

exposure of 10 s covered 0.3° in ω . The crystal-to-detector distance was 5 cm. Coverage of the unique set is over 95% complete out to at least 23° in θ . Crystal decay was found to be negligible by comparison of the intensities of repeated reflections at the end of the data collection. The temperature of the crystal was controlled using the Oxford Cryosystems Cryostream Cooler (Cosier & Glazer, 1986). H atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms; H atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl H atoms) times the equivalent isotropic displacement parameter of the parent atom.

Data collection: *SMART* (Siemens, 1994). Cell refinement: *SAINT* (Siemens, 1995). Data reduction: *SAINT*. Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1995b). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXTL/PC*.

The authors wish to acknowledge the use of the EPSRC's Chemical Database Service at Daresbury (Allen *et al.*, 1991). We also wish to thank the EPSRC and ICI Paints for a Case award (to SW), and EPSRC and Siemens for provision of X-ray facilities.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BS1015). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1034–1036

Tetramethylammonium Bis(coumarin-3-carboxylato)triphenylstannate Ethanol Solvate

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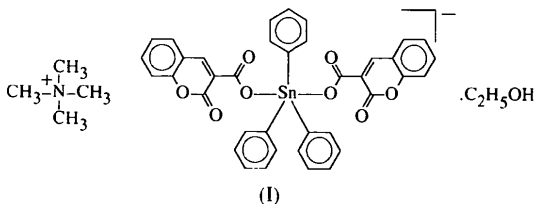
(Received 15 July 1996; accepted 17 March 1997)

Abstract

The title compound, [N(CH₃)₄][Sn(C₆H₅)₃(C₁₀H₅O₄)₂].·C₂H₅OH, crystallizes as non-interacting ammonium cations and stannate anions. The Sn atom which shows *trans*-trigonal bipyramidal coordination is linked axially to two monodentate carboxylato groups [Sn—O 2.232 (2) Å and O—Sn—O 167.1 (1)°].

Comment

Triphenyltin trifluoroacetate forms a stannate derivative with tetramethylammonium trifluoroacetate as a result of the electron-withdrawing ability of the CF₃CO₂ group. The formation of the coumarin-3-carboxylato analog implies an electron-withdrawing ability of the coumarin group, but this is not apparent from the structure of the parent acid. The coordination environment of Sn in the title compound, (I), differs from that in tetramethylammonium bis(trifluoroacetato)triphenylstannate (Ng & Kumar Das, 1997) in that the metal atom lies on a twofold rotation axis, so that the two Sn—O bonds are equivalent [Sn—O 2.232 (2) Å]. The O—Sn—O skeleton is bent [O—Sn—O 167.1 (1)°], whereas that in the trifluoroacetato derivative is almost linear [O—Sn—O 175.1 (1)°].



The carboxyl O2 atom is 3.411 (2) Å from Sn; the absence of any interaction is supported by the carboxyl band of 1742 cm⁻¹ in the IR spectrum.

The structure is best described as comprising anion layers at $x = 0.25$ and 0.75 , and cation and solvent layers at $x = 0$ and 0.5 . The disordered ethanol molecule does not form a hydrogen bond to any of the doubly bonded O atoms. Despite the absence of such an interaction, the compound does not lose the lattice ethanol.

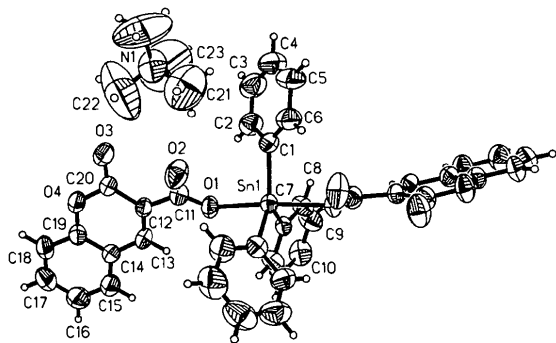
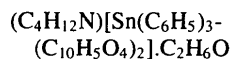


Fig. 1. ORTEP (Johnson, 1976) plot of the title compound with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii. The disordered ethanol molecule is not shown.

Experimental

Tetramethylammonium hydroxide and coumarin-3-carboxylic acid (1:2 molar ratio) were dissolved in ethanol, and an equivalent quantity of triphenyltin hydroxide was added. The solution was heated briefly. Slow cooling of the filtered solution gave large crystals of the ammonium stannate.

