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Outer-sphere coordination of *o*-phenanthroline in bis[aquachlorotri(*p*-chlorophenyl) tin·*o*-phenanthroline]

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Abstract

The crystal structure of bis[aquachlorotri(*p*-chlorophenyl)tin·*o*-phenanthroline] consists of trigonal bipyramidal aquachlorotri(*p*-chlorophenyl)tin units in which the coordinated water is hydrogen bonded to two *o*-phenanthroline bases.

Keywords: Tin; Crystal structure

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1. Introduction

In centrosymmetric bis[aquachlorotriphenyltin·*o*-phenanthroline], the coordinated water appears to form four hydrogen bonds ($O \cdots N = 2.96 - 3.31$ Å) to the two *o*-phenanthrolines [1]. The uncertainty in the hydrogen bonding interactions was attributed to twinning that led to a poor refinement ($R = 12.8\%$) of the model, but nevertheless, the interactions must be weak as the distances exceed distances found in similar aquaorganotin systems [2]. In contrast, the coordinated water in monomeric aquachlorotriphenyltin·3,4,7,8-tetramethyl-*o*-phenanthroline forms only two strong hydrogen bonds to the heterocyclic ligand [3]. The hydrogen bonding scheme suggested for the dimeric compound has been re-examined by a low-temperature study of the analogous aquachlorotri(*p*-chlorophenyl)tin complex.

2. Experimental

The complex was obtained as large colorless crystals from the slow evaporation of an ethanol solution containing equimolar amounts of tri(*p*-chlorophenyl)tin chloride and *o*-phenathroline. A 0.25 × 0.30 × 0.60 mm crystal was used for diffraction analysis. The 8545 reflections were measured at -105°C by ω-scans on a Siemens *P*4 diffractometer (graphite-monochromatized Mo-$K\alpha$ radiation, 0.71073 Å) (collection range: $-13 \le h \le 0$, $-12 \le k \le 11$, $-23 \le l \le 23$) up to $2\Theta = 53°$, and were corrected for absorption (min./max. transmission factors = 0.3826/0.4658). The structure was solved by direct methods [4]. Non-H atoms were refined anisotropically; C-bound H-atoms were generated and allowed to ride on their parent C-atoms with temperature factors 1.5 times those of the C-atoms. The H-atoms of the water molecule were located and refined. Refinement on F^2 [5] over all 8460 independent reflections ($R_{int} = 0.0941$) converged to $R = 0.0657$, $R_w = 0.1322$ for 701 variables and $S = 1.073$; $R = 0.0457$ for the 6665 $F \ge 4\sigma | F_o |$ reflections. Atomic coordinates are listed in Table 1.

Crystal data: $[(p\text{-ClC}_6H_4)_3SnCl \cdot H_2O \cdot o\text{-}C_{12}H_8N_2]_2$, $C_{60}H_{44}Cl_8N_4O_2Sn_2$, $FW = 1373.98$, triclinic, $a = 11.878(5)$, $b = 12.747(4)$, $c = 20.515(6)$ Å, $\alpha = 84.37(1)$, $\beta = 80.74(3)$, $\gamma = 69.39(2)°$, $V = 2867(2)$ Å^3, $D_{calc} = 1.592$ g cm^{-3}, $\mu = 12.91$ cm^{-1}, $F(000) = 1368$ for $Z = 2$.

3. Results and discussion

Bis[aquachlorotri(*p*-chlorophenyl)tin·*o*-phenathroline] crystallizes as a dimer in which the two symmetry-independent [aquachlorotri(*p*-chlorophenyl)tin·*o*-phenanthroline] moieties (*a* and *b*) show *trans*-C_3SnClO trigonal bipyramidal coordination at the tin atoms (molecule *a*: $\Sigma C\text{–}Sn\text{–}C = 358.5(6)$, $O\text{–}Sn\text{–}Cl = 176.2(1)°$; molecule *b*: $\Sigma C\text{–}Sn\text{–}C = 357.5(6)$, $O\text{–}Sn\text{–}Cl = 176.3(1)°$) (Fig. 1). The coordinated water

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Table 1
Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å^2)

