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Nitrogen Donor Chelates of Bivalent Tin Chloride. Part II*. The Crystal Structures of $SnCl_2$·(2,2′-bipyridyl) and $SnCl_2$·(1,10-phenanthroline)**

STEVEN J. ARCHER, KLAUS R. KOCH† and SUSANNE SCHMIDT

School of Chemical Sciences, University of Cape Town, Private Bag, Rondebosch 7700, South Africa

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Abstract

The crystal and molecular structures of dichloro(2,2′-bipyridyl)tin(II), dichloro(1,10-phenanthroline)tin(II) and dichlorobis(8-hydroxyquinolinato)tin(IV) have been determined by means of single crystal X-ray diffraction. The coordination geometry of the two tin(II) complexes is considerably distorted by the presence of a stereochemically active pair of electrons, in contrast to the regular six-coordinate octahedral tin(IV) complex.

Introduction

The structural chemistry of bivalent tin compounds differs markedly from that of tin(IV) compounds, the latter group including a variety of organotin substances such as R_aSnX_{4-a} and $R_aSnX_{4-a}\cdot bL$ (where R = alkyl or aryl group, X = halide ion, L = Lewis base, a = 1–4 and b = 1–2) [1, 2]. In the case of tin(II) compounds, a significant factor determining the structure and chemistry of these substances is the presence of a non-bonding, stereochemically active lone pair of electrons [3], the presence of which has two important consequences. In the first place, while both tin(IV) and tin(II) behave as Lewis acids forming numerous stable complexes [3, 4], tin(II) compounds are also known to behave as Lewis bases, as exemplified by the formation of stable BF_3 [5], BBr_3 and AlX_3 (X = Cl, Br) [6] adducts.

The numerous transition metal complexes involving SnX_2 coordination ($M \leftarrow SnX_2\cdot B$) further emphasise the interesting donor–acceptor behavior of tin(II) compounds [3].

From the structural point of view, tin(II) compounds display an interesting range of coordination polyhedra with coordination numbers of 2, 3, 4, and 6 being common although 7, 8, and even 12 coordination numbers have been reported [3]. Furthermore, the non-bonded pair of electrons is usually responsible for significant distortion of the coordination polyhedra of the tin(II) atom from regular geometry, in contrast to that of tin(IV) compounds which usually display regular tetrahedral, trigonal bipyramidal, and octahedral geometries [1, 3].

We have become interested in structural aspects of tin(II) complexes involving bidentate and tridentate nitrogen donor ligands such as 2,2′:6′,2″-terpyridine, with particular reference to the effect of the stereochemically active lone pair of electrons and its effects on the coordination sphere of the tin(II) atom. Recently we reported a crystal structure of dichloro[2,2′:6′,2″-terpyridyl]tin(II) and found this molecule to be a relatively rare example of a 5-coordinate (Ψ-octahedral) tin(II) complex, with the sixth coordination site occupied by a lone pair of electrons [6]. Although 1:1 2,2′-bipyridyl and 1,10-phenanthroline adducts of $SnCl_2$ have been known for some time, speculation involving a possible 3-coordinate bridging 2,2′-bipyridyl ligand [7] stands in sharp contrast to the suggestion of a 6-coordinate polymeric structure involving halogen bridging [8].

We here report the crystal structures of dichloro(2,2′-bipyridyl)tin(II) (**A**), dichloro(1,10-phenanthroline)tin(II) (**B**) and dichlorobis(8-hydroxyquinolinato)tin(IV) (**C**).

Experimental

Preparation of Sn(2,2′-bipyridyl)Cl₂ (A)

A 5 cm^3 solution of 2.0 mmol (379 mg) anhydrous $SnCl_2$ (ALFA 98% + Sn(II)) in *N,N*-dimethyl-

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*Part I is ref. 6.

**Included is the crystal structure of dichlorobis(8-oxyquinolinato)tin(IV).

†Author to whom correspondence should be addressed. For 1986, address will be: Angewandte Chemie, Universität Gesamthochschule Paderborn, P.O. Box 1621, 4790 Paderborn, F.R.G.

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formamide was added to a 5 cm^3 solution of 2.0 mmol (312 mg) 2,2′-bipyridine (Aldrich). The rapidly formed yellow precipitate was collected by filtration, washed with small portions of ice-cold N,N-dimethylformamide and dried at room temperature under vacuum (yield 187 mg (54%)). *Anal.* Found: C, 34.8; H, 2.4; N, 8.15. Calc. for $C_{10}H_8Cl_2N_2Sn$: C, 34.74; H, 2.33; N, 8.10%. Crystals suitable for X-ray diffraction were grown from dilute solutions of A in *N,N*-dimethylformamide.

*Preparation of Sn(1,10-phenanthroline)Cl₂ (**B**)*

A similar procedure as followed for the preparation of A was followed in the case of 1,10-phenanthroline (Merck). Typical yield of **B** 284 mg (77%). *Anal.* Found: C, 39.0; H, 2.2; N, 7.6. Calc. for $C_{12}H_8N_2Cl_2Sn$: C, 38.94; H, 2.18, N, 7.57%.

Preparation of Sn(8-hydroxyquinoline)₂Cl₂ (C)

A similar procedure as followed for the preparation of **A** above, with no particular precautions to exclude air, yielded relatively small amounts of dichlorobis(8-hydroxyquinolinato)tin(II) as bright yellow crystals (21% of theoretical yield). *Anal.* Found: C, 44.0; H, 2.3; N, 4.18. Calc. for $C_{18}H_{12}N_2O_2Cl_2Sn$: C, 45.2; H, 2.5; N, 5.86%. Recrystallisation from *N,N*-dimethylformamide gave suitable crystals for X-ray diffraction. Several attempts to obtain a Sn(II) adduct with 8-hydroxyquinoline (Merck) in this solvent under anaerobic conditions failed, giving mixtures of products.

Data Collection

Accurate cell parameters were determined for each structure by a least-squares analysis of the setting angles of 24 reflections ($16° \leqslant \theta \leqslant 17°$; graphite monochromated Mo Kα) automatically located and centred on an Enraf-Nonius CAD4 diffractometer. The intensities were collected out to θ = 25° by the ω–2θ scan technique, with a final acceptance limit of 200 at 20 min^{-1} and a maximum recording time of 40 s. The stability of three standard reflections (<2%) monitored periodically during data collection, verified crystal stability. The data were LP processed and an empirical absorption correction applied [9]. Experimental details of the data collection are listed in Table I.

