

Synthesis and crystal structure of a mixed-ligand compound di-*n*-butyl(4-chlorobenzoxy)(4-chlorobenzohydroxamato)tin(IV)

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Abstract

Reaction of dibutyltin dichloride with 4-chlorobenzohydroxamic acid and 4-chlorobenzoic acid in 1:1:1 stoichiometry yields the new title compound di-*n*-butyl(4-chlorobenzoxy)(4-chlorobenzohydroxamato)tin(IV) **1**, which had been characterized by IR and ¹H, ¹³C, ¹¹⁹Sn NMR. Single X-ray crystal structure analysis has been determined for **1**, which crystallizes as the five-coordinate mixed-ligand dibutyltin(IV) complex containing both monodentate and bidentate ligands. The crystal structure of the compound reveals that the tin atom adopts distorted trigonal bipyramidal geometry with the Bu groups trans to each other. The C–Sn–C angle is 145.9(3)°, and the Sn–O bonds are 2.083(4) and 2.158(4) Å in one ligand and 2.242(4) Å in the other. An unusual feature of the structure is the presence of a kind of intermolecular hydrogen bonding which serves to stabilize the crystal structure.

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1. Introduction

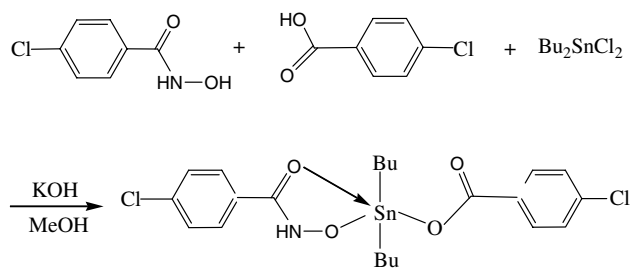
The chemistry of organotin(IV) complexes has developed considerably during last 30 years, highlighting the syntheses of a number of complexes with interesting properties [1–3]. The diorganotin(IV) complex containing carboxylate ligand has been investigated for its antitumor activities [4,5]. Crystallographic studies have revealed that organotin carboxylates adopt structures which are dependent on both the nature of the substituent bound to the tin atom and on the type of carboxylate ligand [6,7]. In recent years, considerable interest has also been shown in diorganotin(IV) derivatives of hydroxamic acids [8] because of their biological proper-

ties such as antifungicidal and the promising antitumor activity in some cases as reported by our group [9,10], several of whose crystal structure data are available [10].

Less attention has been devoted to the mixed-ligand complexes [11]. To the best of our knowledge, no diorganotin(IV) complexes containing both monodentate carboxylate ligand and bidentate O-donors hydroxamic acid ligand as supporting ligands have ever been reported. In general, the antitumor activity of organotin compounds is greatly influenced by the structure of the molecule and the coordination number of the tin atoms [12]. In order to explore the relationship between the biological activity and structure, in this paper, we introduce two different types of ligands into SnBu₂ group to obtain a five-coordinate compound di-*n*-butyl(4-chlorobenzoxy)(4-chlorobenzohydroxamato)tin(IV) (**1**, Scheme 1). The elemental analysis, IR, and ¹H, ¹³C, ¹¹⁹Sn NMR spectra and crystal structure of the new compound have been carried out, and the results of this study are reported herein.

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2. Results and discussion

2.1. Spectroscopy

The assignments of the IR bands of the complex have been made by comparison with the IR spectra of the free ligands. The free ligands show a broad O–H absorption in the regions of $2600\text{--}2900\text{ cm}^{-1}$ and $3210\text{--}3010\text{ cm}^{-1}$ which are absent in the spectrum of the complex, because of their deprotonation and coordination [13]. The N–O absorptions in the free ligand occur in the range of $847\text{--}971\text{ cm}^{-1}$ [14], and at $913\text{--}1043\text{ cm}^{-1}$ in the complex. The shift towards higher frequencies of $\nu(\text{N–O})$ rules out coordination through the N atom [15,16]. Therefore, the IR spectra indicate coordination via both O atoms of the CONHO group. In the $553\text{--}400\text{ cm}^{-1}$ region, the two (or more) strong absorptions of the diorganotin(IV) complexes are assigned to the stretching mode of the Sn–O linkage [17–19]. The presence of more than one Sn–O band, is more obvious for the mixed-ligand complexes, and reflects the different Sn–O bond lengths as proved by the X-ray analysis.

The ^1H NMR spectrum shows the expected resonances with appropriate multiplicities and intensities.

Dibutyltin compounds exhibit resonances in the 0.83–1.74 ppm. For **1** the signals from the other groups, such as phenyl H, appear in similar positions to the free ligand, but exhibit two groups of peaks because the protons on the two p-chlorobenzoyl groups of the compound are chemically different. This finding is consistent with the formulation of **1** as a mixed-ligand complex.

