Isolation and Crystal Structure (130 K) of the First Example of an η^1-O coordinated Sulphine–Metal Complex: $SnMe_2Cl_2[\eta^1\text{-O-}\{Me(Ph)NC(Ph)=S=O\}]$

ROBERT J. F. JANS, GERARD VAN KOTEN*, KEES VRIEZE

Anorganisch Chemisch Laboratorium, University of Amsterdam, Nieuwe Achtergracht 166, 1018 VW Amsterdam, The Netherlands

BISERKA KOJIĆ-PRODIĆ**, ANTHONY L. SPEK

Vakgroep Algemene Chemie, Afdeling Kristal- en Structuurchemie, University of Utrecht, 3508 TB Utrecht, The Netherlands

and JAN L. DE BOER

Material Science Centre, Laboratorium voor Anorganische Chemie, University of Groningen, 9747 AG Groningen, The Netherlands

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Abstract

Aminosulphines coordinate in the η^1-O coordination mode to Me_2SnCl_2 as established by the X-ray structure determination of $SnMe_2Cl_2[\eta^1\text{-O-}\{Me(Ph)\text{-}NC(Ph)=S=O\}]$.

Introduction

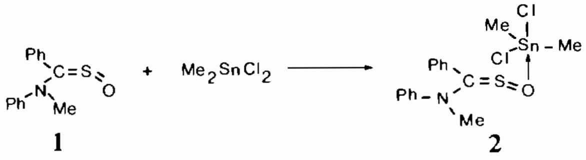
We and others have shown that sulphines, RR′C=S=O, (cf. Scheme 1) can coordinate in a variety of

We and others have shown that sulphines, RR′C=S=O, (cf. eqn. (1)) can coordinate in a variety of modes depending on the nature of the C-substituents R and R′ as well as of the metal fragment involved: *i.e.* via η^2-C=S to $Pt(PR_3)_2$ [1, 2], $Fe(CO)_3$ [3–5] and $W(CO)_5$ [6], η^1-S to $Rh^I(PR_3)_2Cl$ [7] and if R = –SR″ via η^3-S–C=S to $Rh^I(PR_3)Cl$ [7].

However, so far η^1-O coordination has not been realized. Interest in this latter type of coordination relates to research directed towards the preparation of RR′C=S compounds by selective cleavage of the S–O bond† in the sulphine [9].

We report here the isolation and structural characterization of the first example of the η^1-O coordination of a sulphine, which occurs to dimethyltin dichloride.

The addition of phenyl(N-methyl-N-phenylamino)sulphine 1 (1 mmol) to a solution of Me_2SnCl_2 (1 mmol) in CH_2Cl_2 (10 ml) and subsequent addition of pentane (100 ml) results in the precipitation of the yellow complex 2 (Scheme 1)††.



Scheme 1. 1 (1 mmol) and Me_2SnCl_2 (1 mmol); CH_2Cl_2, RT, 10 min.

Recrystallization of 2 from toluene/pentane (1/1 v/v) gave single crystals suitable for X-ray structure analysis.

Crystal Data

130 K, $C_{16}H_{19}Cl_2NOSSn$, M = 463.00, space group *C*2/*c*, $a = 13.806(1)$, $b = 9.265(1)$, $c = 29.221(2)$ Å, $\beta = 93.482(6)°$, $U = 3730.8(6)$ Å^3, $Z = 8$ (monomers), $D_c = 1.648$ g/cm^3, graphite monochromated Mo Kα radiation $\lambda = 0.71073$ Å. 16169 reflections were measured on an ENRAF NONIUS CAD4F diffractometer ($\theta \leqslant 35°$; $\omega/2\theta$ scan mode) and averaged (R = 4.6%) into a unique set of 6742 reflections with $I > 2.5\sigma(I)$. The structure was solved by Patterson and Fourier methods and refined by full matrix least squares (SHELX 76), including positional and anisotropic thermal parameters for the non-hydrogen atoms, hydrogen atoms of phenyl groups with the riding model with one common isotropic temperature parameter, and positional and one common isotropic temperature parameter for the methyl hydrogen atoms, to $R = 0.0397$.

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*Author to whom correspondence should be addressed.

**Permanent address: Rudjer-Bosković Institute, 41000 Zagreb, Yugoslavia.

†Sulphines are converted to the corresponding ketones RR′C=O by exposure to heat or by UV radiation [8].

