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Synthesis of a one-dimensional coordination polymer containing pendant hydrosulfide groups†

Jyotsna Chaturvedi,[a] Subrato Bhattacharya*[a] and M. Nethaji[b]

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In view of the recent interest in compounds containing M–SH units, an organotin hydrosulfide compound, $Me_2Sn(SH)(O_2CMe)$ (**1**) was prepared by controlled hydrolysis of the diorganotin thioacetate. Under similar mild hydrolytic conditions the corresponding benzoate could not be isolated. Instead, the thiobenzoate complex, $Me_2Sn(SOCPh)_2$ (**3**) was obtained in excellent yields indicating that there was no hydrolysis. Both **1** and **3** were characterized by X-ray crystallography. Some properties of the polymeric compound **1**, such as spectral, electrical conductivity and NLO response were also studied. The reactivity and properties were explained using density functional calculations.

Introduction

Coordination polymers built up from organic ligands and inorganic moieties have developed into an important class of solid-state materials. Such materials often form porous metal–organic frameworks (MOFs).[1–6] Over the past few years MOFs have attracted attention in view of their potential for the design of multifunctional materials.[7,8] Though extensive efforts have been devoted to the preparation of new oxygen-based MOFs,[9] analogous sulfur based materials are scanty in the earlier literature. Such materials are expected to be promising candidates for the integration of porosity with electronic and/or optical properties.[6] Metal complexes containing hydrosulfido ligands have, however, recently been used as precursors for metallorganic frameworks and early-late heterobimetallic complexes.[10]

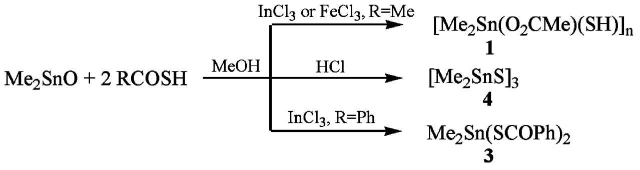
Hydrosulfido complexes of the main group metals are scarce. A monomeric aluminium compound with two terminal SH groups[11] have been prepared by Roesky *et al.* which they have lithiated[12] and very recently utilized in synthesizing bimetallic complexes.[13]

Roper *et al.* have stabilized a terminal Sn–SH moiety for the first time by adequate steric protection using bulky ligands.[14] We have very recently, reported our studies on various hydrolytic reactions of a diorganotin thioacetate with the hope of preparing organotin hydrosulfides.[15] However, all of our attempts were unsuccessful. In this paper we report on a novel route for the synthesis of a one dimensional organotin polymer containing pendant SH groups.

Results and discussion

Syntheses

As described already our recent attempts to prepare hydrosulfide complexes of organotin(IV) by hydrolyzing diorganotin thioacetate under neutral/basic media were unsuccessful. Now we have attempted to carry out the hydrolysis in acidic medium. A reaction of Me_2SnO with thioacetic acid was performed to prepare $Me_2Sn(SOCMe)_2$ which was then treated with dil. HCl in equimolar proportions in methanol. The reaction product was the well known trimeric diorganotin sulfide, $(Me_2SnS)_3$. In order to make the hydrolytic conditions milder we then tried to carry out the complex formation reaction in the presence of a Lewis acid. Interestingly, the reaction was found to take a different route and a complex with the desired functionality was formed (Scheme 1).



Scheme 1

A reaction of Me_2SnO and thioacetic acid in the presence of a Lewis acid such as $InCl_3$ or $FeCl_3$ in methanol resulted in **1**. The plausible mechanism is displayed in Scheme 2. Possibly, the reaction of dimethyltin oxide with thiocarboxylic acid is a step wise one and the initial steps are the same in both cases (HCl catalyzed/Lewis acid mediated). In the first step dimethyl(hydroxo)tin thioacetate is formed. The presence of an acid in (HCl or In^{3+}) induces a partial positive charge on the carbonyl carbon (of the thioacetate group) which is then attacked by the hydroxyl group leading to the formation of dimethyl(hydrosulfido)tin acetate (in the case where a Lewis acid is used). However, in the presence of HCl, deprotonation of acetic acid (*step iii*) is not favored and Sn–S–Sn bonds are formed resulting in the trimeric dimethyltin sulfide (**4**). Formation of Sn–S–Sn bonds is in fact, a general problem associated with the preparation of hydrosulfido complexes. Mononuclear hydrosulfido complexes initially formed are further aggregated leading to the formation of polynuclear sulfido complexes or insoluble metal sulfides.[14,16,17] Encapsulation by sterically hindering bulky groups is expected to provide sufficient inertness of the tin centre so that the decomposition in the form of tin-sulfide should be avoided and the Sn–SH unit should be obtainable.[18] In compound **1** the

