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CRYSTAL STRUCTURE OF 1,10-PHENANTHROLINEDICHLORODI-n-BUTYLTIN

PAOLO GANIS,

Istituto Chimico, Universitá di Napoli, Via Mezzocannone, 4, 80134 Napoli (Italy)

VALERIO PERUZZO *,

Istituto di Chimica Analitica, Universitá di Padova, Via Marzolo, 1, 35100 Padova (Italy)

and GIOVANNI VALLE

Centro di Ricerche sui Biopolimeri del C.N.R., Via Marzolo, 1, 35100 Padova (Italy)

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Summary

The structure of 1,10-phenanthrolinedichlorodi-n-butyltin has been determined by X-ray analysis. The compound crystallizes in the space group $P2_12_12_1$ with *a* 10.785(5), *b* 11.017(5), *c* 18.163(12) Å and $Z = 4$. It consists of distorted octahedral units of $(C_{12}H_8)(C_4H_9)_2SnCl_2$ with *trans* configuration. The structure and the Mössbauer behaviour are compared with those of similar compounds.

Introduction

The relationship between Mössbauer effect and chemistry in six-coordinated organotin(IV) complexes has been subject of intensive research in the last years [1–4]. It has been exhaustively proved that the Mössbauer analysis can allow the solution of geometrical and configurational problems for a number of these complexes having octahedral coordination [2]. Use of the copious Mössbauer data for these compounds in association with X-ray structural data could provide further information for use in theoretical calculations pertinent to the Mössbauer spectroscopy. The lack of appropriate structural data prompted us to undertake the X-ray crystal analysis of suitable complexes. Here we report the crystal structure of the compound 1,10-phenanthrolinedichlorodi-n-butyltin, and compare it with the known structure of 2,2′-bipyridyldichlorodiphenyltin [5], then discuss the implications for Mössbauer data for octahedral coordinated complexes of tin of the type R_2SnCl_2X (X = bidentate ligand) [1–3].

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TABLE 1

FRACTIONAL ATOMIC COORDINATES ($\times 10^4$) AND THERMAL PARAMETERS ($\times 10^3$) [a]

Atom	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Sn	901(4)	982(3)	−123(1)	65(1)	38(1)	47(3)	0(5)	2(2)	0(4)
Cl(1)	−517(13)	427(11)	−1195(3)	49(3)	74(6)	64(4)	1(4)	5(6)	17(3)
Cl(2)	844(18)	3296(9)	−70(4)	87(11)	44(4)	92(8)	6(2)	1(10)	4(6)
N(1)	1277(33)	−1137(28)	179(10)	90(18)					
N(2)	2346(38)	763(32)	838(12)	62(24)					
C(1)	2394(43)	1056(42)	−853(14)	50(16)					
C(2)	2798(62)	−26(48)	−1296(18)	71(21)					
C(3)	4093(71)	162(47)	−1677(20)	79(22)					
C(4)	4374(98)	−1001(85)	−2075(36)	156(19)					
C(5)	−692(51)	1009(48)	652(18)	62(41)					
C(6)	−940(61)	−127(39)	1157(15)	60(31)					
C(7)	−2221(71)	130(54)	1498(22)	88(16)					
C(8)	−2636(76)	−1013(71)	1973(28)	117(24)					
C(9)	926(66)	−2228(45)	−199(24)	71(12)					
C(10)	1097(84)	−3403(54)	46(28)	105(29)					
C(11)	1769(52)	−3643(41)	635(26)	56(13)					
C(12)	2106(53)	−2602(39)	999(20)	56(21)					
C(13)	2959(67)	−2742(54)	1602(31)	85(19)					
C(14)	3508(62)	−1749(49)	2004(24)	75(16)					
C(15)	3347(60)	−538(48)	1697(33)	69(21)					
C(16)	3828(64)	489(47)	2104(29)	63(24)					
C(17)	3820(61)	1576(46)	1743(31)	70(16)					
C(18)	2730(54)	1627(42)	1286(36)	60(19)					
C(19)	2466(46)	−362(35)	1117(19)	43(22)					
C(20)	2004(50)	−1405(38)	765(24)	55(18)					

[a] In parentheses the estimated standard deviations.

