Structural Studies on Indium and Tin Thiobenzoates

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Indium(III) and tin(IV) thiocarboxylates were prepared and characterized on the basis of their IR, ^{13}C- and ^{19}Sn-NMR data. Indium tris(thiobenzoate) (**1**) decomposes into a sulfido complex In(S)[S(O)CPh] (**2a**). The corresponding tris(thioacetate) In[S(O)CMe]$_3$ is thermally too unstable to be isolated. The anionic tetrakis complex [Et$_3$NH]{In[S(O)CPh]$_4$} (**3**) was characterized by X-ray crystallography which revealed a distorted tetrahedral coordination at the In atom. X-ray diffraction analysis of the complexes BuSn[S(O)CPh]$_3$ (**4**) and Cl$_2$Sn[S(O)CPh]$_2$ (**7**) showed distorted tetrahedral and *cis*-octahedral structures, respectively.

In reference to main group elements, the ligating features of asymmetrical sulfur ligands[1] containing both a soft and a hard donor center have largely remained unexplored so far. In the last two decades, the properties of thiocarbamates, [R$_2$NC(O)S]$^-$, which constitute a major class of such ligands, were appreciated regarding mainly transition metals[2]. We recently isolated and spectroscopically characterized tris(thiocarbamates) of In[3] and As[4], Sb and Bi[5]. Among these the arsenic complexes were found to be extremely sensitive to oxygen and moisture and to decompose readily. Thus, there are only few structural data available on the tris(thiocarbamates) of group-13 and -15 elements. Amongst group-14 elements, in a series of R$_{4-n}$Sn[S(O)CNC$_4$H$_4$]$_n$ compounds a successive introduction of the ligand causes discernible changes in the molecular structure[6] making the Sn atom tetra- to hexacoordinate. In contrast to thiocarbamates, the thiocarboxylate anion, [RC(O)S]$^-$, with skeletal and apparent ligational similarities has not yet been exploited as a ligand although a coordination chemistry as rich in variation as R$_2$NC(O)S$^-$ or R$_2$NCS$_2^-$ can be expected. In this paper we report on the results of a study of In(III) and Sn(IV) thiocarboxylates.

Syntheses

The reaction of indium trichloride with potassium thiobenzoate in a 1:3 molar ratio in aqueous medium yields indium tris(thiobenzoate) (**1**), as shown by eq. (1). Thiobenzoate **1** decomposes rapidly in solution to give an insoluble sulfido complex **2** and dibenzoyl sulfide.

$$\mathrm{InCl_3 + 3\ KSOPh} \xrightarrow{-3\,\mathrm{KCl}} \underset{\mathbf{1}}{\mathrm{In[S(O)CPh]_3}} \rightarrow \underset{\mathbf{2a}}{\mathrm{In(S)[S(O)CPh]}} + \mathrm{[PhC(O)]_2S} \quad (1)$$

$$\mathrm{InCl_3 + 4\ PhC(O)SH + 4\ Et_3N} \rightarrow \underset{\mathbf{3}}{\mathrm{[Et_3NH]In[S(O)CPh]_4}} + \mathrm{3\ (Et_3NH)Cl} \quad (2)$$

$$\mathrm{BuSn(O)OH + 3\ PhC(O)SH} \rightarrow \underset{\mathbf{4}}{\mathrm{BuSn[S(O)CPh]_3}} + \mathrm{2\ H_2O} \quad (3)$$

$$\mathrm{SnCl_4 + 4\ KS(O)CPh} \rightarrow \underset{\mathbf{5}}{\mathrm{Sn[S(O)CPh]_4}} + \mathrm{4\ KCl} \quad (4)$$

$$\mathrm{PhSnCl_3 + 3\ KS(O)CPh} \rightarrow \underset{\mathbf{6}}{\mathrm{PhSn[S(O)CPh]_3}} + \mathrm{3\ KCl} \quad (5)$$

$$\mathrm{SnCl_4 + 2\ PhC(O)SH} \rightarrow \underset{\mathbf{7}}{\mathrm{SnCl_2[S(O)CPh]_2}} + \mathrm{2\ HCl} \quad (6)$$

In an attempted preparation from MeC(O)SH in aqueous medium at pH 7, In[S(O)CMe]$_3$ was thermally too unstable for isolation and thus decomposed to the corresponding sulfides. Interestingly, when an excess of thiobenzoic acid was used instead of MeC(O)SH in the presence of triethylamine, triethylammonium tetrakis(thiobenzoato)indate (**3**) was isolated which, in contrast to **1**, turned out to be quite stable.