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[a] *Department of Chemistry, Banaras Hindu University, Varanasi, 221005, India. E-mail: s_bhatt@bhu.ac.in*
[b] *Department of Inorganic and Physical Chemistry, Indian Institute of Science, Bangalore, India*

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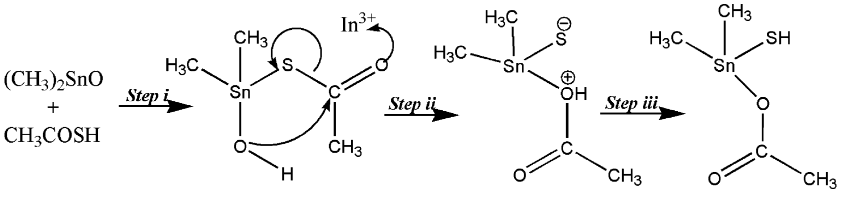


Scheme 2

acetate ligand bridges between two tin centers forming a linear chain which is sufficiently rigid to disallow formation of Sn–S–Sn linkages.

On the other hand, when thiobenzoic acid was used in place of thioacetic acid the corresponding bis-thiobenzoate (**3**) is formed which is quite inert and there is no effect on addition of $InCl_3$. We have tried to follow the reactions by ^1H NMR spectroscopy. When a solution of thioacetic acid was added to Me_2SnO the resulting reaction mixture showed two signals due to the methyl groups of Me_2Sn and SCOMe moieties respectively at 0.96 and 2.41 ppm. The intensity of the signal at 0.96 ppm was observed to increase with time as expected (Me_2SnO has very low solubility in methanol while the product is quite soluble). After attainment of equilibrium (in ~1.5 h) addition of $InCl_3$ resulted in the appearance of a small peak due to the SH proton at 2.01 ppm whose intensity increased with time until equilibrium was reached. On the other hand in the case of the reaction with thiobenzoic acid no change was observed before and after the addition of $InCl_3$.

To understand the differences in reactivity of thioacetate and thiobenzoate ligands we have carried out density functional calculations on $Me_2Sn(OH)(SOCMe)$ (**2A**) and $Me_2Sn(OH)(SOCPh)$ (**2B**). In the optimized structures the thioacetate is monodentate through sulfur ($Sn\cdots O = 2.92$ Å) while the thiobenzoate ligand is bidentate ($Sn–O = 2.52$ Å) respectively in **2A** and **2B**. However, the NBO charges[19] on various atoms of **2A** are not much different from those on the corresponding atoms of **2B**. The difference in reactivity of the compounds originates from the nature and energy levels of the lowest unoccupied orbitals (LUMO) (Fig. 1).

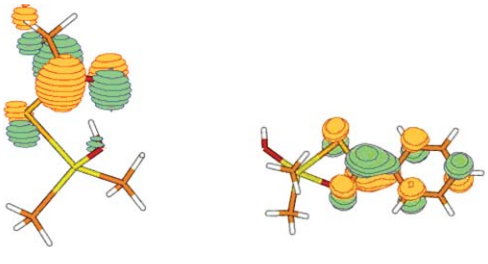
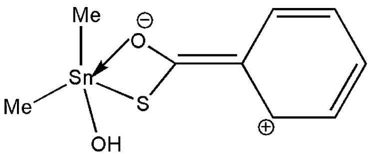


Fig. 1 LUMO of **2A** and **2B** (Orbitals plotted at a contour value of 0.05).

