Synthesis and Structural Studies of Organotin(IV) and Organolead(IV) Thiophene-2-thiocarboxylate

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A few organotin(IV) ([R_2SnCl_2], [R_3SnCl]; R = Me, Ph, *n*Pr, or *n*Bu) and organolead(IV) ([Ph_2PbCl_2], [Ph_3PbCl]) compounds that contain the thiophene-2-thiocarboxylate ligand have been synthesized and characterized by ¹H, ¹³C, ¹¹⁹Sn NMR;

Introduction

Organotin compounds are well known for their synthetic applications^[1] and toxic effects.^[2] A number of studies have been carried out on the structures, bonding patterns, and reactivities of these compounds that contain oxygen or sulfur ligands.^[3] A number of papers related to studies focused on organotin compounds that contain anisobidentate S,Odonor ligands are also available.^[4] Compounds that contain thiocarbamate^[5] and thio-β-diketonate^[6] ligands were reported some time ago. Our early studies with thiocarboxylate ligands have revealed that the ligand may bind to the organotin center either monodentately through S or bidentately by using both O and S atoms.^[7] Tani et al. have studied the extent of Sn–O overlap in triphenyltin thiobenzoate in which the primary bonding of the ligand is essentially through the S atom.^[8] Very recently, we have reported studies on structures of a few organotin thiocarboxylates and their reactivities.^[9,10] It was observed that both structure and reactivity of organotin thiocarboxylates depend not only on the organyl groups (on Sn) but also on the terminal R groups of the RCOS⁻ ligands.^[10] Although we have been able to establish effects of these factors, in a few cases more structural data are essential before any generalization can be made.^[7,10]

We thought it would be worthwhile to study the effect of terminal groups on bonding on organotin(IV) by systematically changing the number/nature of organyl groups. Further, a comparison with analogous organolead compounds would shed light on the role of the metal atom. We report herein the synthesis and structures of a few di- and triorganotin and -lead compounds that contain a new ligand,

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FTIR; and UV/Vis spectroscopy. The molecular structures of some of the compounds were studied by single-crystal X-ray diffraction. Structures and electronic transitions have been explained on the basis of DFT calculations.

thiophene-2-thiocarboxylate. [While compiling our results, a paper appeared that described the synthesis of this ligand (by a different route) and its complexes^[31]]. The thiophene ring, being aromatic in nature, is expected to behave like a phenyl group in which the bidentate bonding mode is a little more favored as compared with the alkyl group of the thiocarboxylate ligand due to the contributions of dianionic canonical forms (as shown in Scheme 1.)



Scheme 1. Dianionic canonical of the thiobenzoate group.

Further, the presence of a sulfur atom at the peripheral position is expected to influence the crystal and molecular structures. In light of the thiophilicity of organotin and -lead centers, one may look for one or more possible modes of bonding of the thiocarboxylate ligand (Scheme 2).



Scheme 2. Possible bonding modes of thiophene-2-thiocarboxylate.

Results and Discussion

Syntheses and Characterization

All the complexes were synthesized by a simple one-step reaction between sodium thiophene-2-thiocarboxylate and organotin or -lead chlorides in methanol (Scheme 3). The compounds were isolated in high yields and were found to be quite stable under ambient conditions.



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Scheme 3. Synthetic route for organotin and -lead compounds.

The IR spectra showed a strong absorption between 1609 and 1557 cm⁻¹ due to C=O stretching vibrations. Two other strong bands were observed in the 1196-1226 and 1045-1053 cm⁻¹ regions. These two correspond to v(th-C) and v(C-S) vibrations, respectively. The infrared spectral features that corroborate the bonding modes of the ligand have been studied in the case of monoorganotin thiobenzoates.^[7] Shifts in the positions of C=O, Ph-C, and C-S bond stretching vibrations can be used as a diagnostic tool to detect the coordination mode of the ligand. A CO stretching band observed around 1600 cm⁻¹ offers strong evidence for the existence of a double bond between the two atoms. A lowering in this frequency is indicative of M···O bonding. Similarly, from the v(C-S) band, an inference can be drawn about the nature of the C-S bond; on chelation, the v(C-S) band shifts to a higher wavenumber. Furthermore, the v(Ph-C) absorption around 1200 cm⁻¹ is also indicative of monodentate attachment of the ligand, since, on chelation, this band shifts to a higher frequency as has been observed in [Cl₂Sn(SOCPh)₂].^[7] From the spectroscopic data of compounds 1-4, one may conclude that bonding of the ligands in these complexes is mainly through the sulfur atoms; however, in 1a-c and 3 significant M···O interactions are expected.

