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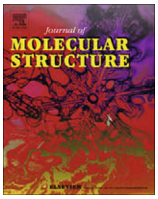

Synthesis and characterization of a diorganotin bis(thioacetate)

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ABSTRACT

Dimethyltin bis(thioacetate) has been prepared by a reaction of dimethyltin dichloride. Attempts to prepare anionic complexes were not successful. The reactions have been explained on the basis of DFT calculations. The compound has been characterized by multinuclear NMR and IR spectral studies. X-ray study revealed that the molecular structure resembled the transition state of the *trans–cis* pathway of a skew trapezoid. Absorption and emission spectra of the compound have also been studied.

1. Introduction

The presence of both hard and soft donor sites has always intrigued chemists towards ligands containing both S and O donor centers [1]. In the past few years, a large number of thiocarboxylate complexes have been reported focusing on their structural aspects [2]. Besides the academic interest, studies on metal thiocarboxylates are due to their potential applications as single source precursors for making binary and ternary metal sulfides [3].

Continuing our studies in organotin thiocarboxylates, we have recently reported the reactions of various nucleophiles with the diorganotin thiocarboxylate, $Me_2SnCl(S\{O\}CMe)$ [4]. Though a thiocarboxylate ion is apparently similar to the corresponding carboxylate ion its ligational abilities are quite different. A carboxylate ion is well known to get chelated with organotin moieties and a large number of molecules with aggregated structures have been reported [5]. On the other hand, organotin thiocarboxylates characterized by X-ray crystallography show that these are monomeric discrete molecules [6,7]. Further, the organotin carboxylates are usually moisture sensitive and undergo hydrolysis under ambient conditions [8]. By contrast, the thiocarboxylates are stable and hydrolytic reactions are very slow [4].

Here, we report the synthesis and structural characterization of a diorganotin thiocarboxylate. We have also attempted to prepare anionic diorganotin thiocarboxylates in view of the fact that anionic complexes of Sn(II) and diorganotin(IV) are well known, respectively, with thiocarboxylate [9] and carboxylate ligands [8], however, no anionic organotin complex containing a thiocarboxylate ligand is known till date.

2. Experimental

2.1. Materials and physical measurements

All solvents were purified by standard methods. Dimethyltin dichloride (Sigma–Aldrich) and sodium acetate (Merck) were used as received. Thioacetic acid (Sigma–Aldrich) was distilled prior to use. Elemental analyses were performed using Exeter Model E-440 CHN analyzer. IR spectra were obtained from KBr pellets on a Varian 3100 FT-IR spectrophotometer in the region 400–4000 cm^{-1}. NMR spectra were recorded in $CDCl_3$ on a Jeol AL300 FT NMR spectrometer.

2.2. Synthesis of $Me_2Sn(SC\{O\}Me)_2$ (**1**)

To a stirred solution of Me_2SnCl_2 (0.260 g, 1.18 mmol) in THF (20 mL) were added thioacetic acid (0.180 g, 2.36 mmol) and triethylamine (0.239 g, 2.36 mmol). Stirring was continued for 3 h. The reaction mixture was filtered off and the solvent from the filtrate was evaporated. The residue was extracted with benzene (20 mL) and the compound was isolated by removing the solvent under reduced pressure. Recrystallized from chloroform. Yield = 80%. Anal. Calcd for $C_6H_{12}O_2S_2Sn$: C, 24.01; H, 4.03. Found: C, 24.07; H, 4.06. ^1H NMR (300 MHz, $CDCl_3$): $\delta = 1.03$ (s, 3H, Me–H), $\delta = 2.44$ ppm

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(s, 3H, Me–H), ^{13}C (112 MHz, $CDCl_3$): $\delta = 3.60, 33.22, 206.42$ ppm. ^{119}Sn (112 MHz, $CDCl_3$, Me_4Sn at $\delta = 0$): $\delta = -47.13$ ppm.

2.3. Attempted synthesis of $[Me_4N][Me_2Sn(SC\{O\}Me)_3]$

To a stirred solution of Me_2SnCl_2 (0.312 g, 1.43 mmol) in chloroform (20 mL) were added thioacetic acid (0.323 g, 4.25 mmol), triethylamine (0.429 g, 4.24 mmol) and tetramethylammonium chloride (0.155 g, 1.41 mmol). The reaction mixture was then stirred overnight. The solvent from the reaction mixture was evaporated under reduced pressure and the residue was extracted with ~10 mL of benzene. Residue obtained on drying the benzene solution was recrystallized from chloroform and found (on the basis of elemental analysis and ^1H NMR spectrum) to be $Me_2Sn(SC\{O\}Me)_2$.

2.4. Attempted synthesis of $[Me_4N][Me_2Sn(SC\{O\}Me)_2(O_2CMe)]$

To a stirred solution of $Me_2Sn(SC\{O\}Me)_2$ (0.136 g, 0.454 mmol) in chloroform (20 mL) were added sodium acetate (0.037 g, 0.454 mmol) and tetramethylammonium chloride (0.049 g, 0.454 mmol). The reaction mixture was then stirred overnight. The insolubles were separated by filtration. The filtrate on standing for 2–3d yielded colorless crystals of $(Me_2SnS)_3$ (**2**). Yield = 60%. Anal. Calcd for $C_6H_{18}S_3Sn_3$: C, 13.28; H, 3.34. Found: C, 13.30; H, 3.34.

