Crystal structure of bis[chloro-1κCl-μ-fluoro-μ-oxo-(tetraphenyl-1κ_2C,2κ_2C)ditin], $[(C_6H_5)_2SnClFOSn(C_6H_5)_2]_2$

I. Ahmed, H. Reuter* and G. Kastner

Universität Osnabrück, Institut für Chemie, Barbarastr. 7, D-49069 Osnabrück, Germany

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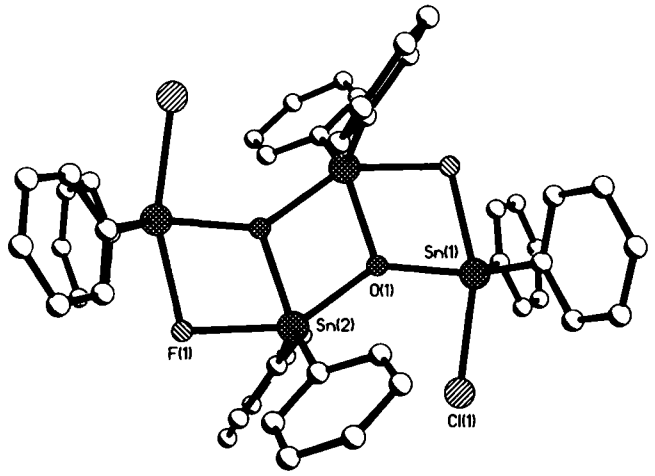

Abstract

$C_{48}H_{40}Cl_2F_2O_2Sn_4$, monoclinic, $P12_1/n1$ (No. 14), $a = 11.113(2)$ Å, $b = 18.360(2)$ Å, $c = 11.877(2)$ Å, $\beta = 91.71(2)°$, $V = 2422.2$ Å^3, $Z = 2$, $R_{gt}(F) = 0.043$, $wR_{ref}(F^2) = 0.115$, $T = 293$ K.

Source of material

All reagents were purchased from Aldrich or Fluka and used without further purification. A solution of Ph_2SnCl_2 (6.63 g, 19.29 mmol) in 100 mL diethylether was slowly added to a solution of KF (1.12 g, 19.26 mmol) in a mixture of ethanol/H_2O. The reaction mixture was stirred for one hour, filtered of and washed with water, ether and acetone (yield: 5.08 g, 84.9 %). The compound melts at 425.9 K with an enthalpy of 122.6 kJ/mol (Setaram calorimeter DSC 92, heat flow rate 5 K/min, calibration of temperature and enthalpy with melting points and enthalpies of indium, bismuth, lead and 1,2-dichloroethane [1,2]). Analysis (Beller Microanalytical Laboratory, Göttingen)/ (calc. data) for $C_{48}H_{40}Cl_2F_2O_2Sn_4$: C 46.78/46.56, H 3.27/3.17, Sn 38.46/38.60. Some of the product was dissolved in toluene and the solvent was allowed to evaporate slowly at room temperature. Colorless crystals were grown within three weeks.

A suitable single crystal was chosen by use of a polarisation microscope and mounted at the top of a glass thread with epoxy resin.

Discussion

The compound exhibits the planar, centrosymmetric ladder structure found for a lot of partial hydrolysis products of diorganotin dihalides, R_2SnX_2, leading to the formation of the three main classes (X = Cl) of the so-called tetra organodistannoxanes: $(R_2SnCl)(R_2SnCl)O$ [3-8], $(R_2SnCl)(R_2SnOH)O$ [3,9-12] and $(R_2SnOH)(R_2SnOH)O$ [6,13]. The atoms of the fused $Sn_4O_2F_2$ ring system lying within 0.043 Å of the least-square plane. The tin atoms are five fold coordinated with the alkyl groups occupying the equatorial positions. The axial positions at Sn(1) and Sn(2) are occupied by Cl(1) and F(1) and by F(1) and O(1), respectively. The distortion is due to the constraints imposed by the fused ring systems as well as the weak interaction between Sn2 and Cl1. The Sn(1)–F(1)–Sn(2) bridge is nearly symmetric with Sn—F distances (2.144(2) Å, 2.147(2) Å) which are in well agreement to those found for $[NH_4][(Ph_2SnF)_2(CH_2)F]$ [14] and $[(t\text{-}Bu_2SnF)_2O]_2$ [15]. Spectroscopic data gives further information about the presence of fluorine. Solid state $^{19}F[1H]$ MAS-NMR-spectroscopy (Bruker-DSX-500; rotational frequencies: 9 and 10 kHz) shows a singulett at –122.9 ppm where as the infrared spectrum (Brucker vector 22 FT spectrometer; KBr-pellet, 4000-400 cm^{-1}, selected bands: 3048m, 2994w, 1961vw, 1892vw, 1578vw, 1481m, 1432s, 1071m, 1022m, 997m, 919w, 730vs, 694vs, 661m, 635m, 577m, 553m, 483vw, 447m cm^{-1}) shows the absence of OH bands.