Atom	x	y	z	U_{eq}
Sn(1a)	7473(1)	943(1)	907(1)	24(1)
Cl(1a)	2033(1)	1814(2)	1533(1)	46(1)
Cl(2a)	8855(2)	4864(2)	−1374(1)	49(1)
Cl(3a)	10966(1)	−3312(2)	2957(1)	47(1)
Cl(4a)	7720(1)	−403(1)	54(1)	36(1)
O(1a)	7375(4)	2202(5)	1697(2)	30(1)
N(1a)	5675(4)	4658(4)	2099(2)	29(1)
N(2a)	7628(4)	4529(4)	1380(2)	30(1)
C(1a)	5713(5)	1259(5)	1098(3)	29(2)
C(2a)	5277(5)	390(5)	1016(3)	27(1)
C(3a)	4144(5)	545(6)	1147(3)	32(2)
C(4a)	3450(5)	1619(6)	1351(3)	34(2)
C(5a)	3851(5)	2520(6)	1428(3)	30(2)
C(6a)	4980(5)	2349(5)	1298(3)	29(1)
C(7a)	7970(5)	2240(5)	238(3)	25(1)
C(8a)	7214(5)	3393(5)	66(3)	27(1)
C(9a)	7471(5)	4217(6)	−418(3)	31(2)
C(10a)	8530(5)	3857(6)	−734(3)	30(2)
C(11a)	9316(5)	2738(6)	−572(3)	36(2)
C(12a)	9029(5)	1939(5)	−76(3)	32(2)
C(13a)	8611(5)	−422(5)	1552(3)	25(1)
C(14a)	9645(5)	−365(5)	1662(3)	30(2)
C(15a)	10377(5)	−1260(6)	2074(3)	37(2)
C(16a)	10075(5)	−2208(6)	2406(3)	32(2)
C(17a)	9045(5)	−2297(6)	2305(3)	36(2)
C(18a)	8320(5)	−1393(5)	1879(3)	31(2)
C(19a)	5642(5)	5490(5)	1554(3)	26(1)
C(20a)	4719(5)	4668(6)	2414(4)	41(2)
C(21a)	3674(6)	5483(8)	2216(4)	55(2)
C(22a)	3636(6)	6348(7)	1691(4)	53(2)
C(23a)	4637(6)	6400(6)	1338(3)	39(2)
C(24a)	4672(7)	7316(6)	804(4)	50(2)
C(25a)	5640(8)	7359(7)	516(4)	50(2)
C(26a)	6691(6)	6435(6)	704(3)	36(2)
C(27a)	7729(8)	6452(7)	416(4)	54(2)
C(28a)	8678(7)	5515(8)	608(4)	55(2)
C(29a)	8591(6)	4566(7)	1076(4)	45(2)
C(30a)	6699(5)	5481(5)	1207(3)	28(1)
Sn(1b)	7347(1)	4416(1)	3980(1)	29(1)
Cl(1b)	12829(2)	3287(2)	3417(1)	57(1)
Cl(2b)	3195(1)	9013(2)	2546(1)	48(1)
Cl(3b)	6674(2)	−701(2)	5455(1)	59(1)
Cl(4b)	7116(1)	5262(2)	5030(1)	47(1)
O(1b)	7437(4)	3616(5)	2980(3)	34(1)
N(1b)	6679(4)	1161(4)	2926(2)	29(1)
N(2b)	8791(4)	1139(5)	3086(3)	34(1)
C(1b)	9076(5)	4222(6)	3766(3)	30(2)
C(2b)	9767(5)	4062(6)	4295(3)	38(2)
C(3b)	10921(5)	3776(6)	4183(3)	41(2)
C(4b)	11376(5)	3658(6)	3559(3)	38(2)
C(5b)	10728(6)	3824(6)	3032(3)	43(2)
C(6b)	9575(6)	4106(6)	3141(3)	36(2)
C(7b)	6034(5)	5907(5)	3521(3)	30(2)
C(8b)	6194(5)	6524(5)	2912(3)	32(2)
C(9b)	5337(5)	7495(6)	2606(3)	35(2)
C(10b)	4282(5)	7815(6)	2929(3)	36(2)
C(11b)	4088(5)	7232(6)	3542(3)	39(2)
C(12b)	4968(6)	6287(6)	3835(3)	40(2)
C(13b)	7086(5)	2793(6)	4434(3)	31(2)
C(14b)	8000(5)	1812(6)	4678(3)	36(2)
C(15b)	7877(6)	737(6)	4980(3)	40(2)
C(16b)	6822(6)	636(6)	5055(3)	43(2)
C(17b)	5892(6)	1595(6)	4810(3)	42(2)
C(18b)	6038(5)	2662(6)	4504(3)	38(2)
C(19b)	7381(5)	184(5)	3302(3)	27(1)
C(20b)	5640(5)	1171(6)	2895(3)	36(2)
C(21b)	5233(6)	276(7)	3209(3)	42(2)
C(22b)	5946(6)	−708(7)	3572(3)	42(2)
C(23b)	7066(5)	−785(6)	3626(3)	33(2)
C(24b)	7854(6)	−1792(6)	3996(3)	41(2)
C(25b)	8916(6)	−1827(6)	4040(3)	43(2)
C(26b)	9261(5)	−855(6)	3746(3)	38(2)
C(27b)	10354(6)	−838(7)	3790(4)	51(2)
C(28b)	10639(6)	106(7)	3504(4)	51(2)
C(29b)	9836(6)	1109(7)	3144(4)	47(2)
C(30b)	8516(5)	172(6)	3372(3)	31(2)

