

Chloro(μ -6-methylpyridine-2-carboxylato)bis(6-methylpyridine-2-carboxylato)triphenylchromium(III)-tin(IV) chlorotriphenyltin(IV)

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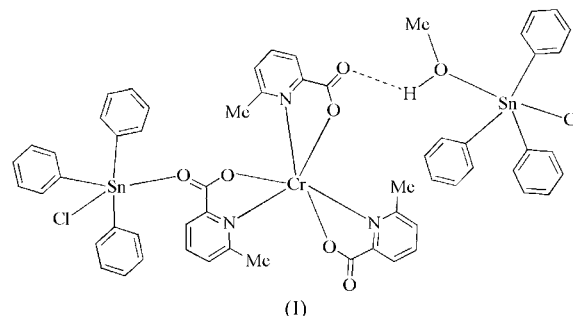
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The title compound, $[\text{CrSn}(\text{C}_6\text{H}_5)_3(\text{C}_7\text{H}_6\text{NO}_2)_3\text{Cl}][\text{Sn}(\text{C}_6\text{H}_5)_3\text{Cl}(\text{CH}_4\text{O})]$, was obtained from the reaction of Ph_3SnCl with the complex $[\text{Cr}(\text{C}_7\text{H}_6\text{NO}_2)_3]$ in methanol. The structure contains $[\text{Ph}_3\text{SnCl}(\text{MeOH})]$ (*A*) and $[\text{Ph}_3\text{SnClCr}(\text{C}_7\text{H}_6\text{NO}_2)_3]$ (*B*) molecules. In molecule *A*, the Sn atom of Ph_3SnCl is coordinated by one methanol molecule. In molecule *B*, the Sn atom of Ph_3SnCl is coordinated by one carboxylate O atom of $[\text{Cr}(\text{C}_7\text{H}_6\text{NO}_2)_3]$. Molecules *A* and *B* are connected through an $\text{O}—\text{H} \cdots \text{O}$ hydrogen bond between a carboxylate O atom and the methanol OH group. Weak $\text{C}—\text{H} \cdots \text{Cl}$ interactions and $\text{O}—\text{H} \cdots \text{O}$ hydrogen bonds extend the components of (I) into a two-dimensional network.

Comment

Organotin compounds have attracted much interest, not only because of their applications as catalysts in organic reactions

(Orita *et al.*, 1998), but also for use in medicinal chemistry (Arakawa, 1998). For example, the triorganotin compounds, R_3SnX , have been known for several years as having a specific action on mitochondrial oxidative phosphorylation (Barnes &



Magos, 1968). To the best of our knowledge, little attention (Döring *et al.*, 1997; Yang *et al.*, 2006) has been given to heterobimetallic organotin compounds. It is known that R_3Sn^+ cations usually prefer a trigonal-bipyramidal (tbp) configuration. Thus, triorganotin compounds are good Lewis acids, despite the fact that they carry three *R* groups. Given the Lewis acidity of triorganotin compounds, a complex with surplus coordinating atoms can react with triphenyltin to form an adduct. We report here the crystal structure of such a compound, $[\text{Ph}_3\text{SnClCr}(\text{C}_7\text{H}_6\text{NO}_2)_3][\text{Ph}_3\text{SnCl}(\text{MeOH})]$, (I).

As shown in Fig. 1, compound (I) possesses two kinds of molecules, *viz.* $[\text{Ph}_3\text{SnCl}(\text{MeOH})]$ (*A*) and $[\text{Ph}_3\text{SnClCr}(\text{C}_7\text{H}_6\text{NO}_2)_3]$ (*B*). In molecule *A*, the Sn atom of Ph_3SnCl is coordinated by one methanol molecule, the C atom of which is disordered over two positions with unequal populations for each orientation (the ratio of the occupancies of C58 and C59 is 1.27:1). Molecule *B* contains Ph_3SnCl which is coordinated by one carboxylate O atom of a $[\text{Cr}(\text{C}_7\text{H}_6\text{NO}_2)_3]$ fragment. In the latter, the Cr centre is six-coordinated by N and O atoms of three 6-methylpyridine-2-carboxylate anions, displaying a distorted octahedral configuration. The three N atoms are meridional, as are the three O atoms.