Structure Solution and Refinement

The position of the tin atom in each structure was located in a Patterson map – in the case of **C**, the metal atom lies on a two-fold axis. After initial emergence of the structures, refinements were carried out with all non-hydrogen atoms treated anisotropically. Hydrogen atoms were refined in constrained positions and their temperature factors treated as single parameters. Table I gives details of final refinements; final atomic parameters are listed in Tables IIa and b. Bond lengths and angles are given in Table III.

TABLE I. Experimental and Refinement Parameters for **A**, **B** and **C**

	A	**B**	**C**
Space group	$P2_1/C$	$C2/C$	$C2/C$
a (A)	8.623(4)	13.688(4)	14.235(2)
b (A)	9.365(1)	11.010(3)	8.207(1)
c (A)	15.056(3)	17.451(4)	15.462(5)
β (°)	106.18(3)	105.92(2)	108.82(2)
M_r (g mol^{-1})	345.8	369.8	477.9
V (A^3)	1167.6	2528.9	1709.9
D_c (Mg m^{-3})	1.18	1.17	1.12
F (000)	664	1424	916
μ(Mo Kα) (mm^{-1})	2.42	2.24	1.67
Crystal dimensions (mm)	0.22 × 0.22 × 0.31	0.13 × 0.22 × 0.31	0.08 × 0.50 × 0.50
$\Delta\omega$ (°)	0.74 + 0.35 tan θ	1.29 + 0.35 tan θ	1.34 + 0.35 tan θ
Aperture length (mm)	4.0	4.0	4.0
Aperture width (mm)	1.26 + 1.05 tan θ	1.78 + 1.05 tan θ	1.25 + 1.05 tan θ
No. of reflections collected	2272	2438	1680
No. of observed reflections	1774	1738	1181
No. of variables	137	155	115
$R = \Sigma \lVert F_o\vert - \vert F_c\rVert / \Sigma \vert F_o\vert$	0.021	0.033	0.031
$R_w = \Sigma W^{1/2} \lVert F_o\vert - \vert F_c\rVert / \Sigma W^{1/2} \vert F_o\vert$	0.021	0.033	0.029
Goodness of fit, S	2.52	2.16	1.16
Weighting scheme	$1.0/\sigma^2 F$	$0.96/\sigma^2 F$	$1.01/\sigma^2 F$
U_{iso} of H atoms (A)	0.084	0.071	0.046

Results and Discussion

All adducts of tin(II) chloride were prepared by the reaction of appropriate amounts of $SnCl_2$ and ligand in pure *N,N*-dimethylformamide solution.

TABLE IIa. Fractional Atomic Coordinates ($\times 10^4$) and Thermal Parameters ($\times 10^3$) for Non-hydrogen Atoms

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
$[Sn(bipy)Cl_2]$				
Sn1	2429(0)	0587(0)	−0026(0)	38.1(1)
Cl1	5096(1)	0724(1)	1214(1)	56.2(4)
Cl2	1309(1)	−1348(1)	1071(1)	59.1(4)
N1	3140(4)	2917(3)	−0498(2)	45(1)
C2	3786(5)	3077(5)	−1215(3)	59(2)
C3	3941(6)	4394(5)	−1581(3)	70(2)
C4	3435(6)	5567(5)	−1208(3)	74(2)
C5	2784(5)	5433(4)	−0466(3)	60(2)
C6	2672(4)	4073(4)	−0126(3)	45(1)
C7	2006(4)	3820(4)	0669(2)	39(1)
C8	1714(5)	4899(5)	1227(3)	58(2)
C9	1093(5)	4590(4)	1944(3)	62(2)
C10	0739(5)	3201(4)	2098(3)	54(2)
C11	1079(5)	2167(4)	1541(3)	47(1)
N12	1716(3)	2442(3)	0841(2)	38(1)
$[Sn(phen)Cl_2]$				
Sn1	6330(0)	3576(0)	0269(0)	39.4(2)
Cl1	4391(1)	3401(2)	−0056(1)	51.6(6)
Cl2	6412(2)	2071(2)	−1044(1)	60.8(7)
N1	6284(4)	3988(5)	1621(3)	43(2)
N10	6256(4)	1754(5)	0953(3)	43(2)
C2	6273(5)	5086(7)	1917(4)	56(3)
C3	6281(5)	5289(7)	2715(4)	55(3)
C4	6321(5)	4299(8)	3193(4)	57(3)
C41	6342(5)	3127(7)	2898(4)	49(3)
C42	6307(5)	3008(6)	2086(4)	39(3)
C5	6358(6)	2063(9)	3361(5)	62(3)
C6	6305(6)	0953(8)	3035(4)	60(3)
C7	6143(6)	−0326(7)	1832(5)	62(3)
C71	6247(5)	0798(7)	2199(4)	49(3)
C72	6278(5)	1830(6)	1744(4)	41(2)
C8	6095(6)	−0398(7)	1031(5)	62(3)
C9	6173(5)	0662(6)	0619(4)	51(3)
$[Sn(8\text{-}HQ)_2Cl_2]$				
Sn1	0000(0)	0721(1)	2500(0)	31.0(2)
Cl1	1254(1)	−1264(2)	3123(1)	44.8(5)
O1	−0453(2)	1059(4)	3605(2)	37(1)
N1	1020(3)	2652(5)	3251(3)	34(1)
C2	1736(3)	3419(7)	3044(4)	44(2)
C3	2362(3)	4537(6)	3642(4)	47(2)
C4	2242(4)	4816(7)	4464(4)	48(2)
C41	1500(3)	3998(6)	4721(3)	38(2)
C42	0895(3)	2940(6)	4077(3)	33(2)
C5	1343(4)	4170(7)	5569(3)	45(2)
C6	0606(4)	3305(7)	5741(4)	48(2)
C7	−0004(4)	2243(6)	5092(3)	40(2)
C8	0121(3)	2049(6)	4253(3)	32(2)

