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Bis(dicyclohexylammonium) tributyl-(nitrilotriacetato)stannate†

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Abstract

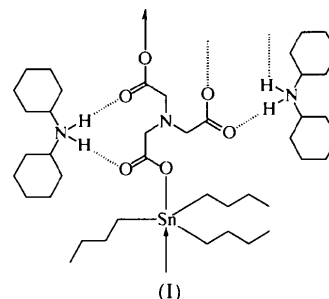
In the title compound, $(C_{12}H_{24}N)_2[Sn(C_4H_9)_3(C_6H_5NO_6)]$, the tributyltin groups are linked by the nitrilotriacetate groups [$Sn-O = 2.281(4)$ and $2.258(3) \text{ \AA}$] into a linear helical chain. Adjacent chains are linked by one of the two dicyclohexylammonium counter-ions [$N \cdots O = 2.727(5)$ and $2.858(5) \text{ \AA}$] into layers.

Comment

Unlike other dicyclohexylammonium hydrogen dicarboxylates (oxalate, malonate and succinate) that condense with bis(tributyltin) oxide to afford ammonium stannate compounds having complex formulations (Ng *et al.*, 1990, 1992; Ng & Holeček, 1998), the mono-(dicyclohexylammonium) derivative of the aminopolycarboxylic acid 2,6-pyridinedicarboxylic acid furnishes a simple ammonium stannate. In this compound, the tributyltin groups are linked axially by the 2,6-pyridinedicarboxylate groups into linear chains. The dicyclohexylammonium cations surround the chains and the cation forms hydrogen bonds with the two carbonyl O atoms of the same carboxylate unit (Ng *et al.*, 1991). The bis(dicyclohexylammonium) salt of tribasic nitrilotriacetic acid also yields a simple ammonium stannate when treated with the organotin oxide. The nitrilotriacetate trianion has been used to chelate to a plethora of metal complexes (Oliver *et al.*, 1984); however, few organometallic derivatives have been prepared and only one, 3-dimethylaminopropyl(nitrilotriacetato)-

tin *N*-oxide, has been crystallographically documented (Dakternieks *et al.*, 1993). In this compound, the nitrilotriacetate group displays tetradentate ($N+3O$) ligating behavior.

In the chiral title compound, bis(dicyclohexylammonium) tributyl(nitrilotriacetato)stannate, (I), the tributyltin and nitrilotriacetate groups are covalently



bonded into a linear helical chain (Fig. 1). The Sn atom shows $trans-C_3SnO_2$ trigonal-bipyramidal coordination [$\Sigma_{C-Sn-C} = 359.8(9)^\circ$ and $O-Sn-O = 176.8(1)^\circ$]. The two $Sn-O$ bonds are longer than the covalent $Sn-O$ bonds but shorter than the carboxylate bridges found in five-coordinate triorganotin carboxylates (Tiekink, 1991, 1994), in agreement with a 1.5 bond order for the $Sn-O$ bond in this stannate.