In **2A** the LUMO is CO π* which is attacked by the OH group as shown in Scheme 2. On the other hand the same orbital (CO π*) is of much higher energy (LUMO +5) in **2B** because of the stabilization of the CO π orbital. The LUMO in **2B** is the Ph–C π orbital which is quite low lying and indicates the contribution of a canonical form with the Ph=C bond[20] (Scheme 3). The same also supports the stabilization of the CO π orbital by conjugation. Thus in **2B** there is no orbital at the carbonyl carbon of suitable energy and symmetry which could be attacked by the OH group.



Scheme 3

Solid state structures of $Me_2Sn(SH)(O_2CMe)$ (1) and $Me_2Sn(SOCPh)_2$ (3). The complex $Me_2Sn(SH)(OOCMe)$ (**1**) crystallizes in the orthorhombic crystal system with the *Pnma* space group. The thermal ellipsoid plot is given in Fig. 2.

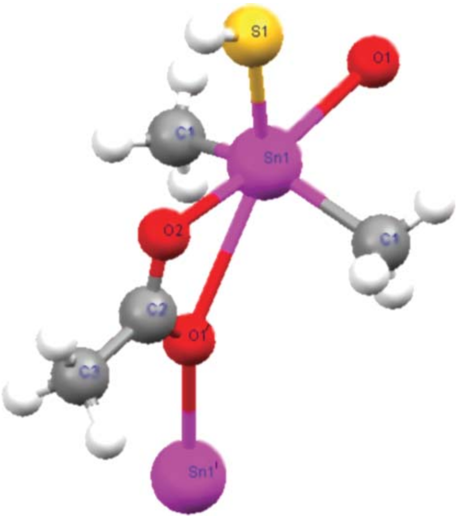


Fig. 2 Thermal ellipsoid plot of **1** (two tin atoms are shown to clarify bridging by the O1′ atom). Selected metric data: Sn1–C1 2.098(4), Sn1–S1 2.37(1), Sn1–O1 2.392(4), Sn1–O2 2.154(3), Sn1–O1′ 2.779, C1–Sn1–C1 140.4(2), C1–Sn1–O2 108.75(12), C1–Sn–O2 97.22(13).

The Sn1 atom appears to be six-coordinated, however, the geometry around the metal centre is highly deviated from that of a regular octahedron and closer to a trapezoidal bipyramid due to the small bite angle of the acetate ligand. A large number of diorganotin compounds have skewed trapezoidal bipyramidal geometry around the tin center.[21] A recent study[22] using the Cambridge structural database has revealed that in skew trapezoidal molecules the *cis*- and *trans*-C–Sn–C angles range between 102–110° and 180–145° respectively. While the same in the transition state of the *cis–trans* pathway ranges between 120° and 134°. The O–Sn–O angle in frozen transition states are > 160° < 170°.[22] Since the C1–Sn–C1 angle in **1** is 140.4°, and the O1–Sn1–O1′ angle is 138.85° the geometry of **1** fits into none of these three categories.

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The acetate ion exhibits an asymmetric mode of bonding with a very long Sn1–O1′ bond (2.779 Å). This is much longer than the sum of the covalent radii of Sn and O (2.14 Å) but quite shorter than the sum of their van der Waals' radii (3.69 Å). It may be noted that almost all diorganotin carboxylates exhibit asymmetric bonding of the carboxylate ligands. The longer Sn–O bond usually ranges from 2.45 to 2.55 Å.[23–26] Amongst the monomeric diorganotin carboxylates, the longest Sn–O bond has been reported to be 2.696 Å in the case of hexamethylenetin *bis*(chloroacetate).[27] A still longer Sn–O1′ distance in **1** is due to the fact that O1′ has a closer contact (2.392 Å) with another tin atom forming a bridge between two Sn centers. The structure is thus comparable to the polymeric tin carboxylates.[28] A better description of the geometry therefore, can be made by considering the longer Sn–O bond as a weak interaction only. The geometry around tin can be described as trigonal bipyramidal. The O1–Sn–O2 angle being 170.24° places the two oxygen atoms at the axial positions. Sn1 is slightly tipped above (by only 0.179) the plane constituted by C1, C1′ and S1 atoms. The three O atoms, S1 and Sn1 lie in a plane which is perpendicular to the C1, C1′, S1 plane. The deviation in the C–Sn–C angle from the expected value of 120° may be attributed to the capping of the C1–C2–O2 face by the O1 atom.