A few tin(IV) thiobenzoates **4**–**7** were prepared according to the routes described by eq. (3)–(6). The only phenyltin derivative which could be isolated from aqueous solutions was PhSn[S(O)CPh]$_3$ (**6**) [eq. (5)].

IR and NMR Spectra

The infrared spectrum of thiobenzoic acid displays three characteristic bands at 1685, 1213, and 950 cm^{-1} due to

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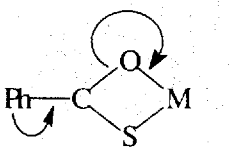
Table 1. Selected IR and NMR data of compounds **1–7**

Compound		ν(N-H)	ν(C=O)	ν(Ph-C)	ν(C=S)	δ(SCO)	ν(In-S) ν(Sn-S)	^{1}H		^{13}C		^{119}Sn
								Bu	Ph	Bu	Ph	
1	In(SOCPh)$_3$		1618	1210	926	650	260					
2a	In(S)(SOCPh)		1611	1206	914	652	393					
							354					
2b	In(S)(SOCMe)		1626		629	669	399					
							375					
3	[Et$_3$NH]$^+$											
	[In(SOCPh)$_4$]$^-$	2853	1615	1204	922	652	310					
4[a]	BuSn(SOCPh)$_3$		1595	1213	938	650	360	0.91-	7.21	13.6		
									-			
								2.78	8.21	25.6	128.13	
										27.5	128.99	
										33.2	133.98	
5[b]	PhSn(SOCPh)$_3$		1620	1211	918	648	355				136.85	
6	Sn(SOCPh)$_4$		1597	1215	927	648	373		7.37			
									8.09			125.3
7[c]	Cl$_2$Sn(SOCPh)$_2$		1466	1230	962	650	375		7.23			
									-			
									8.06		128.49	-555.5
											128.69	
											128.93	
											129.82	
											130.23	
											130.79	
											133.83	
											136.59	

[a] ν(Sn–O) = 615. – [b] ν(Sn–C) = 552, 446, 434. – [c] ν(Sn–Cl) = 337.

ν(C=O), ν(Ph–C), and ν(C–S), respectively (see Table 1). These are the absorptions which are mainly affected on complexation. In the spectra of complexes **1–6** the ν(CO) band is observed in a narrow range between 1593 and 1620 cm^{-1} revealing that the carbonyl oxygen atoms are not essentially involved in coordination to the metal center. However, an appreciable lowering of the ν(C=S) absorption is observed. Bands between 914 and 939 cm^{-1} indicate single bonds between carbon and sulfur substantiating the coordination of thiobenzoate only through its sulfur atom. In addition, the ν(Ph–C) absorption in the region 1204–1209 cm^{-1} in **1–6** reveals monodentate attachment of the ligand since on chelation the π-electron drift, as shown in **A**, would shift this absorption to a higher frequency[7].



A

The data are similar to those of a dinuclear Cu(II) thiobenzoate complex[8], whose crystal structure revealed the presence of a monodentate sulfur-bound thiobenzoate ligand, and to earlier reported complexes containing soft ions such as Hg(II) and Cu(I)[7]. The dichloro complex **6** shows a different infrared spectrum. It displays a much lower ν(CO) absorption at 1466 cm^{-1} and a comparatively higher ν(CS) at 962 cm^{-1} and ν(Ph–C) at 1230 cm^{-1}, suggesting the presence of chelating thiobenzoate ions.

^{119}Sn-NMR spectroscopy is a particularly useful tool for determining the coordination environment around tin atoms. The tetrakis complex **6** shows a signal at $\delta = 125.3$ which is consistent with a tetracoordinated tin tetrathiolate such as Sn(SCH$_2$Ph)$_4$[9] (δ = 132.0). The high-field ^{119}Sn resonance for **7** at $\delta = -497$ (weak) and -555 (strong) indicates a hexacoordinated environment around tin. Moreover, its ^{13}C-NMR spectrum displays two sets of phenyl carbon resonances. Probably the *cis* and *trans* isomers are present in solution.