TABLE IIb. Fractional Atomic Coordinates ($\times 10^4$) for Hydrogen Atoms

Atom	*x/a*	*y/b*	*z/c*
$[Sn(bipy)Cl_2]$			
H2	4162(5)	2212(5)	−1485(3)
H3	4416(6)	4489(5)	−2113(3)
H4	3533(6)	6533(5)	−1470(3)
H5	2410(5)	6288(4)	−0185(3)
H8	1960(5)	5911(4)	1104(3)
H9	0899(5)	5368(5)	2355(3)
H10	0245(5)	2951(4)	2604(3)
$[Sn(phen)Cl_2]$			
H2	6257(5)	5803(7)	1562(4)
H3	6262(5)	6132(7)	2925(4)
H4	6331(5)	4419(8)	3764(4)
H5	6404(6)	2139(9)	3940(5)
H6	6308(6)	0217(8)	3371(4)
H7	6102(6)	−1082(7)	2139(5)
H8	6009(6)	−1200(7)	0752(5)
H9	6171(5)	0602(6)	0047(4)
$[Sn(8\text{-}HQ)_2Cl_2]$			
H2	1831(3)	3197(7)	2442(4)
H3	2891(3)	5114(6)	3463(4)
H4	2686(4)	5618(7)	4891(4)
H5	1771(4)	4922(7)	6042(3)
H6	0499(4)	3431(7)	6346(4)
H7	−0538(4)	1623(6)	5240(3)

TABLE III. Bond Lengths (A) and Angles (°)

Bond lengths		Bond angles	
$[Sn(bipy)Cl_2]$			
Sn1−Cl1	2.529(1)	N12−Sn1−N1	68.0(1)
Sn1−Cl2	2.799(1)	Cl2−Sn1−N12	155.8(8)
Sn1−N1	2.426(3)	Cl2−Sn1−N1	87.9(8)
Sn1−N12	2.355(3)	Cl1−Sn1−N1	85.4(8)
N1−C2	1.354(6)	Cl1−Sn1−N12	83.0(8)
C2−C3	1.373(7)	Cl1−Sn1−Cl2	89.4(4)
C3−C4	1.360(7)	Sn1−N1−C2	121.8(3)
C4−C5	1.389(7)	Sn1−N1−C6	118.5(2)
C5−C6	1.386(6)	C2−N1−C6	119.0(3)
N1−C6	1.332(5)	N1−C2−C3	121.8(4)
C6−C7	1.484(6)	C2−C3−C4	118.8(4)
C7−C8	1.382(6)	C3−C4−C5	120.5(4)
C8−C9	1.363(7)	C4−C5−C6	117.7(4)
C9−C10	1.370(6)	N1−C6−C5	122.1(4)
C10−C11	1.365(6)	C5−C6−C7	121.8(4)
C11−N12	1.342(6)	N1−C6−C7	116.1(3)
N12−C7	1.353(5)	C6−C7−C8	123.4(4)
		C7−C8−C9	120.3(4)
		C8−C9−C10	119.4(4)
		C9−C10−C11	118.2(4)
		C10−C11−N12	123.4(4)
		N12−C7−C8	120.4(4)

(continued)

TABLE III. *(continued)*

Bond lengths		Bond angles	
		N12–C7–C6	116.1(3)
		C7–N12–C11	118.1(3)
		Sn1–N12–C11	121.4(2)
		Sn1–N12–C7	120.4(2)
[Sn(phen)Cl_2]			
Sn1–Cl1	2.565(2)	N1–Sn1–N10	69.4(2)
Sn1–Cl2	2.854(2)	Cl2–Sn1–N10	85.9(1)
Sn1–N1	2.420(6)	Cl2–Sn1–N1	155.3(1)
Sn1–N10	2.351(6)	Cl1–Sn1–N10	82.1(1)
N1–C2	1.316(9)	Cl1–Sn1–N1	85.8(1)
N1–C42	1.345(9)	Cl1–Sn1–Cl2	92.6(6)
N10–C72	1.375(9)	Sn1–N1–C42	115.8(4)
N10–C9	1.327(9)	Sn1–N1–C2	124.1(4)
C2–C3	1.407(1)	C2–N1–C42	120.0(6)
C3–C4	1.365(1)	Sn1–N10–C9	124.1(4)
C4–C41	1.392(1)	Sn1–N10–C72	117.8(4)
C41–C42	1.411(1)	C72–N10–C9	118.1(6)
C41–C5	1.420(1)	N1–C2–C3	122.4(7)
C42–C72	1.424(9)	C2–C3–C4	117.8(7)
C5–C6	1.342(1)	C3–C4–C41	121.0(6)
C6–C71	1.449(1)	C4–C41–C5	123.6(7)
C7–C71	1.383(1)	C4–C41–C42	117.3(7)
C7–C8	1.384(1)	C42–C41–C5	119.1(7)
C71–C72	1.394(1)	N1–C42–C41	121.4(6)
C8–C9	1.390(1)	C41–C42–C72	119.7(6)
		N1–C42–C72	119.0(6)
		C41–C5–C6	121.3(7)
		C5–C6–C71	121.0(8)
		C71–C7–C8	119.3(7)
		C6–C71–C7	122.8(7)
		C7–C71–C72	118.8(7)
		C6–C71–C72	118.4(7)
		C42–C72–C71	120.4(6)
		N10–C72–C71	121.8(6)
		N10–C72–C42	117.8(6)
		C7–C8–C9	119.0(7)
		N10–C9–C8	122.9(6)
[Sn(8-HQ)$_2$$Cl_2$]			
Sn1–Cl1	2.379(2)	O1–Sn1–N1	78.1(1)
Sn1–N1	2.209(4)	Cl1–Sn1–N1	89.9(1)
N1–C2	1.322(7)	Cl1–Sn1–O1	98.8(1)
C2–C3	1.399(7)	Sn1–O1–C8	115.4(3)
C3–C4	1.355(9)	Sn1–N1–C42	110.7(3)
C4–C41	1.413(8)	Sn1–N1–C2	129.9(4)
C41–C42	1.390(6)	C2–N1–C42	117.2(4)
N1–C42	1.366(7)	N2–C2–C3	121.9(5)
C41–C5	1.406(7)	C2–C3–C4	118.9(5)
C5–C6	1.362(9)	C3–C4–C41	121.0(5)
C6–C7	1.399(7)	C4–C41–C42	116.2(4)
C7–C8	1.374(7)	N1–C42–C41	122.7(4)
C8–C42	1.420(7)	C4–C41–C5	125.0(5)
O1–C8	1.343(5)	C42–C41–C5	118.8(4)
		C41–C5–C6	119.6(4)
		C5–C6–C7	121.6(5)
		C6–C7–C8	120.6(5)
		C42–C8–C7	117.8(4)