Experimental

Crystal and intensity data

The title compound was prepared as described in ref. 6. Colorless, neadle-shaped crystals, m.p. 188°C, suitable for X-ray analysis were obtained from methanol.

$C_{20}H_{26}N_2Cl_2Sn$, mol. wt. 484.04, orthorhombic, a 10.785(5), b 11.017(5), c 18.163(12) Å; U 2158.09 Å^3, D_m 1.48 g cm^{-3}, $Z = 4$, D_c 1.49 g cm^{-3}, $F(000)$ 984, λ(Mo-K_α) 0.7107, μ(Mo-K_α) 15.3 cm^{-1}. Space group $P2_12_12_1$. The compound was found to decompose in the X-ray beam and three crystals were used for the data collection. The dimensions of all three crystals were about 0.6 × 0.2 × 0.2 mm. Accurate lattice and orientation parameters were obtained by least squares treatment of 25 symmetry-related reflections. Intensity data were measured by use of ϑ–2ϑ scan method with a Philips PW 100 computer controlled four circle diffractometer, with graphite monochromator. After one third of data collection the intensity dropped to 70% of the initial intensity and the crystal was changed. The intensities were corrected for Lorentz and polarization effects and were scaled using almost 100 common reflections. No absorption corrections were made. The data were scaled to give 1425 independent $F(hkl)$ values for which I was greater than $3\sigma(I)$.

Solution and refinement of the structure

The positions of Sn and Cl atoms were determined from a three-dimensional Patterson synthesis. A difference electron density synthesis, based upon the Sn and Cl contributions, revealed the position of all the non-hydrogen atoms. Six cycles of

TABLE 2

SOME BOND DISTANCES (Å) AND ANGLES (°) IN 1,10-PHENANTHROLINE DICHLORODI-n-BUTYLTIN (A) COMPARED WITH THOSE OF 2,2′-DIPYRIDYLDICHLORODIPHENYLTIN (B) [a]; THE STANDARD DEVIATIONS ARE SHOWN IN PARENTHESES

	A	B
Sn–C(1)	2.09(1)	2.151(7)
Sn–C(5)	2.22(2)	2.153(8)
Sn–N(1)	2.43(1)	2.344(6)
Sn–N(2)	2.35(2)	2.375(6)
Sn–Cl(1)	2.55(1)	2.511(2)
Sn–Cl(2)	2.55(1)	2.508(2)
C(1)–Sn–C(5)	177(2)	173.5(3)
C(1)–Sn–N(1)	93(1)	85.5(2)
C(1)–Sn–N(2)	88(1)	87.0(3)
C(1)–Sn–Cl(2)	90(1)	92.9(2)
C(1)–Sn–Cl(1)	89(1)	92.4(2)
C(5)–Sn–N(1)	90(1)	88.3(2)
C(5)–Sn–N(2)	93(1)	88.9(2)
C(5)–Sn–Cl(1)	91(1)	92.3(2)
C(5)–Sn–Cl(2)	87(1)	90.2(2)
N(1)–Sn–N(2)	68(1)	69.0(2)
N(1)–Sn–Cl(1)	92(1)	95.6(1)
N(2)–Sn–Cl(2)	95(1)	92.0(1)
Cl(1)–Sn–Cl(2)	105(1)	103.5(1)

[a] From ref. 5.

isotropic refinement with unit weights reduced the R value to 0.13.

