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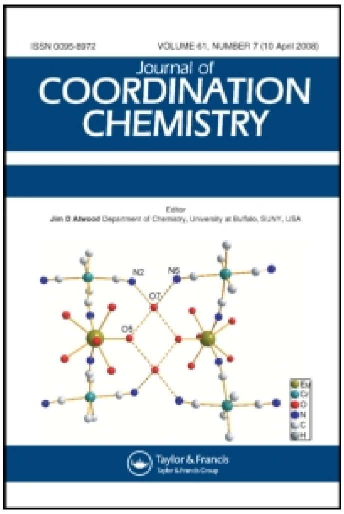

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SYNTHESIS AND CRYSTAL STRUCTURE OF DIMETHYLDI(MONOTHIOBENZOATO)TIN(IV)

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SYNTHESIS AND CRYSTAL STRUCTURE OF DIMETHYLDI(MONOTHIOBENZOATO)TIN(IV)

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The reaction of dimethyltin(IV) dichloride with monothiobenzoic acid results in the formation of dimethyldi(monothiobenzoato)tin(IV), $C_{16}H_{16}O_2S_2Sn$, which crystallizes in the orthorhombic system, space group $Cmc2_1$, $Z = 8$, $a = 20.578(7)$, $b = 7.409(4)$ and $c = 11.270(4)$ Å. Refinement converged to $R = 0.030$ and $R_w = 0.032$ based on 1079 unique reflections such that $3.0° \leq 2\Theta \leq 55.0°$. Each of the two ligands functions as a monodentate anion coordinating to the tin atom through its sulfur atom and conferring a tetrahedral geometry about the tin atom.

KEYWORDS: Dimethyldi(monothiobenzoato)tin(IV), dimethyltin(IV) dichloride, tetrahedral, X-ray analysis

INTRODUCTION

The mode of coordination of monothiocarboxylic acid with several transition metals has been extensively studied.[1–6] However, to-date, few systematic studies have been carried out on the coordinating ability of the monothiocarboxylate ligands to organotin compounds.[7–10]

In this paper, we report the synthesis and a full X-ray structural analysis of the title compound.

EXPERIMENTAL

Synthesis of dimethyldi(monothiobenzoato)tin(IV), $C_{16}H_{16}O_2S_2Sn$

A reaction mixture consisting of dimethyltin(IV) dichloride (0.5 mmol) and monothiobenzoic acid (1 mmol) in 50 cm^3 of ethanol was continuously stirred for

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1 hr at room temperature. The mixture was allowed to stand whereupon the crystals which were formed were filtered and then recrystallized from ethanol. Yield 80%; m.p. 136–137°C.

Anal.: Calcd. for $C_{16}H_{16}O_2S_2Sn$: C, 45.42; H, 3.80; Sn, 28.05%. Found: C, 45.39; H, 3.82; Sn, 28.00%. IR (KBr): v, 1568 ($C = 0_{assym}$); 1448 ($C = O_{symm}$); 931 (C- S); NMR (^1H,$CDCl_3$,25°C): 1.21 (s, 6H, 2{Sn CH_3}); 7.43-8.10 (m, 10H, aromatic) ppm. The carbon, hydrogen and nitrogen analyses were carried out on a Control Equipment Corporation 240 XA elemental analyzer at the School of Chemical Sciences, Universiti Sains Malaysia, Penang, Malaysia. The tin analysis was performed using an Instrumental Laboratory 357 atomic spectrophotometer. IR data were recorded using a Perkin Elmer FTIR 1650 spectrophotometer in the frequency range 4000–450 cm^{-1} with samples in KBr discs. ^1H NMR spectra were recorded on a Bruker AC-P 300 MHz NMR spectrometer.