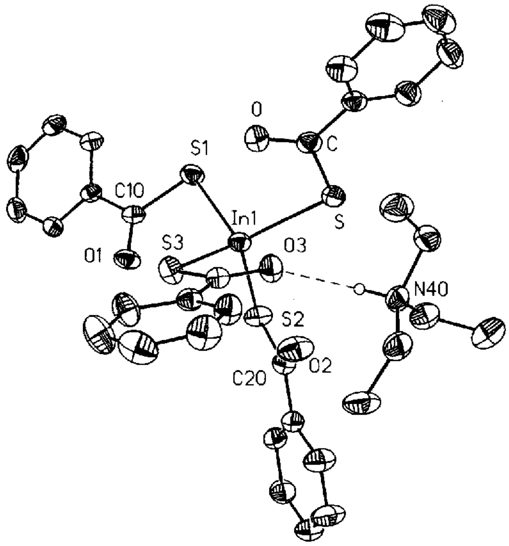
Based on these spectral data, an octahedral structure for **7** and a tetracoordinated environment for all the other tin thiobenzoates with essentially no bonding interaction between tin and oxygen may be possible. The anionic indium complex **3** was also thought to be tetrahedral on similar consideration. The structures of **3**, **4**, and **7** have been established by X-ray crystal structure analysis.

Importantly, a tricoordinated environment with an InS$_3$ core for the tris(thiocarboxylates) as indicated by the IR data is quite surprising. The thermal instability of these compounds may be a consequence of coordination unsaturation. We are further investigating this unusual feature with sterically demanding substituents in the 2,6 positions of the thiobenzoates which might result in a stable product suitable for X-ray diffraction analysis.

Crystal and Molecular Structures

Failure to obtain the structure of In[S(O)CPh]$_3$ gives more importance to the structure of the salt $[Et_3NH]^+\{In[S(O)CPh]_4\}^-$ (**3**). The molecular geometry and atomic labeling scheme of **3** are depicted in Figure 1. Selected bond lengths and angles are given in Table 2. The complex salt **3** crystallizes from dichloromethane/*n*-hexane solution and is the first example of an anionic homoleptic complex of indium carboxylates. There are discrete cationic and anionic molecules in the monoclinic unit cell. The ions $[Et_3NH]^+$ and $\{In[S(O)CPh]_4\}^-$ are connected by a hydrogen bond between the nitrogen atom and an oxygen atom.

Figure 1. ORTEP representation of [Et$_3$NH]In[SC(O)Ph]$_4$ (**3**). Thermal ellipsoids are depicted on a 25% probability level



In the anionic part of **3**, the attachment of the ligands is effected by the sulfur atoms in a monodentate manner. The coordination polyhedron is essentially tetrahedral but distorted from ideal geometry as evidenced by the S−In−S angles ranging from 100.8(1) to 125.8(1)°. Possibly the close proximity of the oxygen atoms to the polyhedral core may be an important factor causing this distortion. Expectedly, the In−S bond lengths (aver. 2.479 Å) are distinctly shorter than those found in penta- and hexacoordinated indium complexes with sulfur ligands and are even shorter than their single bond covalent radii (2.54 Å)[10]. The carbon-oxygen bond lengths (aver. 1.222 Å) correspond with the sum of the double bond radii of carbon and oxygen (1.22 Å)[10] as there exists no significant bonding interaction between the oxygen and the indium atoms.

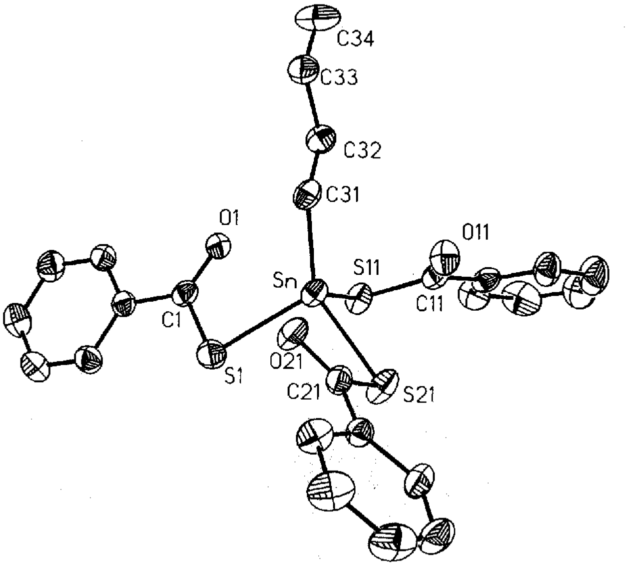
The In−S−C angles (aver. 95.8°) in combination with the S−C−O bond angle (aver. 121.5°) places the oxygen atoms farthest apart from the indium atom. In the cation $[Et_3NH]^+$ the nitrogen atom resides in an essential tetrahedral environment.

