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Acta Cryst. (1998). **C54**, 760–762

[3-(*tert*-Butoxycarbonylamino)-4-pyridyl]trimethyltin(IV), a Tetraorganotin Compound Containing an Unexpected Intramolecular Sn···O Interaction

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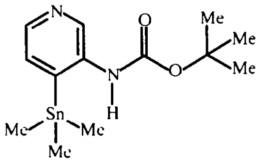
(*Received 19 September 1997; accepted 21 November 1997*)

Abstract

The configuration about the Sn centre in the title compound, $[Sn(CH_3)_3(C_{10}H_{13}N_2O_2)]$, is intermediate between tetrahedral and trigonal bipyramidal. A weak intramolecular Sn···O(carbonyl) interaction of 3.070 (3) Å gives rise to an intramolecular six-membered chelate ring, formed through the carbonyl O atom; this is a unique feature of tetraorganotin compounds. The title compound was prepared by consecutive reaction of 3-(*tert*-butoxycarbonylamino)pyridine with *n*-butyllithium and trimethyltin chloride.

Comment

Our approach to the synthesis of streptonigrin (Godard *et al.*, 1993) and related compounds (Molina *et al.*, 1994) employed, among other methods, the palladium(0)-catalysed cross-coupling of 4-metallated-3-aminopyridine derivatives with appropriate aryl halides. Preparation of one of the starting materials by lithiation of 3-(*tert*-butoxycarbonylamino)pyridine with *n*-butyllithium (Turner, 1983), followed by treatment with trimethyltin chloride, afforded the title compound, (I), which readily crystallized from ethyl acetate–hexane. This compound is markedly less reactive in Stille cross-coupling reactions (Farina, 1996) than the corresponding compound lacking the 3-acylamino substituent. As organotin compounds containing coordinating groups such as a ketone, ester or amine in favourable positions sometimes extend their coordination spheres through intramolecular coordination, this relative stability was tentatively ascribed to an intramolecular Sn···O stabilizing interaction. As good quality crystals were available, a crystal structure determination was performed. The structure reported here confirms the postulated intramolecular interaction between the Sn and carbonyl O atoms, thus explaining the stability of the compound.



(I)

Due to the relatively low Lewis acidity of tin in tetraorganotin compounds, known crystal structures containing pentacoordinated tin are scarce. A search of the April 1997 version of the Cambridge Structural Database (Allen & Kennard, 1993) revealed only a small number containing such Sn···O or Sn···N interactions. Examples were found, however, in which the coordination of tin was increased from four to five (Beak & Lee, 1993; Das, Mun, Wei, Blunden & Mak, 1987; Doidge-Harrison *et al.*, 1991; Fu *et al.*, 1995; Jastrzebski *et al.*, 1991; Jousseaume *et al.*, 1988; Jurkschat *et al.*, 1986; Kayser *et al.*, 1994; Murakami *et al.*, 1995; Pearson *et al.*, 1993; Selvaratnam *et al.*, 1994; Veith *et al.*, 1993), and to six (Das, Mun, Wei & Mak, 1987). Even intermolecular interactions of this type are possible in the solid state (Lorberth *et al.*, 1991).

The effect of additional Sn–ligand interactions on chemical reactivity, affording unique synthetic routes to stable organotin compounds, appears to have been overlooked up to now (Murakami *et al.*, 1995). We are currently investigating the effects on intramolecular association of ligand position and of variation of the Lewis acidity of tin by use of different substituents on the Sn atom.

The Sn···O distance of 3.070 (3) Å observed in this study is quite long, but still within the range of distances observed in the structures quoted above (2.623–3.247 Å), and intermediate between the sum of the covalent radii (2.11 Å) and the sum of the van der Waals radii (3.70 Å). The presence of a definite Sn···O interaction can, however, be clearly seen in the distortion of the Sn coordination polyhedron. If C1 (opposite to O1) is regarded as the apical, and C2, C3 and C4 as the equatorial ligands in a trigonal-bipyramidal configuration, a measure of the deviation from tetrahedral geometry can be established by calculating the difference between the sum of the three equatorial and the sum of the three apical angles (Dräger, 1983). This difference turns out to be 19.63°, intermediate between the ideal value of 0 for tetrahedral and 90° for trigonal-bipyramidal coordination. Further evidence for the formation of a weak bond between the Sn and O1 atoms is the deviation of the torsion angle Sn—C4—C5—N2 of 5.9 (3) from 0°, as the ligand distorts to form the chelate ring.