^{119}Sn NMR spectra of **1** display only one resonance at -157.8 ppm indicating one type of tin site. The chemical shift is in agreement with the penta-coordinated tin atom [20], which shows that the structure of the type of tin atom in the solid state is still retained in solution.

2.2. X-ray crystallography

The molecular structure of **1** is shown in Fig. 1. It can be seen that the tin atom has a coordination number of five. There are two types of chlorophenyl substituted ligands. The chlorobenzohydroxamo is found to be chelating to the Sn atom through the carbonyl O atom and the hydroxyl O atom, and Sn–O bond distances are 2.242(4) and 2.083(4) Å. The carboxylate is monodentate, coordinating to Sn atom through atom O(2), Sn(1)–O(2) 2.158(4) Å. The O(1) and Sn(1) distance of 3.031(4) Å are too long to be a strong covalent bond. However, this Sn–O distance is shorter than the sum of the van der Waals radii for these atoms (3.68 Å) [21], and thus may be considered as a weak bond. We think there are two important reasons for this. Firstly, the strong electron-withdrawing nature of Cl decreases the electron density on the O atom of the C=O and reduces its ability for coordinating to the tin atom. Secondly, steric interactions of two bulky butyl groups and the chelating five membered ring may prevent the formation of the Sn1–O1 bond. In addition, the strain

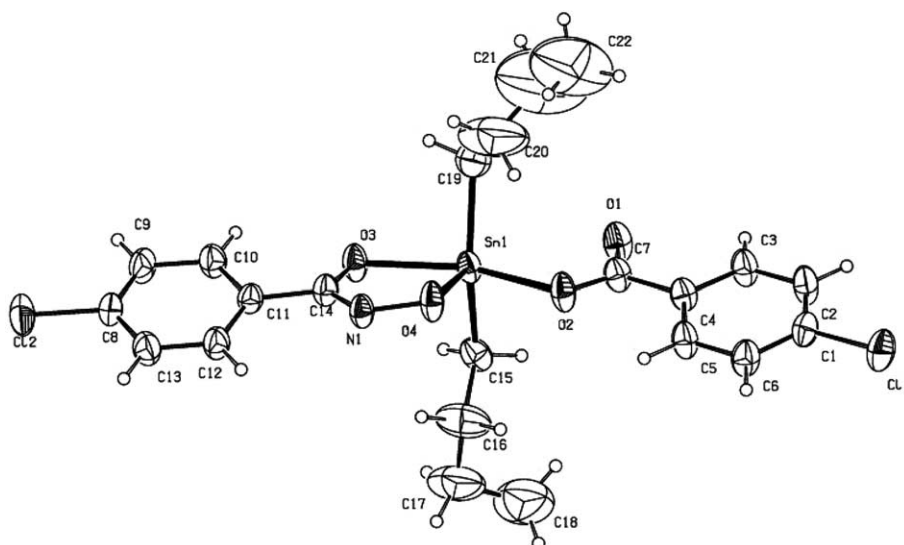


Fig. 1. Molecular structure of **1** with atom labeling.

of the four-member ring that would be formed also needs to be considered.

The C(15)–Sn–C(19) linkage is not linear, having an angle of 145.9(3)°, which is much smaller than the value expected for a regular octahedron. This coordination geometry is best described as distorted trigonal bipyramid. Another important distortion is caused by the asymmetric Sn–O bond lengths, since all three of them are significantly different. Therefore, the bite angle O(4)–Sn(1)–O(3) of **1**, 74.31(15)°, is not consistent with a true trigonal geometry of 120°, but instead with a distorted trigonal bipyramidal geometry. As a result, the Sn atom in **1** exists in a distorted trigonal planar geometry in which the basal plane is defined by the three O atoms, and the axial positions are occupied by the two butyl substituents which are found to be disordered owing to high thermal motion. In addition, the dihedral angles between the O(1)–C(7)–O(2)/C(2)–C(3)–C(4)–C(5) and O(3)–C(14)–N(1)/C(9)–C(10)–C(11)–C(12) planes are 12.1° and 17.3°, respectively, indicating little conjugation between the –COO or –CONH and benzene ring [22].

There are some weak intermolecular interactions in the crystal lattice. Firstly, the oxygen atom(O1) of carbonyl in 4-chlorobenzoic acid participates in intermolecular hydrogen bond formation with the hydrogen atom H(12) of benzene ring; the O(1)···H(12) separation is 2.57 Å (symmetry operation: $x, 1/2 - y, 1/2 + z$). This has the result that the lattice consists of loosely associated dimers linked by hydrogen bonding. Secondly, the dihedral angles between the C9–C11–C13/C9'–C11'–C13' and C1–C3–C5/C1'–C3'–C5' planes are 0° and 0.02°, respectively, indicating the one aromatic ring is parallel to another. The centroid–centroid distances of aromatic ring planes are 4.0318 and 3.8271 Å, suggesting a weak π – π stacking interaction [23].