It is interesting to note that all the O–Sn–OC units lie in the same plane constructing a straight polymeric chain (Fig. 3). The nearest intermolecular Sn–S distance in a chain is 4.438 Å while that between the two chains is 5.325 Å.

Compound **3** crystallizes in discrete molecular units (Fig. 4) It may be noted that the only other structurally characterized tin(IV) *bis*(thiocarboxylate) which we have reported earlier[29] has a distorted octahedral environment around tin. The two thiobenzoate ligands in **3** bind bidentately with Sn–O distances of 2.649 Å and 2.720 Å which are significantly longer than the corresponding distance in the earlier reported $Cl_2Sn(SOCPh)_2$.[29] The difference in the two Sn–O bond lengths in **3** arises possibly due to the weak intermolecular Sn···O interaction. (Fig. 5).

Though the geometry around tin in **3** may also be described as skewed trapezoidal bipyramidal, the two thiocarboxylates groups are not really coplanar (interplanar angle is 4.44°). Moreover, all the four C–Sn–S angles range between 105.26° and 109.44° which are very close to the ideal tetrahedral angle. However, the C–Sn–C angle is quite wider than the tetrahedral angle but does not fit into the skewed trapezoidal model.[22] The deviation of the C–Sn–C angle is also due to the weak Sn···O bonds capping the two faces of the tetrahedron.[26,30]

Electronic absorption spectra

The electronic absorption spectra of **1** and **3** were recorded in DMSO and $CHCl_3$ solutions respectively. In the case of **1** absorption bands were observed at 304 nm and 238 nm, while in the case of **3** these bands arise at 300, 264 and 212 nm. Such bands may arise because of the intra-ligand or ligand to metal charge transfers. Time-dependent density functional calculations reveal that in the case of **1** the calculated absorptions at 308 nm and 249 nm arise because of the ligand to metal charge transfers involving HOMO-4 to LUMO and HOMO to LUMO of the molecule (Fig. 6). In the case of **3** the calculated absorptions at 304, 267 and 214 arise due to intra-ligand n→π* transitions involving HOMO-2 to LUMO+1, HOMO to LUMO+1 and HOMO-1 to LUMO+3 of the molecule (Fig. 7).

Non-Linear optical properties

In comparison with the standard *p*-nitroaniline (29.56×10^{-30} esu) the first static hyperpolarizability in a methanolic solution of **1** was found to be 26.73×10^{-30} esu, thereby revealing a moderate non-linear optical response for this compound. This was further substantiated by theoretical calculations using the finite field perturbation method *i.e.*, by double numerical differentiation of energies. Hyperpolarizability is given by the coefficients in the

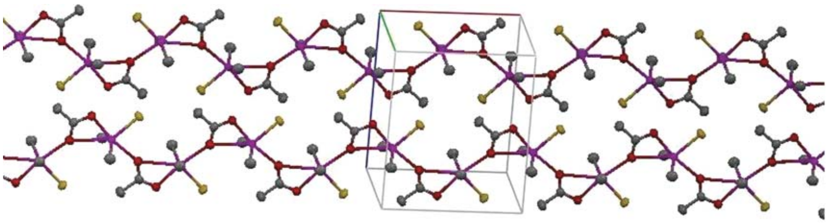

Fig. 3 Orientation of the polymeric chains of **1** in the lattice.