In the ¹H NMR spectrum of thiophene-2-thiocarboxylic acid, two doublets (δ = 7.67, 7.75 ppm) and a triplet (δ = 7.13 ppm) were observed due to the thiophene ring protons, which showed small shifts after complexation. Similarly, the four signals observed due to thiophene carbon atoms (δ = 128.03, 133.88, 134.09, 141.54 ppm) in the ¹³C NMR spectrum of the free acid were also observed in the complexes. One would expect the signals of the carbon atoms at the 2- and 5-positions of the thiophene ring to show smaller downfield shifts relative to those of the ones in the free acid if the thiophene sulfur atom is involved in bonding with the metal atom. Small changes were observed in the δ values of C-2 of the ring, but the signal of the carbon atom at position 5 appeared at the same position. The shift in the former case may also arise due to bonding with the metal atom through the S/O-donor atoms. As expected, significant changes in the chemical-shift values of the COS carbon atom were noticed in the complexes when compared to that of the free acid ($\delta = 182.18$ ppm). From these data, it appears that there is no significant bonding between the metal atom and the ring sulfur atom.

¹¹⁹Sn NMR spectral studies were carried out to understand the structure of compounds **1a–1c**. The single resonance observed in the spectra of all the three compounds rules out any possibility of the existence of more than one isomer in solution. The peak at $\delta = -190.10$ ppm in the spectrum of **1c** indicates a five-coordinate environment around the tin center.^[11] ¹¹⁹Sn signals for four-coordinate compounds are observed in the range of $\delta = +200$ to -60 ppm.^[11] Signals at $\delta = -69.68$ and -77.71 ppm, respectively, in the cases of **1a** and **1b** indicate higher (>4) coordination numbers around the tin atom, which is possibly due to the existence of weak Sn–O bonds (the primary bonding of ligands is through the sulfur atoms).

This could be further substantiated by variable-temperature (VT) ¹¹⁹Sn NMR spectroscopic studies (Table 1). At -30 °C, **1b** showed a signal at $\delta = -83.77$ ppm, which shifted downfield on an increase in the temperature. Similar temperature-dependent shifts in the NMR spectroscopic signals have also been observed for **1a** and **1c**. Such shifts in ¹¹⁹Sn NMR spectroscopic signals evince weakening of Sn–O interactions with an increase in temperature.

Table 1. Variable-temperature ¹¹⁹Sn NMR spectroscopic data of **1a–1c**.

Compound	<i>T</i> [°C]	$\delta(^{119}\text{Sn})$ [ppm]
1a	+24	-69.66
	+46	-64.40
1b	-30	-83.77
	0	-80.10
	+24	-77.71
	+46	-73.52
1b	+24	-190.10
	+46	-186.76

Crystal and Molecular Structures

All the complexes except 2a (liquid) and 2b (insoluble solid) have been characterized by single-crystal X-ray diffraction. Suitable single crystals of 1a were grown from a chloroform solution by layering with *n*-hexane. The compound crystallized in the triclinic system with *P*1 space group. A molecular structure and atomic labeling scheme of 1a are depicted in Figure 1.



Figure 1. Molecular structure of 1a.

Selected bond lengths and angles are given in Table 2. There are two molecules in the unit cell that lie almost perpendicular to each other (the interplanar angle between the two $C_2S_2O_2Sn$ units is 81.54°). The central tin atom is sur-



rounded by two carbon, two sulfur, and two oxygen atoms. The thiocarboxylate ligands are bonded to the metal atom mainly through the S atoms and have longer distances between the oxygen and tin atoms. The average Sn–O distance 2.778 Å is significantly longer than the corresponding distances in the earlier reported molecule [Cl₂Sn(SCOPh)₂] with distorted octahedral structure. The geometry around Sn1 may be described as skewed trapezoidal-bipyramidal. The C11–Sn1–C12 angle is 125.5(3)°, which corresponds to the geometry of the transition state in the *cis/trans* pathway of the skewed trapezoidal-bipyramidal structures.^[12] However, the O1-Sn1-O2 angle (153.49°) is quite smaller than that of the transition state (160-170°), and the two SCO units of two thiocarboxylate groups deviate slightly from planarity (the interplanar angle is 14.74°). Notably, the two thiophene rings are twisted to opposite directions from each

Table 2. Selected bond lengths and angles of the complexes.