The unusual Sn···O interaction is illustrated in Fig. 1. Intermolecular N—H···N hydrogen bonding between N1 and N2 leads to one-dimensional chains (Table 1).

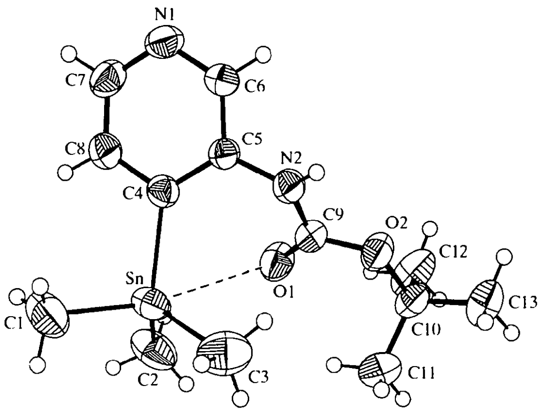


Fig. 1. Perspective view of the title compound showing the non-H atoms as displacement ellipsoids at the 50% probability level; H atoms are drawn as small circles of arbitrary radii.

Experimental

The synthesis of (I) was carried out by adding ^{n}BuLi (9.2 ml, 10.95 mmol) to a solution of 3-(*tert*-butoxycarbonylamino)pyridine (0.85 g, 4.38 mmol) and TMEDA (1.63 ml, 10.95 mmol) in THF (10 ml) at 195–208 K. After stirring for 2 h at 263 K, the reaction vessel was cooled to 195–208 K and Me_3SnCl (1.3 g in 3 ml THF, 6.57 mmol) was added dropwise. The reaction mixture was quenched with H_2O (50 ml) and extracted with ether (3 × 50 ml). The combined organic layers were dried ($MgSO_4$) and concentrated. The white solid residue was filtered through a short silica plug and crystallized from hexane–ethyl acetate (1:1) to give compound (I) as colourless prisms (m.p. 407–408 K), pure according to ^{1}H NMR ($CDCl_3$, 300 MHz): δ 0.32 (9H, *s*), 1.47 (9H, *s*), 6.56 (1H, *bs*), 7.31 (1H, *d*), 8.26 (1H, *d*), 8.48 p.p.m. (1H, *s*). The yield before crystallization was 1.25 g (3.5 mmol, 79%).

Crystal data

$[Sn(CH_3)_3(C_{10}H_{13}N_2O_2)]$
$M_r = 357.01$
Monoclinic
$P2_1$
$a = 8.7829\,(7)$ Å
$b = 9.622\,(2)$ Å
$c = 9.8535\,(11)$ Å
$\beta = 92.948\,(8)^\circ$
$V = 831.6\,(2)$ Å^3
$Z = 2$
$D_x = 1.426$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 18.0–19.8^\circ$
$\mu = 1.534$ mm^{-1}
$T = 293\,(2)$ K
Prism
0.65 × 0.40 × 0.35 mm
Colourless

Data collection

Enraf–Nonius CAD-4*F* diffractometer
ω–2θ scans
Absorption correction: ψ scan (North *et al.*, 1968)
$T_{\min} = 0.553$, $T_{\max} = 0.585$
5396 measured reflections
4842 independent reflections (including Friedel pairs)

4720 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.016$
$\theta_{\max} = 29.90^\circ$
$h = -12 \rightarrow 12$
$k = 0 \rightarrow 13$
$l = -13 \rightarrow 13$
3 standard reflections every 345 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.069$
$S = 1.114$
4842 reflections
169 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0374P)^2 + 0.0994P]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.011$
$\Delta\rho_{\max} = 0.839$ e Å^{-3}
$\Delta\rho_{\min} = -0.497$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = −0.03 (2)