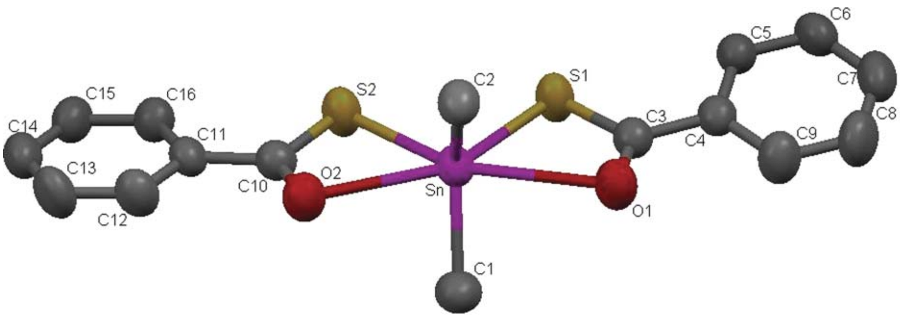

Fig. 4 Thermal ellipsoid plot of **3**. Selected metric data: Sn–C1 2.112(4), Sn–S1 2.4918(12), Sn–S2 2.4923(12), Sn–O1 2.720, Sn–O2 2.649, C1–Sn–C2 129.62(19), C1–Sn–S1 109.44(14), S1–Sn–S2 90.68(4), O1–Sn–O2 149.61, O1–Sn–S1 59.37, O1–Sn–S2 1.

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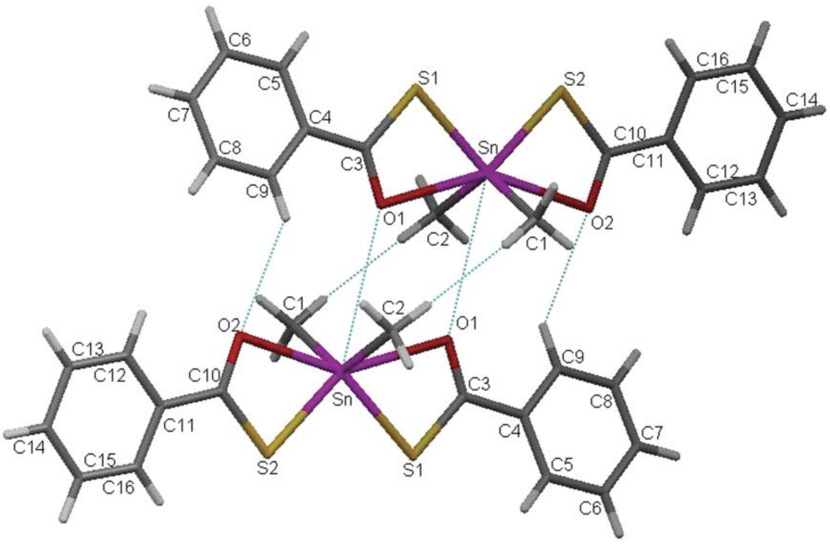

Fig. 5 A pair of molecules of **3** showing intermolecular interactions.

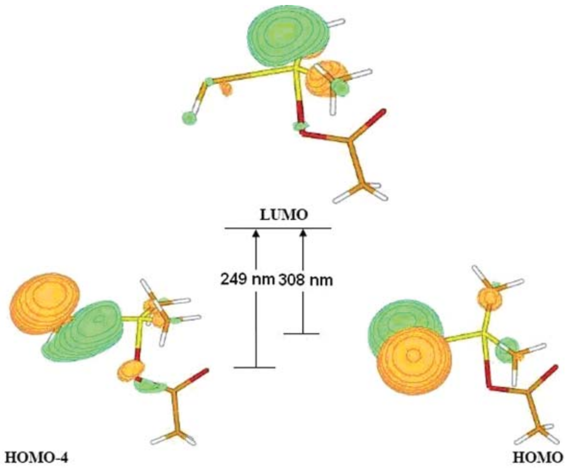

Fig. 6 Selected orbital transitions for **1** (orbital contour value 0.05).

Taylor series expansion[31] of the energy in the external electric field. If the external electric field is weak and homogeneous the expansion becomes:

$$E = E^{\circ} - \mu_{\alpha}F_{\alpha} - 1/2\alpha_{\alpha\beta}F\alpha F_{\beta} - 1/6\beta_{\alpha\beta\gamma}F_{\alpha}F_{\beta}F_{\gamma} + \ldots\ldots.. \quad (1)$$