Bond	l lengths [Å]			
1a	Sn1–S1	2.467(16)	Sn1-S3	2.470(17)
	Sn1-C11	2.105(6)	Sn1-C12	2.085(6)
	S1-C1	1.745(5)	O1–C1	1.227(6)
	C1–C2	1.469(7)		
1b	Sn1–S1	2.473(3)	Sn1–S1	2.473(3)
	Sn1–C6	2.136(10)	Sn1–C6	2.136(10)
	S1-C1	1.751(10)	Ol-Cl	1.243(12)
	C1–C2	1.453(13)	G 1 G 2	2 402(7)
Ic	Sn1–S1	2.480(7)	Sn1-S2	2.483(7)
	SnI-CII	2.135(3)	SnI-CI/	2.122(2)
	SI-CI	1.750(5) 1.457(4)	01–C1	1.228(3)
2	C2-CI Db1_S1	1.437(4) 2.574(2)	Db1 62	2 596(2)
3	Pb1 C11	2.374(3) 2.207(10)	P01-32	2.380(3) 2.182(0)
		1.767(10)	01 C1	1.234(14)
	$C^{2}-C^{1}$	1.767(12) 1.456(13)	Ph1-O1	2.743(8)
4	Pb01_S01	2 550(5)	S01-C01	1.751(18)
-	Pb01-C06	2.330(3) 2.189(15)	Pb01-C12	2.202(17)
	Pb01-C18	2.170(15)	O01-C01	1.21(2)
	C01-C02	1.50(2)		
Bond	l angles [°]			
1a	S1–Sn1–S3	88.88(5)	C11-Sn1-S1	112.75(18)
	C12-Sn1-S1	105.43(19)	C11-Sn-C12	125.5(3)
	C1-S1-Sn	189.94(17)	O1C1S1	121.6(4)
	C2C1S1	115.9(4)	O1–C1–C2	122.6(4)
1b	S1–Sn1–S1	87.73(12)	C6–Sn1–S1	108(3)
	C6–Sn1–S1	111.5(3)	C6–Sn1–C6	122.9(8)
	C1–S1–Sn1	90.2(3)	Ol-Cl-Sl	120.3(8)
	C2-C1-S1	117.4(7)	Ol-Cl-C2	122.3(9)
Ic	SI-Sn1-S2	89./3(2)	CII-SnI-SI	10/.22(/)
	CI / - SnI - SI	110.59(7)	CI/-SnI-CII	127.59(9)
	C1-S1-Sn1	87.07(9)	01-01-51	119.4(2) 122.1(2)
3	$S_{1} = 01 - 31$	80.05(0)	C_{11} Pb1 S1	122.1(3) 105.4(2)
3	$C17_Ph1_S1$	108 1(3)	$C17_Pb_C11$	103.4(2) 133.8(4)
	C1-S1-Pb1	87 7(3)	01-C1-S1	120 5(8)
	$C_{2}-C_{1}-S_{1}$	117.2(8)	01 - C1 - C2	122.3(10)
	01–Pb1–O2	153.1(2)	S1-Pb1-O1	58.90(18)
	S2-Pb1-O1	143.63(18)	C11-Pb1-O1	88.1(3)
	C17–Pb1–O1	88.0(3)		
4	C01-S01-Pb01	98.7(6)	C06-Pb01-S01	105.4(4)
	C12-Pb01-S01	108.7(4)	C18-Pb01-S01	92.7(4)
	C06-Pb01-C12	118.0(6)	C06-Pb01-C18	112.6(6)
	C12-Pb01-C18	115.8(6)	O01-C01-S01	123.2(4)
	C02-C01-S01	115.4(11)	O01-C01-C02	121.4(14)

other with an interplanar angle of 44.92°. This indicates that the delocalization of the thiophene π -electrons does not extend up to the donor atoms (O/S) by conjugation, and as a result the bidentate binding of the ligand is not favored.

An alternative and better description of the geometry thus can be made by considering the Sn–O distances as nonbonding interactions only. The Sn1 atom is tetrahedrally surrounded by two sulfur and two carbon atoms. The C–Sn–S bond angles (which vary between 105.43 and 112.88°) are very close to the ideal tetrahedral angle. The large deviation of the C–Sn–C angle is due to the capping of the CCS faces by the oxygen atoms.^[13]

There are two types of intermolecular hydrogen bonds, one between a methyl hydrogen atom and the thiophene sulfur atom (2.985 Å) along the *b* axis and the other between a hydrogen atom of the thiophene ring and a carbonyl oxygen atom (2.654 Å). Sulfur, which has less electronegativity, forms weaker hydrogen bonds relative to oxygen, and the C–H donor strength is known to vary along the order $C_{(sp)}$ –H > $C_{(sp^2)}$ –H > $C_{(sp^3)}$ –H.^[14] The S···H $C_{(sp^3)}$ distance in the present case indicates a strong hydrogen bond. Due to two types of hydrogen bonding, it acquires a sheetlike structure along the *a* axis (Figure 2).



