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The crystal structure of butylchlorobis(8-quinolinate)tin(IV)

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Abstract

A single crystal X-ray diffraction study has shown that in butyl-chloro-bis(8-quinolinate)tin(IV) the coordination geometry around the tin atom is distorted octahedral; two O atoms, a N atom of the *cis*-chelated 8-quinolinate ligands, and a chlorine atom are in equatorial sites. The apical sites are occupied by the N atom of the other *cis*-chelate 8-quinolinate group and the butyl group. The apical groups form a C–Sn–N angle of 172.3(2)°. The two Sn–O distances are effectively equal [2.054(4) Å and 2.059(3) Å], but the axial Sn–N bond [2.223(5) Å] is slightly longer than the equatorial Sn–N bond [2.201(4) Å]. The Sn–Cl and Sn–C distances [2.429(2) Å; 2.073(6) Å] are similar to those in related complexes.

Keywords: Tin; Quinolate; Crystal structure; Main group elements; Anticancer; X-ray diffraction

1. Introduction

The chemical, biological and pharmaceutical properties of diorganotin(IV) complexes have been extensively studied. Recently, structure — anti-tumour activity relations — have been studied for di- and triorganotin(IV) oxinates and thiooxinates [1]. Because of the important applications of organotin-bischelates the structures of this class of compound has received considerable attention and the ^{119}Sn, ^{15}N, ^{13}C and ^{1}H NMR, as well as the solid-state ^{119}Sn CP/MAS NMR spectra, have been used to study the structures of many such species [2,3]. The organotin(IV) compounds crystallize as molecular complexes, which retain their structure in solutions in non-coordinating solvents. However, derivation of the coordination number of the tin and the type of distortion of coordination polyhedron of diorganotin complexes with S, N or O chelate ligands from ^{119}Sn NMR shift data is not wholly reliable. By use of IR and Mössbauer spectroscopy, octahedral coordination could be established for diorganotin(IV) complexes, but a decision as to whether the chelating ligands are *cis* or *trans* chelated required crystal structure determinations. For diorganotin(IV) bischelates the coordination around the tin is that of a regular *trans* or *cis* octahedron or distorted skew-trapezoidal bipyramid (STB); which form is adopted depends on the nature of the carbon- and hetero-atom-donor ligands [4]. The STB geometry is associated with a small chelate bite angle and carbon–tin–carbon angle (135–155°) intermediate between the ideal *cis* and *trans*-SnR_2 octahedral angles [5]. Octahedral geometries distorted towards the STB form were proposed for many diorganotin(IV) dithiocarbamates; such as $(n\text{-Bu})_2Sn(morph)_2$ [6], $(n\text{-Bu})_2Sn(S_2CNEt_2)_2$ [7], $Me_2Sn(S_2CNMe_2)_2$ [8] or for bis(2-pyridinethiolato)tin(IV) complexes $Ph_2Sn(2\text{-SPy})_2$ [9], $(n\text{-Bu})_2Sn(2\text{-Spy-5-NO}_2)_2$ [10], and $Me_2Sn(2\text{-SPyO})_2$ [11], having sulphur, nitrogen or oxygen atoms in the trapezoidal plane and carbon atoms in apical positions. In the mixed alkyl $Et(n\text{-Pr})Sn(Meox)_2$ (Meox = 2-methyl-8-hydroxyquinolinate) [12], the two alkyl groups are approximately *trans* to each other, with C–Sn–C 145.2(3)°, and perpendicular to the 2-methyl-quinolinate groups. The *trans* preference of the Et(*n*-Pr)Sn moiety is the result of steric effects of the quinolinate ligands. *Cis*-octahedral geometry was found for $Me_2Sn(ox)_2$ [13] and *p*-chlorophenyl-Sn(ox)2-*p*-tolyl [14], with C–Sn–C angles of 111.0(1)° and 106.8(2)°, respectively. The bischelates $Me[(Me_3Si)_2CH]Sn(ox)_2$ [14] and $(p\text{-ClC}_6H_4)(p\text{-MeC}_6H_4)Sn(ox)_2$ [14] are distorted towards

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the *cis* configuration, with C–Sn–C angles between 101° and 109°.

2. Experimental details

The yellow compound $BuSnCl(ox)_2$ (ox = 8-hydroxyquinolinate) was as described previously [15] and gave a satisfactory C, H and N analysis. Single crystals were obtained by slow evaporation from a mixture of $CHCl_3$ and *n*-hexane at room temperature. The crystal density was measured by flotation in $ZnSO_4$ solution.