Where E° is the energy of unperturbed molecules, F_{α} is the field of origin, μ_{α}, $\alpha_{\alpha\beta}$ and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability and the first hyperpolarizability respectively. The mean first hyperpolarizability is defined as,[32]

$$\beta_0=(\beta_x{}^2+\beta_y{}^2+\beta_z{}^2)^{1/2},$$

where the β_x, β_y and β_z components can be described by,

$$\beta_x= \beta_{xxx} +\beta_{xyy} +\beta_{xzz}$$

$$\beta_y= \beta_{yyy} +\beta_{yxx} +\beta_{yzz}$$

$$\beta_z= \beta_{zzz} +\beta_{zxx} +\beta_{zyy}$$

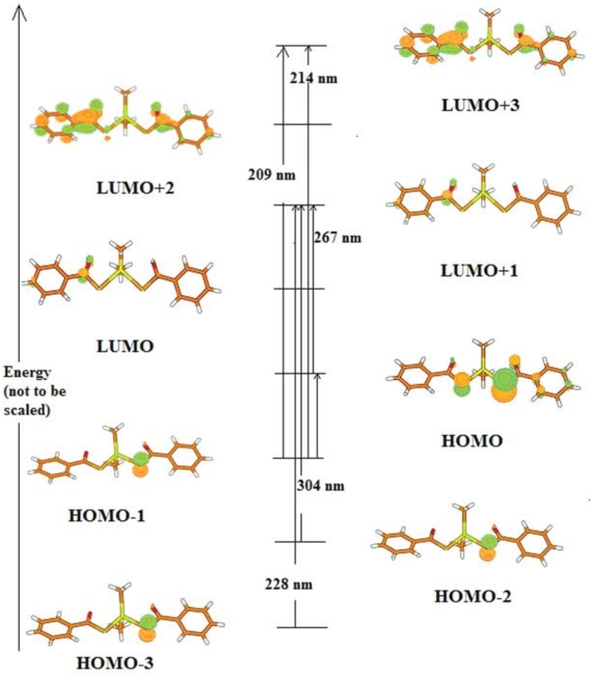

Fig. 7 Selected orbital transitions for **3** (orbital contour value 0.05).

The solvent parameters used were of methanol. The β_o value calculated for the monomeric unit **1** was found to be 5.02×10^{-30} esu in methanol but the same for a trimeric chain was calculated to be 409.41×10^{-30} esu. It is interesting to note that the monomeric unit of **1** does not possess a chiral center, however, the presence of the lone pair of electrons on the oxygen atoms are rather delocalized over the molecular skeleton which is possibly responsible for the NLO response. In the case of **3** the molecules are discrete (except for the weak O–Sn interactions which couples up two molecules together) and the calculated β_{vec} value was only 4.72×10^{-30}esu.

Computed hyperpolarizability values of **1** and **3** and its components are shown in Table 1. Compared with that of *p*-nitroaniline (*p*NA) computed at the same level of theory the trimeric unit of **1**

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Table 1 Computed dipole moment (μ) and hyperpolarizabilities

	System	(μ)	β_x	β_y	β_z	β_0
*p*NA		7.53	−13.70	0.03	0.49	13.72
1	Monomeric	1.57	3.14	1.72	−3.52	5.02
	Trimeric	9.42	350.80	−40.36	207.20	409.41
3		0.85	−0.53	−4.69	−0.056	4.72

showed an excellent first order non linear optical response while in the case of **3** only a weak hyperpolarizability was calculated.

Pressed pellet conductivity

The pressed pellet electrical conductivity value of **1** was determined to be 8.13×10^{-9} S cm^{-1} at room temperature (38 °C) which was increased to 1.14×10^{-7} S cm^{-1} at 60 °C. The variation of electrical conductivity with temperature for complex **1** (Fig. 8) reveals that the compound is a semiconductor with a band gap of 1.01 eV.

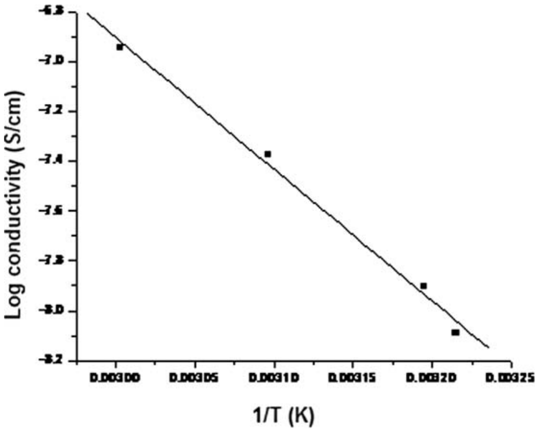

Fig. 8 Plot of log conductivity of **1** *vs* $1/T$.