3. Experimental

3.1. General

Dibutyltin(IV) dichloride and 4-chlorobenzoic acid were purchased from Aldrich Chemical Co. They are used as received. The other reagents were of analytical grade. 4-Chlorobenzohydroxamic acid was prepared according to the literature method [24].

Elemental analyses were performed on PE-2400-II elemental analyzer. IR spectra in the range 4000–400 cm^{-1} were recorded on Perkin–Elmer one FT-IR spectrophotometer with samples investigated as KBr discs. ^1H , ^{13}C , ^{119}Sn NMR spectra were recorded on a Varian INOVA 600 spectrometer (600.0 MHz for ^1H , 150.8 MHz for ^{13}C , 223.6 MHz for ^{119}Sn) at ambient temperature [δ values in ppm relative to Me_4Si (^1H , ^{13}C) or Me_4Sn (^{119}Sn)].

3.2. Synthesis of di-*n*-butyl(4-chlorobenzoxy)(4-chlorobenzohydroxamato)tin(IV)

Dibutyltin dichloride (0.303 g, 1.0 mmol) was added to an anhydrous methanolic solution (30 ml) of 4-chlorobenzohydroxamic acid (HL_1 , 0.172 g 1.0 mmol), 4-chlorobenzoic acid (HL_2 , 0.157 g 1.0 mmol) and KOH (0.112 g 2.0 mmol). The solution was stirred under N_2 at room temperature overnight. Water (30 ml) was added to form a white precipitate, which was separated by filtration, washed with water and cold methanol. The white solid was then recrystallized from ethanol. Colorless needle-shaped crystals of ${}^n\text{BuSn}(\text{L}_1)(\text{L}_2)$ were collected, washed with ethanol and dried under reduced pressure. Yield: 0.20 g, 36%. M.p. 148–149 °C. Anal. Calc. for $\text{C}_{22}\text{H}_{26}\text{Cl}_2\text{NO}_4\text{Sn}$: C, 47.35; H, 4.70; N, 2.51. Found: C, 47.17; H, 4.77; N, 2.47%. IR(KBr): $\nu = 3205$ s (N–H); 1559 m and 1594 vs (CO)/(NC); 1363 m (COO) 913 s (N–O); 421 m and 527 s (Sn–O); 553 s and 572 w (Sn–C) cm^{-1} ; ^1H NMR (CDCl_3) for $(\text{H}_3\text{C}^4\text{H}_2\text{C}^3\text{H}_2\text{C}^2\text{H}_2\text{C}^1)_2\text{Sn}[\text{OC}(\text{O})\text{C}_6\text{H}_4\text{Cl-4}][\text{O-NH-C}(\text{O})\text{C}_6\text{H}_4\text{Cl-4}]$: δ (t, 6H, $2\text{C}^4\text{H}_3$) 0.85; δ (m, 4H, $2\text{C}^3\text{H}_2$) 1.38; δ (m, 8H, $2\text{C}^2\text{H}_2\text{C}^1\text{H}_2$) 1.68; δ (m, 8H, $2\text{C}_6\text{H}_4$) 7.40–7.98 ppm. ^{13}C NMR (CDCl_3) δ 176.1, 168.2 (CO); 139.2, 132.0, 129.8, 128.9 and 128.2 (C_{arom}); 27.32–14.12 ppm (m, Sn–R); ^{119}Sn NMR (CDCl_3): δ –157.8 ppm.

3.3. Crystal structure determination

A colorless crystal of approximately $0.40 \times 0.10 \times 0.08$ mm³ was mounted in a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo $\text{K}\alpha$ radiation at room temperature. A preliminary orientation matrix and unit cell parameters were determined from three runs of 15 frames each, each frame corresponding to a 0.3° scan in 15 s, followed by spot integration and least-squares refinement. Data were measured using an ω scan of 0.3° per frame for 5 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART [25] software and refined with SAINT on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS. The structures were solved by direct methods with the SHELX-97 program and refined by full-matrix least-squares methods on F^2 with SHELXL-PC V. Details of the crystal data, data collection, structure solution and refinement are reported in Supplementary materials.

4. Supplementary materials

CCDC No. 268394 contains the supplementary crystallographic data for this paper. These data can be

obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif or by emailing data_request@ccdc.cam.ac.uk or by contacting The Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033.

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