Figure 2. Packing of 1a along the *a* axis showing hydrogen bonds.

Molecular structures and atomic labeling schemes of 1b and 1c are depicted in Figure 3. Both compounds 1b and 1c have similar structures. Notable features include better planarity of the two thiocarboxylate groups relative to that in 1a. The SCO units are rather coplanar, whereas the twists between the thiophene rings are less significant (5.40° in 1b and 10.68° in 1c). Both O···H- and S···H-type hydrogen bonds are present in 1b; however, these are in the same direction. As a result, the molecules form long strips along the *b* axis (Figure 4) Apart from the H···O hydrogen bonding, there is significant CH···π(phenyl) interaction in 1c (Figure 5).

Compound **3** is isostructural to **1c** (Figure 6). Small differences in bond lengths and angles arise due to the difference in size and electronegativities of Sn^{IV} and Pb^{IV} , which do not necessitate further comment. There are two distinct





Figure 5. Intermolecular hydrogen bonding and CH– π interactions in 1c.

Figure 3. Molecular structures of 1b and 1c.



Figure 4. Arrangement of 1b molecules forming a strip.

CH··· π interactions; one that involves the phenyl ring (as in the case of 1c) and the other that uses the π -electrons of the thiophene ring. H···O hydrogen bonds between a pair of molecules are present as observed in the tin compounds 1a–1c.

In compound 4 (Figure 6), the central Pb atom is bonded with three carbon atoms and one sulfur atom and has a distorted tetrahedral coordination geometry around it. The angles subtended at Pb range from 92.7(4) to 118.0(6)°. The thiocarboxylate ligand is bonded to the metal atom through the S atom only. The oxygen atom is quite far away from the Pb center (3.191 Å), and there is no possibility of any bonding between the two.

This is the only molecule that shows a weak interaction of the thiophene sulfur atom with the neighboring Pb atom. The intermolecular S–Pb distance is 3.74 Å, which is slightly shorter than the sum of the van der Waals radii of the Pb and S atoms (3.82 Å) (Figure 7). The corresponding M–S distances in compounds 1–3 vary within a range of 5.324–6.988 Å, thus ruling out any possibility of an interaction between the two atoms. Possibly, there is also a π – π interaction between a phenyl ring and a thiophene ring of the adjacent molecule. The two rings have a displaced parallel arrangement^[15] with a centroid–centroid distance of 4.04 Å.



Figure 6. Molecular structures of 3 and 4.





Figure 7. Pair of molecule **4** showing interaction between S (thiophene) and Pb. Thermal ellipsoid plot at 30% probability.

Theoretical Studies

Natural Bond Orbital Analyses

Theoretical calculations have been performed by using the density functional theory (DFT) method^[16] to understand the nature of bonding, particularly those that are



Figure 8. Selected orbitals for 1c (orbital contour value = 0.05).

noncovalent and weak. Besides the sulfur atom, which is the primary bonding site with the metal atom, the thiocarboxylate ligand possesses two other atoms that can possibly act as donor sites. These are the oxygen atom of the thiocarboxylate group and the sulfur atom of the thiophene ring. As described in the preceding sections, no M…S(thiophene) interaction was detected in the molecular structures of the complexes except in 4. It was found by natural bond orbital (NBO) analysis that the sulfur atom of the thiophene ring has +0.5 natural charges, and as a result a dative bond formation is not favored. Thus, there is no bonding interaction of the thiophene sulfur atom with the metal ions. In the case of 4, although there is a weak interaction between the lead atom and the sulfur atom of the thiophene ring, the stabilization energies associated with ns $\rightarrow \pi^*_{Pb}$ electron delocalizations are very low (2.47 and 3.34 kcalmol⁻¹, which are even less than commonly observed hydrogen-bonding energies). Calculations on a pair of molecules in the gas phase also supported the existence of very weak interactions. The energy difference between a pair of molecules and two isolated molecules is $-2.62 \text{ kcal mol}^{-1}$.

In the case of **1c**, the oxygen atom of each thiocarboxylate group has a substantial interaction with the tin atom (Sn1–O1 2.63 Å) due to considerable charge transfers from both the nonbonding orbitals (lone pairs) of the oxygen atom to the tin atom. The stabilization energies associated with electron transfers from n_{O33} to σ^*_{Sn-S24} and σ^*_{Sn-S25} orbitals are 11.03 and 9.75 kcal mol⁻¹, respectively. Since **1a** and **1b** are structurally similar to **1c**, one would expect similar Sn···O interactions in these compounds. An analogous result was also found in the case of **3**, in which the energy due to electron transfers from n_{O14} to σ^*_{Pb-S9} and σ^*_{Pb-S18} orbitals is 9.08 and 10.79 kcal mol⁻¹, respectively. In the



Figure 9. Selected molecular orbitals for 3 (orbital contour value = 0.05).