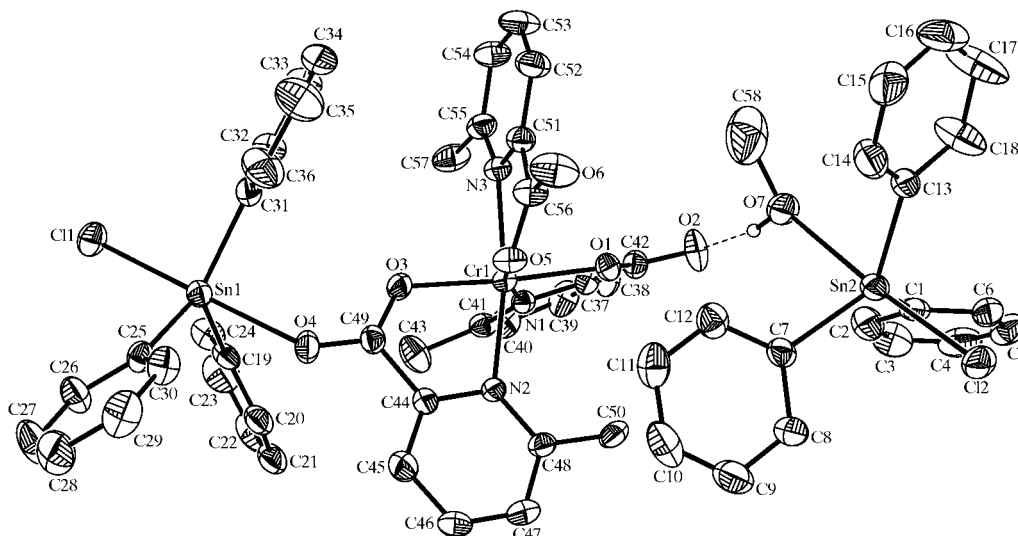


Figure 1

The structure of (I). Displacement ellipsoids are drawn at the 30% probability level. Only one disorder component is shown. The hydrogen bond between molecules is drawn as a dashed line and H atoms not involved in this interaction have been omitted.

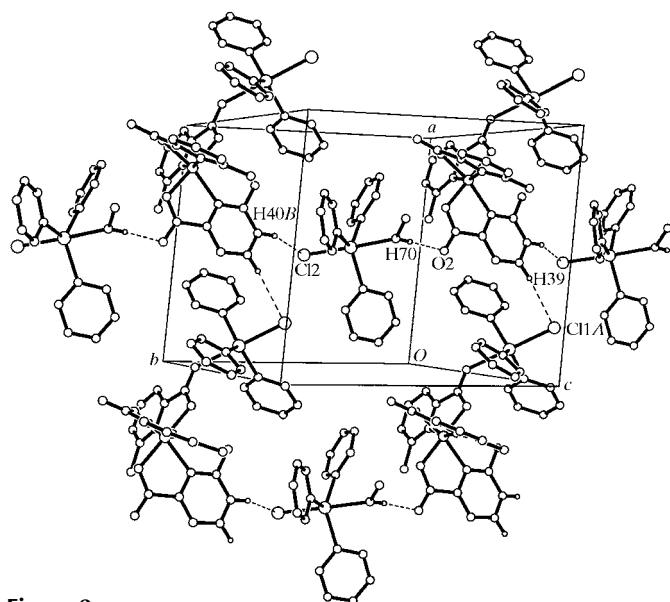


Figure 2
A packing diagram for (I), showing the two-dimensional network formed via weak C—H...Cl interactions and O—H...O hydrogen bonds (dashed lines). [Symmetry codes: (A) $x - 1, y, z$; (B) $x, y + 1, z$.]