Anisotropic temperature factors of the form $\exp[-2\pi^2(U_{11}h^2a^{\star 2} + U_{22}k^2b^{\star 2} + \cdots + 2U_{12}hka^{\star}b^{\star})]$ were assigned to the tin and chlorine atoms and four more cycles of least squares lowered R to 0.108. Hydrogen atoms were not included in the calculations. The weighting scheme used in the very last calculations was of the form $W^{-1} = a_i|F_0|^i$. The a_i parameters were calculated using the program PESO [7]. Scattering factors for the atoms were taken from Cromer and Waber [8]; the scattering factor of the Sn atom was corrected for the real and imaginary parts of anomalous dispersion using Cromer's values [9]. Final atomic coordinates and temperature factors are listed in Table 1; bond distances and angles are shown in Table 2 and 3, the atom numbering being shown in Fig. 1. The mode of packing shows no relevant features, the structure consists of discrete $(n\text{-}C_4H_9)_2SnCl_2$(1,10-phenanthroline) units; all the intermolecular contact distances are larger than the sum of the Van der Waals radii.

All calculations were carried out on a CDC Cyber 76 computer, using a program of ref. 10. A list of the observed and calculated structure factors is available from the authors on request.

TABLE 3

OTHER INTERNAL GEOMETRICAL PARAMETERS OF 1,10-PHENANTHROLINEDICHLORODI-n-BUTYLTIN WITH ESTIMATED STANDARD DEVIATIONS

Atoms	Bond distances (Å)	Atoms	Bond angles (°)
C(1)–C(2)	1.50(3)	Sn–N(1)–C(9)	131(2)
C(2)–C(3)	1.57(2)	Sn–N(1)–C(20)	119(2)
C(3)–C(4)	1.50(3)	Sn–N(2)–C(6)	116(3)
C(5)–C(6)	1.57(3)	Sn–N(2)–C(18)	126(2)
C(6)–C(7)	1.54(3)	N(1)–C(9)–C(10)	127(1)
C(7)–C(8)	1.59(2)	C(9)–C(10)–C(11)	121(1)
		C(10)–C(11)–C(12)	111(2)
C(9)–C(10)	1.38(1)	C(11)–C(12)–C(20)	129(1)
C(10)–C(11)	1.32(2)	C(11)–C(12)–C(13)	117(1)
C(11)–C(12)	1.37(1)	C(12)–C(20)–N(1)	119(2)
C(12)–C(13)	1.44(3)	C(12)–C(13)–C(14)	124(1)
C(12)–C(20)	1.39(2)	C(13)–C(14)–C(15)	117(1)
C(13)–C(14)	1.44(1)	C(14)–C(15)–C(19)	119(2)
C(14)–C(15)	1.46(2)	C(14)–C(15)–C(16)	119(1)
C(15)–C(16)	1.45(2)	C(15)–C(19)–C(20)	117(1)
C(15)–C(19)	1.43(1)	C(15)–C(19)–N(2)	118(2)
C(16)–C(17)	1.37(2)	C(15)–C(16)–C(17)	117(1)
C(17)–C(18)	1.44(2)	C(16)–C(17)–C(18)	108(2)
		C(17)–C(18)–N(2)	126(1)
N(1)–C(9)	1.43(1)	C(12)–N(2)–C(19)	114(3)
N(1)–C(20)	1.36(1)	Sn–C(1)–C(2)	122(2)
N(2)–C(18)	1.32(2)	C(1)–C(2)–C(3)	113(1)
N(2)–C(19)	1.34(1)	C(2)–C(3)–C(4)	106(1)
		Sn–C(5)–C(6)	120(2)
		C(5)–C(6)–C(7)	104(2)
		C(6)–C(7)–C(8)	109(1)

