270-901, Brazil

**Introduction**

Compounds containing \textit{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 [\textit{n}-\textit{Pr}_2\textit{NH}_2]_2\textit{C}_2\textit{O}_4 and \textit{SnPh}_2\textit{Cl}_2, which have yielded crystals of [\textit{n}-\textit{Pr}_2\textit{NH}_2]_2[(\textit{C}_2\textit{O}_4)_2\textit{SnPh}_2] (1). The dioxalatodiphenyltin (IV) anion [\textit{SnPh}_2(\textit{C}_2\textit{O}_4)_2]^2- has previously been reported (Ng and Kumar-Das, 1993; Xu et al., 2003), with the supporting cation being either [\textit{i}-\textit{Pr}_2\textit{NH}_2]^+ or [\textit{Cy}_2\textit{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 (\textit{n}-\textit{Pr}_2\textit{NH}_2)\textit{C}_2\textit{O}_4\textit{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 [\textit{Sn}(1)-\textit{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 [\textit{Sn}(1)-\textit{O}(1) 2.181 (3) Å, \textit{Sn}(1)-\textit{O}(3) 2.138 (3) Å, \textit{Sn}(1)-\textit{O}(7) 2.202 (3) Å, and \textit{Sn}(1)-\textit{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 \textit{cis} conformation [\( \angle \text{C(1)-Sn(1)-C(7)} \) 105.07° (15°); \( \angle \text{C(23)-Sn(2)-C(17)} \) 107.43° (16°)]. Compared with the data reported by Ng and Kumar-Das (1993), the \textit{Sn(1)-O} distances in 1 are longer–2.181 (3) and 2.132 (3) Å–and shorter–2.138 (3) and 2.202 (3) Å (the same observations can also be made for \textit{Sn(2)}); i.e., the chelation is more asymmetric for 1 than in the [\textit{i}-\textit{Pr}_2\textit{NH}_2]^+ analogue.
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···O hydrogen bond network, which links neighboring \([\text{SnPh}_2(\text{C}_2\text{O}_4)_2]^2\) anions.

**Selected bonds (Å)**

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

**Conclusion**

[n-Pr$_2$NH$_2$]$_2$[(C$_2$O$_4$)$_2$SnPh$_2$] has a structure consisting of alternating infinite chains of organotin units differentiated by their C-Sn-C angles. The chains comprise [(C$_2$O$_4$)$_2$SnPh$_2$]$^b$ 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), 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; Г, full width at half-height).

**Synthesis**

All chemicals were purchased from Aldrich (Germany) and used without any further purification. [n-Pr$_2$NH$_2$]$_2$C$_2$O$_4$ was prepared by completely neutralizing oxalic acid with Pr$_2$NH in water. The white powder collected after slow evaporation is [n-Pr$_2$NH$_2$]$_2$C$_2$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-Pr$_2$NH$_2$]$_2$C$_2$O$_4$ was mixed with SnPh$_2$Cl$_2$ in a 2:1 ratio, in ethanol, a colorless solution was obtained, which gave, after a slow solvent evaporation, crystals of suitable for X-ray diffraction (yield 71%, m.p. = 100°C). Analytical data were as follows: % calculated (% found): C 57.50 (57.39), H 11.03 (10.95), N 9.59 (9.45).

Infrared (cm$^{-1}$) and Mossbauer data (mm/s) for [n-Pr$_2$NH$_2$]$_2$[(C$_2$O$_4$)$_2$SnPh$_2$] (1).