Each Sn atom of (I) shows a *trans*-ClSnR₃O trigonal-bipyramidal coordination environment, with three phenyl groups in equatorial positions (those joined at C19, C25 and C31 for Sn1, and at C1, C7 and C13 for Sn2) and Cl and O atoms in axial (ax) positions (Cl1 and O4 for Sn1, and Cl2 and O7 for Sn2). The O_{ax}—Sn—Cl_{ax} angles are 179.14 (7) (O4—Sn1—Cl1) and 175.21 (7)° (O7—Sn2—Cl2), so the structures can be described as slightly distorted trigonal bipyramids. Molecules A and B are connected through an O—H...O hydrogen bond between the carboxylate O atom and the hydroxyl H atom of methanol.

In the fragment [Cr(C₇H₆NO₂)₃], the Cr—O distances of 1.944 (2), 1.957 (2) and 1.931 (2) Å are near the values found in other chromium complexes with pyridine-2-carboxylate (Steams & Armsbong, 1992). However, the Cr—N distances of 2.115 (3), 2.090 (3) and 2.088 (3) Å are somewhat longer. The Sn—O bond distances of (I) are longer than the value found in (Ph₃Sn)₂O (1.955 Å; Glidewell & Liles, 1978), but shorter than the value in [Sn₂(C₆H₅)₆(C₈H₄O₄)] (2.724 Å; Zhang *et al.*, 2006). The Sn—Cl bond distances are significantly longer than those found for Ph₃SnCl (2.321 and 2.315 Å; Bokii *et al.*, 1970).

As shown in Fig. 2 and Table 2, B molecules form a one-dimensional zigzag chain via weak C—H...Cl interactions between the C atoms of the pyridine rings and Cl[−] anions bound to Sn atoms. Adjacent one-dimensional chains are parallel to each other. The zigzag chains are connected through O—H...O hydrogen bonds and weak C—H...Cl interactions between molecules A and B to form a two-dimensional network. There are no π — π interactions between the aromatic rings in the structure of (I).

The molecular structure of (I) can be viewed as a donor-acceptor adduct, in which the electron-rich Cr complex interacts with the electrophilic Sn centre, without causing the loss of Cl[−] anions. It can be predicted that the Lewis acidity of

organotin can facilitate the formation of adducts. Thus, it is conceivable that compounds with new properties can be prepared by introducing a second metal into organotin compounds.

Experimental

A mixture of NaOH (0.012 g, 0.3 mmol) and 6-methylpyridine-2-carboxylic acid (0.041 g, 0.3 mmol) in water (10 ml) was stirred for 10 min, and then CrCl₃·6H₂O (0.027 g, 0.1 mmol) was added. A purple solid was collected by filtration after stirring for 30 min. The solid was redissolved in methanol (15 ml), and Ph₃SnCl (0.039 g, 0.1 mmol) was added to the purple solution. After refluxing for 2 h, the mixture was filtered. Purple block-shaped crystals of (I) were obtained by evaporating the filtrate at room temperature for several days.

Crystal data

[CrSn(C ₆ H ₅) ₃ (C ₇ H ₆ NO ₂) ₃ Cl]· [Sn(C ₆ H ₅) ₃ Cl(CH ₄ O)]	$\gamma = 94.944 (5)^\circ$
$M_r = 1263.31$	$V = 2843.9 (17) \text{ \AA}^3$
Triclinic, $P\bar{1}$	$Z = 2$
$a = 12.767 (5) \text{ \AA}$	$D_x = 1.475 \text{ Mg m}^{-3}$
$b = 14.095 (5) \text{ \AA}$	Mo $K\alpha$ radiation
$c = 15.967 (5) \text{ \AA}$	$\mu = 1.21 \text{ mm}^{-1}$
$\alpha = 96.122 (5)^\circ$	$T = 293 (2) \text{ K}$
$\beta = 91.784 (5)^\circ$	Block, purple
	$0.52 \times 0.40 \times 0.32 \text{ mm}$