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case of 4, however, the Pb–O distance is quite large and the total stabilization energy associated with $n_O \rightarrow \sigma^*{}_{Pb-S}$ delocalizations is only 3.07 kcal mol⁻¹, thus indicating very weak interaction between the two atoms. Although Tani et al. have reported^[8] the existence of a weak interaction between the metal atom and the oxygen atom that lead to short M–O distances in RC(O)S-MR₃-type compounds on the basis of very low stabilization energies (2.05 kcal mol⁻¹), we have recently shown that such interactions may not be responsible for closeness of the two atoms.^[17] This is because the energies associated with crystal packing and π -stacking are often larger and influence the structure to a greater extent.

TD-DFT Calculations

The results of time-dependent DFT calculations on 1c at the B3LYP^[18,19] level revealed that all absorption bands



Figure 10. Selected molecular orbitals for 4 (orbital contour value = 0.05).

arise due to inter- and intraligand charge transfers (Figure 8).

The results of TD-DFT calculations on compound **3** (Figure 9) revealed that the lower energy band calculated at 321 nm is due to the admixture of intraligand $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions in which the comparatively higher-energy band calculated at 266 nm is due to electron transfers from a coordinated sulfur atom of the thiocaboxylate moiety and (C^{...}C) π orbitals of the phenyl ring to two different orbitals, namely, an antibonding orbital of the thiocarboxylate group and an RY* of Pb.

The calculations reveal that, in the case of **4** (Figure 10), the lower-energy band (calculated at 304 nm) is due to the intermolecular $\pi \rightarrow \pi^*$ transitions from a phenyl ring of the triphenyllead moiety to the π^* -orbitals of thiophene and phenyl rings of another molecule. However, a comparatively higher-energy band calculated at 256 nm is due to intramolecular ligand-to-metal charge transfers from a sulfur atom of the thiocarboxylate group and a π -orbital of the thiophene ring to the Pb–S antibonding orbitals.

Nonlinear Optical Properties

The nonlinear optical property of **4** was calculated by double numerical differentiation of energies (finite-field perturbation method). Hyperpolarizability is given by the coefficients in the Taylor series expansion of the energy in the external electric field.^[20] If the external electric field is weak and homogeneous the expansion is [Equation (1)]:

$$E = E^0 - \mu_{\alpha} F_{\alpha} - \frac{1}{2} a_{\alpha\beta} F_{\alpha} F_{\beta} - \frac{1}{6} \beta_{\alpha\beta\gamma} F_{\alpha} F_{\beta} F_{\gamma} \dots$$
(1)

in which E^0 is the energy of unperturbed molecules, F_{α} is the field of origin, and $\mu_{\alpha,} a_{\alpha\beta}$, and $\beta_{\alpha\beta\gamma}$ are the components of dipole moment, polarizability, and first hyperpolarizability, respectively. The mean first hyperpolarizability is defined as shown in Equation (2):^[21]

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

in which the β_x , β_y , and β_z components can be described by $\beta_x = \beta_{xxx} + \beta_{xyy} + \beta_{xzz}$, $\beta_y = \beta_{yyy} + \beta_{yxx} + \beta_{yzz}$, and $\beta_z = \beta_{zzz} + \beta_{zxx} + \beta_{zyy}$.

The solvent parameters used were those of chloroform. The β_0 value calculated for one molecule of **4** was found to be 8.70×10^{-30} esu in chloroform, which is less than *p*-nitroaniline (*p*NA, Table 3). The value marginally increases for a pair of molecules (as shown in Figure 7), which was calculated to be 9.86×10^{-30} esu. This small increase in the hyperpolarizability is possibly due to weak interactions between the sulfur atom of the thiophene ring of one molecule and the lead atom of the other molecule.

Table 3. Calculated dipole moment and hyperpolarizabilities of 4.