<table>
<thead>
<tr>
<th>D-H…A</th>
<th>H…A</th>
<th>D-A</th>
<th>&lt;D-H…A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N$_3$H$<em>7$A…O$</em>{10}$</td>
<td>1.888</td>
<td>2.786</td>
<td>164.54</td>
</tr>
<tr>
<td>N$_3$H$<em>7$B…O$</em>{10}$</td>
<td>1.972</td>
<td>2.886</td>
<td>172.46</td>
</tr>
<tr>
<td>N$_3$H$<em>7$A…O$</em>{5}$</td>
<td>2.065</td>
<td>2.977</td>
<td>171.04</td>
</tr>
<tr>
<td>N$_3$H$<em>7$B…O$</em>{5}$</td>
<td>1.897</td>
<td>2.766</td>
<td>156.70</td>
</tr>
<tr>
<td>N$_3$H$<em>7$B…O$</em>{12}$</td>
<td>2.497</td>
<td>2.963</td>
<td>111.68</td>
</tr>
<tr>
<td>N$_3$H$<em>7$A…O$</em>{12}$</td>
<td>1.970</td>
<td>2.838</td>
<td>156.67</td>
</tr>
<tr>
<td>N$_3$H$<em>7$A…O$</em>{12}$</td>
<td>2.315</td>
<td>2.847</td>
<td>116.51</td>
</tr>
<tr>
<td>N$_3$H$<em>7$B…O$</em>{12}$</td>
<td>1.915</td>
<td>2.811</td>
<td>163.76</td>
</tr>
<tr>
<td>N$_3$H$<em>7$A…O$</em>{12}$</td>
<td>2.008</td>
<td>2.928</td>
<td>178.26</td>
</tr>
<tr>
<td>N$_3$H$<em>7$B…O$</em>{12}$</td>
<td>1.931</td>
<td>2.820</td>
<td>161.70</td>
</tr>
</tbody>
</table>

**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 MoKα radiation at λ=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. C28H42N2O8Sn, formula weight: 653.33; crystal system: orthorhombic; space group: Pbc2 1; a (Å): 11.95490 (10); b (Å): 15.70510 (10); c (Å): 32.6221 (3); V (Å3): 6124.89 (9); Z = 8;

Data completeness: 0.994; maximum, minimum transmission: (I>2σ(I)) 0.0966; reflections observed: (>2 sigma) 10,322; reflections collected: 70,741; independent reflections: [R(int)] 13,902 [0.0966]; data completeness: 0.994; maximum, minimum transmission: 0.8790, 0.7476; refinement method: full-matrix least squares on F².

Received June 28, 2013; accepted September 14, 2013; previously published online October 11, 2013

Acknowledgements: We thank Dr Raymundo Cea, OLIVERES, Instituto de Química-UNAM, Mexico, for recording the infrared spectra and performing the elemental analyses.

References

Alcock, N. W.; Culver, J.; Roe, S. M. J. Bis(acetate-O,O′)-

Cruz-Huerta, J.; Carillo-Morales, M.; Santacruz-Juarez, E.;
Hernandez-Ahuaczi, I. F.; Escalante-Garcia, J.; Godoy-Alcata, C.;
Guerrero-Alvarez, J. A.; Hopfi, H.; Morales-Rojas, H.; Sanchez, M.
Bisµ2-(benzyl(carbodithioato)amino)butanoato)-tetraphenyl-

De Sousa, G. F.; Deflon, 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.

Diop, C. A. K.; Qamar, H.; Cissé, I.; Diop, L.; Russo, U.
(R,R,)[aqua(oxalato-
1999, 592, 41–44.

Evans, C. J.; Karpel, S. Organotin compounds in modern technology.

Farrugia, L. J. Suite for single crystal small molecule crystallography.

Gueuye, O.; Qamar, H.; Diop, L.; Diop, C. A. K. A new synthetic route
for mono- and poly-Tin(IV) oxalate adducts: IR and Mossbauer

Gueuye, N. D.; Diop, L.; Molloy, K. C.; Kociok-Köhn, G.
Bis(dicyclohexylammonium)μ-oxalato –κ-O2:O:O′-
ten(tetraphenylstannate(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)bisoxalatodiphenylstannate. Main

Otwinowski, Z.; Minor, W. Processing of X-ray Diffraction Data
276, Macromolecular Crystallography, Part A. Carter, C. W. Jr;
p. 1307.

Schränzer, 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.