Suitable single crystals of BuSn[S(O)CPh]$_3$ (**4**)[4] were grown by slow evaporation of an ethereal solution. The compound crystallizes in the monoclinic system with space group $P2_1/n$ and $Z = 4$. Figure 2 shows the molecular structure and numbering scheme of the complex. Bond lengths and bond angles are listed in Table 2. The coordination polyhedron consists of one carbon atom and three sulfur atoms around the central tin atom and can be best described as a distorted tetrahedron with approximate C_{3v}

Table 2. Selected bond lengths [Å] and bond angles [°]. Estimated standard derivations in parenthesis

Complex				
	A. Selected bond lengths [Å]			
3	In1-S1	2.478(1)	In1-S1	2.496(1)
	In1-S2	2.493(1)	In1-S3	2.451(1)
	S-C	1.754(5)	O-C	1.222(5)
	C-C1	1.491(6)		
4	Sn-S1	2.447(1)	Sn-S11	2.464(1)
	Sn-S21	2.464(1)	Sn-C31	2.133(4)
	S1-C1	1.759(4)	O1-C1	1.227(5)
	C1-C2	1.485(5)		
7	Sn1-O1	2.267(2)	Sn-Cl1	2.357(1)
	Sn1-S1	2.468(1)	C1-C2	1.474(4)
	S1-C1	1.732(3)	O1-C1	1.262(3)
	B. Selected bond angles [°]			
3	S-In1-S1	102.11(4)	S-In1-S2	103.81(5)
	S1-In1-S2	100.78(4)	S-In1-S3	125.83(4)
	S1-In1-S3	107.37(4)	S2-In1-S3	113.68(5)
	In1-S-C	94.10(2)	S-C-O	121.14(4)
	S-C-C1	117.9(3)	O-C-C1	121.0(4)
	In1-S1-C10	95.0(1)	In1-S2-C20	93.4(2)
	In1-S3-C30	100.8(2)	S3-C30-O3	122.5(3)
4	S1-Sn-S11	101.28(4)	S1-Sn-S21	97.81(4)
	S11-Sn-S21	97.25(4)	S1-Sn-C31	116.7(1)
	S11-Sn-C31	117.5(1)	S21-Sn-C31	122.1(1)
	Sn-S1-C1	91.1(1)	S1-C1-O1	119.8(3)
	S1-C1-C2	118.2(3)	O1-C1-C2	122.0(4)
7	O1-Sn1-O1A	83.4(1)	O1-Sn1-Cl1	165.36(5)
	O1A-Sn1-Cl1	90.58(6)	Cl1-Sn1-Cl1A	98.21(4)
	O1-Sn1-S1	65.54(5)	O1A-Sn1-S1	89.22(5)
	Cl1-Sn1-S1	101.16(3)	Cl1A-Sn1-S1	100.45(3)
	S1-Sn1-S1A	146.73(4)	C1-S1-Sn1	79.29(9)
	C1-O1-Sn1	97.7(2)	O1-C1-S1	117.4(2)

Figure 2. Molecular structure of BuSn[SC(O)Ph]$_3$ (**4** in the crystal. Thermal ellipsoids are depicted on a 25% probability level

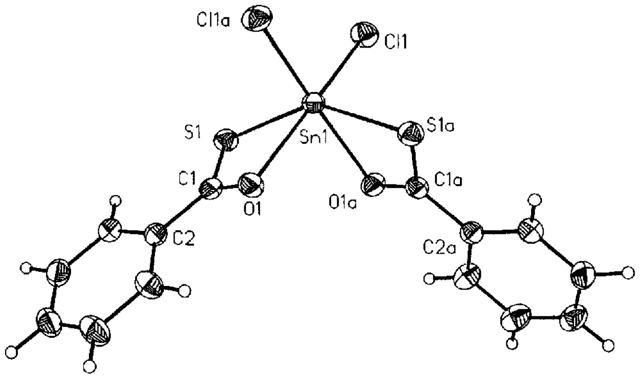


symmetry. This is in sharp contrast to the structure of analogous triscarboxylates $MeSn(O_2CPh)_3$[11] where the three benzoate ligands are bidentate leading to a heptacoordinated tin atom.

