Crystal structure of bis{(ethanol)[2-(salicylhydrazono)propionato]-di(2-fluorobenzyl)tin(IV)}, $[(FC_6H_4CH_2)_2Sn(C_2H_5OH)(C_{10}H_8N_2O_4)]_2$

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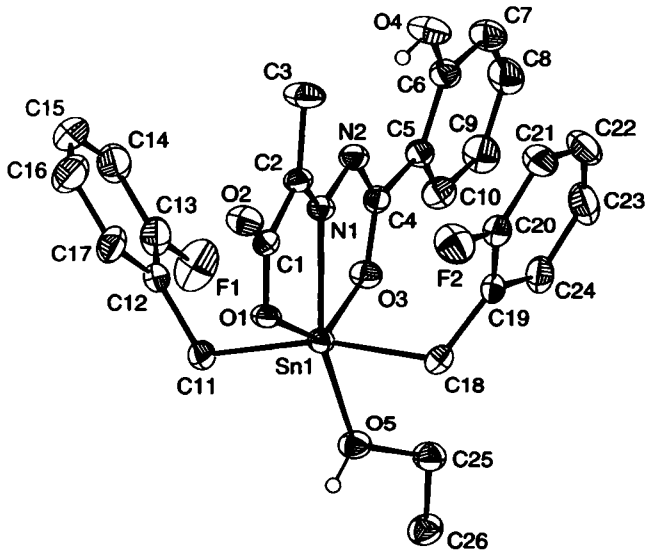

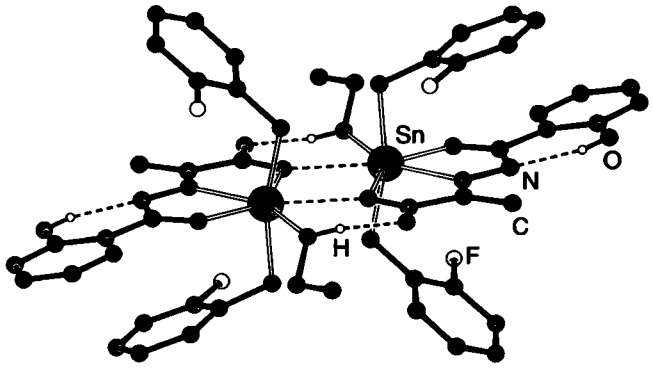

Abstract

$C_{52}H_{52}F_4N_4O_{10}Sn_2$, monoclinic, $P12_1/n1$ (no. 14), $a = 11.112(1)$ Å, $b = 17.939(3)$ Å, $c = 12.612(3)$ Å, $\beta = 92.407(2)°$, $V = 2511.9$ Å^3, $Z = 2$, $R_{gt}(F) = 0.046$, $wR_{ref}(F^2) = 0.124$, $T = 298$ K.

Source of material

The pyruvic acid salicylhydrazone (1 mmol) and sodium ethoxide (1 mmol) was added to the solution of dry benzene (20 ml) in a Schlenk flask and stirred for 0.5 h. After the di-*o*-fluorobenzyltin dichloride (1 mmol) was added to the reactor, the reaction mixture was stirred for 12 h at 40 °C and then filtered. The solvent was gradually removed by evaporation under vacuum until a solid product was obtained. The solid was then recrystallized from ethanol and the colorless crystal suitable for X-ray diffraction was obtained (m.p. 413 K).

Elemental analysis: found – C, 51.87 %; H, 4.23 %; N, 4.68 %; calc. for $C_{52}H_{52}F_4N_4O_{10}Sn_2$ – C, 51.73 %; H, 4.31 %; N, 4.64 %. ^{1}H NMR and IR data are available in the CIF file.

Discussion

Studies on diorganotin(IV) complexes of carboxylic acid having carboxylate ligands with additional donor atom, such as nitrogen, revealed new structural types which may lead to complexes with different activities [1-3]. In line with these developments, we have recently reported some diorganotin complexes of pyruvic acid isonicotinyl hydrazone [4].

In the title complex, the Sn atom exists in a seven-coordinate environment in which one ethanol molecule, two tridentate pyruvic acid salicylhydrazone ligands, and two *trans* *o*-fluorobenzyl groups coordinate to each Sn center (figure, top). The atoms O1, O5, O1^i, O3 and N1 are coplanar within 0.046 Å, which form the equatorial plane. The angle of the axial C11–Sn1–C18 is 165.0(2)°, which deviates from the linear angle of 180°. These data indicate that the tin atom of this complex has in a distorted pentagonal bipyramid environment. The O1 atom of the carboxylate residue also binds another tin atom, Sn1^i, generating a Sn_2O_2 four-membered ring. Thereby the structure of this complex can be described as a dimer (figure, bottom). The forming of the dimer leads to the shorter interaction between O and O^i (symmetry code: $-x+2,-y+2,-z+1$), because the interaction of two monomers surpass the repelling effect of two O atoms.