(continued)

TABLE III. *(continued)*

Bond angles	
O1–C8–C7	122.8(4)
O1–C8–C42	119.4(4)
C41–C42–C8	121.6(4)
N1–C42–C8	115.7(4)

In the case of 2,2′-bipyridyl and 1,10-phenanthroline yielding $SnCl_2 \cdot C_{10}H_8N_2$ (**A**) and $SnCl_2 \cdot C_{12}H_8N_2$ (**B**) it was not necessary to perform the reaction under nitrogen to obviate any possible atmospheric oxidation of $SnCl_2$. In these cases, good yields of the tin(II) adducts were readily obtained. In the case of 8-hydroxyquinoline, however, attempts to isolate tin(II) adducts failed under aerobic conditins, while a mixture of substances was obtained under anaerobic conditions. The crystals obtained under any of our conditions were invariably adducts of tin(IV), $SnCl_2(C_8H_6NO)_2$ (**C**). Evidently, Sn(II) is oxidized to Sn(IV) in the presence of 8-hydroxyquinoline in *N,N*-dimethylformamide solution. Similar oxidations of Fe(II) and Mn(II) at pH 4 in the

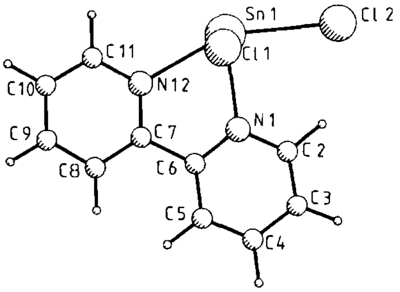

Fig. 1. Molecular structure of [Sn(bipy)Cl_2].

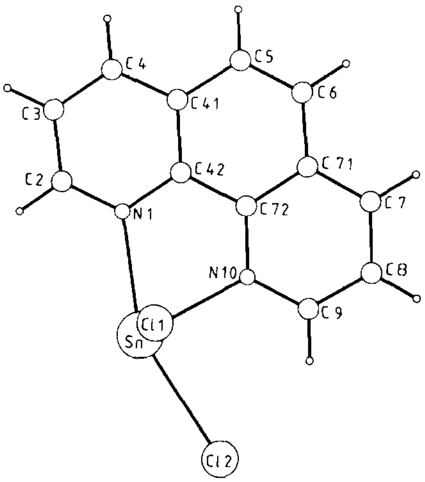

Fig. 2. Molecular structure of [Sn(phen)Cl_2].

TABLE IV. Comparison of Interatomic Distances (A) with the Sn(II) Coordination Sphere in **A** and **B**, with Corresponding Distances in Other Compounds

	Sn–Cl	Sn---Cl	Sn–N	Reference
$SnCl_2 \cdot 2H_2O$	2.500(2) 2.562(2)	3.209(2) 3.336(2) 3.416(2)		11
$CsSnCl_3$	2.52(1)	3.21(1) 3.45(1) 3.77(1)		12
$Sn(1,4\text{-dioxane})_2Cl_2$	2.474(2)	3.451(2)		13
$Sn(terpyridyl)Cl_2$	2.687(1)		2.315(5) 2.384(4)	6
A	2.53(1) 2.80(1)	3.25(1) 3.38(1)	2.35(3) 2.42(3)	this work
B	2.57(2) 2.86(2)	3.10(2) 3.42(2)	2.36(6) 2.41(6)	this work
$H_2Sn(EDTA)$			2.389(5) 2.445(5)	14
(2-aminobenzothiazolato)-nitratotin(II)			2.23(1)	15

presence of 8-hydroxyquinoline have been reported, although the role of 8-hydroxyquinoline is not clear [10].

Dichloro(2,2'-bipyridyl)tin(II) (A) (Fig. 1) and Dichloro(1,10-phenanthroline)tin(II) (B) (Fig. 2)

The compounds **A** and **B** are remarkably similar, both in molecular and in crystal structure. In both cases, the geometry about the tin atom could be described as distorted octahedral, the stereochemically active lone pair of electrons being in part at least responsible for the distortion from regular octahedral geometry. Veith and Recktenwald [3] have listed the most commonly occurring forms of tin(II) coordination polyhedra. All three tin(II) compounds studied by us to data are covered by their classification; **A** and **B** are distorted octahedral while the previously reported $Sn(terpy)Cl_2$ displays a five coordinate, Ψ-octahedral geometry [3, 6].

In contrast with $Sn(terpy)Cl_2$, **A** and **B** cannot be described as hemispherical molecules; the space available for their lone pairs is much less than that in $Sn(terpyl)Cl_2$ and probably lies in the region between the atoms Cl1, Cl2 and Cl1a. In both **A** and **B**, each tin atom is involved in contacts with four chlorine atoms (see Figs. 3 and 4), each of the four tin to chlorine distances being unequal, two of these distances <3 Å; the other two being >3 Å (long interactions). The spread of the tin to chlorine distances involved makes it difficult to distinguish between bonded and non-bonded interactions (Table IV). The shortest Sn–Cl bonds (2.53(1) Å, **A** and 2.57(2) Å, **B**) fall well within the expected range, while the Sn---Cl contacts which we have classified as long interactions, are comparable in length with other Sn---Cl non-bonded interactions. An interesting intermediate Sn–Cl distance of 2.80(1) Å and 2.86(2) Å in each molecule of **A** and **B** respectively appears to be unprecedented in tin(II) chemistry (Table IV).

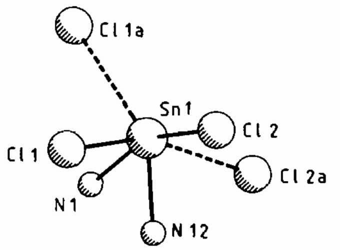

Fig. 3. Coordination sphere of $[Sn(bipy)Cl_2]$.