Crystal data



$M_r = 848.48$

Orthorhombic

Cmca

$a = 29.608 (2) \text{ \AA}$

$b = 23.6935 (9) \text{ \AA}$

$c = 11.8195 (5) \text{ \AA}$

$V = 8291.5 (7) \text{ \AA}^3$

$Z = 8$

$D_x = 1.359 \text{ Mg m}^{-3}$

D_m not measured

Data collection

Enraf-Nonius CAD-4
diffractometer

ω scans

Absorption correction:

ψ scans (North, Phillips
& Mathews, 1968)

$T_{\min} = 0.654$, $T_{\max} = 0.791$

5631 measured reflections

3725 independent reflections

Mo $K\alpha$ radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 25

reflections

$\theta = 12\text{--}13^\circ$

$\mu = 0.671 \text{ mm}^{-1}$

$T = 298 (2) \text{ K}$

Irregular block

$0.55 \times 0.45 \times 0.35 \text{ mm}$

Colorless

2449 reflections with
 $I > 2\sigma(I)$

$R_{\text{int}} = 0.040$

$\theta_{\text{max}} = 25^\circ$

$h = 0 \rightarrow 35$

$k = -28 \rightarrow 28$

$l = -14 \rightarrow 0$

3 standard reflections

frequency: 60 min

intensity decay: none

Refinement

Refinement on F^2

$R[F^2 > 2\sigma(F^2)] = 0.036$

$wR(F^2) = 0.099$

$S = 0.997$

3725 reflections

253 parameters

H atoms riding; $U(\text{H}) =$

$1.5U_{\text{eq}}(\text{C}, \text{O})$.

$w = 1/[\sigma^2(F_o^2) + (0.0546P)^2]$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\text{max}} = 0.001$

$\Delta\rho_{\text{max}} = 0.507 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.330 \text{ e \AA}^{-3}$

Extinction correction: none

Scattering factors from

*International Tables for
Crystallography (Vol. C)*

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters (\AA^2)

$$U_{\text{eq}} = (1/3)\sum_i \sum_j U^{ij} a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j$$

	<i>x</i>	<i>y</i>	<i>z</i>	U_{eq}
Sn1	0.15641 (1)	0	0	0.0419 (1)
O1	0.1645 (1)	0.0729 (1)	-0.1177 (2)	0.056 (1)
O2	0.0933 (1)	0.1025 (1)	-0.1268 (3)	0.087 (1)
O3	0.0903 (1)	0.2127 (1)	-0.2210 (2)	0.082 (1)
O4	0.1310 (1)	0.2218 (1)	-0.3744 (2)	0.064 (1)
N1	0	0.1828 (3)	0.0379 (6)	0.101 (2)
C1	0.1273 (1)	0.0498 (2)	0.1297 (3)	0.051 (1)
C2	0.1442 (2)	0.1043 (2)	0.1479 (4)	0.070 (1)
C3	0.1299 (2)	0.1366 (2)	0.2377 (5)	0.095 (2)
C4	0.0986 (2)	0.1166 (3)	0.3110 (5)	0.107 (2)
C5	0.0809 (2)	0.0639 (3)	0.2963 (4)	0.099 (2)
C6	0.0950 (2)	0.0311 (2)	0.2053 (4)	0.077 (1)
C7	0.2285 (1)	0	0	0.043 (1)
C8	0.2525 (1)	0.0127 (2)	0.0953 (3)	0.063 (1)
C9	0.2994 (1)	0.0132 (2)	0.0962 (4)	0.074 (1)
C10	0.3224 (2)	0	0	0.078 (2)
C11	0.1328 (1)	0.1042 (2)	-0.1569 (3)	0.054 (1)
C12	0.1471 (1)	0.1429 (1)	-0.2518 (3)	0.045 (1)
C13	0.1832 (1)	0.1310 (1)	-0.3160 (3)	0.051 (1)
C14	0.1946 (1)	0.1628 (1)	-0.4154 (3)	0.051 (1)
C15	0.2306 (1)	0.1509 (2)	-0.4863 (3)	0.067 (1)
C16	0.2373 (2)	0.1820 (2)	-0.5824 (4)	0.078 (1)
C17	0.2095 (2)	0.2271 (2)	-0.6071 (3)	0.075 (1)
C18	0.1738 (2)	0.2399 (2)	-0.5378 (3)	0.067 (1)
C19	0.1669 (1)	0.2083 (2)	-0.4425 (3)	0.053 (1)
C20	0.1204 (1)	0.1928 (2)	-0.2776 (3)	0.055 (1)
C21	0	0.1199 (6)	0.048 (1)	0.197 (5)
C22	0	0.193 (1)	-0.074 (1)	0.30 (1)
C23	0.0410 (3)	0.2009 (5)	0.080 (1)	0.254 (6)
O1' [†]	-0.029 (1)	0.413 (1)	0.081 (3)	0.41 (2)
C2' [†]	0.010 (3)	0.419 (2)	0.172 (3)	0.39 (2)
C3' [†]	0.033 (1)	0.375 (1)	0.131 (3)	0.30 (2)

[†] Site occupancy = 0.50.