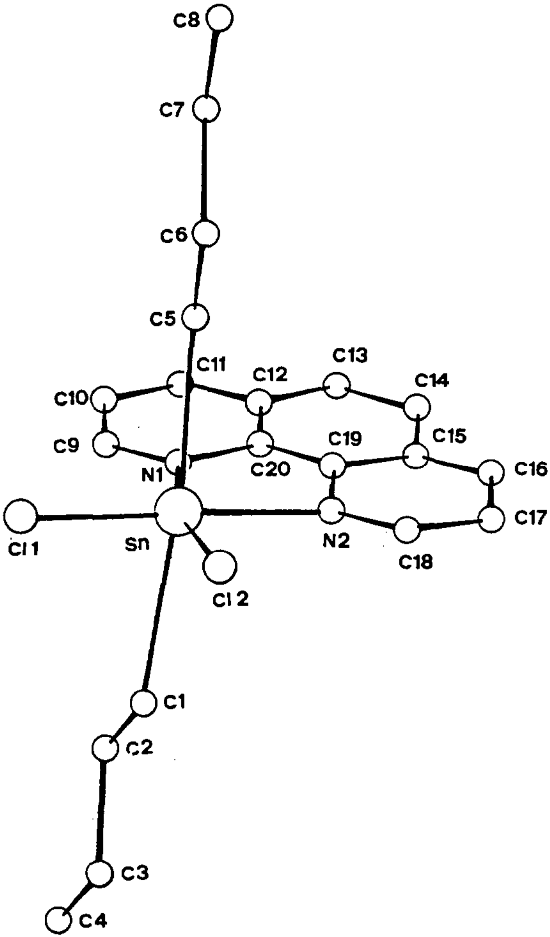

Fig. 1. Structure of 1,10-phenanthrolinedichlorodi-n-butyltin with the atom numbering scheme used in the Tables.

Results and discussion

The internal geometrical parameters indicate a distorted octahedral geometry about the tin atom with a *trans*-configuration, as predicted from Mössbauer measurements [2,3]. It is of interest to compare these data with those of 2,2′-bipyridyldichlorodiphenyltin [6]. In spite of the larger standard deviations estimated for the present structure, the parameters considered indicate a virtually identical geometry about tin (see Table 2). The other molecular parameters (see Table 3) can be considered quite normal. A few deviations from the normal values of bond distances and angles are to be ascribed to the decomposition of the crystals which reduces the accuracy of the measured intensities. From the data reported in literature it is reasonable to assume that the influence on the quadrupole splitting Δq of the dipyridyl and phenanthroline ligands is the same: e.g. $(CH_3)_2SnCl_2$(bipyridyl) and $(CH_3)_2SnCl_2$(phenanthroline) have Δq of 4.09 and 4.03 mm/sec, respectively, $(n\text{-}C_4H_9)_2SnBr_2$(bipyridyl) and $(n\text{-}C_4H_9)_2SnBr_2$(phenanthroline) have Δq of 3.95

and 3.94 mm/sec, respectively [2]. Therefore it is to be expected that the Mössbauer behaviour of the title compound with respect to 2,2'-dipyridyldichlorodiphenyltin will mostly depend on the replacement of the phenyl groups by butyl groups. The quadrupole splitting is in fact, more sensitive to chemical nature of the ligands bonded to tin than to relatively small differences of the bond angles and distances about tin [11–13]. For this reason we have not attempted a further refinement of the structure by collecting the intensities at low temperature. The quadrupole splitting of 2,2'-bipyridyldichlorodiphenyltin and of 1,10-phenanthrolinedichlorodi-n-butyltin are 3.90 and 4.07 mm/sec, respectively. The lower value for 2,2'-bipyridyldichlorodiphenyltin is due to the higher electronegativity of the phenyl group leading to a diminution of *s*-electron density at the tin nucleus. Similar effects have been noted previously, for example in the case of $(C_6H_5)_2Sn$(8-hydroxyquinolate)$_2$ and (n-$C_4H_9)_2Sn$(8-hydroxyquinolate)$_2$ where the Δq values are 1.78 and 2.21 mm/sec, respectively [2].

On the basis of the above arguments we expect that replacement of the bipyridyl ligand by the phenanthroline ligand in complexes of type $R_2SnCl_2(X)$ does not affect the Δq values provided that the geometrical parameters about the tin atom are unchanged. In the case of the pairs of complexes (a) Bu_2SnCl_2(bipyridyl) and Bu_2SnCl_2(phenanthroline), with Δq values of 3.83 and 4.07 mm/sec, respectively, and (b) $(C_6H_5)_2SnCl_2$(bipyridyl) and $(C_6H_5)_2SnCl_2$(phenanthroline), with Δq 3.90 and 3.70 mm/sec, respectively [2], we suggest that the octahedral geometry is distorted in a different way in the two components of each pair.

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