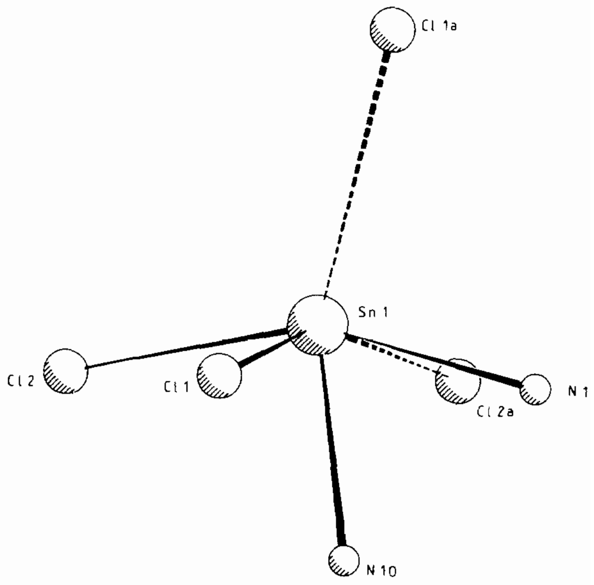

Fig. 4. Coordination sphere of $[Sn(phen)Cl_2]$.

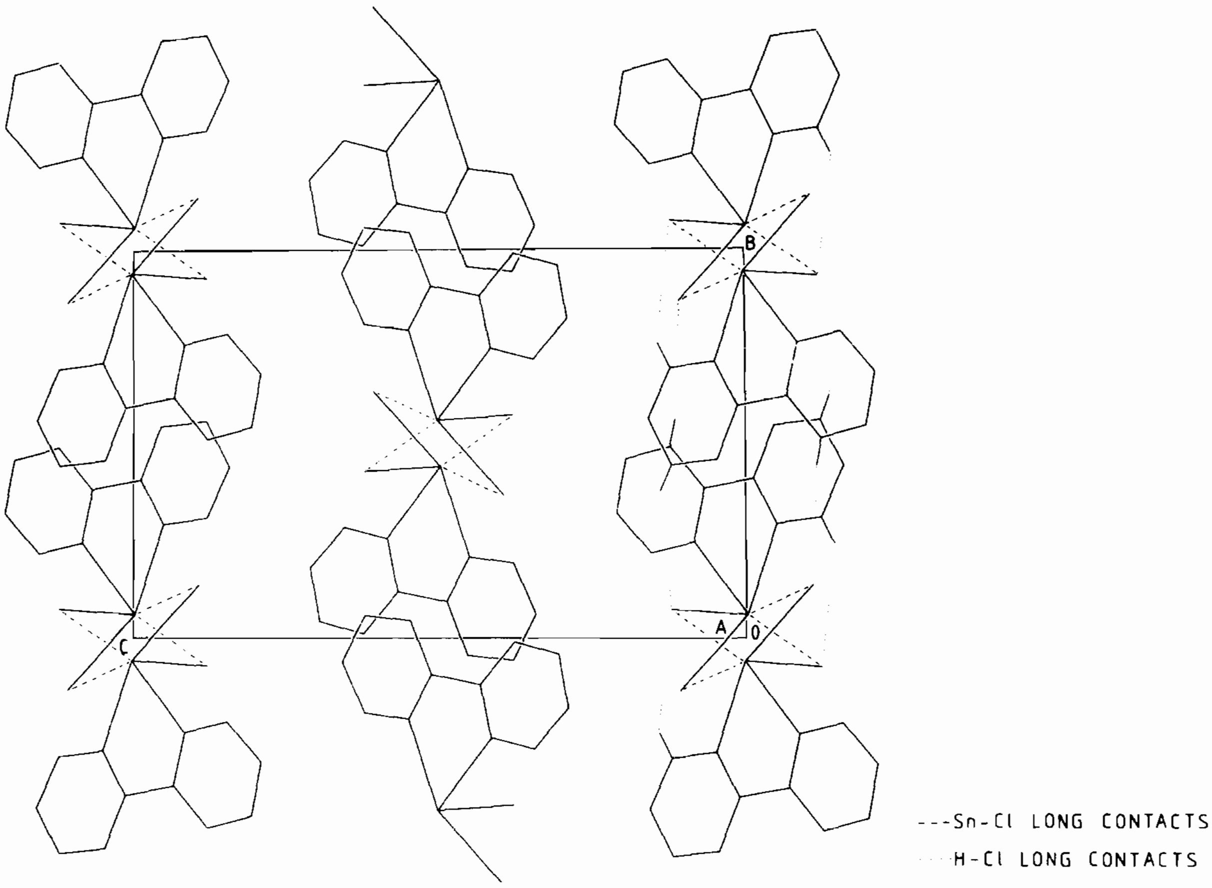

Fig. 5. Crystal structure of [Sn(bipy)Cl_2] viewed down the *a*-axis.

The Sn–N bond lengths in **A** and **B** fit very well into the existing collection of Sn(II)–N bond lengths (see Table IV and other examples in ref. 3). The bond lengths in the coordination spheres of **A** and **B**, excluding one intermediate Sn- - -Cl contact, are equal within 2%. The lengths of the remaining Sn- - - Cl contacts agree within 5%.

The chelate rings in **A** and **B** hardly deviate from planarity; in **A** the greatest deviation of an atom in the chelate ring from the mean plane of the ring is 0.05 Å and in **B**, 0.04 Å. The bond lengths and angles in the chelate ring of **A** resemble those in Sn(terpy)Cl_2 much more closely than those in **B**. In particular, the Sn–N–C angles in **A** and in Sn(terpy)Cl_2 are larger, and the N–C–C angles smaller, than the corresponding angles in **B**. These differences are no doubt due to the extra rigidity of the phenanthroline ligand, arising from the C5–C6 bridge in its fused ring system. In support of this, the ligand 'bite' in **A** (2.674(5) Å) is closer to that in Sn(terpy)Cl_2 (2.642(5) Å) [6] than to that in **B** (2.718(8) Å). The ligand rings in **A** and **B** are planar, and their bond lengths and angles are unremarkable.

