

Catalytic oxidation of diorganotin(IV) carboxylates to mixed-ligand monoalkyltin(IV) carboxylates by Ag^+ and structure characterization of the mixed-ligand monoalkyltin(IV) 2-pyridinecarboxylate $(2\text{-}C/\text{PhCH}_2)\text{Sn}(2\text{-}C/\text{PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-}2)_2$

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Abstract

The complexes of the type $(\text{ArCH}_2)_2\text{SnO}$ were catalytic-oxygenated by Ag^+ and yielded mixed-ligand organotin(IV) complexes $(\text{ArCH}_2)(2\text{-C}_5\text{H}_4\text{NCO}_2)_2(\text{ArCOO})\text{tin(IV)}$ ($\text{Ar} = \text{C}_6\text{H}_5$ (**1**), $2\text{-}C/\text{C}_6\text{H}_4$ (**2**), $2\text{-}C/\text{NC}_6\text{H}_4$ (**3**), $4\text{-}C/\text{C}_6\text{H}_4$ (**4**), $4\text{-}C/\text{NC}_6\text{H}_4$ (**5**), $2\text{-}F/\text{C}_6\text{H}_4$ (**6**)). The complexes **1–6** are characterized by elemental analyses, IR and NMR (^1H , ^{13}C , ^{119}Sn) spectroscopies. Single X-ray crystal structure analysis has been determined, which reveals that the center tin atom of complex **2** is seven-coordinated geometry.
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Keywords: Diorganotin oxide; Mixed-ligand; 2-Pyrazinecarboxylic acid; Synthesis; Catalytic oxidation; Crystal structure

1. Introduction

The chemistry of organotin(IV) complexes has developed considerably during last 30 years, highlighting the syntheses of a number of complexes with interesting properties [1–3]. Organotin carboxylates are widely used owing to their potential biocidal activity [4] and cytotoxicity [5] as well as their industrial and agricultural applications [6–10]. In general, the biocidal activity of organotin complexes is greatly influenced by the molecular structures and coordination number of the tin atoms [11]. Crystallographic studies have reveal that organotin carboxylates adopt structures which are dependent on both the nature of the substitute bond to the tin atom and on the type of carboxylate ligand [12,13]. Studies on organotin(IV) derivatives containing carboxylate ligands with additional donor atom, such as nitrogen, have revealed new structural types

which may lead to complexes with different activity [9,11,13,14].

Less attention has been devoted to the mixed-ligand complexes [15]. To the best of our knowledge, no organotin(IV) complexes presenting as the seven-coordinate mixed-ligand complex has ever been obtained by means of catalytic oxidation: oxidating R_2Sn group. Differing from the methods of adding two different types of ligands into SnR_2 group to obtain a mixed-ligand complex, in this paper, we introduce a novel means and obtained new mixed-ligand complexes (Scheme 1). All the complexes had been characterized by FT-IR, ^1H , ^{13}C , and ^{119}Sn NMR spectroscopies, elemental analyses. They are stable in air. Single X-ray crystal structure analyses have been determined for complex **2**, and the result of this study is reported herein.

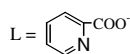
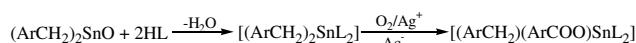
2. Experimental

2.1. Materials and measurements

The $(\text{ArCH}_2)_2\text{SnO}$ was prepared by the reported method [16]. The melting points were obtained with Kofler

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Scheme 1.

micro-melting points apparatus and were uncorrected. Infrared spectra were recorded on a Nicole-460 spectrophotometer using KBr discs and sodium chloride optics. ^1H , ^{13}C and ^{119}Sn NMR spectra were recorded on a Mercury Plus-400 NMR spectrometer. Chemical shifts are given in ppm relative to Me_4Si and Me_4Sn in CDCl_3 solvent. Elemental analyses were performed on PE-2400-II elemental analyzer.