Table 2. Selected geometric parameters (\AA , $^\circ$)

Sn1—C1	2.117 (4)	Sn1—C7	2.135 (4)
Sn1—C1'	2.117 (4)	Sn1—O1	2.232 (2)
C1—Sn1—C1'	131.9 (2)	C1'—Sn1—O1	91.3 (1)
C1—Sn1—C7	114.0 (1)	C1'—Sn1—O1'	93.7 (1)
C1—Sn1—O1	93.7 (1)	C7—Sn1—O1	83.84 (6)
C1—Sn1—O1'	91.3 (1)	C7—Sn1—O1'	83.84 (6)
C1'—Sn1—C7	114.0 (1)	O1—Sn1—O1'	167.7 (1)

Symmetry code: (i) $x, -y, -z$.

The presence of ethanol was not suspected in the earlier refinements, which consistently showed two strong peaks in the difference Fourier maps; however, a broad band around 3500 cm⁻¹ in the infrared spectrum proved its existence in the crystal structure. The ethanol molecule is disordered over a mirror plane, with the C2' atom lying on the mirror plane.

Data collection: *CAD-4 VAX/PC Software* (Enraf-Nonius, 1988). Cell refinement: *CAD-4 VAX/PC Software*. Data reduction: *NRCVAX* (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *SHELXS86* (Sheldrick,

1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SK1052). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). **C53**, 1036–1037

A Tetrahydrofuran Ring-Opening Product: *trans*-Tetrachloro{4-[2-(phenylamino)pyridinio]butoxido-*O*}(tetrahydrofuran-*O*)-zirconium(IV)

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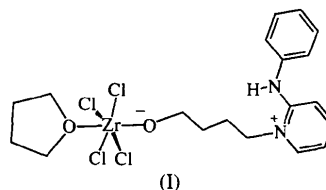
Abstract

The title compound, $[ZrCl_4(C_{15}H_{18}N_2O)(C_4H_8O)]$, was formed *via* tetrahydrofuran (thf) ring opening when $ZrCl_4$ and 2-(phenylamino)pyridine were heated in a thf-containing reaction medium. The molecule is zwitterionic, with distorted octahedral coordination at the negatively charged zirconium(IV) centre. A 2-(phenylamino)pyridinium cation is connected to the metal

centre by a residue formed through opening of a thf ring.

Comment

We have recently synthesized chlorobis[2-(phenylamino)pyridinato] complexes by direct reaction of 2-(phenylamino)pyridine and the appropriate metal halide in toluene under reflux (Polamo & Leskelä, 1996). The direct reaction gave the desired bis complexes of Nb and Ta with reasonable yields, unlike zirconium chloride, which produced only a low yield. Nb and Ta complexes are monomeric in the solid state, whereas the corresponding monomeric Zr complex would be coordinatively unsaturated. The bis[2-(phenylamino)pyridinato]zirconium complex was found to be a dimer, with two bridging chloro ligands (Polamo & Leskelä, 1996). It is likely that the low yields of the Zr complex may be related to oligomerization. In order to obtain monomeric complexes, a tetrahydrofuran/toluene mixture was used as a reaction medium. The reaction between 2-(phenylamino)pyridine and zirconium tetrachloride resulted in a thf ring-opening product, (I), instead of the expected dichlorobis[2-(phenylamino)pyridinato]-(tetrahydrofuran)zirconium(IV).



Only a few thf ring-opening products have been previously reported. The formation of a pentamethylcyclopentadienyl complex of Sm (Ewans, Ulibarri,

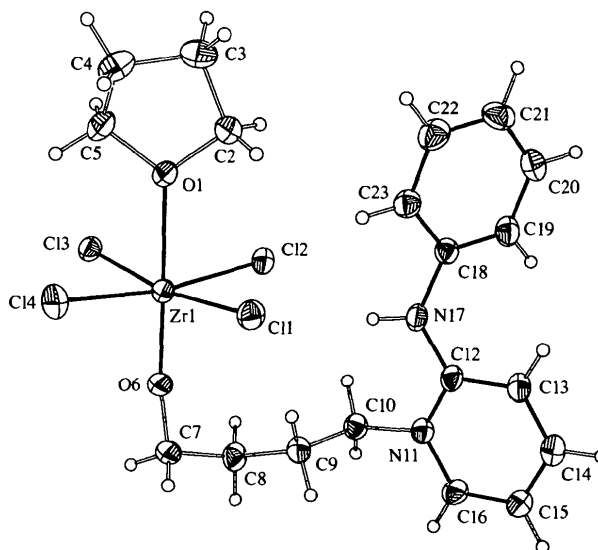


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.