††Correct elemental analytical data were obtained $C_{16}H_{19}Cl_2NOSSn$ % calc.: C 41.51; H 4.14; Cl 15.31; N 3.03; S 6.92. % found: C 41.46; H 4.17; Cl 15.13; N 2.90; S 6.99. ^1H NMR ($CDCl_3$, RT, δ (ppm) TMS (internal standard): aromatic-H 7.2–7.6, N–Me 3.67, Sn–Me 1.24 $^3J(Sn\text{–}H)$ 79.8 Hz.

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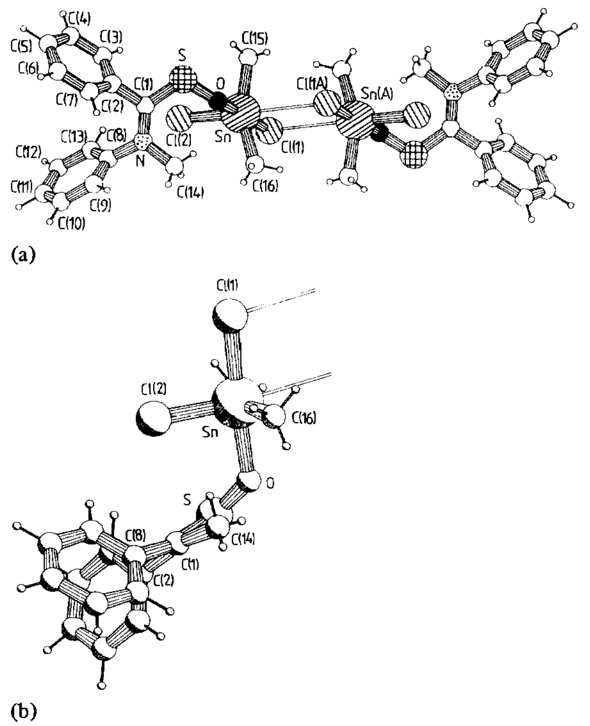

Fig. 1. (a) Pluto drawing of the dimeric solid state structure of 2. Selected bond distances (Å) and angles (°) (see other page). (b) View of the monomeric unit along the C(1)–N bond.

Figure 1 shows the dimeric molecular unit with relevant bond lengths and angles. Each Sn atom is surrounded by essentially five atoms at short distances, *i.e.* Cl(1), Cl(2), C(15), C(16) and the O atom of an intact sulphine. The Sn coordination sphere is completed by a second SnMe$_2$Cl$_2$·ligand unit with a long Sn····Cl(1A) interatomic distance of 3.307(1) Å. The latter weak interaction also occurs from Cl(1) to Sn(A), which results in formation of an associated dimer in the solid-containing pseudo-hexacoordinate Sn centres. The Sn–O distance is 2.268(3) Å. The C(15)–Sn–C(16) angle has opened up from the value of 120° expected for this angle between two methyl groups in a TBP arrangement, to 153.4(2)° in the present complex 2.

The structure of 2 is unique because it contains: (a) an aminosulphine that is O-coordinated and (b) a planar OSC(1)NC(2) sulphine skeleton as shown by the interbond angles around each of these nuclei as well as dihedral angles within this moiety[*].

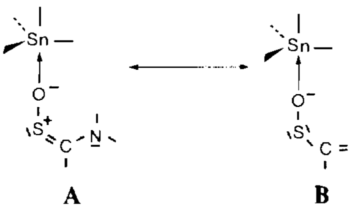

Fig. 2. Canonical structures of 2.

Each Sn centre possesses two different Sn–Cl bonds with the Sn–Cl(1) bond, which is *trans* to the η^1-O sulphine and which is also involved in the bridge, being 0.14 Å longer than Sn–Cl(2). The η^1-O coordination of 1 to SnMe$_2$Cl$_2$ results in a change of the bond lengths and angles within the sulphine. As compared to the free ligand [10] both the S–O (1.547(3) *vs.* 1.50 Å) and the S–C(1) 1.689(3) *vs.* 1.64 Å) bond distances increase with metal coordination. These observations, together with the shortening of the C(1)–N bond (1.328(4) *vs.* 1.34 Å), indicate an enhanced contribution of canonical structure **B** (see Fig. 2) to the bonding in the sulphine and account for the observed planarity of the sulphine skeleton in 2. The importance of the availability of the canonical structures A and **B**, allowing extensive electron delocalisation, for the stability of these complexes is reflected by the observation that, so far, 9-fluorenon-S-oxide is the only other sulphine that we have found to form a stable η^1-O-coordinated complex with Me$_2$SnCl$_2$.