2.2. Synthesis of $(\text{ArCH}_2)(2\text{-C}_5\text{H}_4\text{NCO}_2)_2(\text{ArCOO})\text{tin-}$ (IV) ($\text{Ar} = \text{C}_6\text{H}_5$ (1), 2- ClC_6H_4 (2), 2- CNC_6H_4 (3), 4- ClC_6H_4 (4), 4- CNC_6H_4 (5), 2- FC_6H_4 (6))

The diorganotin oxide (2.0 mmol) and the 2-pyrazine-carboxylic acid (4.0 mmol) were dissolved in dry benzene (37 ml) and stirred at reflux for 7 h under nitrogen atmosphere. After cooling to room temperature, then, the Silver(I) sulfite (0.312 g, 1.00 mmol) and CH_3COONa (0.06 g, 0.1 mol) were added to the solution and stirring for 5 h under oxygen atmosphere. After cooling to room temperature, the solvent was filtrated and evaporated under vacuum. The crude adduct was recrystallized from dichloromethane–hexane to give colorless crystals.

2.2.1. $\text{PhCH}_2\text{Sn}(\text{PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (1)

Yield: 55%. M.p. 201–203 °C. Anal. Calc. for $\text{C}_{26}\text{H}_{20}\text{N}_2\text{O}_6\text{Sn}$: C, 54.29; H, 3.50; N, 4.87. Found: C, 54.32; H, 3.53; N, 4.86%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1643, 1573; $\nu_{\text{s}}(\text{COO})$, 1405, 1326; $\nu(\text{C}=\text{N})$, 1547; $\nu(\text{Sn}-\text{C})$, 568; $\nu(\text{Sn}-\text{O})$, 480; $\nu(\text{Sn}-\text{N})$, 448. ^1H NMR (CDCl_3 , ppm): δ 3.07 (s, 2H, $J_{\text{Sn-H}} = 75$ Hz, SnCH_2), 7.17–7.65 (m, 10H, Ph-H), 8.60–8.73 (m, 8H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 29.55 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 589 Hz), 126.41, 126.71, 127.54, 127.92, 129.15, 129.97, 132.05, 132.32, 133.45, 133.89, 135.63, 136.08 (Ar-C), 139.10, 142.43, 145.91, 146.58, 150.74 ($\text{C}_5\text{H}_4\text{N}_1$), 175.31, 178.27 (COO). ^{119}Sn NMR (CDCl_3 , ppm): –432.1.

2.2.2. $(2\text{-Cl-PhCH}_2)\text{Sn}(2\text{-Cl-PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (2)

Yield: 37%. M.p. 189–191 °C. Anal. Calc. for $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_6\text{Sn}$: C, 48.49; H, 2.82; N, 4.35. Found: C, 48.46; H, 2.85; N, 4.36%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1669, 1569; $\nu_{\text{s}}(\text{COO})$, 1401, 1337; $\nu(\text{C}=\text{N})$, 1557; $\nu(\text{Sn}-\text{C})$, 564; $\nu(\text{Sn}-\text{O})$, 487; $\nu(\text{Sn}-\text{N})$, 454. ^1H NMR (CDCl_3 , ppm): δ 3.30 (s, 2H, $J_{\text{Sn-H}} = 74$ Hz, SnCH_2), 7.39–7.71 (m, 8H, Ph-H), 8.62–9.23 (m, 8H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 27.6 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 586 Hz), 127.01, 127.40, 128.28, 128.73, 129.83, 130.14, 134.02, 134.45, 136.10, 136.31, 138.0, 138.51 (Ar-C),

140.23, 143.8, 146.1, 147.7, 150.7 ($\text{C}_5\text{H}_4\text{N}_1$), 177.04, 180.27 (COO). ^{119}Sn NMR (CDCl_3 , ppm): –412.5.