2.5. X-ray structure determination

X-ray diffraction data were collected on an Enraf Nonius Kappa CCD diffractometer operating with Mo Kα radiation in the hemisphere mode and were reduced by using the program SMART [10]. The SHELX system of programs [11] was used for structure solution and refinement. The crystallographic data for **1** are given in Table 1.

Table 1
Crystallographic data for **1**.

Empirical formula	$C_6H_{12}O_2S_2Sn$
Formula weight	298.97
Crystal system	Triclinic
Lattice parameters	
a (Å)	6.742(1)
b (Å)	8.791(2)
c (Å)	10.240(2)
a (°)	81.85(3)
b (°)	73.21(3)
c (°)	73.08(3)
V (Å^3)	549.1(2)
Space group	$P\bar{1}$
Z	2
ρ(calc) (g/cc)	1.808
λ (Mo Kα) (mm^{-1})	0.71073 Å
F(0 0 0)	292
Abs. coeff. (μ)	2.665
Temperature (K)	200
$2\theta_{max}$ (°)	54.88
Refl. limits	$-8 < h < 8$
	$-11 < k < 11$
	$-12 < l < 13$
Refl. coll.	2521
No. obs. ($I > 2\sigma(I)$)	2304
No. of parameters	101
Goodness of fit	1.055
Max. shift in last cycle	0.000
Residuals: R_1 and wR_2	0.0227 and 0.0558
Absorption corr. max/min	0.7452/0.5431
Largest peaks in final diff. map (e$^-$/Å^3)	0.79, −0.46

2.6. Theoretical calculations

Density functional calculations at B3LYP level were performed with GAUSSIAN 03W set of programs [12]. The effective core potential standard basis set LANL2DZ was used for all the atoms.

3. Results and discussion

When dimethyltin dichloride was treated with thioacetic acid and triethylamine in 1:2:2 stoichiometric ratio, the expected product dimethyltin bis(thioacetate), $Me_2Sn(SC\{O\}Me)_2$ (**1**) was obtained in high yields. It is known that when a bis-carboxylate, $R_2Sn(O_2CMe)_2$ is treated with another mole of acetate salt, the corresponding anionic complex $[R_2Sn(O_2CMe)_3]^-$ is obtained [8]. However, on the one hand, when **1** was treated with sodium acetate in equimolar proportions the product was not the expected anionic complex but the cyclic dimethyltin sulfide, $(Me_2SnS)_3$ [4]. On the other hand, a reaction of Me_2SnCl_2 with thioacetate ligand even in 1:3 molar ratio ended with the formation of **1** and the desired anionic complex $[Me_2Sn(SC\{O\}Me)_3]^-$ was not obtained.

$$Me_2SnCl_2 + 2(\text{or } 3)\ MeC\{O\}SH \overset{2Et_3N}{\rightarrow} Me_2Sn(SC\{O\}Me)_2$$
$$Me_2Sn(SC\{O\}Me)_2 + NaO_2CMe \rightarrow (Me_2SnS)_3$$

3.1. Theoretical calculations

To understand these differences in reactivity of $Me_2Sn(O_2CMe)_2$ and $Me_2Sn(SC\{O\}Me)_2$ we have performed density functional calculations [13]. The structure of $Me_2Sn(O_2CMe)_2$ has been fully optimized while that of **1** was obtained from the X-ray coordinates for the calculations. The calculated NBO [14] charges on different atoms of **1** and the corresponding acetate, $Me_2Sn(O_2CMe)_2$ are given in Fig. 1. A high positive charge on the tin atom in the acetate compound is responsible for its reaction with another molecule of acetate ion. Expectedly, in **1** the charge on Sn atom is comparatively less owing to its bonding with highly polarizable sulfur atoms. Additionally, the steric bulk of the sulfur atoms possibly also hinders the closer approach of sulfur atom of the third thioacetate ligand. An acetate ligand, however, takes an entirely different route and attacks the carbonyl carbon of the thioacetate groups [4].

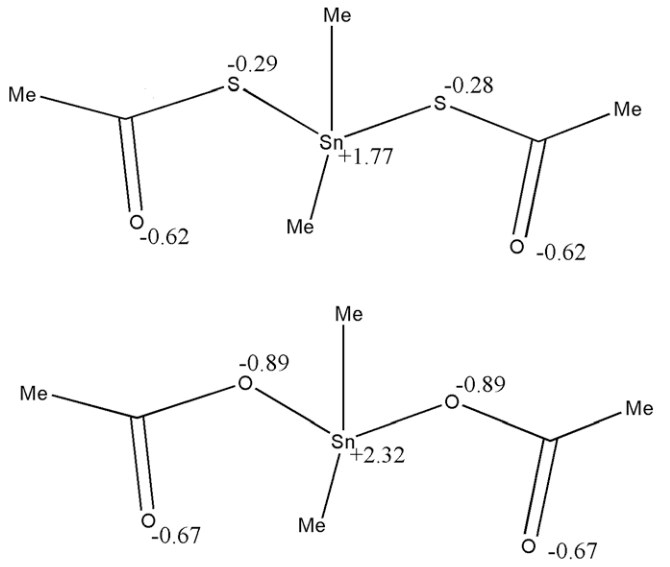

Fig. 1. Calculated (NBO) charges on various atoms of $Me_2Sn(O_2CMe)_2$ and $Me_2Sn(SC\{O\}Me)_2$.