



Structural and spectral studies of diorganotin(IV) complexes containing bis-tridentate *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene) oxalohydrazide ligand

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ABSTRACT

Three new symmetrical binuclear diorganotin(IV) complexes with the symmetrical bis-tridentate Schiff base, *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene)oxalohydrazide, (R₂Sn)₂[Ph–C(O)=CH–C(Me)=N–N=C(O)–C(O)=N–N=C(Me)–CH=C(O)–Ph] (R = Ph: **1a**; R = Me: **1b**; R = *n*-Bu: **1c**) have been synthesized by reaction with corresponding diorganotin(IV) dichloride at room temperature in methanol in presence of triethylamine. The complexes have been characterized by elemental analyses, IR, ¹H, ¹³C, ¹⁵N and ¹¹⁹Sn NMR spectroscopy. Two dimensional H,H-COSY, NOESY, H,C-COSY, gs (gradient selected)-HMQC and gs-HMBC techniques were applied in order to assign proton and carbon chemical shifts unambiguously. The δ(¹¹⁹Sn) values for the complexes **1a–1c** are –320.1, –181.9 and –150.7 ppm respectively, indicating penta-coordinated tin centres. The C–Sn–C angles calculated from ¹J(¹¹⁹Sn, ¹³C) for **1a**, **1b** and **1c** are found to be 135.6°, 133.85° and 135.0° respectively. From the ²J(¹¹⁹Sn, ¹H) value, the Me–Sn–Me angle for **1b** is found to be 130.46°. From NMR spectra a distorted trigonal-bipyramidal geometry at each tin centre is proposed. The structures of the complexes have been confirmed by single crystal X-ray diffraction analysis of one representative compound **1a**. The ligand, *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene)oxalohydrazide (H₄L) coordinates to the metal centre in enolate form via the phenolic O, imino N and enolic O atoms. The X-ray structure indicates that the coordination geometry of tin atoms are intermediate between trigonal bipyramid and a square pyramid. The oxygen atoms are in axial positions while the imino nitrogen atom of the ligand and two phenyl groups occupy the equatorial sites.

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1. Introduction

Tin(IV) complexes containing (O,O) [1]; (N,O) and (O,S) [2–5] donor atoms are noteworthy for their excellent activities as fungicides, bacteriocides and anti-inflammatory agents [6–9]. A series of organotin(IV) derivatives and a number of diorganotin halides and pseudohalides [SnR₂X₂L₂] [L = amino ligand, e.g. pyridine(py); bipyridyl(bpy); 1,10-phenanthroline(phen); ethylenediamine(en)]

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have displayed modest antitumour activity in vitro and in vivo [10–14]. These di and tri-organotin(IV) complexes show important anti-tumour activities combined with low toxicity due to their abilities to form complexes with biologically important compounds like DNA. In addition to the aforesaid applications, organotin compounds are also of interest in view of their considerable structural diversity. This aspect has been attracting the attention of a number of researchers to discover a number of structural types [15]. A series of diorganotin carboxylates have been synthesised, either for investigating their structural chemistry [16,17], or for assessing their performance as PVC (Polyvinyl Chloride) stabilizers [18], biocides, metal-based drugs [19], anion-recognition agents [20] and catalysts for polyurethane foams [21], for room temperature vulcanisation of silicone rubbers [22], for trans-esterifications [23], for acetylations of alcohols [24], for dehydration of alcohols to

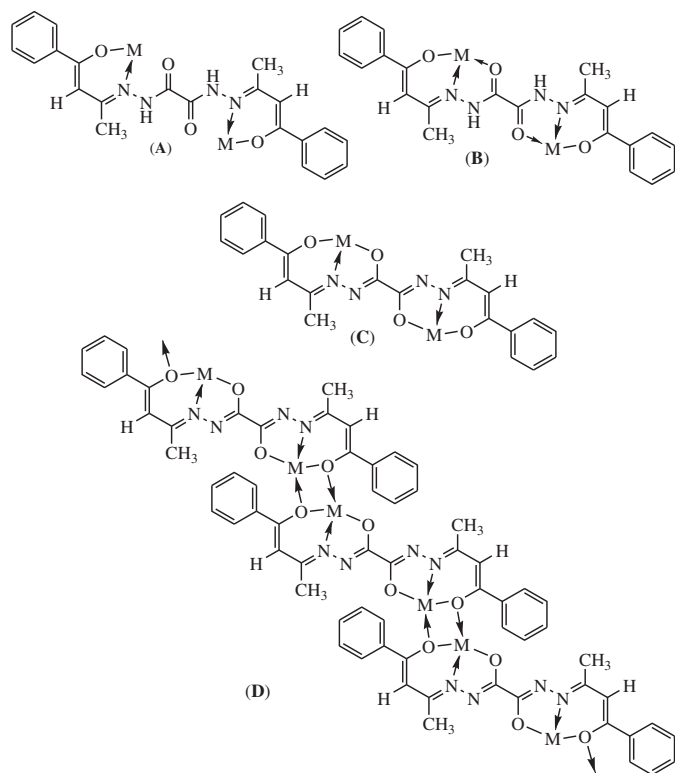


Fig. 1. Different possible binding modes of the ligand, *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene)oxalohydrazide (**I**).