2.2.3. $(2\text{-CN-PhCH}_2)\text{Sn}(2\text{-CN-PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (3)

Yield: 56.4%. M.p. 192–194 °C. Anal. Calc. for $\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_6\text{Sn}$: C, 53.79; H, 2.90; N, 8.96. Found: C, 53.78; H, 2.93; N, 8.96%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1654, 1576; $\nu_{\text{s}}(\text{COO})$, 1403, 1329; $\nu(\text{C}=\text{N})$, 1550; $\nu(\text{Sn}-\text{C})$, 560; $\nu(\text{Sn}-\text{O})$, 485; $\nu(\text{Sn}-\text{N})$, 456. ^1H NMR (CDCl_3 , ppm): δ 3.25 (s, 2H, $J_{\text{Sn-H}} = 77$ Hz, SnCH_2), 7.04–7.69 (m, 8H, Ph-H), 8.63–9.22 (m, 8H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 29.61 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 588 Hz), 129.02, 129.62, 131.15, 131.46, 133.43, 133.71, 136.00, 136.37, 137.92, 138.45, 140.11, 140.32 (Ar-C), 146.47, 146.94 (CN-), 141.15, 144.03, 146.17, 147.72, 150.52 ($\text{C}_5\text{H}_4\text{N}_1$), 172.55, 177.09 (COO). ^{119}Sn NMR (CDCl_3 , ppm): –403.7.

2.2.4. $(4\text{-Cl-PhCH}_2)\text{Sn}(4\text{-Cl-PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (4)

Yield: 56.5%. M.p. 197–199 °C. Anal. Calc. for $\text{C}_{26}\text{H}_{18}\text{Cl}_2\text{N}_2\text{O}_6\text{Sn}$: C, 48.49; H, 2.82; N, 4.35. Found: C, 48.43; H, 2.86; N, 4.39%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1663, 1567; $\nu_{\text{s}}(\text{COO})$, 1404, 1335; $\nu(\text{Sn}-\text{C})$, 563; $\nu(\text{Sn}-\text{O})$, 488; $\nu(\text{Sn}-\text{N})$, 454. ^1H NMR (CDCl_3 , ppm): δ 3.22 (s, 2H, $J_{\text{Sn-H}} = 74$ Hz, SnCH_2), 7.36–7.68 (m, 8H, Ph-H), 8.612–9.20 (m, 8H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 27.61 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 583 Hz), 127.02, 127.41, 128.25, 128.77, 129.80, 130.14, 134.01, 134.44, 136.12, 136.30, 138.05, 138.54 (Ar-C), 139.97, 143.82, 146.15, 147.78, 150.71 ($\text{C}_5\text{H}_4\text{N}_1$), 177.01, 180.24 (COO). ^{119}Sn NMR (CDCl_3 , ppm): –426.1.

2.2.5. $(4\text{-CN-PhCH}_2)\text{Sn}(4\text{-CN-PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (5)

Yield: 66.1%. M.p. 200–202 °C. Anal. Calc. for $\text{C}_{28}\text{H}_{18}\text{N}_4\text{O}_6\text{Sn}$: C, 53.79; H, 2.90; N, 8.96. Found: C, 53.74; H, 2.95; N, 8.95%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1650, 1579; $\nu_{\text{s}}(\text{COO})$, 1409, 1327; $\nu(\text{Sn}-\text{C})$, 561; $\nu(\text{Sn}-\text{O})$, 484; $\nu(\text{Sn}-\text{N})$, 454. ^1H NMR (CDCl_3 , ppm): δ 3.26 (s, 2H, $J_{\text{Sn-H}} = 76$ Hz, SnCH_2), 7.03–7.69 (m, 8H, Ph-H), 8.65–9.27 (m, 8H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm): δ 29.57 (CH_2Ar , $^1J(^{119}\text{Sn}-^{13}\text{C})$, 589 Hz), 129.10, 129.60, 131.14, 131.45, 133.44, 133.71, 136.03, 136.37, 137.92, 138.48, 140.10, 140.33 (Ar-C), 146.49, 146.98 (CN-), 142.88, 144.09, 146.17, 147.78, 150.53 ($\text{C}_5\text{H}_4\text{N}_1$), 172.55, 177.04 (COO). ^{119}Sn NMR (CDCl_3 , ppm): –419.5.