Determination of crystal structure of $C_{16}H_{16}O_2S_2Sn$

A single crystal of dimensions 0.4 x 0.4 x 0.1 mm was mounted on a thin glass fibre on a Siemens P_4 diffractor fitted with graphite monochromated Mo-K_α radiation λ = 0.71073 Å. The Θ-2Θ scan method was employed to measure a total of 1079 reflections in the 3.0° ≤ 2Θ ≤ 55.0° shell. Corrections were applied for Lorentz and polarization effects but not for absorption. There were 1079 unique data of which 983 satisfied the $F>4.0\sigma(F)$ criterion of observability and these were used the subsequent analysis. The structure was solved by direct methods using Siemens SHELXTL Plus[11] and refined by a full-matrix least-squares procedure. The crystal data and refinement parameters are given in Table 1. Fractional atomic coordinates and their equivalent isotropic displacement parameters are given in Table 2 and

Table 1 Crystal data and refinement details for $C_{16}H_{16}O_2S_2Sn$.

Formula	$C_{16}H_{16}O_2S_2Sn$
Formula weight	211.5
Crystal system	Othorhombic
Space group	*Cmc*2$_1$
Cell constants	a = 20.578(7)Å b = 7.409(4)Å c = 11.270(4)Å V = 1718.3(13)Å
Z	8
F(000)	840
Density,D_c	1.636 g cm^{-1}
μ	1.730 mm^{-1}
Radiation	Mo-K_α (λ = 0.71073Å)
Temperature	25°C
Range of h k l	h: 0→26; k: 0→9; l: -14→0
Orientation reflections	1025
No. of unique reflections	1079
No. of observed reflections	983 ($F>4.0\sigma(F)$)
No. of variables	123
R	0.030
R_w	0.032, $w = 1/[\sigma^2(F) + (0.003)F^2]$
Fourier difference	max. 1.3 e/Å^3; min. -0.40 e/Å^3

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement coefficients (Å^2 × 10^3).

Atoms	x/a	y/b	z/c	$U_{(eq)}$
Sn(1)	0	926(1)	2459	47(1)
S(1)	853(1)	1493(3)	939(2)	60(1)
O(1)	1264(4)	709(8)	3047(7)	60(2)
C(1)	2136(3)	1195(7)	1720(6)	40(2)
C(2)	2351(4)	1694(10)	616(6)	51(2)
C(3)	3005(4)	1819(11)	371(8)	60(2)
C(4)	3445(3)	1392(10)	1242(8)	57(2)
C(5)	3242(3)	880(9)	2353(20)	60(3)
C(6)	2577(3)	794(9)	2609(10)	48(2)
C(7)	1425(5)	1081(10)	2043(8)	48(2)
C(8)	0	2955(18)	3758(12)	75(4)
C(9)	0	-1865(13)	2867(10)	59(3)

* Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

bond distances and angles in Table 3. The molecular structure of $C_{16}H_{16}O_2S_2Sn$ with atom labelling is shown in Figure 1.

RESULTS AND DISCUSSION

As shown in Figure 1, the structure of dimethyldi(monothiobenzoato)tin(IV) shows a distorted tetrahedron about the tin atom which is coordinated to two methyl and two monothiobenzoate groups. Each of the two monothiobenzoate ligands functions as a unidentate anion coordinating to tin through its sulfur atom, leaving its carbonyl group free. The average Sn-S distance (2.488(2) Å) is close to the sum of the covalent radii of Sn and S (2.44 Å)[12] and is comparable to those observed for diorganotin compounds with sulphur containing ligands.[13–16]

Table 3 Selected bond distances (Å) and angles (°) with c.s.d.'s in parentheses for non-hydrogen atoms.

