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Crystal structure of (4-fluorobenzyl-κC)(bis(2-hydroxyethyl)carbamodithioato-κ²S,S')(2,2′-imino-diethanolato-κ³N,O,O')tin(IV), C₁₆H₂₅FN₂O₄S₂Sn

Abstract

C₁₆H₂₅FN₂O₄S₂Sn, monoclinic, P2₁/n (no. 14), a = 11.2227(1) Å, b = 12.6793(1) Å, c = 13.8731(1) Å, β = 98.282(1)°, V = 1953.50(3) Å³, Z = 4, Rgt(F) = 0.0198, wR(ref)(F²) = 0.0507, T = 100(2) K.

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The molecular structure is shown in the figure. Table 1 contains crystallographic data and Table 2 contains the list of the atoms including atomic coordinates and displacement parameters.

Source of material

All chemicals and solvents were used as purchased without purification. The melting point was determined using a

Table 1: Data collection and handling.

| Atom | x     | y     | z     | Ueq(%) |
|------|-------|-------|-------|--------|
| Sn   | 0.33289(2) | 0.30356(2) | 0.40915(2) | 0.00921(6) |
| S1   | 0.45184(4)  | 0.42766(4)  | 0.30926(3)  | 0.01390(11) |
| S2   | 0.43980(5)  | 0.19570(4)  | 0.28780(3)  | 0.01364(11) |
| F1   | 0.89803(12) | 0.11300(13) | 0.48966(10) | 0.0395(4)   |
| O1   | 0.82094(13) | 0.37685(12) | 0.25974(10) | 0.0211(3)   |
| O2   | 0.70132(15) | 0.05587(12) | 0.14059(10) | 0.0237(3)   |
| N1   | 0.57226(16) | 0.31851(13) | 0.18900(12) | 0.0141(3)   |
| C1   | 0.49787(18) | 0.31489(15) | 0.25473(14) | 0.0120(4)   |
| H2A  | 0.186(2)   | 0.3042(17)  | 0.2309(3)   | 0.017*      |

Table 2: Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

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Mel-temp II digital melting point apparatus and was uncorrected. The IR spectrum was obtained on a Bruker Vertex 70v FTIR Spectrometer. The $^1$H and $^{13}$C($^1$H) spectra were recorded at room temperature in DMSO-d$_6$ solution on a Bruker Ascend 400 MHz NMR spectrometer with chemical shifts relative to tetramethylsilane.

Di(4-fluorobenzyl)tin dichloride was synthesized by the direct reaction of 4-fluorobenzyl chloride (Merck) and metallic tin powder (Merck) in toluene according to a literature procedure [5]. The dithiocarbamate ligand was prepared in situ (methanol; 15 mL) from the reaction of CS$_2$ (Merck, 0.25 mmol) with diethanolamine (Merck, 0.25 mmol) and NaOH (0.02 mL; 50% w/v); CS$_2$ was added dropwise into the methanol solution. The resulting solution was kept at 273 K for 1 h. Next, di(4-fluorobenzyl)tin dichloride (Merck, 0.25 mmol, 0.10 g) in methanol (10 mL) was added into the solution and the resulting mixture was stirred for 3 h. The filtrate was evaporated until an off-white precipitate was obtained. The precipitate was washed with n-hexane and recrystallised from a methanol-acetone solution. Crystals of the title compound were obtained from the slow evaporation of the solvent; the 2,2′-imino-diethanolate di-anion is derived from diethanolamine. Yield: 0.010 g (7.8%). M.pt: 377–379 K. IR (cm$^{-1}$): 3360(br) ν(NH, OH), 1501(m) ν(CN), 1064(s) ν(CS), 1022(s) ν(CS). $^1$H NMR (DMSO-d$_6$, ppm): δ 50.0 (CH$_2$), 58.4 (NCH$_2$), 59.0 (NCH$_2$), 62.1 (OCH$_3$), 66.9 (OCH$_3$), 114.5, 128.5, 130.1, 138.5 (Ph-C), 187.5 (CS).

**Experimental details**

The C-bound H atoms were geometrically placed (C–H = 0.95–0.99 Å) and refined as riding with $U_{iso}$(H) = 1.2$U_{eq}$(C). The O- and N-bound H-atoms were located in a difference Fourier map but, were refined with distance restraints of O–H = 0.84 ± 0.01 Å and N–H = 0.88 ± 0.01 Å, respectively, and with $U_{iso}$(H) set to 1.5$U_{eq}$(O) and 1.2$U_{eq}$(N), respectively.