The angles between tin and sulfur atoms in compound **4** lie in the range of 97.3(1)−101.3(1)° while those between carbon and sulfur comprise 116.6(1)−122.2(1)°. As a result of these two sets of angles, the C31 atom can be considered to occupy the axial position in the approximate C_3 symmetrical core.

Two of the three Sn−S atom distances are of identical length [aver. 2.464(1) Å] while the third is slightly shorter [2.445(1) Å]. The latter corresponds to the sum of their covalent radii (2.44 Å)[10]. The C=O bond lengths (aver. 1.226 Å) are similar to those found in $\{In[S(O)CPh]_4\}^-$ (aver. 1.222 Å). The C−S bond lengths (aver. 1.759 Å) are quite close to those in organotin(IV) thiocarbamates, e.g. $Ph_3Sn[S(O)CNC_4H_4]$ (1.762 Å)[6], where ligand bonding is effected by means of sulfur only. In the ligand skeleton, Sn−S−C angles (aver. 90.7°) are a bit more acute than the In−S−C angles in **3** (aver. 95.8°) and so are the S−C−O angles (aver. 119.4°) in **4** and 121.5° in **3**.

Figure 3. Molecular structure of $Cl_2Sn[SC(O)Ph]_2$ (**7**) in the crystal. Thermal ellipsoids are drawn on a 25% probabiltiy level



The molecular structure and numbering scheme of compound **7** are given in Figure 3. There are discrete molecular units, but these have distinct intramolecular sulfur-sulfur contacts. Interestingly, the thiobenzoate ligand is bidentate in this complex. This may arise from the inductive effect of the chloro ligands on the Sn atom. The molecule has a distorted octahedral structure with the two chlorine atoms in a *cis* position subtending an angle of 98.21(4)° at the Sn atom. The bite angles are very small [65.54(5)°] which is obviously an important factor causing distortion from an ideal octahedral symmetry. The molecule possesses true C_2 symmetry due to the position of the Sn atom on a crystallographic twofold axis as found also in some other dichlorotin bis-chelate complexes[12].

The Sn−O distances in **7**, 2.267(2) Å, are intermediate between the short and long Sn−O bonds in $Bu_2Sn(O_2C\text{-}CEt_2CO_2)_2$[13]. Also this distance is longer as compared to the sum of their covalent radii (2.11 Å)[10]. As a consequence of the chelating nature of the ligand, the carbon-oxygen bond [1.262(3) Å] is distinctly longer than those of **3** and **4** (aver. 1.222 and 1.226 Å, respectively). These facts suggest a strong dative bond between tin and oxygen atoms[14].

The sulfur-carbon bond lengths [1.732(3) Å] in **7** are shorter than those in **3** and **4** indicating delocalization of π electrons in the S−C−O moiety. Sn−S bond lengths [2.468(8) Å] are comparable to those in **4**. As a result of chelation the Sn−S−C angles are acute [79.29(9)°]. Even the S−C−O angles are a little smaller [117.4(2)°] than in **4** (aver. 119.5°).

Conclusions

It may be concluded that thiocarboxylates, particularly thiobenzoates, are usually sulfur-bound to indium(III) and tin(IV) thus providing a low-coordinate environment for them. The fact that **3** is tetrahedral furnishes an indirect but strong evidence for a highly coordinatively unsaturated environment around indium in **1**. It may, however, be mentioned here that $In[S(O)CNR_2]_3$ also shows unusual but similar spectral features suggesting to a comparable situation. In contrast to the transition metal complexes wherein higher coordination numbers are stabilized by thiocarbamates, the situation is different amongst main group elements investigated here. It is only in the presence of electron-withdrawing atoms, such as in **7**, that the thiobenzoate tends to become bidentate. The crystal structure of it documents this and offers the first known example of a complex in which the thiobenzoate is bound as a bidentate anion to a main group metal center. It may be emphasized that for the thiobenzoate ion the position of ν(C=O) in the IR spectra could be taken as diagnostic for identifying the bonding pattern. Studies of other main group elements will be reported in subsequent publications.