The Sn—O bond lengths are in the range of previous investigations [3-13,15]. The Sn(1)—Cl(1) bond distance (240.9(3) pm) in the title compound is one of the shortest ones found in this class of compounds.

Table 1. Data collection and handling.

Crystal:	colourless transparent plate, size 0.11 × 0.29 × 0.34 mm
Wavelength:	Mo K_α radiation (0.71073 Å)
μ:	21.92 cm^{-1}
Diffractometer, scan mode:	Siemens P4, $2\theta/\omega$
$2\theta_{max}$:	46.02°
$N(hkl)_{measured}$, $N(hkl)_{unique}$:	4247, 3361
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\,\sigma(I_{obs})$, 2590
$N(param)_{refined}$:	263
Program:	SHELXTL [16]

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

Atom	Site	x	y	z	U_{iso}
H(11A)	4e	0.2880	0.2247	0.2298	0.239
H(11B)	4e	0.2406	0.2379	0.0404	0.322
H(114)	4e	0.1596	0.1468	–0.0550	0.198
H(11C)	4e	0.1377	0.0401	0.0267	0.307
H(11D)	4e	0.2005	0.0223	0.2134	0.238
H(12A)	4e	0.0951	0.0318	0.5502	0.108
H(12B)	4e	0.1046	0.2506	0.7396	0.125
H(12C)	4e	–0.0244	0.1618	0.7939	0.113
H(12D)	4e	–0.0341	0.0551	0.6984	0.138

* Correspondence author (e-mail: hreuter@uos.de)

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(12E)	4e	0.2250	0.2324	0.5893	0.107
H(21A)	4e	0.8476	0.1316	0.4627	0.120
H(21B)	4e	0.9497	0.1622	0.3026	0.167
H(21C)	4e	0.8653	0.1355	0.1300	0.172
H(21D)	4e	0.6827	0.0831	0.1142	0.158
H(21E)	4e	0.5700	0.0605	0.2720	0.121

Table 2. Continued.

Atom	Site	x	y	z	U_{iso}
H(22A)	4e	0.4051	0.1121	0.6749	0.133
H(22B)	4e	0.3718	0.1576	0.8531	0.176
H(22C)	4e	0.5326	0.1853	0.9712	0.146
H(22D)	4e	0.7237	0.1697	0.9083	0.161
H(22E)	4e	0.7522	0.1176	0.7347	0.144