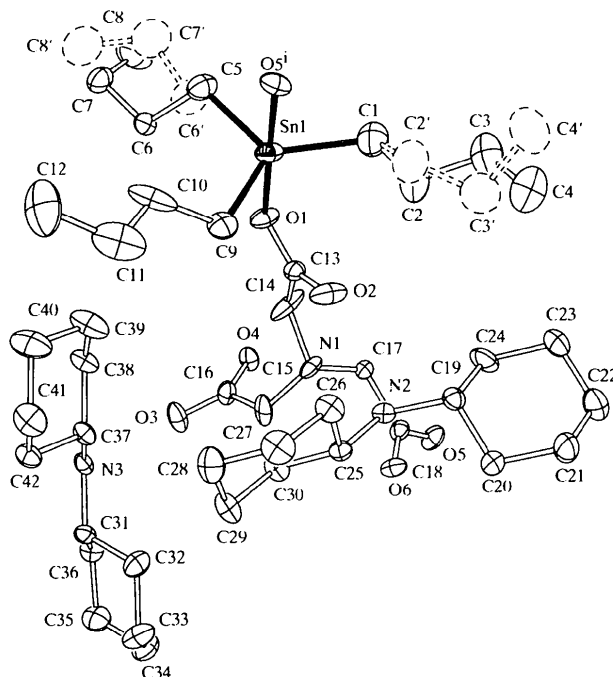


Fig. 1. ORTEP (Johnson, 1976) plot of bis(dicyclohexylammonium) tributyl(nitrilotriacetato)stannate at the 50% probability level. H atoms are not shown. The two orientations of the disordered *n*-butyl groups are shown. [Symmetry code: (i) $2 - x, \frac{1}{2} + y, \frac{1}{2} - z$].

† Alternative name: *catena*-poly[bis(dicyclohexylammonium) [[tributyltin(IV)]- μ -[nitrilotriacetato(3-)-*O*:*O'*]]].

The carboxyl group (C16, O3 and O4) not involved in bonding to tin has essentially equal C—O distances (Table 1), consistent with it being an ionized system, and it is involved in N—H···O hydrogen bonding with a pair of symmetry-related cations to form an infinite hydrogen-bonded chain. The other cation uses its NH_2 group to form two N—H···O hydrogen bonds to two carbonyl O atoms of one nitrilotriacetate moiety. Hydrogen-bonding details are given in Table 2. The tertiary N atom is not involved in any hydrogen bonding and its geometry is a flattened pyramid as all three C—N—C angles [111.3(5), 112.6(4) and 112.7(5)°] exceed the idealized value of 109.5°. The central N atom of the parent nitrilotriacetic acid, which exists as the zwitterion $(HO_2CCH_2)_2NH^+(CH_2CO_2^-)$, also displays similarly large angles [112.3(1), 113.2(1) and 113.6(1)°; Skrzypczak-Jankun *et al.*, 1994]. Trisodium nitrilotriacetate monohydrate represents another rare example of the nitrilotriacetate group whose tertiary N atom is neither protonated nor involved in bonding. In this compound, one of the C—N—C angles is compressed whereas one is opened up [105.6(5), 111.0(5) and 115.9(6)°; Daly, 1967].

Experimental

Dicyclohexylamine, nitrilotriacetic acid and bis(tributyltin) oxide in a 4:2:1 molar ratio were heated in a small volume of ethanol until the acid had dissolved completely. The ammonium stannate precipitated as colorless crystals when the filtered solution was left to cool slowly.

Crystal data

| | |
|---|---|
| $(C_{12}H_{24}N)_2[Sn(C_4H_9)_3(C_6H_6NO_6)]$ | Mo $K\alpha$ radiation |
| $M_r = 842.79$ | $\lambda = 0.71073 \text{ \AA}$ |
| Orthorhombic | Cell parameters from 6607 reflections |
| $P2_12_12_1$ | $\theta = 2.15\text{--}25.00^\circ$ |
| $a = 9.443(2) \text{ \AA}$ | $\mu = 0.599 \text{ mm}^{-1}$ |
| $b = 20.758(4) \text{ \AA}$ | $T = 162(2) \text{ K}$ |
| $c = 23.478(5) \text{ \AA}$ | Plate |
| $V = 4602.2(16) \text{ \AA}^3$ | $0.70 \times 0.40 \times 0.12 \text{ mm}$ |
| $Z = 4$ | Colorless |
| $D_x = 1.216 \text{ Mg m}^{-3}$ | |
| D_m not measured | |

Data collection

| | |
|--|--|
| Siemens CCD area-detector diffractometer | 6038 reflections with $I > 2\sigma(I)$ |
| ω scans | $R_{int} = 0.045$ |
| Absorption correction: empirical (SADABS; Sheldrick, 1996) | $\theta_{max} = 25^\circ$ |
| $T_{min} = 0.606$, $T_{max} = 0.932$ | $h = -11 \rightarrow 11$ |
| 19 318 measured reflections | $k = -24 \rightarrow 10$ |
| 4492 independent reflections (plus 3533 Friedel-related reflections) | $l = -25 \rightarrow 27$ |