U_{eq} is defined as one third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

(Sn–O = 2.351(4) Å) in molecule *a* forms a hydrogen bond to the nitrogen atom of its own heterocycle (O ⋯ N = 3.083(8) Å), and another (O ⋯ N = 2.873(7) Å) to the nitrogen atom belonging to the base of molecule *b*. The coordinated water (Sn–O = 2.351(5) Å) of molecule *b* in similarly linked to its own *o*-phenathroline (O ⋯ N = 3.000(8) Å) and to the *o*-phenanthroline (O ⋯ N = 2.864(8) Å) of the other molecule (Fig. 2). Several chlorine-chlorine contacts ranging from 3.762 to 3.903 Å are present in the unit cell. The two pairs of hydrogen bonds hold together the flat heterocyclic bases [1], which are twisted with respect to each other (dihedral angle = 31.1(1)°) in a propeller-like conformation. The hydrogen bonding distances exceed those found in aquachlorotriphenyltin·3,4,7,8-tetramethyl-*o*-phenanthroline (O ⋯ N = 2.661(3), 2.767(3) Å; N ⋯ O ⋯ N = 60.9(1)°), whose five-membered C–N ⋯ O$_{water}$ ⋯ N–C ring is planar (Σangles = 540(1)°) [3]. The packing appears to be less efficient compared with that of the title complex, as suggested by its density (1.415 g cm^{-3}). The distances in the title complex also exceed those found in monomeric aquachlorotriphenyltin·2,2′:6′,2″-terpyridyl (O ⋯ N = 2.766(2), 2.807(2) Å; N ⋯ O ⋯ N = 107.0(2)°); in this complex, hydrogen bonding involves only the two outer pyridyl groups of the non-planar terpyridyl ligand [6].

The hydrogen bonding scheme of the complex prompted a re-investigation of crystal structure of

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[1] *o*-Phenanthroline crystallizes as a monohydrate in the trigonal $P3_1$ or $P3_2$ space group but no structural details were given in S. Nishigaki, H. Yoshioka and K. Nakatsu, *Acta Cryst.*, B31 (1975) 1220; G. Thevenet, P. Toffoli, R. Ceolin and N. Rodier, *C.R. Hebd. Sci., Ser. C*, 283 (1976) 671.