Experimental

All solvents were of reagent grade and were purified by standard methods.[33] Anhydrous $InCl_3$, thiobenzoic acid (98%) and dimethyltin(IV) oxide (all Aldrich) were used as received. Thioacetic acid (96%, Aldrich) was distilled before used.

IR spectra were recorded using Perkin-Elmer RX-1, FT-IR spectrometer and Varian-3100 FTIR instruments. NMR spectra were obtained using a JEOL AL300 FT NMR spectrometer. Electronic absorption spectra were recorded using a Shimadzu UV-1700 PharmaSpec Spectrophotometer. Pressed pellet electrical conductivity was recorded on a Kiethley-236 source measurement unit by employing a conventional two-probe technique in the temperature range 311–333 K. The first hyperpolarizability of the complex **1** was measured by hyper-Rayleigh scattering using a Q-switched Nd:YAG Laser at 1064 nm.[34,35] The laser beam was focused 2–3 cm away from a cylindrical sample cell placed in front of a monochromator. No collection optics were used. The dispersed second harmonic scattered light signal at 532 nm was collected through the monochromator using a photomultiplier tube, averaged over 512 laser shots and stored in a digital storage oscilloscope. Methanol was the solvent of choice and *p*-nitroaniline was used as the external reference.

Table 2 Crystal data and structure refinement of **1** and **3**

	1	**3**
Empirical formula	$C_4H_{10}O_2S_1Sn$	$C_{16}H_{16}O_2S_2Sn$
M	240.90	423.11
T/K	293	153
Crystal system	Orthorhombic	Monoclinic
Space group	*Pnma*	$P2_1/c$
a/Å	9.310(3)	10.546 (3)
b/Å	7.671(3)	14.516(4)
c/Å	11.045(4)	12.049(4)
β/°	90	107.702(4)
V/Å^3	788.8(5)	1757.2(9)
Z	4	4
μ (Mo-Kα)/mm^{-1}	3.428	1.692
Final R indices	$R_1 = 0.0282$	$R_1 = 0.0370$
[$I > 2\sigma(I)$]	$wR_2 = 0.0651$	$wR_2 = 0.0868$
R indices(all data)	$R_1 = 0.0364$	$R_1 = 0.0399$
	$R_2 = 0.0688$	$R_2 = 0.0882$
GOF on F^2	0.959	1.300

Single crystal X-ray data of **1** and **3** were collected at room temperature on Bruker SMART APEX CCD diffractometers using graphite monochromated Mo*K*α radiation (λ = 0.71073 Å). Data integration and reductions were processed with SAINT+ software.[36] Structures were solved by the direct method and then refined on F^2 by the full matrix least square technique with SHELX-97 software[37] using the WinGX program package.[38] A summary of crystallographic data and the structure solution are given in Table 2.

Computational details

Optimized molecular geometries were calculated using the B3LYP[39,40] exchange–correlation functional. The effective core potential (ECP) standard basis set LANL2DZ was utilized for Sn atoms while the 6-31g** basis set was used for C, H, O and S atoms. The optimized structures of the complexes were used for molecular orbital analyses. The energies and intensities of the 30 lowest-energy spin allowed electronic excitations were calculated using the TD-DFT at the same level of theory with the polarized continuum model (PCM).[41,42] The solvent parameter was that of methanol. The first static hyperpolarizability (β_0) for both the complexes where calculated by using the finite field perturbation method by implementing the PCM model. X-ray coordinates were used for calculation of electronic excitations and hyperpolarizability. Natural bond orbital (NBO) calculations were performed using the LANL2DZ(*d,p*) basis set for all the atoms. All theoretical calculations were performed using the GAUSSIAN 03 W set of programs.[43] Molecular orbital plots were generated using the program MOLDEN.[44]

Synthesis of [$Me_2Sn(OOCMe)(SH)$] (1). To a stirred suspension of dimethyltin(IV) oxide (0.165 g, 1 mmol) in methanol (10 ml) was added a methanolic (10 ml) solution of thioacetic acid (0.152 g, 2 mmol). The reaction mixture was stirred at 18 °C for 30 min. A methanolic solution of $InCl_3$ (0.110 g, 0.5 mmol) was then added and the reaction mixture stirred for 4 h. The solvent was then evaporated under reduced pressure and the residue was extracted with $CHCl_3$ (20 ml). The precipitate was filtered off and solvent