2.2.6. $(2\text{-FPhCH}_2)\text{Sn}(2\text{-FPhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (6)

Yield: 35%. M.p. 172–174 °C. Anal. Calc. for $\text{C}_{26}\text{H}_{18}\text{F}_2\text{N}_2\text{O}_6\text{Sn}$: C, 51.10; H, 2.97; N, 4.58. Found: C, 50.05; H, 3.00; N, 4.58%. IR (KBr, cm^{-1}): $\nu_{\text{as}}(\text{COO})$, 1667, 1572; $\nu_{\text{s}}(\text{COO})$, 1404, 1337; $\nu(\text{Sn}-\text{C})$, 558; $\nu(\text{Sn}-\text{O})$, 488; $\nu(\text{Sn}-\text{N})$, 452. ^1H NMR (CDCl_3 , ppm): δ 3.28 (s, 2H, $J_{\text{Sn-H}} = 79$ Hz, SnCH_2), 7.49–7.89 (m, 6H, Ph-H), 8.63–9.23 (m, 8H, pyrazine-H). ^{13}C NMR (CDCl_3 , ppm):

Table 1
Crystal data collection and structure refinement parameters for complex **2**

Empirical formula	C ₂₆ H ₁₈ Cl ₂ N ₂ O ₆ Sn
<i>M</i>	644.01
<i>T</i> /K	298(2)
Crystal system, space group	Monoclinic, <i>P</i> 2(1)/ <i>c</i>
<i>a</i> (Å)	7.555(2)
<i>b</i> (Å)	16.317(6)
<i>c</i> (Å)	20.152(7)
β (°)	92.682(4)
<i>V</i> (Å ³)	2481.4(14)
<i>Z</i>	4
Calculated density (Mg m ^{−3})	1.724
<i>F</i> (000)	1280
μ (mm ^{−1})	1.291
Scan range θ (°)	2.02–5.01
Reflections collected/unique [<i>R</i> _{int}]	12367/4299 [0.0566]
Data/restraints/parameters	4299/126/334
Maximum/minimum transmission	0.7384, 0.6131
GOF	0.999
<i>R</i> ₁ , <i>wR</i> ₂ [<i>I</i> > 2σ(<i>I</i>)]	0.0610, 0.1530
<i>R</i> ₁ , <i>wR</i> ₂ (all data)	0.0948, 0.1750
Largest difference peak, hole (e Å ^{−3})	2.208, −0.726

δ 35.0 (CH₂Ar, ¹*J*(¹¹⁹Sn–¹³C), 594 Hz), 129.34, 129.95, 138.51, 139.018, 140.66, 141.14, 141.75, 142.51, 135.31, 135.87, 131.64, 132.29 (Ar–C), 142.95, 143.53, 146.71, 148.26, 150.82 (C₅H₄N₁–), 173.54, 175.08 (COO). ¹¹⁹Sn NMR (CDCl₃, ppm): −438.9.

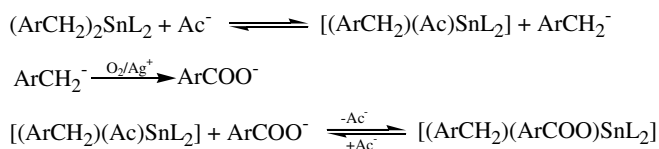
2.3. X-ray crystallographic studies

X-ray crystallographic data for complexes **2** were collected on a Bruker Smart-1000 CCD diffractometer using Mo K α radiations (0.71073 Å). The structures were solved by direct method and difference Fourier map using SHELXL-97 program, and refined by full-matrix least-squares on *F*². All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and refined isotropically. Further details are given in Table 1.

3. Results and discussion

3.1. Preparations

The diorganotin(IV) carboxylates, (ArCH₂)₂(2-C₅H₄-NCO₂)₂tin(IV) were produced by the reaction of 2-pyrazinecarboxylic acid with dibenzyltin oxide or bis(substituted-benzyl)tin in 2:1 molar ratio, and the complexes (ArCH₂)₂(2-C₅H₄NCO₂)₂(ArCOO)tin(IV) were produced by dibenzyltin carboxylates through oxidative cleavage of one of benzyl-tin bonds. It is clear that the CH₃COO[−] ion accelerates cleavage of one of benzyl-tin bonds, and



Scheme 2.

C₆H₅CH₂[−] is replaced by CH₃COO[−], and the active C₆H₅CH₂[−] ion were catalytic oxidated to C₆H₅COO[−] by Ag⁺ under oxygen atmosphere, then, the C₆H₅COO[−] replaces CH₃COO[−] as bidentate ligand and yielded mixed-ligand organotin(IV) complexes (ArCH₂)₂(2-C₅H₄-NCO₂)₂(ArCOO)tin. The possible mechanism is given in Scheme 2.