2.1. X-ray analysis

Diffraction measurements on the title compound were carried out on a Syntex $P2_1$ four-circle diffractometer using monochromated Mo $K\alpha$ radiation ($\lambda = 0.7107$ Å). Approximate values of lattice parameters were obtained from rotation and Weissenberg patterns. Accurate lattice parameters were refined by least-squares on the basis of 15 precisely centred reflections with $6 < 2\Theta < 16°$. All intensities were corrected for Lorentz and polarization effects, but not for absorption or extinction. There was no significant variation in intensities of two standard reflections measured after 98 reflections. Data reductions were performed with the program XP21 [16]. The structure was solved by the heavy-atom method and refined on F by the block-diagonal least-squares method using 1234 observed reflections and anisotropic temperature factors for all non-H atoms. The H-atoms were placed in calculated positions and given isotropic thermal parameters. Positional and anisotropic thermal parameters for non-H atoms were refined. The absolute structure was checked by inverting the structure and comparing the residuals. The residuals of the final least-squares cycle and other parameters are listed in Table 1, the atomic coordinates in Table 2, and bond lengths and angles in Table 3. Scattering factors for uncharged atoms and real and imaginary dispersion terms were taken from international Tables for X-ray Crystallography [17]. The calculations were performed on the CDC computer using a local version of the NRC system [18] and PARST [19]. Tables of hydrogen atom coordinates and anisotropic thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

3. Results and discussion

As shown in Fig. 1, the structure of butyl-chloro-bis (8-quinolinate)tin(IV) consists of discrete hexacoordinated molecules with oxinate ligands in chelating mode. The coordination geometry is distorted octahedral. The two oxinate ligands are in a *cis* arrangement with the

Table 1
Data collection and processing parameters

Molecular formula	$C_{22}H_{21}N_2ClSn$			
Molecular weight	499.56			
Unit cell parameters	a 8.856(6) Å		V	2033(2) Å^3
	b 13.472(9) Å		Z	4
	c 17.038(12) Å		$F(000)$	1000
Density (calc.)	1.632 g cm^{-3}			
Crystal system	orthorombic			
Space group	$Pna2_1$			
Standard reflections	$(\bar{1}3\bar{1}; \bar{2}4\bar{2})$			
R_{int} (from merging of equivalent reflections)	0.013			
Absorption coefficient	1.412 mm^{-1}			
Crystal size	0.20 × 0.20 × 0.30 mm			
Scan type and rate	$\Theta/2\Theta$; 4.88–29.30 deg min^{-1}			
Collection range	$2\Theta_{max} = 55°$			
	$h \rightarrow 0$–11			
	$k \rightarrow 0$–17			
	$l \rightarrow 0$–22			
No. of reflections measured	2756			
No. of independent reflections	2422			
No. of observed reflections	1234			
Criterion of observed $I \geq 1.96\sigma(I)$				
No. of parameters refined	252			
$R = \Sigma(\lvert F_o \rvert - \lvert F_c \rvert)/\Sigma \lvert F_o \rvert$	0.041			
Weighting scheme	$w = [\sigma^2(F_o) + 0.015 \lvert F_o \rvert^2]^{-1}$			
$R_w = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/\Sigma w \lvert F_o \rvert^2]^{1/2}$	0.042			
$S = [\Sigma w(\lvert F_o \rvert - \lvert F_c \rvert)^2/(n-p)]^{1/2}$	1.148			
Electron density in final difference Fourier map	+0.944 to −0.786 e Å^{-3}			

Table 2
Final atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters B_{eq}(Å^2) with e.s.d.'s in parentheses

Atom	x	y	z	B_{eq}
Sn(1)	2353(0.4)	4716(0.2)	0	4.12(1)
Cl(1)	3263(2)	4548(1)	1338(1)	5.29(5)
N(1)	1126(5)	4498(3)	−1111(3)	3.90(13)
N(2)	156(5)	4292(4)	535(3)	3.96(13)
O(1)	2550(4)	3220(2)	−210(2)	4.30(11)
O(2)	1222(4)	6043(2)	112(2)	4.24(10)
C(1)	1945(6)	2886(4)	−856(3)	3.61(15)
C(2)	2003(6)	1916(4)	−1058(4)	5.03(19)
C(3)	1272(9)	1626(5)	−1775(4)	7.21(27)
C(4)	539(10)	2254(5)	−2238(4)	7.99(32)
C(5)	468(7)	3249(5)	−2034(3)	5.60(20)
C(6)	−318(7)	3957(5)	−2471(4)	5.92(25)
C(7)	−358(8)	4902(5)	−2234(4)	6.45(24)
C(8)	379(7)	5146(5)	−1526(4)	5.49(20)
C(9)	1151(6)	3537(4)	−1359(3)	3.83(16)
C(10)	−84(6)	6029(4)	425(3)	3.97(17)
C(11)	−945(8)	6856(4)	555(3)	4.43(18)
C(12)	−2310(7)	6800(5)	928(4)	5.26(19)
C(13)	−2933(7)	5933(5)	1155(4)	5.96(22)
C(14)	−2081(7)	5033(4)	1038(4)	4.71(18)
C(15)	−2549(6)	4117(5)	1277(4)	5.17(16)
C(16)	−1704(7)	3310(4)	1135(3)	4.85(19)
C(17)	−381(7)	3420(4)	759(3)	4.26(18)
C(18)	−743(7)	5107(4)	673(3)	4.07(17)
C(19)	4348(7)	5300(5)	−438(4)	5.54(19)
C(20)	4255(8)	5965(6)	−1142(4)	7.45(28)
C(21)	5730(10)	6458(7)	−1355(5)	10.38(36)
C(22)	5673(12)	7047(7)	−1964(6)	13.20(44)