Refinement

| | |
|---|--|
| Refinement on F^2 | $(\Delta/\sigma)_{max} = 0.001$ |
| $R[F^2 > 2\sigma(F^2)] = 0.044$ | $\Delta\rho_{max} = 0.772 \text{ e \AA}^{-3}$ |
| $wR(F^2) = 0.100$ | $\Delta\rho_{min} = -0.943 \text{ e \AA}^{-3}$ |
| $S = 0.942$ | Extinction correction: none |
| 8025 reflections | Scattering factors from |
| 523 parameters | <i>International Tables for</i> |
| H atoms riding, $U(H) = 1.5U_{eq}(C,N)$ | <i>Crystallography</i> (Vol. C) |
| $w = 1/[\sigma^2(F_o^2) + (0.0545P)^2]$ | Absolute structure: Flack & Schwarzenbach (1988) |
| where $P = (F_o^2 + 2F_c^2)/3$ | Flack parameter = $-0.02(2)$ |

Table 1. Selected geometric parameters (\AA , $^\circ$)

| | | | |
|------------------------|-----------|------------------------|-----------|
| Sn1—C1 | 2.119 (6) | O2—C13 | 1.236 (5) |
| Sn1—C5 | 2.137 (5) | O3—C16 | 1.238 (6) |
| Sn1—C9 | 2.125 (6) | O4—C16 | 1.242 (6) |
| Sn1—O1 | 2.258 (3) | O5—C18 | 1.264 (6) |
| Sn1—O5 ⁱ | 2.281 (4) | O6—C18 | 1.245 (6) |
| O1—C13 | 1.272 (5) | | |
| C1—Sn1—C5 | 121.6 (2) | C5—Sn1—O1 | 88.5 (2) |
| C1—Sn1—C9 | 123.8 (2) | C5—Sn1—O5 ⁱ | 94.3 (2) |
| C1—Sn1—O1 | 92.9 (2) | C9—Sn1—O1 | 93.8 (2) |
| C1—Sn1—O5 ⁱ | 87.0 (2) | C9—Sn1—O5 ⁱ | 83.6 (2) |
| C5—Sn1—C9 | 114.3 (2) | O1—Sn1—O5 ⁱ | 176.8 (1) |

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

Table 2. Hydrogen-bonding geometry (\AA , $^\circ$)

| D—H···A | D—H | H···A | D···A | D—H···A |
|--------------------------|------|-------|-----------|---------|
| N2—H2A···O6 | 0.92 | 1.85 | 2.752 (6) | 168 |
| N2—H2B···O2 | 0.92 | 1.79 | 2.698 (6) | 169 |
| N3—H3A···O3 | 0.92 | 1.81 | 2.727 (5) | 178 |
| N3—H3B···O4 ⁱ | 0.92 | 1.97 | 2.858 (5) | 167 |

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

Two of the three butyl chains (C1—C4 and C5—C8) are disordered over two positions and each was refined as two half-site-occupancy chains sharing a common C_α atom. Distance restraints (C—C = $1.54 \pm 0.01 \text{ \AA}$ and C—C—C = $2.52 \pm 0.02 \text{ \AA}$) were imposed on all three butyl chains. The displacement parameters of the C atoms along the disordered butyl chains were restrained by $SIMU = 0.01$ and $ISOR = 0.01$ instructions (SHELXL97; Sheldrick, 1997a). An $ISOR = 0.01$ instruction was imposed on the C14 atom to prevent the maximum/minimum atomic displacement parameter ratio from exceeding 3. The compound crystallizes in a chiral space group and the diffraction analysis establishes the chirality of the structure in the crystal chosen for the analysis.

Data collection: SMART (Siemens, 1996). Cell refinement: SAINT (Siemens, 1996). Data reduction: SAINT. Program(s) used to solve structure: SHELXS97 (Sheldrick, 1997b). Program(s) used to refine structure: SHELXL97. Molecular graphics: ORTEPII (Johnson, 1976). Software used to prepare material for publication: SHELXL97.