Sn(1)-S(1)	2.488(2)	S(1)-Sn(1)-S(1A)	89.7(1)
Sn(1)-S(1A)	2.488(2)	S(1)-Sn(1)-C(8)	111.1(3)
Sn(1)-C(8)	2.099(14)	S(1)-Sn(1)-C(9)	108.3(2)
Sn(1)-C(9)	2.118(10)	C(8)-Sn(1)-C(9)	123.2(5)
S(1)-C(7)	1.740(10	C(8)-Sn(1)-S(1A)	111.1(3)
O(1)-C(7)	1.211(12)	C(9)-Sn(1)-S(1A)	108.3(2)
C(1)-C(2)	1.372(9)	Sn(1)-S(1)-C(7)	87.4(3)
C(1)-C(6)	1.385(11)	C(2)-C(1)-C(6)	120.1(6)
C(1)-C(7)	1.509(12)	C(2)-C(1)-C(7)	123.2(6)
C(2)-C(3)	1.376(11)	C(6)-C(1)-C(7)	116.7(7)
C(3)-C(4)	1.373(11)	C(1)-C(2)-C(3)	121.1(7)
C(4)-C(5)	1.374(23)	C(2)-C(3)-C(4)	119.0(7)
C(5)-C(6)	1.400(11)	C(3)-C(4)-C(5)	121.1(7)
		C(4)-C(5)-C(6)	119.8(13)
		C(1)-C(6)-C(5)	118.9(12)
		S(1)-C(7)-O(1)	121.5(8)
		S(1)-C(7)-C(1)	118.3(6)
		O(1)-C(7)-C(1)	120.2(8)

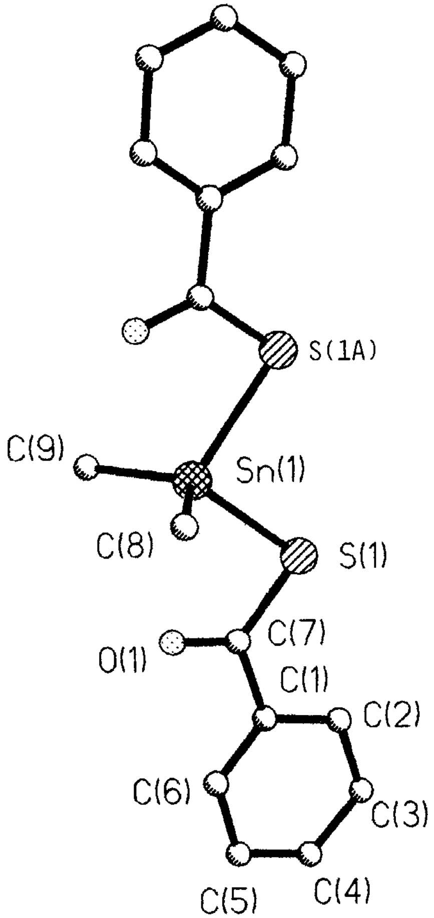

Figure 1 The molecular structure of $C_{16}H_{16}O_2S_2Sn$.

On the basis of IR and ^1H NMR spectroscopic evidence, it has been postulated by Tsipis[7] that in diorganotin(IV) monothiocarboxylates, the ligands are bidentate and coordinate to tin through their sulphur and oxygen atoms. However, it has been found[10] that alkyl thiocarboxylic acids coordinate to dimethyltin(IV) through sulphur atoms while the carboxylate groups are uncoordinated.

The X-ray crystal structure of diaquabis(monothiobenzoato)zinc(II)[3] has shown explicitly that the sulfur atom of each of the ligands is bonded to the central metal atom as observed in the present complex. While the two sulfur atoms are relatively close and the S(1)-Sn(1)-S(1A) angle is relatively small (89.7(1)°), the corresponding angle in the zinc(II) complex is much larger (125.7(2)°) and the two sulfur atoms are farther apart as a result of hydrogen bonding between the coordinated water and the carboxylate oxygen of the ligand.

It is found that $\nu_{S\text{-}H}$ in the IR spectrum of the free monothiobenzoic acid disappears upon complexation with $(CH_3)_2$ $SnCl_2$ while the S-H signal at δ = 4.50

ppm in the ^1H NMR spectrum of the ligand is absent in the spectrum of the complex. Such observations are in accord with the deprotonation of the thiol proton and the coordination of sulfur to tin. In terms of the concept of hard and soft donors and acceptors, the dimethyltin(IV) moiety acts as a soft acceptor which combines with the soft sulfur donor of the monothiobenzoate ligand.

Supplementary material

Tables of hydrogen coordinates and their corresponding atomic displacement parameters, anisotropic atomic displacements for the non- hydrogen atoms and structural factors are available from the authors.

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