$B_{eq} = (4/3)\Sigma_i \Sigma_j \beta_{ij} \boldsymbol{a}_i \cdot \boldsymbol{a}_j$

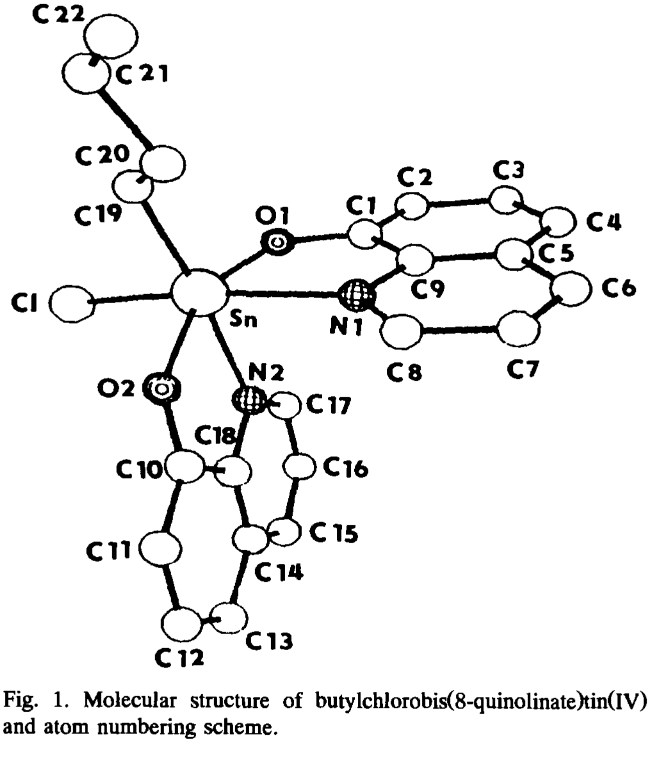

Fig. 1. Molecular structure of butylchlorobis(8-quinolinate)tin(IV) and atom numbering scheme.

Table 3
Bond lengths (Å) and bond angles (°)