We are currently investigating the behaviour of 2 and related compounds in solution. Like the five other known Me$_2$SnCl$_2$·L compounds with weak donor ligands (RR'C=O, RR'C=S, RR'S=O, pyridine N-oxide) [11, 12], 2 dissociates in solution and is in equilibrium with free sulphine 1 and Me$_2$SnCl$_2$[†].

Moreover, both in the solid and in solution, 2 is converted into a 1:2 mixture of: Me$_2$SnCl$_2$·Ph(Me)NC(Ph)=S, 3, and Me$_2$SnCl$_2$·Ph(Me)NC(Ph)=O, 4 (see Scheme 2)[††]. It is noteworthy that pure **1** decomposes slowly mainly via S-elimination into N-methylbenzanilide, *i.e.* the η^1-O coordination to the Sn centre as in 2 has a pronounced effect on the reactivity of the (RR')CSO group.

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[*] Also C(8) and C(14) are almost in the OSC(1)NC(2) plane with the C(8)–NC(14) group rotated by 17° about the C(1)–N bond out of this plane. Summation of the angles for the respective nuclei in the OSC(1)NC(2) fragment gives values close to 360°, with dihedral angles close to 0° or 180°.

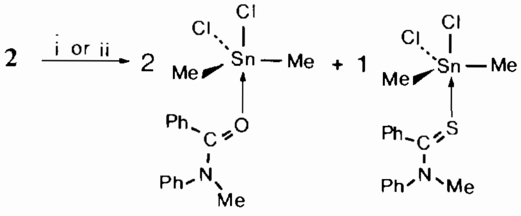
[†] The ^{119}Sn chemical shift depends on the concentration of the sulphine relative to the concentration of Me$_2$SnCl$_2$.

[††] Me$_2$SnCl$_2$·Ph(Me)NC(Ph)=S, 3. ^{1}H NMR (CDCl$_3$, δ (ppm) TMS (internal standard)) aromatic-H 7.32–6.90 ppm, NMe 3.83, Sn–Me 0.73 ppm, ^{3}J(Sn–H) = 71 Hz). Me$_2$SnCl$_2$·Ph(Me)NC(Ph)=O, 4; ^{1}H NMR (CDCl$_3$, δ(ppm) TMS (internal standard)) aromatic-H 7.32–6.90, NMe 3.44, SnMe 0.73 ppm ^{3}J(Sn–H) = 73 Hz). Samples of 3 and 4 were prepared via an independent route, involving the 1/1 reaction of the corresponding ketone or thioketone with Me$_2$SnCl$_2$, and gave identical NMR data.

Work is continuing into the potentiality of the reactions (underlying Scheme 2), that also proceed with catalytic amounts of R_2SnCl_2, for the selective cleavage of the SO bond in sulphines.

TABLE I. Selected Bond Distances (Å) and Angles (°).

Within Sn coordination			
Sn–Cl(1)	2.544(1)	Cl(1)–Sn–Cl(2)	93.65(4)
Sn–Cl(1A)	3.307(1)	Cl(1A)–Sn–Cl(2)	174.15(3)
Sn–Cl(2)	2.4043(9)	Cl(1)–Sn–O	175.86(7)
Sn–O	2.268(3)	Cl(1)–Sn–C(15)	93.7(1)
Sn–C(15)	2.109(4)	Cl(1)–Sn–C(16)	90.0(1)
Sn–C(16)	2.109(4)	Cl(2)–Sn–O	88.92(7)
		Cl(2)–Sn–C(15)	99.2(2)
		Cl(2)–Sn–C(16)	106.9(2)
		O–Sn–C(15)	89.1(1)
		O–Sn–C(16)	86.2(1)
		C(15)–Sn–C(16)	153.4(2)
Within sulphine			
O–S	1.547(3)	Sn–O–S	129.1(2)
S–C(1)	1.689(3)	O–S–C(1)	112.3(2)
N–C(1)	1.328(4)	S–C(1)–N	129.3(2)
N–C(8)	1.445(4)	S–C(1)–C(2)	111.1(2)
N–C(14)	1.471(5)	N–C(1)–C(2)	119.5(3)
C(1)–C(2)	1.483(4)	C(1)–N–C(8)	120.5(3)
		C(1)–N–C(14)	123.8(3)



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Scheme 2. (i) Solid state, 100 °C, 1/2 h (ii) solution in toluene, 70 °C, 15 min.

Acknowledgements

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