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Experimental

All experimental manipulations were carried out under anhydrous conditions. Solvents were purified and dried by standard methods. Indium(III) chloride (Alfa-Chem) was used without further purification. $BuSnCl_3$ (Aldrich, b.p. 93 °C/10 Torr) was distilled before use. $SnCl_4$ (b.p. 114 °C)[15], $PhSnCl_3$ (b.p. 75 °C/0.1 Torr)[16] and butylstannoic acid[17] were prepared by literature methods as were thiobenzoic acid (b.p. 85−87 °C/10 Torr) and potassium thiobenzoate[18].

Indium and tin were determined as In_2O_3 and SnO_2, respectively. Sulfur was estimated by the Messenger method and chlorine gravimetrically as silver chloride. − IR: Region 4000−400 cm^{-1} with Jasco FT/IR-5300 (KBr disks), region 600−200 cm^{-1} with Perkin-Elmer 883 (nujol mull over CsI plates or polystyrene sheets). − NMR (^1H, ^{13}C, and ^{119}Sn): Jeol FX 90Q and Bruker 400-MHz, $CDCl_3$ solutions, internal reference TMS for ^1H and ^{13}C, external reference Me_4Sn in a sealed capillary tube for ^{119}Sn. − Elemental analyses: Perkin-Elmer 240 C. Data collection for the single-crystal X-ray diffraction of $BuSn[S(O)CPh]_3$ was performed by using a Siemens R3m four-circle automated diffractometer operating with a graphite monochromator and Mo-K_α radiation, $\lambda = 0.71073$ Å, while a Siemens P4 diffractometer was used for $[Et_3NH]^+\{In[S(O)CPh]_4\}^-$ and $Cl_2Sn[S(O)CPh]_2$. Computations

Table 3. Data concerning the preparation and characterization of compounds **1**–**7**

	Reactans (g; mmol)		Product (yield %)	Nature	M. p. [°C]	Anal. Found (Calcd.) C	H	In/Sn	S
1	$InCl_3 \cdot 4\,H_2O$ (1.38; 4.71)	+ PhCOSK (2.50; 14.2)	$In(SOCPh)_3$ (94)	Yellow solid	58 - 60	–	–	21.1 (21.8)	17.7 (18.2)
2a	$In(SOCPh)_3$ (0.99; 1.88)		In((S)(SOCPh) (90)	White solid	158	–	–	40.7 (40.4)	22.5 (21.8)
2b	$InCl_3 \cdot 4\,H_2O$ (0.33; 1.12)	+ CH_3COSH (0.27; 3.55)	In(S)(SOCMe) (83)	Yellow solid	230	–	–	51.5 (51.8)	29.1 (28.8)
3	$InCl_3$ (0.15; 0.68)	+ PhCOSH 0.85, 6.16)	$(Et_3NH)^+$ $[In(SOCPh)_4]^-$ (74)	White solid	118 - 119	51.00 (53.33)	4.49 (4.74)	15.3 (15.0)	18.0 (16.7)
4	BuSn(O)(OH) (0.99; 4.74)	+ PhCOSH (1.95; 14.13)	$BuSn(SOCPh)_3$ (90)	Brown solid	80 - 82	51.11 (51.08)	4.02 (4.09)	20.3 (20.2)	–
5	$PhSnCl_3$ (0.35; 1.16)	+ PhCOSK (0.63; 3.58)	$PhSn(SOCPh)_3$ (87)	Brown solid	45 - 48	–	–	18.8 (19.5)	16.1 (15.8)
6	$SnCl_4$ (0.23; 0.88)	+ PhCOSK (0.62; 3.52)	$Sn(SOCPh)_4$ (86)	Yellow solid	104 - 106	50.12 (50.38)	3.40 (3.02)	17.8 (18.2)	19.2 (19.2)
7	$SnCl_4$ (0.57; 2.18)	+ PhCOSH (0.59; 4.28)	$Cl_2Sn(SOCPh)_2$ (93)	Pale yellow solid	170	–	–	26.58 (25.65)	– [a]

[a] Cl Found/Calcd. 16.6/15.3.