3.2. Spectroscopic studies

3.2.1. IR spectra

The stretching frequencies of interesting are those associated with the acid COO, Sn–C, Sn–O and Sn–N groups. The spectra of the complexes **1–6** show some common characters. The assignments of the IR bands of the complexes **1–6** have been made by comparison with the IR spectra of the free ligands. The free acid shows a broad O–H absorption at 3000–2500 cm^{−1}, which is absent in the spectra of the eight title compounds, showing the deprotonation of the COOH groups, during the reactions. The explicit feature in the infrared spectra of the complexes, strong absorption appearing at 480–488 cm^{−1} in the respective spectra of the complexes, which is absent in the free ligand, is assigned to the Sn–O stretching mode of vibration. Compared with the free ligand the new occurrence of the bands in the region of 448–456 cm^{−1} for all the eight compounds were assigned to the Sn–N vibrations, which provides prove for the existence of Sn–N bonds for all of the six complexes [17].

The $\Delta\nu$ ($\nu_{\text{as}}(\text{CO}_2) - \nu_{\text{s}}(\text{CO}_2)$) value is used to determine the type of bonding between metal and carboxyl group [18]. It is generally believed that the difference in $\Delta\nu$ between asymmetric $\nu_{\text{as}}(\text{CO}_2)$ and symmetric $\nu_{\text{s}}(\text{CO}_2)$ absorption frequencies below 200 cm^{−1} for the bidentate carboxylate moiety, but greater than 200 cm^{−1} for the unidentate carboxylate moiety [19,20]. Some obvious differences among the spectra of the complexes are also observed. In complexes **1–6**, the presence of two values for each of $\nu_{\text{as}}(\text{CO}_2)$ and $\nu_{\text{s}}(\text{CO}_2)$ indicates that there are two different types of carboxylate groups. The two bands which occur at 1643–1667 and 1567–1579 cm^{−1} were assigned to $\nu_{\text{as}}(\text{CO}_2)$, while the bands at 1326–1337 and 1401–1409 cm^{−1} were assigned to $\nu_{\text{s}}(\text{CO}_2)$. The magnitudes of $\Delta\nu^1$ [$\nu_{\text{as}}(\text{CO}_2)^1 - \nu_{\text{s}}(\text{CO}_2)^1$] and $\Delta\nu^2$ [$\nu_{\text{as}}(\text{CO}_2)^2 - \nu_{\text{s}}(\text{CO}_2)^2$] for complexes **1–6** are 317–332 and 163–173 cm^{−1} which indicate the presence of bidentate and monodentate carboxylate groups in these complexes [21,22].

3.2.2. NMR spectroscopic

In ¹H NMR spectra of the free ligand, single resonances are observed at 8.43 ppm, which are absent in the spectra of the complexes **1–6**, indicating the replacement of the carboxylic acid proton by a organotin moiety. The spectra show that the chemical shifts of the phenyl or the substituted phenyl, 7.03–7.89 and 8.60–9.27 ppm for the Py group. All upfield shifts as compared with those of their corresponding precursors. The six complexes generally

show broad signals for the protons of Py ligands, shifted to high field with respect to the value for Py, which could be interpreted in terms of the Sn \leftarrow N interaction.

The ^{13}C NMR spectra of the complexes show a significant upfield shift of all carbon resonance, compared with the free ligand. The shift is a consequence of an electron density transfer from the ligand to the acceptor.

^{119}Sn NMR spectra of **1–6** display only one resonance and the ^{119}Sn chemical shift values in complexes **1–6** are found to be in the range of -403.7 to -438.9 ppm. The appearance of chemical shift values in this region is agreement with the seven-coordinated tin atom [23].