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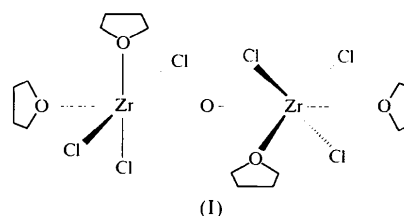
Supplementary data for this paper are available from the IUCr electronic archives (Reference: FG1549). Services for accessing these data are described at the back of the journal.

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Comment

The title complex, $[\text{ZrCl}_3(\text{C}_4\text{H}_8\text{O})_2]_2\text{O}$, (I), was obtained quite unexpectedly when the reaction product of $\text{Na}[\text{C}_5\text{H}_4(\text{CH}_2)_2\text{OME}]$ and C_7H_9 (spiro-cyclopentadienyl-[1,1']-cyclopropane) was reacted with ZrCl_4 in $\text{C}_4\text{H}_8\text{O}$ (THF). The use of carefully dried chemicals under strictly purified N_2 and yields of (I) up to 20% (reference: ZrCl_4) make it unlikely that impurities of H_2O have been the only source of the metal-bridging O atoms. Similarly, the reaction of ZrCl_4 with neat 1,2-dimethoxyethane (dme) under argon was shown to afford the related complex $[\text{ZrCl}_3(\text{dme})_2]_2\text{O}$, (II) (Babaiian-Kibala *et al.*, 1991). However, the comparable reaction of ZrCl_4 with neat THF has not yet been similarly investigated.



The crystal structure of (I) (Fig. 1) involves an uncharged dinuclear molecule, the only non-trivial symmetry element of which is a C_2 axis passing through

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μ -Oxo-bis[mer-trichlorobis(tetrahydrofuran-O)zirconium(IV)]

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Abstract

The crystal structure of the title compound, $[\text{ZrCl}_3(\text{C}_4\text{H}_8\text{O})_2]_2\text{O}$ or $[\text{Zr}_2\text{Cl}_6\text{O}(\text{C}_4\text{H}_8\text{O})_4]$, (I), was solved at room temperature and compared with that of the earlier reported complex $[\text{ZrCl}_3(\text{MeOCH}_2\text{CH}_2\text{OME})_2]_2\text{O}$, (II). In both molecules, two equivalent quasi-octahedral fragments involving one axial (ax) and one equatorial (eq) ether oxygen share one bridging oxide functionality. However, the point symmetry of (I) is only C_2 , while that of (II) is C_{2h} . The dihedral angle of the $\text{O}_{\text{eq}}-\text{Zr}-\text{Zr}-\text{O}_{\text{eq}}$ fragment of (I) [symmetry code: (i) $1-x, y, \frac{1}{2}-z$] is $115.3(1)^\circ$ [180.0° in (II)] and the $\text{Zr}-\text{O}-\text{Zr}$ angle is $174.8(2)^\circ$ [180.0° in (II)].

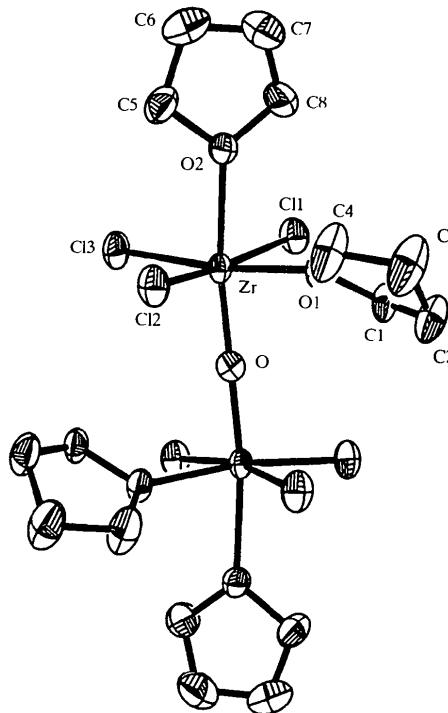


Fig. 1. The molecular structure of (I) showing 30% probability displacement ellipsoids. H atoms have been omitted for clarity.