Table 4. Data of the X-ray structure determinations

	3	**4**	**7**
Crystal data			
Formula	$C_{34}H_{36}InNO_4S_4$	$C_{25}H_{24}SnO_3S_3$	$C_{14}H_{10}SnCl_2O_2S_2$
M	765.7	587.3	463.93
a [Å]	11.783(1)	8.957(1)	18.033(2)
b [Å]	20.143(3)	19.935(3)	9.193(1)
c [Å]	14.861(4)	15.207(2)	13.039(3)
β [°]	91.99(1)	104.25(2)	129.59(1)
V [$Å^3$]	3525(1)	2631.8(6)	1665.8(5)
D_c [Mg m^{-3}]	1.443	1.482	1.850
Z	4	4	4
Space group	$P2_1/n$	$P2_1/n$	$C2/c$
μ(Mo-K_α) [mm^{-1}]	0.944	1.232	2.104
F(000)	1568	1184	904
Crystal size [mm]	0.22×0.3×0.35	0.25×0.30×0.35	0.45×0.4×0.35
Data collection			
2θ range [°]	3.00-50.00	2.00-50.00	5.32-49.98
h, k, l	$0 \le h \le 13$, $-1 \le k \le 23$, $-16 \le l \le 16$	$0 \le h \le 10$, $-1 \le k \le 23$, $-18 \le l \le 17$	$-21 \le h \le 21$, $-9 \le k \le 1$, $-15 \le l \le 15$
Scan speed [° min^{-1}]	2.50-60.00	2.00-60.00	3.00-60.00
No. measured refl.	5984	5122	3026
No. unique refl.	4107	4609	1415
No. for $F > 4\sigma(F)$		3523	1301
Min./max. transmission	0.4501/0.3567	0.6327/0.6950	0.614/0.748
Structure solution	Direct method	Direct method	Heavy-atom method
No. of variables	460	361	111
R	3.35	3.17	0.0222
wR_2	4.04	8.03	0.0538
GOF	1.09	0.836	1.117
Largest residual electron density [e $Å^{-3}$]	0.37	0.24	0.22

were performed by using the SHELXTL PC[19] or SHELXL 93[20] program packages.

Data referring to the preparation and analytical characterization of compounds **1**–**7** are compiled in Table 3.

General Procedure for the Preparation of Indium Tris(thiobenzoate) (**1**) *and Phenyltin Tris(thiobenzoate)* (**6**): A solution of potassium thiobenzoate in ca. 30 ml of water was added to a solution of indium trichloride in ca. 20 ml of water (or to phenyltin trichloride) with vigorous stirring at room temp. Precipitation started immediately. After stirring for 30–60 min the precipitate was filtered off and dried in vacuo for 4–5 h at 0.01 Torr/30 °C. $PhSn[S(O)CPh]_3$ was crystallized from dichloromethane/petroleum ether (40–60 °C).

General Procedure for the Preparation of Butyltin Tris(thiobenzoate) (**4**) *and Dichlorotin Bis(thiobenzoate)* (**7**): A solution of a stoichiometric amount of thiobenzoic acid in dichloromethane (ca. 10 ml) was added to a stirred suspension of butylstannoic acid [or tin(IV) chloride] in the same solvent. Stirring was continued for 1–12 h followed by solvent evaporation under reduced pressure. The resulting residue was dried in vacuo for 2–6 h at 0.05 Torr/28 °C. Crystallization was achieved by slow evaporation of a diethyl ether or dichloromethane solution.

Decomposition of $In[SC(O)Ph]_3$ (**1**): A chloroform solution (ca. 15 ml) of **1** was stirred for 3 d. A white precipitate formed which was collected by filtration and dried in vacuo for 1 h at 0.01 Torr/30 °C. Its analytical data are in agreement with an indium sulfido complex In(S)(SOCPh) (**2a**). From the filtrate the solvent was evaporated and the residue (dibenzoyl sulfide) was crystallized from benzene/petroleum ether.

Attempted Preparation of $In[S(O)CMe]_3$: In an attempt to prepare indium tris(thioacetate), a solution of thioacetic acid in ca. 10 ml of water was added to a solution of indium trichloride tetrahydrate in ca. 25 ml of water followed by the addition of ammonia with stirring until the pH reached 7.0. At that point a white product started to precipitate. It was isolated by filtration and dried overnight in a vacuum desiccator over P_2O_5. The analytical data are in agreement with the product indium sulfido thioacetate, In(S)[S(O)CMe] (**2b**).