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	0.29029(5)	0.11220(3)	0.41728(4)	0.0610(4)	0.0717(4)	0.0586(4)	0.0063(3)	-0.0001(3)	0.0070(3)
Sn(2)	4e	0.60785(5)	0.05963(3)	0.52998(4)	0.0574(3)	0.0615(3)	0.0585(3)	-0.0056(3)	0.0002(2)	-0.0016(3)
Cl(1)	4e	0.4211(2)	0.2157(1)	0.4448(2)	0.097(2)	0.083(2)	0.106(2)	-0.004(1)	0.009(1)	0.014(1)
O(1)	4e	0.4321(4)	0.0491(3)	0.4664(4)	0.058(3)	0.060(3)	0.061(3)	-0.002(2)	-0.008(2)	0.003(2)
F(1)	4e	0.7685(4)	0.0034(3)	0.5927(4)	0.063(3)	0.083(3)	0.064(3)	-0.004(2)	-0.003(2)	-0.005(2)
C(111)	4e	0.2500(8)	0.1226(6)	0.2448(7)	0.070(5)	0.095(6)	0.064(5)	0.007(5)	-0.005(4)	0.009(5)
C(112)	4e	0.259(2)	0.1843(8)	0.190(1)	0.41(3)	0.10(1)	0.081(9)	0.03(1)	-0.02(1)	0.021(8)
C(113)	4e	0.228(3)	0.193(1)	0.076(2)	0.54(5)	0.15(2)	0.10(1)	0.03(2)	-0.12(2)	0.03(1)
C(114)	4e	0.183(2)	0.141(1)	0.020(1)	0.15(1)	0.28(3)	0.066(9)	0.03(2)	-0.010(8)	0.04(1)
C(115)	4e	0.171(2)	0.079(2)	0.068(2)	0.31(3)	0.33(3)	0.12(2)	-0.15(2)	-0.10(2)	0.05(2)
C(116)	4e	0.207(2)	0.068(1)	0.182(1)	0.30(2)	0.19(2)	0.09(1)	-0.10(2)	-0.06(1)	0.04(1)
C(121)	4e	0.1717(7)	0.1311(5)	0.5527(6)	0.060(5)	0.081(6)	0.054(5)	0.006(4)	-0.001(4)	0.002(4)
C(122)	4e	0.0962(8)	0.0768(6)	0.5863(9)	0.067(6)	0.111(8)	0.092(7)	-0.019(5)	0.018(5)	-0.034(6)
C(123)	4e	0.101(1)	0.2066(6)	0.7008(9)	0.125(9)	0.098(8)	0.089(7)	0.004(7)	0.017(7)	-0.020(6)
C(124)	4e	0.0249(9)	0.1541(6)	0.7330(8)	0.090(7)	0.119(9)	0.073(6)	-0.011(7)	0.016(5)	-0.011(6)
C(125)	4e	0.020(1)	0.0906(7)	0.677(1)	0.092(8)	0.13(1)	0.123(9)	-0.038(7)	0.042(7)	-0.035(8)
C(126)	4e	0.173(1)	0.1954(5)	0.6111(8)	0.116(8)	0.074(6)	0.078(6)	-0.001(6)	0.011(6)	0.001(5)
C(211)	4e	0.6985(7)	0.0920(4)	0.3852(7)	0.059(5)	0.063(5)	0.079(6)	0.008(4)	0.014(4)	0.013(4)
C(212)	4e	0.8121(9)	0.1226(6)	0.392(1)	0.083(7)	0.104(8)	0.114(8)	-0.014(6)	0.028(6)	0.019(6)
C(213)	4e	0.874(1)	0.1402(8)	0.297(2)	0.099(9)	0.13(1)	0.20(2)	-0.008(8)	0.06(1)	0.05(1)
C(214)	4e	0.824(2)	0.1248(9)	0.195(1)	0.15(1)	0.16(1)	0.12(1)	0.04(1)	0.06(1)	0.07(1)
C(215)	4e	0.715(1)	0.0944(9)	0.185(1)	0.14(1)	0.18(1)	0.081(8)	0.01(1)	0.032(8)	0.026(8)
C(216)	4e	0.648(1)	0.0791(6)	0.2799(9)	0.106(8)	0.121(9)	0.077(7)	-0.002(7)	0.023(6)	0.007(6)
C(221)	4e	0.5812(8)	0.1085(5)	0.6871(7)	0.068(5)	0.080(6)	0.059(5)	0.003(4)	-0.003(4)	-0.010(4)
C(222)	4e	0.4708(9)	0.1219(7)	0.7228(9)	0.077(7)	0.18(1)	0.076(7)	0.027(7)	-0.003(5)	-0.036(7)
C(223)	4e	0.450(1)	0.1503(9)	0.830(1)	0.107(9)	0.25(2)	0.083(8)	0.03(1)	0.005(7)	-0.05(1)
C(224)	4e	0.545(1)	0.1670(8)	0.8995(9)	0.12(1)	0.17(1)	0.075(7)	0.021(9)	-0.001(7)	-0.033(8)
C(225)	4e	0.658(1)	0.1565(8)	0.863(1)	0.11(1)	0.19(1)	0.095(8)	-0.02(1)	-0.017(7)	-0.063(9)
C(226)	4e	0.674(1)	0.1262(7)	0.7576(9)	0.088(7)	0.17(1)	0.103(9)	-0.015(8)	0.000(6)	-0.059(8)

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