In **A** intermolecular Sn- - -Cl contacts result in the formation of infinite chains of molecules, which lie parallel to **a** (Figs. 5 and 6). Intermolecular Sn- - - Cl contacts occur between enantiomers related by inversion centres located at Wyckoff positions a and b of space group $P2_1/C$. Each chain has close contacts with its neighbour in the *b* direction through van der Waals' interactions between parallel aromatic rings. There is, however, no identifiable interaction between adjacent chains in the *c* direction. Aromatic overlap takes place only between pairs of molecules related by centres of symmetry Wyckoff position d. The ligand rings are about 3.58 Å apart in the region of overlap.

Similar intermolecular Sn- - -Cl contacts occur in the case of **B** resulting also in infinite chains (Fig. 7). One set of chains lies in the (001) plane, parallel to $(1\bar{1}0)$, and the other set lies in the plane (002), parallel to (110). In fact, the two sets are related by the two-fold axis in the cell. Therefore, when viewed down the *c* axis, the two sets of chains appear to intersect each other in a right-angled grid.

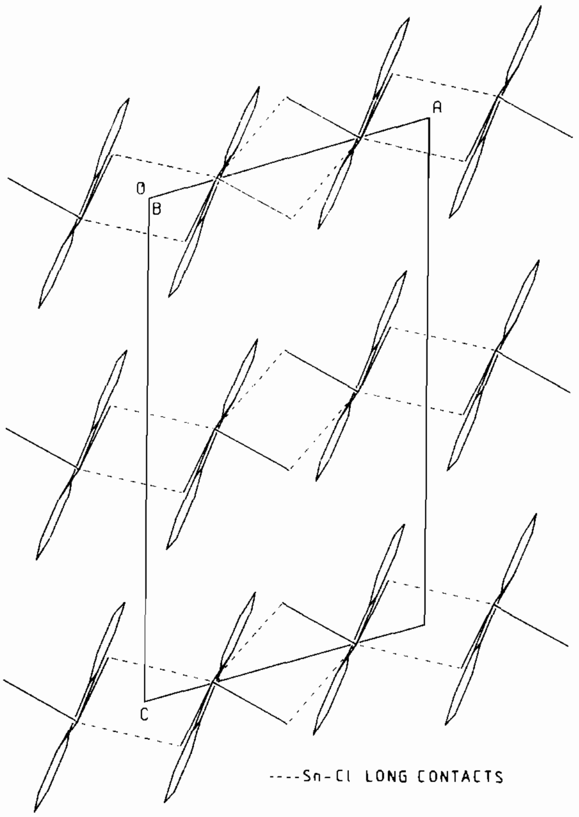

Fig. 6. Crystal structure of [Sn(bipy)Cl$_2$] viewed down the *b*-axis.

Regarding the chains in the *ab* plane, intermolecular Sn---Cl interactions take place between pairs of enantiomers related by inversion centres at (0, 0, 0), (¼, ¾, 0), (½, ½, 0) and (¾, ¼, 0). The long Sn---Cl contacts responsible for the chains lying in the (002) plane occur between pairs of molecules related by centres of symmetry at (0, 0, ½), (¼, ¼, ½), (½, ½, ½) and (¾, ¾, ½).

Although these chains of molecules, as a result of long Sn---Cl contacts, are not all mutually parallel, the phenanthroline rings are all aligned in parallel layers (Fig. 8). The two sets of chains are, in fact, linked to each other by van der Waals' contacts between the parallel aromatic rings. This ring overlap takes place between pairs of molecules related by a two-fold axis; the rings are held about 3.56 Å apart in the region of overlap. There is no overlap of ligand rings between chains within the same set. It is interesting that the degree of overlap of phenanthroline rings is large.

In the crystal structures of both **A** and **B**, there is a third type of intermolecular close contact: that between chlorine atoms and aromatic hydrogen atoms. In **A** networks of H•••Cl contacts of 2.625(4) Å, 2.809(5) Å, and 2.827(5) Å, run through the structure parallel to *b* (Fig. 5). In **B** the molecular chains mentioned, are further strengthened by H•••Cl interactions of 2.680(7) Å and 2.698(8) Å, slightly less than the van der Waals' distances (Fig. 7).

cis-Dichlorobis(8-hydroxyquinoline)tin(IV) (C)

The tin atom in **C** lies on a two-fold axis so that the two 8-hydroxyquinoline ligands are related by symmetry (Fig. 9). The complex is six-coordinate and has an irregular *cis*-octahedral structure. As Table V shows, six-coordinate tin(IV) complexes exhibit wide ranges of Sn–Cl, Sn–O and Sn–N bond lengths. The reasons for such diversity are obviously many and complex. The Sn-Cl, Sn–O and Sn–N bonds in **C** are all among the shortest bonds listed. It is noteworthy that most of the bonds in Table V which are longer than the corresponding bonds in **C**, are found in organotin compounds.

The molecular structure of **C** is very similar to that of dimethylbis(8-hydroxyquinoline)tin(IV) [16]; both complexes have the *cis*-configuration, bond lengths around the metal atom are of similar length, and the angular distortion from octahedral geometry at the metal centre is similar in both complexes.

The chelate ring in **C** deviates only slightly from planarity. The largest deviation of an atom in the chelate ring from the least-squares plane through this ring is 0.071(5) Å. The ligand is also almost planar, the largest deviation from the mean ring plane being 0.034(6) Å. This is similar to the ligand planarity in dimethylbis(8-hydroxyquinoline)tin(IV), where the largest deviation is 0.04(2) Å. Bond lengths and angles within the ligand in **C** have expected values [11].

Van der Waals' interactions between overlapping ligand rings link molecules of **C** together to form infinite stair-cases parallel to (1$\bar{1}$0). The planes of the two symmetry-related ligand rings are almost perpendicular to each other. Thus, the crystal structure is composed of two mutually perpendicular systems of parallel-packed aromatic rings. Each ligand is involved in two non-bonded stacking interactions with its neighbours. Both two-ring and one-ring overlap occurs, and the extent of overlap is generally small (Fig. 10).

Supplementary Material

Tables of structure factors, anisotropic temperature factors, deviations from planarity and other intermolecular distances have been deposited with the Editor-in-Chief.