	System	μ	β_x	β_y	β_z	β_0
<i>p</i> NA 4	single molecule paired molecules	7.53 2.05 4.10	-13.70 -5.39 -7.39	0.03 -3.22 -6.48	0.04 -6.03 0.72	13.72 8.70 9.86

Conclusion

Organotin ($[R_2SnCl_2]$, $[R_3SnCl]$; R = Me, Ph, *n*Pr, and *n*Bu) and organolead ([Ph₂PbCl₂], [Ph₃PbCl]) compounds of the thiocarboxylate ligand that contain a donor atom at the terminal R group (thiophene) have been synthesized. In all the compounds the binding of the thiocarboxylate ligand is primarily through the sulfur atom of the thiocarboxylate group; however, M···O interactions are strong enough to affect the molecular geometry. Notably, significant interaction of the terminal sulfur atom (thiophene) with the metal atom is absent in all the cases except in [Ph₃Pb(SCOth)], in which weak intermolecular interaction is present that amounts to a maximum energy lowering of $3.34 \text{ kcal mol}^{-1}$. The molecules exhibited electronic transitions in the UV region due to inter- and intraligand charge transfers; however, in the case of [Ph₃Pb(SCOth)], intermolecular $\pi \rightarrow \pi^*$ transitions were responsible for an absorption at 304 nm. Theoretical calculations revealed that hyperpolarizability of this molecule is 8.7×10^{-3} esu in chloroform, which increases slightly in its dimeric form.

Experimental Section

General: All the reactions were carried out under ambient conditions. Solvents were purified by using standard methods. Organotin and -lead chlorides and thiophene-2-carbonyl chloride were purchased from Sigma Aldrich and used as received. IR spectra were recorded with Varian 3100 FTIR instruments. NMR spectra were obtained with a JEOL AL300 FT NMR spectrometer. Elemental analyses were performed with an Exeter model E-440 CHN analyser. Electronic absorption spectra were recorded with a Shimazdu UV-1700 PhermaSpec spectrophotometer. Single-crystal X-ray data of 1a and 4 were collected with Enraf Nonius Kappa and Bruker SMART APEX CCD diffractometers, respectively, whereas those of 1b, 1c, and 3 were collected with an Xcalibur Oxford Diffractometer by using graphite-monochromated Mo- K_a radiation (λ = 0.7107 Å). Data collections for **1a** and **4** were carried out at 100 K, whereas those for 1b, 1c, and 3 were carried out at 293 K. The SHELX program^[22] was used for structure solution and refinement. A summary of crystallographic data and structure solutions are listed in Table 4. The molecular structure plot of the compound was created with Diamond software.[23] CCDC-771048 (1a) -771049 (1b), 771050 (1c), 771051 (3), and -771052 (4) contain the supple-

Table 4. Crystallographic data of compounds.

mentary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Thiophene-2-thiocarboxylic Acid: For the synthesis, a method similar to that reported for thiobenzoic acid^[24] was applied. Thiophene-2-carbonyl chloride (2.930 g, 20.0 mmol) was added dropwise with stirring to a solution of KSH (5.760 g, 40.0 mmol) in methanol (30.0 mL) over a period of 30 min. The reaction mixture was stirred for 1 h, and then the precipitated KCl was removed by filtration. The filtrate was dried under reduced pressure, and the residue was dissolved in water (50 mL), which was washed with benzene (20 mL). The aqueous solution was acidified with 6 \times HCl and extracted with diethyl ether (2 \times 30 mL). The ethereal layer wasdried under reduced pressure. A yellow oily liquid was obtained. Yield: 2.275 g (79%). The sodium salt of the acid was obtained by treating it with sodium methoxide in a stoichiometric ratio.

[Me₂Sn(SCOth)₂] (1a): A methanolic (5 mL) solution of sodium thiophene-2-thiocarboxylate (0.339 g 1.02 mmol) was added with stirring to a stirred solution of dimethyltin(IV) dichloride (0.123 g, 0.56 mmol) in methanol (5 mL). After stirring the reaction mixture for 2 h, the solvent was evaporated under reduced pressure. The yellow residue was dried under vacuum, dissolved in chloroform, and separated from the sodium chloride by filtration. The filtrate was layered with *n*-hexane and kept for crystallization. After 2 d, light yellow crystals were obtained. Yield: 0.195 g (80%). M.p. 108–110 °C. C₁₂H₁₂O₂S₄Sn (435.16): calcd. C 33.12, H 2.78; found C 33.41, H 2.76. IR (KBr): $\tilde{v} = 1575$ [v(CO)], 1217 [v(th–C)], 1048 [v(C–S)] cm⁻¹. ¹H NMR (CDCl₃): $\delta = 1.21$ (6 H of Me), 7.09–7.87 (6 H of thiophene rings) ppm. ¹³C NMR (CDCl₃): $\delta = 5.22$, 5.25 (Me), 128.18–143.12 (thiophene ring), 192.92, 192.97 (COS) ppm. ¹¹⁹Sn NMR (CDCl₃): $\delta = -69.68$ ppm.