Preparation of $[Et_3NH]^+\{In[S(O)CPh]_4\}^-$ (**3**): A methanolic solution (5 ml) of thiobenzoic acid was added to a stirred solution of indium(III) chloride in the same solvent (ca. 20 ml) followed by the addition of a soluton of triethylamine in ca. 5 ml of methanol.

The reaction mixture was stirred overnight during which time a white precipitate formed which was isolated by filtration and dried in vacuo for 1 h at 0.05 Torr/33°C. The product was crystallized from CH_2Cl_2/petroleum ether (60–80°C).

Preparation of $Sn[S(O)CPh]_4$ (**5**): To the stirred suspension of potassium thiobenzoate in dichloromethane (ca. 20 ml) a solution of $SnCl_4$ (ca. 15 ml) in the same solvent was added. Stirring was continued for 3 h and KCl which had formed was filtered off. Then the solvent was removed from the filtrate under reduced pressure and the residue thus obtained dried in vacuo for 2 h at 0.01 Torr/30°C to give **5** which was crystallized from dichloromethane/*n*-hexane.

X-Ray Structure Determinations: Data relevant to crystallography and data collection are displayed in Table 4. Further details of the X-ray structure determinations are deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, and may be requested by quoting the depository number CSD-405315 (**7**), -405316 (**4**), -405317 (**3**), the authors and the journal citation.

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[1] T. N. Lockyer, R. L. Martin, *Prog. Inorg. Chem.* **1980**, *27*, 153.

[2] B. J. McCormick, R. D. Bereman, D. M. Baird, *Coord. Chem. Rev.* **1984**, *54*, 99–130.

[3] S. Bhattacharya, N. Seth, V. D. Gupta, H. Nöth, M. Thomann, *Z. Naturforsch., Part B*, **1994**, *49*, 193–198.

[4] D. K. Srivastava, Ph. D. Thesis, Banaras University, India, **1986**.

[5] D. K. Srivastava, R. P. Singh., V. D. Gupta, *Polyhedron* **1988**, 483–487.

[6] D. K. Srivastava, V. D. Gupta, H. Nöth, W. Rattay, *J. Chem. Soc., Dalton Trans.* **1988**, 1533–1541.

[7] V. V. Savant, J. Gopalakrishnan, C. C. Patel, *Inorg. Chem.* **1970**, *9*, 748–751.

[8] G. Speier, V. Vülöp, G. Argay, *Transition Met. Chem.* **1991**, *16*, 576–578.

[9] P. J. Smith, A. P. Tupciauskas, *Ann. Rev. NMR Spectrosc.* **1978**, *8*, 291.

[10] *Lange's Handbook of Chemistry* (Ed.: J. A. Dean), 13th ed., McGraw-Hill, **1972**.

[11] R. R. Holmes, *Acc. Chem. Res.* **1989**, *22*, 190, citing C. K. Kumaraswami, R. O. Day, R. R. Holmes, unpublished results.

[12] S. Bhattacharya, N. Seth, V. D. Gupta, H. Nöth, K. Polborn, M. Thomann, H. Schwenk, *Chem. Ber.* **1994**, *127*, 1895–190X.

[13] J. H. Wengrovius, M. F. Gabauskas, *Organometallics* **1992**, *11*, 1334–1342.

[14] A. Haaland, *Angew. Chem.* **1989**, *101*, 1917–1933; *Angew. Chem. Int. Ed. Engl.* **1989**, *28*, 992–1007.

[15] G. Brauer, *Handbook of Preparative Inorganic Chemistry*, Academic Press, New York and London, **1963**, vol. VI, p. 729.

[16] H. Gilman, L. A. Gist, *J. Org. Chem.* **1957**, *22*, 368–378.

[17] P. Dunn, T. Norris, Australia, Commonwealth, Dept. Supply Defence Std. Lab. Rept. **1964**, *269*, 21.

[18] P. Noble, Jr., D. S. Tarbell in *Organic Synthesis* (Ed.: N. Rabjohn), Interscience, New York, **1963**, vol. 4, p. 924.

[19] SHELXTL PLUS, Siemens Analytical X-Ray Instruments, Inc. Release 4.1, **1990**.

[20] SHELXL 93, G. M. Sheldrick, University of Göttingen, **1993**.

[96056]