Sn(1)–O(1)	2.054(4)	Sn(1)–Cl(1)	2.429(2)
Sn(1)–O(2)	2.059(3)	Sn(1)–C(19)	2.073(6)
Sn(1)–N(1)	2.201(4)	Sn(1)–N(2)	2.223(5)
O(1)–Sn(1)–N(1)	76.2(2)	N(1)–Sn(1)–Cl(1)	163.4(1)
O(1)–Sn(1)–Cl(1)	92.5(1)	N(1)–Sn(1)–N(2)	83.5(2)
O(1)–Sn(1)–N(2)	83.9(2)	N(1)–Sn(1)–O(2)	87.5(2)
O(1)–Sn(1)–O(2)	155.5(2)	N(2)–Sn(1)–Cl(1)	83.2(1)
O(2)–Sn(1)–Cl(1)	98.9(1)	N(2)–Sn(1)–C(19)	172.3(2)
O(2)–Sn(1)–N(2)	76.1(2)	Cl(1)–Sn(1)–C(19)	95.2(2)
O(2)–Sn(1)–C(19)	96.8(2)	O(1)–Sn(1)–C(19)	103.7(2)
N(1)–Sn(1)–C(19)	99.3(2)		
C(1)–O(1)	1.305(6)	C(10)–O(2)	1.274(6)
C(1)–C(2)	1.353(8)	C(10)–C(11)	1.368(8)
C(2)–C(3)	1.437(9)	C(10)–C(18)	1.436(8)
C(3)–C(4)	1.327(10)	C(11)–C(12)	1.368(9)
C(4)–C(5)	1.386(9)	C(12)–C(13)	1.347(9)
C(5)–C(6)	1.397((9)	C(13)–C(14)	1.442(9)
C(5)–C(9)	1.356(8)	C(14)–C(15)	1.365(9)
C(6)–C(7)	1.336(10)	C(15)–C(16)	1.341(9)
C(7)–C(8)	1.411(9)	C(16)–C(17)	1.343(9)
N(1)–C(8)	1.304(8)	C(18)–C(14)	1.341(9)
N(1)–C(9)	1.362(7)	N(2)–C(17)	1.324(8)
C(1)–C(9)	1.414(7)	N(2)–C(18)	1.377(8)
O(1)–C(1)–C(2)	122.1(5)	O(2)–C(10)–C(11)	124.2(5)
O(1)–C(1)–C(9)	120.1(5)	O(2)–C(10)–C(18)	120.4(5)
C(2)–C(1)–C(9)	117.7(5)	C(10)–C(11)–C(12)	121.5(5)
C(1)–C(2)–C(3)	117.4(6)	C(11)–C(12)–C(13)	122.9(6)
C(2)–C(3)–C(4)	123.6(6)	C(12)–C(13)–C(14)	118.3(6)
C(3)–C(4)–C(5)	119.3(7)	C(13)–C(14)–C(15)	124.1(6)
C(4)–C(5)–C(6)	123.3(6)	C(13)–C(14)–C(18)	117.6(6)
C(5)–C(6)–C(7)	120.2(6)	C(18)–C(14)–C(15)	118.3(6)
C(4)–C(5)–C(9)	118.0(6)	C(14)–C(15)–C(16)	120.7(6)
C(6)–C(5)–C(9)	118.7(6)	C(15)–C(16)–C(17)	118.9(6)
C(6)–C(7)–C(8)	118.0(6)	C(16)–C(17)–N(2)	123.3(6)
C(7)–C(8)–N(1)	122.9(6)	C(17)–N(2)–C(18)	116.8(5)
C(8)–N(1)–C(9)	118.4(5)	N(2)–C(18)–C(10)	113.8(5)
N(1)–C(9)–C(5)	121.9(5)	N(2)–C(18)–C(14)	122.1(5)
N(1)–C(9)–C(1)	114.1(5)	C(10)–C(18)–C(14)	124.0(5)
C(19)–C(20)	1.509(10)	Sn(1)–C(19)–C(20)	117.9(4)
C(20)–C(21)	1.509(12)	C(19)–C(20)–C(21)	114.0(6)
C(21)–C(22)	1.307(14)	C(20)–C(21)–C(22)	115.1(8)

O(1)–Sn(1)–N(2) angle 83.9(2)° and the Cl(1)–Sn(1)–C(19) angle 95.2(2)°. The dihedral angle between the least-squares planes formed by the atoms of oxinate group is 86.4(1)° and the relevant torsions are N(1)–Sn(1)–N(2)–C(18) 90.6(4)° and N(1)–Sn(1)–O(2)–C(10) 85.5(4)°. The equatorial plane contains the O(1) and N(1) atoms of one oxinate ligand, and the O(2) atom of the other oxinate ligand and the chlorine atom. The tin is 0.32 Å above this plane. The N(2) and C(19) atoms form the largest angle at tin [N(2)–Sn(1)–C(19) 172.3(2)°] and occupy the apical positions of the distorted octahedron. The sum of the equatorial angles is 355.1°. The bond distances Sn(1)–O(1) and Sn(1)–O(2) are nearly equal [2.054(4) Å; 2.059(3) Å] and the bite angles of the ligands 76.2(2)° and 76.1(2)° are similar to those in $Me_2Sn(ox)_2$ [13], in (n-Pr)EtSn(2-Meox)$_2$ [11] or in (p-chlorophenyl)(p-tolyl)Sn(ox)$_2$ [14]. The bond distances Sn(1)–N(1) 2.201(4) Å and Sn(1)–N(2) 2.223(5) Å are significantly shorter than the Sn–N bonds in the skew trapezoidal pyridine thiolate complexes $Ph_2Sn(2\text{-}SPy)_2$ [9] [2.636(4) Å; 2.698(4) Å] and $(n\text{-}Bu)_2Sn(2\text{-}Spy\text{-}5\text{-}NO_2)_2$ [10] [2.77(1) Å], but are comparable with those in $Cl_2Sn(2\text{-}SPy)_2$ [20], (2.271(9) Å and 2.256(9) Å). The apical distances Sn(1)–Cl(1) 2.429(2) Å and Sn(1)–C(19) 2.073(6) Å are within the range commonly observed for five- and six-coordinated diorganotin(IV) chloride complexes. The shortest intermolecular contact 3.153(7) Å is between O(1)...C(16) $[x + 1/2;\ 1/2 - y;\ z]$ atoms.

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