The C—O bond length (C4—O3, 1.274(6) Å), lies in between double-bond length of 1.224 Å and single-bond length of 1.430 Å. Compared with the length of C=N 1.270 Å and that of C—N 1.470 Å, the bond C4—N2 (1.339(7) Å) are rather close to C=N. The length of C2—N1 (1.282(7) Å) is similar to that of C4—N2. And the N1—N2 bond (1.371(6) Å) belongs to the scope of single-bonds [5,6]. These data indicate that Schiff base ligand forms C=N–N=C conjugated system, which is introduced into the inner coordination sphere and functions as a tridentate chelate with O, N and O atoms in enol dehydrogenized form. Meanwhile, studies show that the phenolic oxygen atoms are also in non-participation in coordination to tin atoms. Each Sn atom is also coordinated by an ethanol molecule, the Sn—$O_{ethanol}$ bond distance is 2.429(4) Å being relatively longer than those in the analogous [3], due to the formation of intra-dimeric hydrogen bonds, O2···O5^i (and O2^i···O5) with 2.635 Å (symmetry code: $-x+2,-y+2,-z+1$). There are also strong intramolecular O–H···N hydrogen bonds involving N2 atom and phenolic hydroxy oxygen atom non-coordinating to the Sn center.

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Table 1. Data collection and handling.

Crystal:	colorless block, size 0.17 × 0.32 × 0.38 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	10.72 cm^{-1}
Diffractometer, scan mode:	Bruker SMART CCD, φ/ω
$2\theta_{max}$:	50.04°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	12442, 4294
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 3326
$N(param)_{refined}$:	325
Programs:	SHELXS-97 [7], SHELXL-97 [8]

Table 2. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{iso}
H(1)	4e	0.9430	0.9240	0.7520	0.050
H(4)	4e	0.8107	0.6854	0.3000	0.092
H(3A)	4e	0.8498	0.7946	0.1917	0.087
H(3B)	4e	0.9614	0.8395	0.1544	0.087
H(3C)	4e	0.8322	0.8743	0.1425	0.087
H(7)	4e	0.7361	0.5143	0.3625	0.070
H(8)	4e	0.6958	0.4740	0.5303	0.075
H(9)	4e	0.7026	0.5549	0.6719	0.072
H(10)	4e	0.7603	0.6773	0.6463	0.058
H(11A)	4e	0.7281	0.9414	0.6338	0.047
H(11B)	4e	0.7772	1.0092	0.5705	0.047
H(14)	4e	0.4230	0.8431	0.4249	0.096
H(15)	4e	0.4182	0.9163	0.2736	0.101
H(16)	4e	0.5651	1.0031	0.2492	0.091
H(17)	4e	0.7132	1.0227	0.3772	0.069
H(18A)	4e	1.1555	0.8889	0.5150	0.046
H(18B)	4e	1.1291	0.8465	0.6201	0.046
H(21)	4e	1.1606	0.7140	0.2549	0.077
H(22)	4e	1.1166	0.6021	0.3393	0.097
H(23)	4e	1.0757	0.6016	0.5150	0.085
H(24)	4e	1.0738	0.7110	0.6119	0.064
H(25A)	4e	1.0532	0.8117	0.7799	0.058
H(25B)	4e	0.9252	0.7745	0.7724	0.058
H(26A)	4e	0.9854	0.7911	0.9493	0.079
H(26B)	4e	0.8715	0.8404	0.9230	0.079
H(26C)	4e	0.9997	0.8770	0.9306	0.079

Table 3. Atomic coordinates and displacement parameters (in $Å^2$).