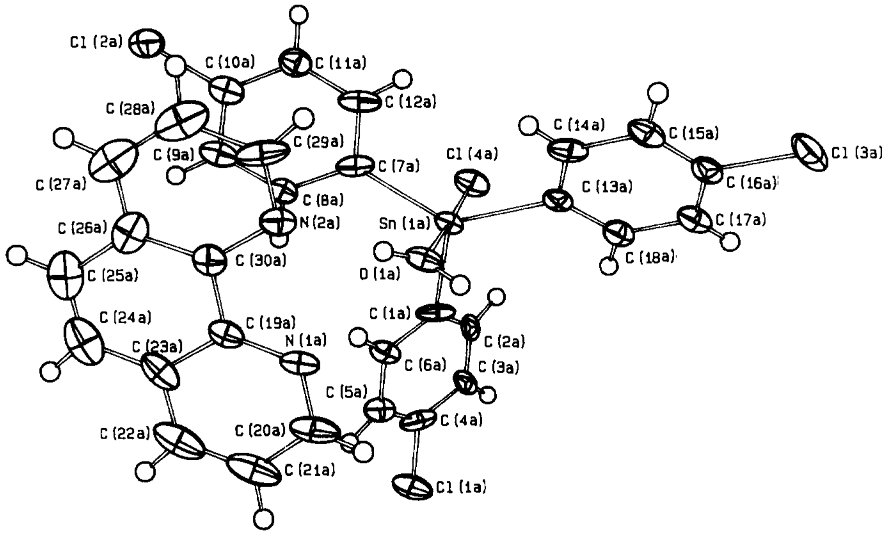

Fig. 1*a*. Geometry of the tin atom in molecule *a* of bis[aquachlorotri(*p*-chlorophenyl)tin·*o*-phenanthroline]. Selected bond distances and angles: Sn(1a)–C(1a) = 1.964(6), Sn(1a)–C(7a) = 2.225(6), Sn(1a)–C(13a) = 2.252(6), Sn(1a)–O(1a) = 2.351(4), Sn(1a)–Cl(4a) = 2.482(2) Å; C(1a)–Sn(1a)–C(7a) = 113.3(2), C(1a)–Sn(1a)–C(13a) = 115.6(2), C(1a)–Sn(1a)–O(1a) = 91.3(2), C(1a)–Sn(1a)–Cl(4a) = 92.5(2), C(7a)–Sn(1a)–C(13a) = 129.6(2), C(7a)–Sn(1a)–O(1a) = 80.6(2), C(7a)–Sn(1a)–Cl(4a) = 97.6(2), C(13a)–Sn(1a)–O(1a) = 86.9(2), C(13a)–Sn(1a)–Cl(4a) = 91.7(2), O(1a)–Sn(1a)–Cl(4a) = 176.2(1)°.

bis(aquachlorotriphenyltin·*o*-phenanthroline) [2]. On an image plate system, a super-structure lattice has been discerned from the diffraction pattern [3], and preliminary refinements reveal five independent aquachlorotriphenyltin·*o*-phenanthroline units, so that the reported bond dimensions are subject to errors inherent in averaging over five units.

Acknowledgments

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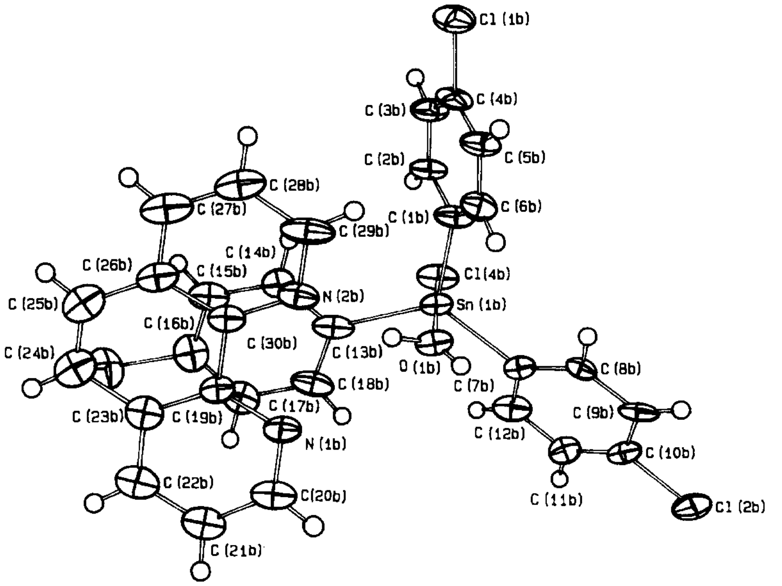