3.3. Crystal structure of $(2\text{-Cl-PhCH}_2)\text{Sn}(2\text{-Cl-PhCO}_2)(\text{O}_2\text{CC}_5\text{H}_4\text{N-2})_2$ (**2**)

The molecular structure of **2** is shown in Fig. 1 and selected bond lengths and bond angles are presented in Table 2. It can be seen that the tin atom has a coordination number of seven. There are two types of ligands, two 2-pyridinecarboxylate and 2-chlorobenzoxylate, which are found to be chelating to the Sn atom, respectively. The Sn atom exists in a distorted-pentagonal-bipyramidal geometry, with the axial positioning occupied by the 2-chlorobenzyl and one O-atom of one 2-pyridinecarboxylate moiety. And the O(5)–Sn(1)–C(20) linkage is not linear, having an angle of $176.4(3)^\circ$, which is smaller than the value expected for a regular pentagonal-bipyramid. This coordination geometry is best described as distorted-pentagonal-bipyramid. Another important distortion is caused by the asymmetric Sn–O bond lengths, since there are two types of O atoms. The pentagonal plane is defined by the O(1) and O(2) atoms of the 2-chlorobenzoxylate group, the N(2) atom of the 2-pyridinecarboxylate moiety, the O(3) and N(1) atoms of the other 2-pyridinecarboxylate moiety. The O(2)–Sn(1) distance of $2.522(6)$ Å is longer than O(1)–Sn(1) and O(3)–Sn(1) and O(5)–Sn(1) distances; of $2.147(6)$, $2.143(5)$ and $2.087(5)$ Å, respectively.

Table 2

Selected bond lengths (Å) and bond angles ($^\circ$) of the complex **2**

Sn(1)–O(5)	2.087(5)
Sn(1)–O(3)	2.143(5)
Sn(1)–O(1)	2.147(6)
Sn(1)–C(20)	2.164(8)
Sn(1)–N(2)	2.253(6)
Sn(1)–N(1)	2.255(6)
Sn(1)–O(2)	2.522(6)
O(5)–Sn(1)–C(20)	176.4(3)
O(1)–Sn(1)–O(2)	54.5(2)
O(3)–Sn(1)–N(1)	74.0(2)
O(1)–Sn(1)–N(1)	80.6(2)
N(2)–Sn(1)–O(2)	71.7(2)
O(3)–Sn(1)–N(2)	77.2(2)

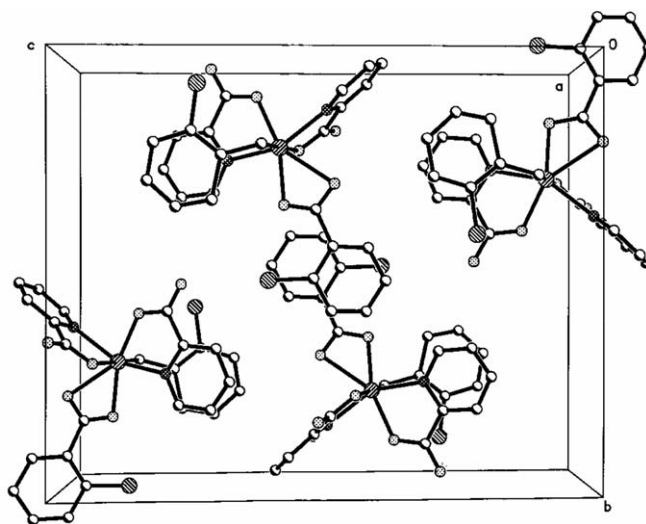


Fig. 2. The unit cell of complex **2**.

The unit cell of complex **2** is shown in Fig. 2.

4. Supplementary material

Crystallographic data for complex **2** has been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC 291882. Copies of available material may be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).

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References

- [1] M.J. Clarke, Fuchun Zhu, D.R. Frasca, Chem. Rev. 99 (1999) 2511.
- [2] J. Beckmann, K. Jurkschat, Coord. Chem. Rev. 215 (2001) 267.