Table 1. *Selected geometric parameters and hydrogen-bonding geometry (Å, °)*

Sn—C2	2.134 (3)	Sn—C4	2.163 (2)
Sn—C1	2.142 (4)	Sn···O1	3.070 (3)
Sn—C3	2.145 (5)		
C2—Sn—C1	108.22 (17)	C2—Sn—C4	114.02 (15)
C2—Sn—C3	112.9 (2)	C1—Sn—C4	101.97 (14)
C1—Sn—C3	108.03 (19)	C3—Sn—C4	110.93 (15)
Sn—C4—C5—N2	5.9 (3)		

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2···N1$^{\rm i}$	0.86	2.152	2.971 (3)	159.14

Symmetry code: (i) $1 - x, y - \frac{1}{2}, 1 - z$.

The measured data set contained all Friedel pairs, allowing the determination of the absolute configuration of the structure by the refinement of the Flack (1983) parameter. The H atoms were included in calculated positions and refined using a riding model, including free rotation about $X—CH_3$ bonds, and with $U_{iso}(H) = 1.2U_{eq}(X)$ ($1.5U_{eq}$ for methyl H atoms).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software*. Data reduction: *CAD*-4 *Software*. Program(s) used to solve structure: *SHELXL*97 (Sheldrick, 1997). Program(s) used to refine structure: *SHELXL*97. Molecular graphics: *Xtal*3.4 (Hall *et al.*, 1995). Software used to prepare material for publication: *Xtal*3.4.

The authors wish to thank Professor P. H. van Rooyen of the Department of Chemistry of the University of Pretoria, South Africa, for collecting the diffraction data.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: CF1218). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 762–764

trans-Diaquadichlorobis(6-methyl-2-pyridone-*O*)cobalt(II) Bis(6-methyl-2-pyridone) Solvate

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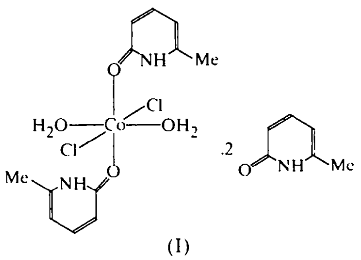
(*Received 8 August 1997; accepted 7 January 1998*)

Abstract

The crystal structure of the title compound, $[CoCl_2(C_6H_7NO)_2(H_2O)_2].2C_6H_7NO$, consists of a one-dimensional hydrogen-bonded polymer in which $[CoCl_2(Hmhp)_2(H_2O)_2]$ complexes alternate with pairs of unbound Hmhp molecules (Hmhp = 6-methyl-2-pyridone).

Comment

We have recently reviewed the extensive structural chemistry of complexes of the late first row transition metals with 6-substituted pyridonate ligands (Parsons & Winpenny, 1997). The immense structural diversity of these systems can be illustrated by reference to cobalt, which forms complexes ranging from one-dimensional polymers (Blake *et al.*, 1998) to one in which a fragment of $Co(OH)_2$ containing 24 Co centres is encapsulated by 6-methyl-2-pyridonate (mhp), OH and Cl ligands (Brechin *et al.*, 1997). We now report the crystal structure of $[CoCl_2(Hmhp)_2(H_2O)_2].2Hmhp$, (I), containing a simple mononuclear complex of Hmhp co-crystallized with free Hmhp. Interest in the structure of this material stems from the relationship between the complex and the uncomplexed Hmhp, and from the presence of both complexed and uncomplexed Hmhp within the same structure.



(I)

The octahedral Co centre in (I) occupies a crystallographic inversion centre, and adopts quite typical bond lengths and angles to the Cl, H_2O and Hmhp ligands. The Hmhp binds through the exocyclic O atom and this

Acta Crystallographica Section C
ISSN 0108-2701 © 1998