[*n*Pr₂Sn(SCOth)₂] (1b): A solution of sodium thiophen-2-thiocarboxylate (0.208 g, 1.25 mmol) in methanol (5.0 mL) was added with stirring to a stirred solution of [*n*Pr₂SnCl₂] (0.191 g, 0.628 mmol) in methanol (10 mL). The reaction mixture was stirred for 1 h, during which a white precipitate appeared, which was collected by filtration. The solid was dried and dissolved in chloroform, layered with petroleum ether (boiling range 60–80 °C), and kept for crystallization. After 2 d, colorless crystals suitable for single-crystal X-ray diffraction were obtained. Yield: 0.290 g (89%). M.p. 86– 88 °C. $C_{16}H_{20}O_2S_4Sn$ (491.26): calcd. C 39.11, H 4.10; found C 40.23, H 4.24. IR (KBr): $\tilde{v} = 1571$ [v(CO)], 1213 [v(th–C)], 1047 [v(C–S)] cm⁻¹. ¹H NMR (CDCl₃): $\delta = 1.04$ (6 H of *n*Pr), 1.81 (4 H

	1a	1b	1c	3	4
Empirical formula	$C_{12}H_{12}O_2S_4Sn$	$C_{16}H_{20}O_2S_4Sn$	$C_{22}H_{16}O_2S_4Sn$	$C_{22}H_{16}O_2PbS_4$	$C_{23}H_{18}OPbS_2$
<i>T</i> [K]	100	293	293	293	100
Crystal system	triclinic	monoclinic	triclinic	triclinic	monoclinic
Space group	<i>P</i> 1	C2/c	$P\overline{1}$	ΡĪ	$P2_1/n11$
<i>a</i> [Å]	5.9330(12)	15.4722(10)	10.1857(3)	10.4143(6)	11.785(4)
b [Å]	7.6190(15)	6.0028(4)	10.7413(3)	10.6226(7)	13.402(5)
c [Å]	18.418(4)	21.2495(12)	11.8598(3)	11.7566(8)	14.743(5)
β [°]	90.03	103.553(6)	107.174	104.481(6)	63.463(6)
V[Å ³]	832.6(3)	1918.6(2)	1138.51(5)	1156.24(13)	2083.4(13)
Z	2	4	2	3	4
$\mu [{\rm mm}^{-1}]$	2.030	1.772	1.505	7.672	8.308
<i>R</i> indices $[I > 2\sigma(I)]$	0.0240	0.0781	0.0363	0.0698	0.0503
R indices (all data)	0.0269	0.0815	0.0496	0.1059	0.0948
GOF on F^2	1.007	1.238	1.055	1.077	1.001

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of *n*Pr), 1.95 (4 H of *n*Pr), 7.09–7.88 (6 H of thiophene ring) ppm. ¹³C NMR (CDCl₃): δ = 17.85 (CH₃ of *n*Pr), 19.55 and 27.56 (CH₂ of *n*Pr), 128.13–143.30 (thiophene ring), 193.24 (COS) ppm. ¹¹⁹Sn NMR (CDCl₃): δ = -77.71 ppm.

[Ph₂Sn(SCOth)₂] (1c): The same procedure as for **1b**, but instead of [*n*Pr₂SnCl₂], [Ph₂SnCl₂] (0.219 g, 0.637 mmol) and sodium thiophene-2-thiocarboxylate (0.211 g, 1.27 mmol) were used. Colorless crystals were obtained from a chloroform solution layered with petroleum ether (boiling range 60–80 °C). Yield: 0.283 g (80%). M.p. 162–164 °C. C₂₂H₁₆O₂S₄Sn (559.30): calcd. C 47.24, H 2.88; found C 46.90, H 2.90. IR (KBr): $\tilde{v} = 1559$ [v(CO)], 1226 [v(th–C)], 1053 [v(C–S)] cm⁻¹. ¹H NMR (CDCl₃): $\delta = 7.06-8.06$ (6 H of thiophene ring and 10 H of phenyl ring) ppm. ¹³C NMR (CDCl₃): $\delta = 128.13-142.58$ (thiophene ring and phenyl ring), 190.90 (COS) ppm. ¹¹⁹Sn NMR (CDCl₃): $\delta = -190.10$ ppm.

[*n*Bu₃Sn(SCOth)] (2a): A solution of sodium thiophene-2-thiocarboxylate (0.109 g, 0.659 mmol) in methanol (5.0 mL) was added with stirring to a stirred solution of [*n*Bu₃SnCl] (0.214 g, 0.657 mmol) in methanol (5.0 mL). A light yellow solution was obtained. The reaction mixture was stirred for 2 h. It was then dried under reduced pressure, and the residue was dissolved in chloroform to separate NaCl by filtration. The filtrate was dried under reduced pressure, then in vacuo to obtain a viscous yellow-orange liquid. Yield: 0.219 g (76%). IR (KBr): $\tilde{v} = 1606$ [v(CO)], 1204 [v(th–C)], 1045 [v(C–S)] cm⁻¹. ¹H NMR (CDCl₃): $\delta = 0.88-1.66$ (27 H of *n*Bu), 7.05–7.84, (3 H of thiophene ring) ppm. ¹³C NMR (CDCl₃): $\delta = 6.99$, 13.61, 15.09, and 28.72 (*n*Bu) 127.77–144.73 (thiophene ring), 188.52 (COS) ppm. ¹¹⁹Sn NMR (CDCl₃): $\delta = -80.68$ ppm.