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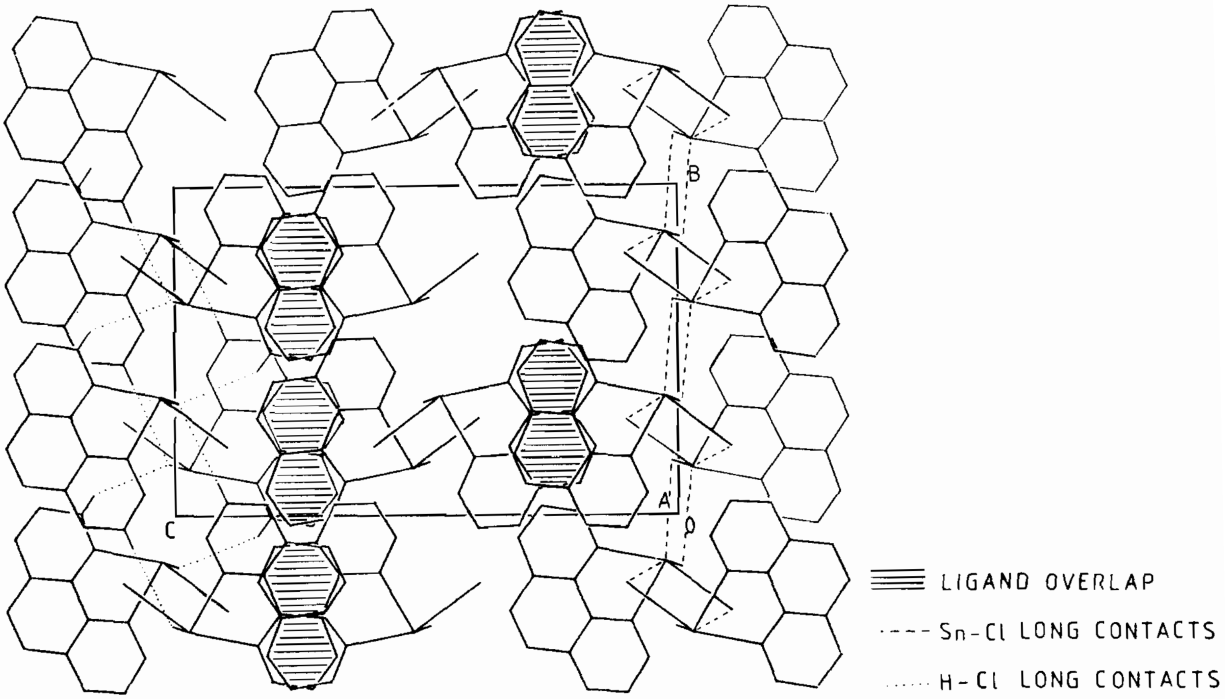

Fig. 7. Crystal structure of [Sn(phen)Cl$_2$] viewed down the *a*-axis.

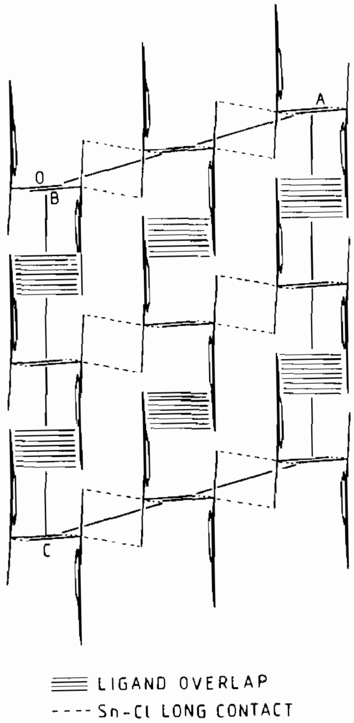

Fig. 8. Crystal structure of [Sn(phen)Cl$_2$] viewed down the *b*-axis.

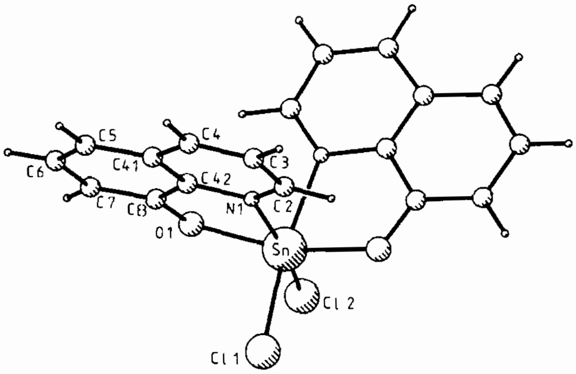

Fig. 9. Molecular structure of [Sn(8-HQ)$_2$Cl$_2$].