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from the filtrate was evaporated under reduced pressure. The colourless product was dried under vacuum for 2 h. Recrystallized by slow evaporation of a dilute chloroform solution. (61% yield); Mp: 189 °C. Anal. Calcd for $SnC_4H_{10}O_2S$: C, 19.94; H, 4.18, found: C, 19.67; H, 4.10. ^1H NMR ($CDCl_3$, ppm): 1.19 (6H, Me), 2.45 (3H, Me). IR (KBr, cm^{-1}):1557 *v*(CO), 465 *v*(Sn–O) and 279 *v*(Sn–C).

Attempted synthesis of $Me_2Sn(SH)(O_2CPh)$ 1A [Synthesis of $Me_2Sn(SOCPh)_2$ (3)]. A similar procedure described in the synthesis of **1** was adopted for the synthesis of **1A**. Thiobenzoic acid (0.280 g, 2 mmol) was used instead of thioacetic acid. Elemental analysis of the residue after recrystallizing from chloroform (0.388 g) was found to be in good agreement with the formula $Me_2Sn(SOCPh)_2$. (91% yield) Mp: 143° C. Anal. Calcd for $SnC_{16}H_{16}O_2S_2$: C, 45.42; H, 3.81; found: C, 45.40; H, 3.70. ^1H NMR ($CDCl_3$, ppm): 1.19 (6H, Me), 7.4–8.09 (10 H, Ph) ^{13}C NMR ($CDCl_3$, ppm):4.6 (CH_3), 128–137 (C_6H_5), 201.87 (COS). ^{119}Sn NMR ($CDCl_3$, Me_4Sn, ppm): −76.66. IR (KBr pellet cm^{-1}): 1628 *v*(CO), 1210 *v*(Ph–C), 929 *v*(C–S), 362 *v*(Sn–S).

Attempted preparation of 1 using HCl [Synthesis of $(Me_2SnS)_3$ (4)]. A similar procedure described in the synthesis of **1** was adopted. However, instead of $InCl_3$, HCl (0.1 N, 0.1 mL) in 10 mL methanol was used. Elemental analysis of the residue after recrystallizing from chloroform (0.321 g) was found to be in good agreement with the molecular formula $(Me_2SnS)_3$. (59.2% yield) Mp: 147 °C (reported: 148 °C). Anal. calcd for $Sn_3C_6H_{18}S_3$: C, 13.28; H, 3.34; found: 12.97; H, 3.22; ^1H NMR ($CDCl_3$, ppm) 0.8 (18H, Me). ^{13}C NMR ($CDCl_3$, ppm) 4.77. ^{119}Sn NMR ($CDCl_3$, Me_4Sn, ppm) 134.22.

NMR studies to explore reaction pathways

To 0.0010 g of dimethyltin oxide in an NMR tube a solution of thioacetic acid (0.9 µL) in 0.5 mL CD_3OD was added. ^1H NMR data was collected after 30 min. Two more spectra of the same reaction mixture were recorded each with a gap of 1 h. A very small quantity of anhydrous indium trichloride was then added to the NMR tube and ^1H NMR spectra were recorded after 15 min, 1 h and 4 h.

The same experiment was repeated using thiobenzoic acid in place of thioacetic acid.

Conclusions

An organotin hydrosulfide compound, $Me_2Sn(SH)(O_2CMe)$ (**1**) was prepared by hydrolysing organotin thioacetate under controlled conditions. Under similar mild hydrolytic conditions the corresponding benzoate could not be isolated. Instead, the thiobenzoate complex, $Me_2Sn(SOCPh)_2$ was obtained in excellent yield indicating that there was no hydrolysis. The reaction mechanisms could be explained on the basis of DFT calculations. X-ray crystallography revealed a one dimensional polymeric structure of $Me_2Sn(SH)(O_2CMe)$. As a result of the polymeric structure the compound showed an NLO response as well as semiconducting behaviour (in the solid state) with a band gap of 1.01 eV.

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