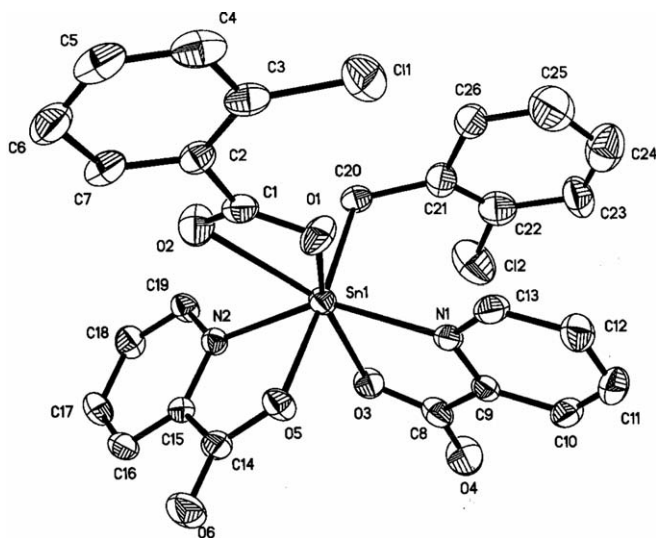


Fig. 1. Molecular structures of complex **2**.

- [3] L. Pellerito, L. Nagy, *Chem. Rev.* 224 (2002) 111.
- [4] K.C. Molloy, T.G. Purcell, E. Hahn, H. Schumann, J.J. Zuckerman, *Organometallics* 5 (1986) 85.
- [5] M. Gielen, *Appl. Organomet. Chem.* 16 (2002) 481.
- [6] J.A. Zubita, J.J. Zuckerman, *Inorg. Chem.* 24 (1987) 251.
- [7] G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish, *Polyhedron* 4 (1985) 81.
- [8] G.K. Sandhu, R. Gupta, S.S. Sandhu, R.V. Parish, K. Brown, *J. Organomet. Chem.* 279 (1985) 372.
- [9] T.P. Lochhart, F. Davidson, *Organometallics* 6 (1987) 2471.
- [10] I.W. Nowell, J.S. Brooks, G. Beech, R. Hill, *J. Organomet. Chem.* 244 (1983) 119.
- [11] Q.L. Xie, X.H. Xu, H.G. Wang, X.K. Yao, R.J. Wang, Z.G. Zhang, J.M. Hu, *Acad. Chim. Sin.* 49 (1991) 1085.
- [12] (a) E.R.T. Tiekink, *Appl. Organomet. Chem.* 5 (1991) 1;
(b) E.R.T. Tiekink *Trends in Organometallic chemistry*, vol. 1, Council of Scientific Research Integration, Trivandrum, India, 1994, p. 71.
- [13] C.S. Parulekar, V.K. Jain, T.K. Das, A.R. Gupta, B.F. Hoskins, E.R.T. Tiekink, *J. Organomet. Chem.* 372 (1989) 193.
- [14] C. Vatsa, V.K. Jain, T. Kesavadas, E.R.T. Tiekink, *J. Organomet. Chem.* 410 (1991) 135.
- [15] T.S. Basu Baul, W. Rynjah, E. Rivaola, C. Pettinari, A. Linden, *J. Organomet. Chem.* 690 (2005) 1413.
- [16] H.D. Yin, Q.B. Wang, S.C. Xue, *J. Organomet. Chem.* 690 (2005) 831.
- [17] H.D. Yin, C.H. Wang, C.L. Ma, D.Q. Wang, *J. Organomet. Chem.* 689 (2004) 246.
- [18] V. Chandrasekhar, V. Bhaskar, A. Steiner, S. Zacchini, *Organometallics* 21 (2002) 4528.
- [19] K.C.K. Swamy, M.A. Said, S. Nagabrahmanandachari, D.M. Poojary, *J. Chem. Soc., Dalton Trans.* (1998) 1645.
- [20] X.N. Fang, X.Q. Song, Q.L. Xie, *J. Organomet. Chem.* 619 (2001) 43.
- [21] H.D. Yin, C.H. Wang, Q.J. Xing, *Polyhedron* 23 (2004) 1805.
- [22] S.P. Narula, S.K. Bharadwaj, Y. Sharda, D.C. Povey, G.W. Smith, *J. Organomet. Chem.* 430 (1992) 167.
- [23] T.S.B. Baul, S. Dhar, S.M. Pyke, E.R.T. Tiekink, E. Rivaola, R. Butcher, F.E. Smith, *J. Organomet. Chem.* 633 (2001) 7.