Fig. 1*b*. Geometry of the tin atom in molecule *b* of bis[aquachlorotri(*p*-chlorophenyl)tin·*o*-phenanthroline]. Selected bond distances and angles: Sn(1b)–C(1b) = 1.961(6), Sn(1b)–C(7b) = 2.229(6), Sn(1b)–C(13b) = 2.286(7), Sn(1b)–O(1b), 2.351(5), Sn(1b)–Cl(4b) = 2.436(2) Å; C(1b)–Sn(1b)–C(7b) = 117.4(2), C(1b)–Sn(1b)–C(13b) = 111.0(2), C(1b)–Sn(1b)–O(1b) = 89.6(2), C(1b)–Sn(1b)–Cl(4b) = 94.1(2), C(7b)–Sn(1b)–C(13b) = 129.1(2), C(7b)–Sn(1b)–O(1b) = 82.6(2), C(7b)–Sn(1b)–Cl(4b) = 95.5(2), C(13b)–Sn(1b)–O(1b) = 83.1(2), C(13b)–Sn(1b)–Cl(4b) = 95.7(2), O(1b)–Sn(1b)–Cl(4b) = 176.3(1)°.

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[2] Monoclinic, $P2_1/c$, $a = 11.960(1)$, $b = 12.220(1)$, $c = 17.854(1)$ Å, $\beta = 92.409(6)°$.

[3] Monoclinic, $P2_1/n$, $a = 21.01(1)$, $b = 12.184(7)$, $c = 51.52(2)$ Å, $\beta = 101.47(1)°$.

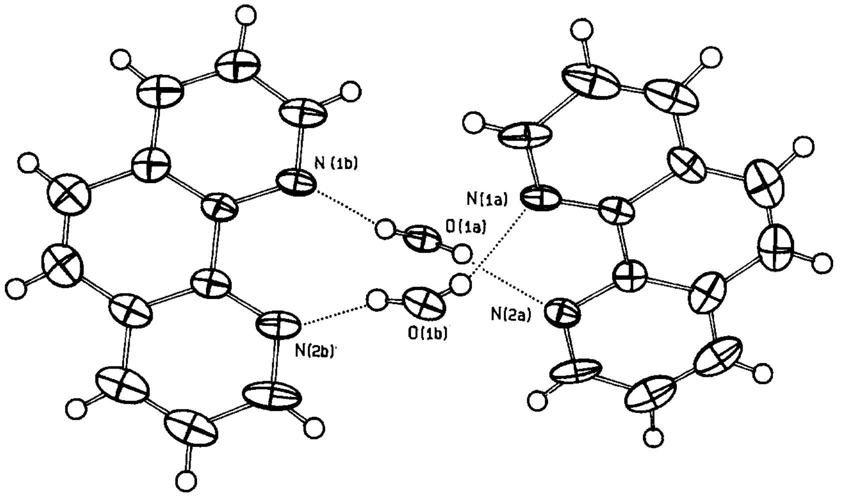

Fig. 2. Hydrogen bonds involving the water and *o*-phenanthroline molecules. O(1a) ··· N(1b) = 2.873(7), O(1b) ··· N(1a) = 2.864(8), O(1a) ··· N(2a) = 3.083(8), O(1b) ··· N(2b) = 3.000(8) Å; N(1b) ··· O(1a) ··· N(2a) = 130.9(2), N(1a) ··· O(1b) ··· N(2b) = 124.2(2)°.

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References

[1] E.J. Gabe, F.L. Lee and F.E. Smith, *Inorg. Chim. Acta*, 90 (1984) L11.

[2] V.G. Kumar Das, W. Chen, S.W. Ng and T.C.W. Mak, *J. Organomet. Chem.*, 322 (1976) 33.

[3] S.W. Ng, *Acta Cryst.*, C51 (1995) 0000.

[4] G.M. Sheldrick, *Acta Cryst.*, A46 (1990) 467.

[5] G.M. Sheldrick, *SHELXL-93*, University of Göttingen, Göttingen, Germany.

[6] L. Prasad, F.L. Lee, Y. Le Page and F.E. Smith, *Acta Cryst.*, B38 (1982) 259.