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Sulfur(IV) Compounds as Ligands. VIII*. Adducts of Tin(IV) Halides with Thiirane-1-oxide

WOLFDIETER A. SCHENK**
and ALMUETASSEM KHADRA

*Institut für Anorganische Chemie der Universität Würzburg,
Am Hubland, D-8700 Würzburg, F.R.G.*

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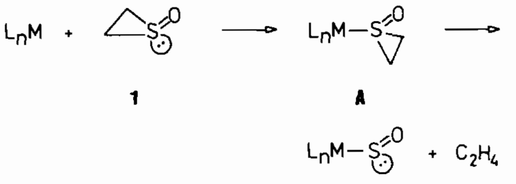
It is well known that sulfoxides form coordination compounds with a wide variety of metal fragments. Hard Lewis acids coordinate at oxygen whereas soft centers such as transition metals in low oxidation states in general prefer the more polarizable sulfur atom [2]. Thiirane-1-oxide (**1**) has been used as a reagent to introduce the sulfur monoxide ligand into transition metal complexes [3–7]. The occurrence of a rather unstable intermediate in this reaction, probably a sulfoxide-S-complex, has been inferred from low-temperature NMR observations (eqn. (1)) [4].



(1)

The synthesis of a stable complex of type **A**, $[Pt(PPh_3)_2(C_2H_4SO)]$, has been claimed [8]. However, the somewhat unusual spectral characteristics reported for this compound and the fact that no other platinum(0) complexes of sulfoxides are known [2] leaves some doubt concerning the exact nature of this material [7].

If at all, coordination via oxygen seemed to offer a chance to obtain isolable complexes of **1**. Indeed,

$$Ph_nSnX_{4-n} + 2\ C_2H_4SO \longrightarrow Ph_nSnX_{4-n}(C_2H_4SO)_2 \qquad (2)$$

	2	**3**	**4**	**5**	**6**
X	Cl	Br	Cl	Cl	Br
n	0	0	1	2	2

$$Ph_3SnCl + C_2H_4SO \longrightarrow \underset{\mathbf{7}}{Ph_3SnCl(C_2H_4SO)} \qquad (3)$$

we found that **1** readily forms 2:1 addition products with SnX_4, $PhSnCl_3$, and Ph_2SnX_2, whereas Ph_3SnCl gives a 1:1 adduct (eqns. (2) and (3)).

Evidently, **1** resembles dimethyl sulfoxide in its behaviour towards tin(IV) halides [9–17]. The new compounds were characterized by elemental and thermal analyses (see 'Experimental') and infrared spectroscopy (Table I). The observation of at least three different Sn–Cl stretching absorptions clearly establishes a *cis*-octahedral structure for **2** which has also been found by X-ray crystallography for the analogous compounds $SnCl_4(Me_2SO)_2$ [9] and $SnBr_4(Me_2SO)_2$ [18]. Similarly the two Sn–Cl stretches of **5** have to be taken as evidence for the usual [15] *trans*-diphenyl-*cis*-dichloro structure. Due to limitations in our instrumentation we have not been able to locate the Sn–Br frequencies of **6** which are expected to occur below 200 cm^{-1}. Since analogous chloro and bromo complexes are not necessarily isostructural [17] a definite assignment is not warranted at this time.

The S–O stretching frequencies of the adducts are as expected some 100 to 150 cm^{-1} lower than that of the free ligand (1060 cm^{-1}, in dichloromethane). This mode is strongly coupled with the CH_2 rocking modes which are also shifted and gain in intensity upon coordination. A notable difference between **2**–**7** and the corresponding Me_2SO adducts is the distinctly lower Sn–O stretching frequencies (*cf.* 482 cm^{-1} in $SnCl_4(Me_2SO)_2$ [13]). Obviously **1** is a weaker donor than dimethyl sulfoxide which may be taken as a consequence of its lower HOMO energy [19].

The new addition compounds **2**–**7** are labile; differential thermal analyses show strongly exo-

TABLE I. Infrared Spectra of the Tin Adducts **2**–**7**[a]

Compound		$\nu(SO)$ (cm^{-1})	$\nu(SnO)$ (cm^{-1})	$\nu(SnX)$ (cm^{-1})
$SnCl_4(C_2H_4SO)_2$	(**2**)	915(vs)	446(s,br)	322(vs,br), 310(sh), 280(w)
$SnBr_4(C_2H_4SO)_2$	(**3**)	910(vs)	437(s)	235(vs,br)
$PhSnCl_3(C_2H_4SO)_2$	(**4**)	950(vs)	425(s)	290(vs,br)
$Ph_2SnCl_2(C_2H_4SO)_2$	(**5**)	967(vs)	382(m)	284(s), 258(s)
$Ph_2SnBr_2(C_2H_4SO)_2$	(**6**)	964(vs)	384(m)	
$Ph_3SnCl(C_2H_4SO)$	(**7**)	987(s)	338(m)	270(s)

[a] Taken from nujol mulls.

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*Part VII is ref. 1.

**Author to whom correspondence should be addressed.

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TABLE II. Yields, Elemental Analyses and Decomposition Points (by DTA) of the Tin Adducts **2**–**7**

Compound	Yield (%)	Analysis: found (calc.) (%)				Decomposition points (°C)
		C	H	S	Sn	
2	85	11.08 (11.64)	2.13 (1.95)	15.80 (15.53)	29.00 (28.76)	49
3	90	8.01 (8.14)	1.48 (1.37)	11.87 (10.86)	19.43 (20.10)	56
4	96	26.20 (26.43)	3.23 (2.88)	14.20 (14.11)	25.20 (26.12)	30
5	84	38.46 (38.74)	3.46 (3.65)	12.70 (12.93)	23.74 (23.93)	84
6	76	32.33 (32.85)	3.10 (3.10)	11.27 (10.96)	20.01 (20.29)	51
7	76	51.97 (52.04)	4.29 (4.15)	6.65 (6.95)	25.35 (25.72)	80[a]

[a] Sharp endothermic melting point followed by rapid exothermic decomposition.

thermic peaks at slightly elevated temperatures (Table II). Ring opening seems to be the main pathway of decomposition as judged by the disappearance of the C–H stretching vibrations of the three-membered ring at 3090 and 2990 cm^{-1}. Similarly **1** is known to decompose upon protonation [20] and addition of copper halides [21], and in view of this it is surprising that complexes such as **2**–**7** could be isolated at all. We have also observed adduct formation between **1** and alkyltin halides in solution by NMR techniques which will be the subject of a study forthcoming from our laboratory.

Experimental

All reactions were carried out under nitrogen in water-free solvents. Thiirane-1-oxide was prepared by a published procedure [22], the tin halides were obtained commercially. IR spectra: Perkin-Elmer 283, DTA: DuPont 990 Thermal Analyzer.

Synthesis of the Adducts 2–7

Solutions of 1.0 mmol of the tin compound in 2 ml of dichloromethane and 2.0 mmol of thiirane-1-oxide in 1 ml of the same solvent (toluene is used instead for **5**, **6** and **7**) are combined at 0 °C. A white precipitate is formed almost immediately. Complete separation of the product is achieved by addition of a few ml of pentane. The product is filtered off, washed with a few ml of cold dichloromethane (toluene, respectively) and dried in a vacuum at 0 °C. Yields, elemental analyses, and decomposition points are reported in Table II.

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