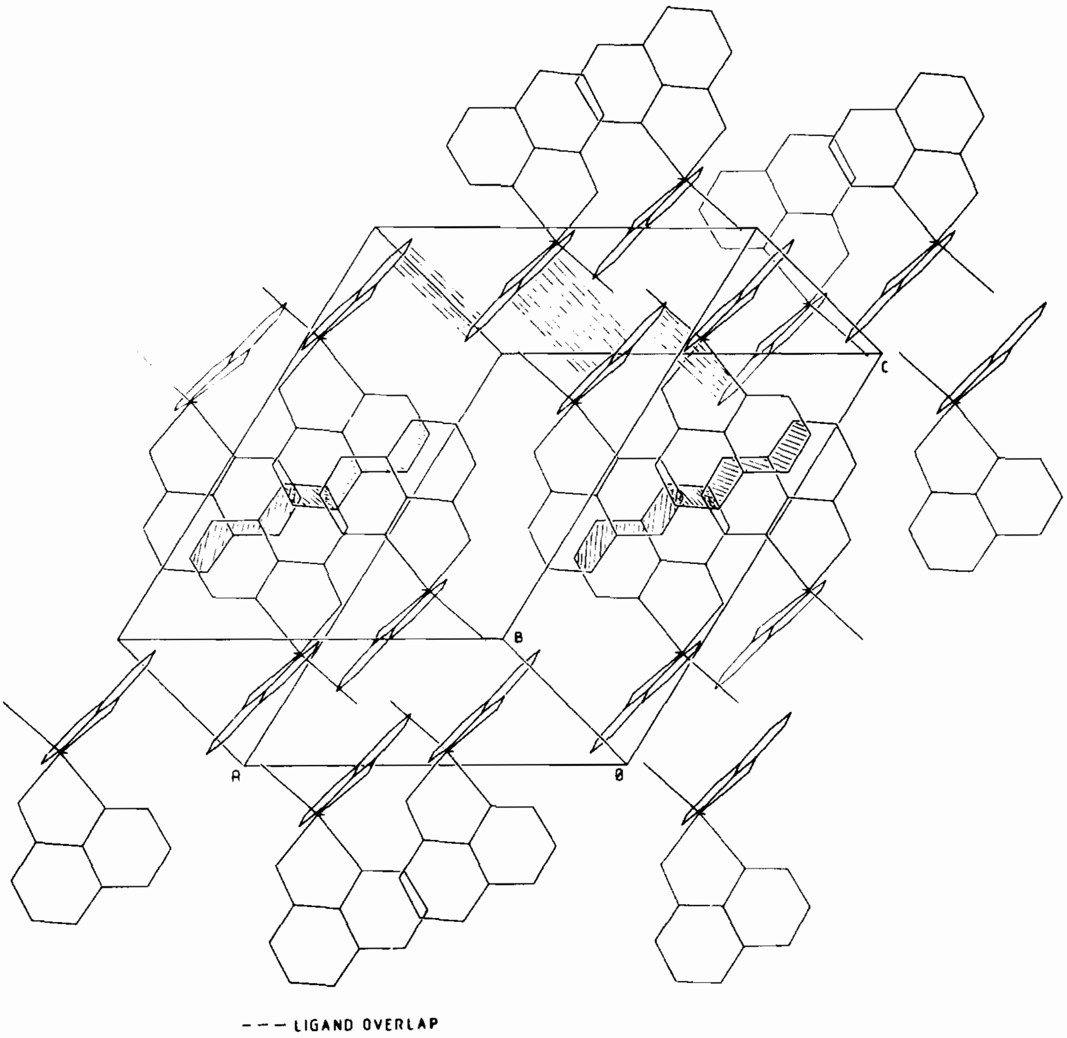

Fig. 10. Crystal structure of [$Sn(8\text{-}HQ)_2Cl_2$] viewed perpendicular of C2 C3 C41.

TABLE V. Comparison of Sn–X Bond Lengths (Å) in some Six-coordinate Sn(IV) Complexes

Complex	Sn–N	Sn–O	Sn–Cl	Reference
C	2.209(4)	2.030(3)	2.379(2)	this work
dimethylbis(8-hydroxyquinoline)tin(IV)	2.38(1) 2.31(1)	2.10(1) 2.11(1)		16
dichlorodiethyl-3(2-pyridyl)-5,6-diphenyl-1,2,4-triazinetin(IV)	2.45(1) 2.55(1)		2.451(5) 2.506(5)	17
dichlorodimethylbis(4-nitroso-*N*,*N*-dimethyl–aniline)tin(IV)		2.277(4)	2.578(1)	18
dichlorobis(β-carbo-methoxyethyl)tin(IV)		2.520(4) 2.524(4)	2.401(2) 2.409(2)	19
dichlorobis(β-amido-ethyl)tin(IV)		2.327(16) 2.321(18)	2.460(7) 2.464(7)	19
dichlorodiethyl-2,2′-bipyridyl-tin(IV)	2.382(4) 2.368(4)		2.529(1) 2.545(1)	20

(continued)

TABLE V. *(continued)*

Complex	Sn–N	Sn–O	Sn–Cl	Reference
tetrachloro-1,3-dicyano-propane-tin(IV)	2.29(2)		2.36(1) 2.35(1)	1
tetrachlorobis(cyanomethane)tin(IV)	2.336(23) 2.326(25)		2.341(7) 2.339(8)	1
$SnCl_2[ONPhC(O)Ph]_2$		2.04(2) 2.11(2)	2.366(5) 2.356(6)	1
$Sn[(OC_2H_4)_2NC_2H_4OH]_2$	2.332(10) 2.383(10)	2.024(8) 2.043(8)		1

References

1 J. A. Zubieta and J. J. Zuckerman, 'Progress in Inorganic Chemistry', Vol. 24, Interscience, Wiley, New York, 1978, p. 251.

2 J. D. Donaldson, 'Progress in Inorganic Chemistry', Vol. 8, Interscience, Wiley, New York, 1967, p. 287.

3 M. Veith and O. Recktenwald, 'Topics in Current Chemistry Organotin Compounds', Vol. 104, Springer, Berlin, 1982, p. 1.

4 A. F. Wells, 'Structural Inorganic Chemistry', 5th edn., Clarendon, Oxford, 1984, p. 1175.

5 C. C. Hsu and R. A. Geanangel, *Inorg. Chem., 19,* 110 (1980).

6 S. A. Archer, K. R. Koch and L. R. Nassimbeni, *J. Crystallogr. Spectrosc. Res., 16,* 449 (1986).

7 J. S. Morrison and H. M. Haendler, *J. Inorg. Nucl. Chem., 29,* 393 (1967).

8 G. W. A. Fowles and I. A. Khan, *J. Less-Common Met., 15,* 209 (1968).

9 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A, 24,* 351 (1968).

10 J. Stavy, 'The Solvent Extraction of Metal Chelates', Pergamon, Oxford, 1964, p. 86, 88.

11 H. Kiriyama, K. Kitahama, O. Nakamura and R. Kiriyama, *Bull. Chem. Soc. Jpn., 46,* 1389 (1973).

12 F. R. Poulsen and S. E. Rasmussen, *Acta Chem. Scand., 24,* 50 (1970).

13 E. Hough and D. G. Nicholson, *J. Chem. Soc., Dalton Trans.,* 1782 (1976).

14 K. G. Shields, R. C. Seccombe and C. H. Kennard, *J. Chem. Soc., Dalton Trans.,* 741 (1973).

15 M. Nardelli, C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.,* 1595 (1975).

16 E. O. Schlemper, *Inorg. Chem., 6,* (11), 2012 (1967).

17 L. Prasad and Y. Le Page, *Inorg. Chim. Acta, 68,* 45 (1983).

18 G. Matsubayashi and K. Nakatsu, *Inorg. Chim. Acta, 64,* L163 (1982).

19 P. G. Harrison, T. J. King and M. A. Healy, *J. Organomet. Chem., 182,* 17 (1979).

20 S. L. Chadha, P. G. Harrison and K. C. Molloy, *J. Organomet. Chem., 202,* 247 (1980).