Data collection

Siemens P4 diffractometer	9854 independent reflections
ω scans	7137 reflections with $I > 2\sigma(I)$
Absorption correction: ψ scan (North <i>et al.</i> , 1968)	$R_{\text{int}} = 0.020$
$T_{\text{min}} = 0.228$, $T_{\text{max}} = 0.303$ (expected range = 0.512–0.680)	$\theta_{\text{max}} = 25.0^\circ$
11436 measured reflections	3 standard reflections every 97 reflections intensity decay: none

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.033$	$w = 1/[\sigma^2(F_o^2) + (0.0263P)^2]$
$wR(F^2) = 0.070$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 0.88$	$(\Delta/\sigma)_{\text{max}} = 0.006$
9854 reflections	$\Delta\rho_{\text{max}} = 0.60 \text{ e \AA}^{-3}$
673 parameters	$\Delta\rho_{\text{min}} = -0.36 \text{ e \AA}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Cr1—O1	1.944 (2)	Cr1—N3	2.088 (3)
Cr1—O3	1.957 (2)	Sn1—O4	2.419 (2)
Cr1—O5	1.931 (2)	Sn1—Cl1	2.4963 (11)
Cr1—N1	2.115 (3)	Sn2—O7	2.423 (3)
Cr1—N2	2.090 (3)	Sn2—Cl2	2.4786 (11)
O4—Sn1—Cl1	179.14 (7)	O7—Sn2—Cl2	175.21 (7)

Table 2

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
O7—H7O...O2	0.873 (18)	1.87 (2)	2.714 (4)	163 (3)
C39—H39...Cl1 ⁱ	0.93	2.78	3.702 (4)	169
C40—H40...Cl2 ⁱⁱ	0.93	2.90	3.730 (4)	150

Symmetry codes: (i) $x - 1, y, z$; (ii) $x, y - 1, z$.

The H atoms of the disordered methyl group of methanol were not located. Other H atoms bound to carbon were refined using a riding model, with C—H = 0.93 Å and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ for aromatic, and C—H = 0.96 Å and $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{C})$ for methyl H atoms. The hydroxy H atom was located in a difference Fourier map; the coordinates were refined and the $U_{\text{iso}}(\text{H})$ value set at $1.5U_{\text{eq}}(\text{O})$.

Data collection: *XSCANS* (Siemens, 1996); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1994); software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: FA3038). Services for accessing these data are described at the back of the journal.

References

- Arakawa, Y. (1998). *Chemistry of Tin*, edited by P. J. Smith, ch. 10, pp. 388–428. London: Blackie Academic and Professional.
- Barnes, J. M. & Magos, L. (1968). *Organomet. Chem. Rev.* **3**, 137–150.
- Bokii, N. G., Zakharova, G. N. & Struchkov, Y. T. (1970). *Zh. Strukt. Khim.* **11**, 895–902. (In Russian.)
- Döring, M., Hahn, G., Stoll, M. & Wolski, A. C. (1997). *Organometallics*, **16**, 1879–1883.
- Glidewell, C. & Liles, D. C. (1978). *Acta Cryst.* **B34**, 1693–1695.
- North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* **A24**, 351–359.
- Orita, A., Mitsutome, A. & Otera, J. (1998). *J. Org. Chem.* **63**, 2420–2421.
- Sheldrick, G. M. (1994). *SHELXTL-Plus*. PC Version 4.21. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Siemens (1996). *XSCANS*. Version 2.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Stearns, D. M. & Armsbong, W. H. (1992). *Inorg. Chem.* **31**, 5178–5184.
- Yang, Z., Ma, X., Jancik, V., Zhang, Z., Roesky, H. W., Magull, J., Noltemeyer, M., Schmidt, H.-G., Cea-Olivares, R. & Toscano, R. A. (2006). *Inorg. Chem.* **45**, 3312–3315.
- Zhang, W.-L., Ma, J.-F. & Jiang, H. (2006). *Acta Cryst.* **E62**, m460–m461.