**Comment**

The 1,1-dithiolate, e.g. dithiocarbamate (−S$_2$CNR$_2$), compounds of the zinc-triad elements [5], main group elements [6, 7], including tin [8], are well-known to form secondary M···S bonding interactions in their crystal structures [9, 10]. However, when concurrently bound to potentially bidentate, bridging bi-pyridyl ligands, with the aim of increasing the dimensionality of the supramolecular association, the secondary bonding is generally lost, as amply demonstrated in the structural chemistry of the zinc-triad 1,1-dithiolenes [11]. One way of overcoming this limitation is to introduce hydrogen bonding functionality in the R groups, e.g. hydroxyethyl groups, as the resultant hydrogen bonding can lead to one-, two- and, sometimes, three-dimensional aggregation in the solid-state [5–8, 11]. In the title mixed ligand, organotin compound, (4-FC$_6$H$_4$CH$_2$)$_2$Sn[OCH$_2$CH$_2$N(H)CH$_2$H$_2$O][S$_2$C(NH$_2$CH$_2$OH)$_2$], (I), the dithiocarbamate ligand bears two hydroxyethyl groups, each capable of hydrogen bonding. Herein, the crystal and molecular structures of (I) are described along with an analysis of the calculated Hirshfeld surfaces.

The molecular structure of (I) is shown in the figure (70% displacement ellipsoids). The tin atom is coordinated by the methylene-carbon atom of the 4-fluorobenzyl substituent, two sulphur atoms of the dithiocarbamate ligand along with the imino-nitrogen and two ethoxide-oxygen atoms of the di-anionic, tridentate 2,2′-imino-diethanolate ligand. The dithiocarbamate ligand chelates in a symmetric mode as seen in the equivalence of the Sn–S$_1$ [2.5906(5) Å] and Sn–S$_2$ [2.5934(5) Å] bond lengths; this equivalence is reflected in the equality of the associated C–S bonds [C1–Sn–O3 [2.0624(13) Å] and C1–Sn–O4 [2.0360(14) Å], respectively. The resultant CNO$_2$S$_2$ donor set defines an approximate octahedron with the major distortion related to the acute S$_1$–Sn–S$_2$ chelate angle of 69.564(15)$^\circ$. The N1–Sn–C10 [167.65(7)$^\circ$] and, in particular, S1–Sn–O4 [158.40(4)$^\circ$]
and S2–Sn–O3 [157(4)°] trans angles deviate from the ideal 180°. To a first approximation, the O2S2 atoms define a square-plane [r.m.s. deviation = 0.0348 Å] and the Sn atom lies 0.2859(6) above this plane in the direction of the 4-fluorobenzyl-C10 atom. The tridentate mode of coordination for the 2,2′-imino-diethanolate ligand gives rise to two five-membered SnO2N,C2 rings, which adopt distinct conformations. Thus, the O3-chelate is twisted about the C7–N2 bond. By contrast, the O4-ring has an envelope conformation with the flap atom, C9, lying 0.555(3) Å out of the least-squares plane through the remaining four atoms [r.m.s. deviation = 0.044 Å].

Tin(II), tin(IV) and organotin(IV) dithiocarbamate compounds are well known in the literature with coordination modes ranging from symmetric as in (I) to effectively monodentate in triorganotin derivatives but often adopt asymmetric modes of coordination [8]. By contrast, there is only one literature precedent for a tin compound with the 2,2′-imino-diethanolate ligand, namely in the structure of Sn(OCH2CH2N(H)CH2CH2O)(CH2Si(Me3)2OSi(Me3)CH2)2 [12].

The crystal of (I) features conventional O–H···O hydrogen bonding leading to a supramolecular layer parallel to (1 0 1). Thus, hydroxy-O–H···O(hydroxy) [O1–H1o···O22; H1o···O22 = 1.86(2) Å, O1···O22 = 2.688(2) Å with angle at H1o = 117(2)° for symmetry operation (i) 3/2 – x, 1/2 + y, 1/2 – z] and hydroxy-O–H···O(ethanolate) [O2–H2o···O3ii; H2o···O3ii = 1.801(15) Å, O2···O3ii = 2.6336(19) Å with angle at H2o = 174(3)° for (ii) 1/2 + x, 1/2 – y, –1/2 + z] hydrogen bonds feature in the molecular packing. The formation of the latter hydrogen bonding interaction provides a rationale for the elongation of the Sn–O3 bond length with respect to the Sn–O4 bond. The connections between layers to consolidate the three-dimensional molecular packing are imino-N–H···π(phenyl) interactions [N2–H2n···Cg(C11-C16)3ii; H2n···Cg(C11-C16)3ii = 2.946(18) Å with angle at H2n = 166.7(18)° for (iii) –1/2 + x, 1/2 – y, –1/2 + z].

In order to analyse the molecular packing further, in particular the influence of other non-covalent interactions operating in the crystal of (I), an analysis of the calculated Hirshfeld surfaces/two-dimensional fingerprint plots (overall and individual surface contacts) was conducted employing Crystal Explorer 17 [13] and literature procedures [14]. Reflecting the significant O–H···O hydrogen bonding interactions along with some C–H···O contacts shorter than the sum of the respective van der Waals radii in the crystal, O···H/H···O contacts, at 17.8%, are a major contributor to surface contacts, as are C···H/H···C contacts [70%] but neither match the dominance of H···H contacts, i.e. 57.5%.

The other major contributions come from F···H/H···F [9.2%] and S···H/H···S [21%], with some F···H contacts within distances less than the sum of their van der Waals radii.

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