[Ph₃Sn(SCOth)] (2b): The same procedure was applied as for **1c**, except [Ph₃SnCl] (0.207 g, 0.536 mmol) and sodium thiophene-2thiocarboxylate (0.089 g, 0.536 mmol) were used. A yellow insoluble precipitate was obtained. Yield: 0.209 g (79%). C₂₃H₁₈OS₂Sn (493.20): calcd. C 56.01, H 3.68; found C 55.43, H 3.64. IR (KBr): $\tilde{v} = 1609 [v(CO)], 1205 [v(th-C)], 1069 [v(C-S)] cm^{-1}$.

[Ph₂Pb(SCOth)₂] (3): A solution of sodium thiophene-2-thiocarboxylate (0.155 g, 0.936 mmol) was added with stirring to stirred suspension of [Ph₂PbCl₂] (0.202 g, 0.468 mmol) in methanol (10 mL). A white precipitate appeared immediately. The reaction mixture was stirred for another 1 h, and the precipitate was filtered off. The latter was dried under vacuum, dissolved in chloroform, and kept for crystallization. After 2 d, colorless crystals were obtained that were suitable for single-crystal X-ray diffraction. Yield: 0.266 g (88%). M.p. 156–158 °C. C₂₂H₁₆O₂PbS₄ (647.81): calcd. C 40.79, H 2.49; found C 41.03, H 2.56. IR (KBr): $\tilde{v} = 1557$ [v(CO)], 1218 [v(th–C)], 1050 [v(C–S)] cm⁻¹. ¹H NMR (CDCl₃): $\delta = 7.06$ –8.21 (6 H of thiophene rings and 10 H of phenyl rings) ppm. ¹³C NMR (CDCl₃): $\delta = 127.99$ –158.04 (thiophene ring and phenyl ring), 192.99 (COS) ppm.

[Ph₃Pb(SCOth)] (4): A solution of sodium thiophene-2-thiocarboxylate (0.143 g, 0.862 mmol) was added with stirring to a stirred turbid solution of [Ph₃PbCl] (0.408 g, 0.861 mmol) in methanol (10 mL). The turbid solution became clear immediately. The reaction mixture was stirred for 1 h, during which a cream-colored precipitate formed. The precipitate was collected by filtration, dried under vacuum, dissolved in chloroform, and kept for crystallization. After 2 d, colorless crystals were obtained that were suitable for single-crystal X-ray diffraction. Yield: 0.449 g (90%). M.p. 120– 122 °C. C₂₃H₁₈OPbS₂ (581.71): calcd. C 47.49, H 3.12; found C 46.98, H 3.14. IR (KBr): $\tilde{v} = 1597$ [v(CO)], 1194 [v(th–C)], 1045 [v(C–S)] cm⁻¹. ¹H NMR (CDCl₃): $\delta = 7.03-7.94$ (3 H of thiophene ring and 15 H of phenyl ring) ppm. ¹³C NMR (CDCl₃): δ = 127.79–157.63 (thiophene ring and phenyl ring), 188.27 (COS) ppm.

Theoretical Calculations: The optimized geometry of tributyltin thiophene-2-thiocarboxylate was calculated by using the B3LYP exchange correlation functional. The effective core potential (ECP) standard basis set LANL2DZ(d,p)^[25] was utilized for Sn atoms, whereas the 6-31g**[26] basis set was used for C, H, O, and S atoms. The energies and intensities of the 20 lowest-energy spin-allowed electronic excitations were calculated by using TD-DFT at the same level of theory. Natural bond orbital (NBO) calculations were performed by using the LANL2DZ(d,p) basis set for all the atoms. The first static hyperpolarizability (β_0) for compound 4 was calculated by using the finite field perturbation method by implementing the PCM model.^[27,28] The solvent parameters were those of chloroform. X-ray coordinates were used for the calculation of electronic excitation, natural bond orbital, and hyperpolarizability, except for 2a, which was optimized. All the theoretical calculations were performed by using the Gaussian 03 W set of programs.^[29] Molecular orbital plots were generated by using the program MOLDEN.^[30]

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