ethers [25] and as homogeneous catalysts [26]. At present, the synthesis of tin(II) and diorganotin(IV) derivatives with polydentate Schiff bases has become a popular topic of research. A systematic study of the coordination chemistry of diorganotin(IV) complexes with biologically or pharmacologically active ONO, NNS and ONS tridentate ligands may provide further information concerning the structural characteristics required for their antitumour and cytotoxic activities. Recently, the coordination chemistry and mode of interaction of the tridentate ONO donor ligand *N*-(2-carboxyphenyl)salicylideneimine dianion and *N*-(2-carboxyphenyl)-5-bromosalicylideneimine dianion towards diorganotin have been reported [27,28]. However, few investigations have been devoted to the diorganotin(IV) complexes derived from benzoic acid hydrazone [6]. Recently our group have presented work on the structure and spectra of diorganotin(IV) complexes derived from benzoic acid hydrazone and related ONO donor ligands [29–32]. All the above mentioned hydrazone ligands behaving as tridentate chelators. However, no study has been conducted so far on the coordination chemistry of symmetrical bis-tridentate hydrazone ligands towards diorganotins. No examples were found in the November 2012 issue of the Cambridge Structural Database. The ligand, *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene)oxalohydrazide (H₄L) can either act as monobasic bis-bidentate (**A**) or monobasic bis-tridentate (**B**) or dibasic bis-tridentate (**C**) chelators or it may form polymeric chain (**D**) as illustrated in Fig. 1. To resolve these possibilities, we wanted to observe the mode of coordination of the ligand, *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene)oxalohydrazide (**I**) with diorganotin(IV) dichlorides in both solid and solution state.

In continuation of our previous studies on diorganotin(IV) complexes derived from tridentate ONO hydrazone and related ligands [27–32], the present study describes the syntheses of the ligand, *N,N*-bis(4-oxo-4-phenylbutan-2-ylidene)oxalohydrazide

(**I**) and first report of three new dinuclear diorganotin(IV) complexes, (R₂Sn)₂[Ph–C(O)=CH–C(Me)=N–N=C(O)–C(O)=N–N=C(Me)–CH=C(O)–Ph] (R = Ph: **1a**; R = Me: **1b**; R = *n*-Bu: **1c**) derived from this ONO donor bis-tridentate ligand. This study also describes detailed NMR studies of the complexes and solid state structure by doing X-ray crystallography of one representative complex, (Ph₂Sn)₂[Ph–C(O)=CH–C(Me)=N–N=C(O)–C(O)=N–N=C(Me)–CH=C(O)–Ph] (**1a**).

2. Experimental

2.1. Materials

All chemicals and reagents were of reagent grade quality. Diphenyltin dichloride (Sigma), di-*n*-butyltin dichloride (Alfa, USA), dimethyltin dichloride (Fluka), 1-benzoylacetone (Sigma) and oxalylidihydrazide (Sigma) were used as received. Triethylamine (s.d. fine chemicals, India) was dried over KOH. Methanol (Ranbaxy, India) was dried over CaO. All solvents were distilled prior to use. Other solvents were dried and purified by standard procedures.

2.2. Physical measurements

Infrared spectra were recorded on a Perkin–Elmer 883 infrared spectrophotometer from 4000 to 200 cm^{–1} as KBr discs. Tin was estimated gravimetrically as SnO₂ after decomposition with concentrated HNO₃. Carbon, hydrogen and nitrogen analyses were carried out on a Perkin–Elmer 2400 II elemental analyser. Melting points (uncorrected) were recorded on an electrical heating coil apparatus.

¹H (400.15 MHz), ¹³C (100.61 MHz), NMR spectra of ligand (**I**) were recorded at 300 K in DMSO-*d*₆ on a Spect 400 spectrometer. The ¹H (360.13 MHz), ¹³C (90.566 MHz) and ¹⁵N (36.50 MHz) NMR spectra of the complexes (**1a–1c**) were recorded at 300 K on a Bruker AMX 360 spectrometer equipped with 5 mm broadband inverse probe and a Silicon Graphic Indy computer. The compounds studied were measured in deuteriochloroform and ¹H and ¹³C chemical shifts were referred to the central signal of the solvent ($\delta = 7.25$ (¹H) and 77.00 (¹³C)). The ¹⁵N and ¹¹⁹Sn chemical shifts were referred to external nitromethane and tetramethylstannane, respectively, ($\delta = 0.0$) placed in a coaxial capillary. Positive values of chemical shifts denote downfield shifts with respect to standards. Two dimensional H,H-COSY, NOESY, H,C-COSY, gs (gradient selected)-HMQC and gs-HMBC techniques were measured using standard microprograms provided by Bruker [33]. The ¹⁵N NMR spectra were measured using gs-HMBC technique the experiment being optimized for 6 Hz ¹J(¹⁵N, ¹H) coupling constant.

2.3. X-ray structure analysis of **1a**

Single crystals of (Ph₂Sn)₂[Ph–C(O)=CH–C(Me)=N–N=C(O)–C(O)=N–N=C(Me)–CH=C(O)–Ph] (**1a**), suitable for X-ray crystallography were obtained from CHCl₃/petroleum ether (40–60 °C) mixture. Diffraction measurements on **1a** were made on a Bruker-APEX2 CCD area detector diffractometer at 100(2) K using graphite-monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) from a sealed tube and were corrected for absorption. The structure was solved by direct methods 'SHELXS-97 [34] (**1a**) and subsequently refined by full-matrix least-squares procedures on F² SHELXTL [35]. Hydrogen atom positions were calculated assuming ideal geometry and using appropriate riding models. No significant peak appeared on the N atom with a coordination number of two, and no evidence of an N–H stretch was reported in the infrared spectrum so it was considered not to be protonated. There is disordered CH₂Cl₂ solvent located over a centre of inversion with one C position at occupancy

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