Atom	Site	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Sn(1)	4e	0.92146(3)	0.89579(2)	0.53954(3)	0.0391(2)	0.0301(2)	0.0284(2)	0.0008(2)	−0.0004(1)	−0.0015(2)
F(1)	4e	0.5728(4)	0.8515(3)	0.5816(4)	0.072(3)	0.093(4)	0.114(4)	−0.018(2)	−0.003(3)	0.045(3)
F(2)	4e	1.1674(4)	0.8418(2)	0.3362(3)	0.092(3)	0.071(3)	0.054(2)	0.007(2)	0.017(2)	0.004(2)
N(1)	4e	0.8757(4)	0.8445(2)	0.3800(3)	0.039(3)	0.031(2)	0.033(2)	−0.001(2)	−0.004(2)	−0.002(2)
N(2)	4e	0.8310(4)	0.7733(2)	0.3776(3)	0.039(3)	0.035(2)	0.037(2)	−0.004(2)	−0.003(2)	−0.004(2)
O(1)	4e	0.9693(3)	0.9774(2)	0.4025(3)	0.048(2)	0.033(2)	0.027(2)	−0.002(2)	−0.002(2)	−0.005(2)
O(2)	4e	0.9814(4)	0.9873(2)	0.2264(3)	0.078(3)	0.039(2)	0.034(2)	−0.007(2)	0.002(2)	0.005(2)
O(3)	4e	0.8377(3)	0.7882(2)	0.5604(3)	0.049(2)	0.035(2)	0.035(2)	−0.007(2)	0.003(2)	0.000(2)
O(4)	4e	0.7946(4)	0.6408(3)	0.3019(3)	0.088(3)	0.050(3)	0.048(3)	−0.017(2)	0.005(2)	−0.014(2)
O(5)	4e	0.9238(4)	0.8809(2)	0.7311(3)	0.063(3)	0.040(2)	0.032(2)	−0.002(2)	−0.005(2)	0.003(2)
C(1)	4e	0.9538(5)	0.9535(3)	0.3065(4)	0.042(3)	0.036(3)	0.028(3)	0.005(2)	−0.005(2)	0.001(2)
C(2)	4e	0.9005(5)	0.8767(3)	0.2928(4)	0.041(3)	0.036(3)	0.028(3)	−0.001(2)	−0.004(2)	−0.002(2)
C(3)	4e	0.8846(7)	0.8433(4)	0.1860(5)	0.097(5)	0.046(4)	0.031(3)	−0.012(3)	−0.006(3)	−0.005(3)
C(4)	4e	0.8177(4)	0.7494(3)	0.4770(4)	0.032(3)	0.030(3)	0.041(3)	−0.002(2)	−0.003(2)	0.001(2)
C(5)	4e	0.7785(4)	0.6704(3)	0.4885(4)	0.029(3)	0.034(3)	0.044(3)	−0.004(2)	0.001(2)	−0.003(2)
C(6)	4e	0.7722(5)	0.6208(3)	0.4026(5)	0.038(3)	0.044(3)	0.054(4)	−0.003(2)	−0.002(3)	−0.010(3)
C(7)	4e	0.7408(6)	0.5475(4)	0.4191(6)	0.059(4)	0.044(4)	0.071(5)	−0.011(3)	−0.004(3)	−0.011(3)
C(8)	4e	0.7162(6)	0.5236(4)	0.5197(6)	0.060(4)	0.036(4)	0.091(5)	−0.011(3)	−0.002(4)	−0.003(4)
C(9)	4e	0.7212(6)	0.5715(4)	0.6047(6)	0.059(4)	0.044(4)	0.076(5)	−0.013(3)	0.004(3)	0.009(4)
C(10)	4e	0.7543(5)	0.6448(4)	0.5889(5)	0.043(3)	0.051(4)	0.051(4)	−0.008(3)	0.001(3)	0.002(3)
C(11)	4e	0.7586(5)	0.9564(3)	0.5662(4)	0.039(3)	0.042(3)	0.038(3)	0.006(2)	0.002(2)	−0.002(2)
C(12)	4e	0.6625(5)	0.9444(3)	0.4811(4)	0.038(3)	0.040(3)	0.044(3)	0.009(2)	−0.001(2)	−0.006(3)
C(13)	4e	0.5738(6)	0.8927(3)	0.4928(7)	0.045(4)	0.045(4)	0.083(5)	0.002(3)	−0.001(3)	0.007(3)
C(14)	4e	0.4810(7)	0.8796(4)	0.4154(8)	0.051(4)	0.057(5)	0.130(8)	−0.001(3)	−0.020(5)	−0.020(5)
C(15)	4e	0.4793(7)	0.9227(6)	0.3254(8)	0.064(5)	0.092(6)	0.093(6)	0.019(5)	−0.038(5)	−0.027(5)
C(16)	4e	0.5664(7)	0.9750(5)	0.3112(6)	0.063(5)	0.103(7)	0.061(5)	0.018(4)	−0.013(4)	−0.002(4)
C(17)	4e	0.6555(6)	0.9862(4)	0.3877(5)	0.055(4)	0.065(4)	0.051(4)	0.013(3)	−0.008(3)	0.012(3)
C(18)	4e	1.1026(4)	0.8529(3)	0.5464(4)	0.036(3)	0.043(3)	0.035(3)	0.000(2)	−0.004(2)	0.006(2)
C(19)	4e	1.1131(5)	0.7804(3)	0.4902(4)	0.032(3)	0.038(3)	0.046(3)	0.008(2)	−0.004(2)	−0.001(3)
C(20)	4e	1.1406(5)	0.7770(4)	0.3855(5)	0.041(3)	0.052(4)	0.050(4)	0.009(3)	−0.004(3)	−0.005(3)
C(21)	4e	1.1426(6)	0.7130(4)	0.3263(6)	0.059(4)	0.066(5)	0.066(4)	0.011(3)	0.000(3)	−0.025(4)
C(22)	4e	1.1169(7)	0.6467(5)	0.3770(8)	0.062(5)	0.059(5)	0.120(8)	0.013(4)	−0.011(5)	−0.047(5)
C(23)	4e	1.0919(6)	0.6466(4)	0.4818(8)	0.053(4)	0.042(4)	0.118(7)	0.008(3)	0.000(4)	−0.008(4)
C(24)	4e	1.0901(5)	0.7122(3)	0.5402(6)	0.039(3)	0.043(4)	0.078(5)	0.005(3)	−0.005(3)	0.004(3)
C(25)	4e	0.9688(6)	0.8194(3)	0.7933(4)	0.061(4)	0.044(3)	0.039(3)	0.000(3)	−0.001(3)	−0.002(3)
C(26)	4e	0.9551(6)	0.8332(4)	0.9095(5)	0.063(4)	0.055(4)	0.041(3)	−0.001(3)	−0.005(3)	0.004(3)

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