POLYSULFONYLAMINES. Part CIV [1]. SERENDIPITOUS ISOLATION AND CRYSTAL STRUCTURE OF THE NOVEL IONIC DIMETHYLTIN(IV) COMPLEX $[Me_2Sn(pyridine\text{-}1\text{-}oxide)_4]^{2+} \bullet 2\ (MeSO_2)_2N \bullet 2\ MeCN$

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Abstract: The title complex is the first authenticated example of a 1:4 adduct formed between a diorganyltin(IV) salt and an amine *N*-oxide. It was obtained adventitiously on treating the dimeric hydroxide $[Me_2Sn\{(MeSO_2)_2N\}(\mu\text{-}OH)]_2$ with four equivalents of pyridine-1-oxide (*pyo*) in acetonitrile, the co-products being Me_2SnO and water. The crystal structure, as determined by X-ray difraction at -100 °C (triclinic, space group P$\bar{1}$, Z = 1), consists of *trans*-octahedral, centrosymmetric $[Me_2Sn(pyo)_4]^{2+}$ cations, non-coordinating $(MeSO_2)_2N^-$ anions and non-coordinating MeCN molecules. Characteristic bond lengths and angles are as follows: Sn-C 211.6, Sn-O 221.0 and 223.1, N-O 134.8 and 134.5 pm, Sn-O-N 123.5 and 119.3, *cis*-angles at tin in the range 90 ± 4.5°; N-S 159.0 and 159.4 pm, S-N-S 121.3°.

Introduction

The coordination chemistry of aromatic amine *N*-oxides is a long-established field of research [2]. With diorganyltin(IV) compounds R_2SnX_2, these *O*-donors are known to form 1:1 and 1:2 complexes, and X-ray structures are available for the following four examples containing 2,6-lutidine-1-oxide (*luO*), pyridine-1-oxide (*pyO*) or quinoline-1-oxide (*quO*): $[Ph_2SnCl_2(luO)]$ (**1**) [3], $[Me_2SnCl_2(luO)]$ (**2**) [4, 5], $[Me_2SnCl_2(pyO)_2]$ (**3**) [6], and $[Me_2SnCl_2(quO)_2]$ (**4**) [7]. In the solid state, **1**-**4** exist as *uncharged* molecules. The monomeric complex **1** contains five-coordinated, trigonal-bipyramidal tin with the ligand oxygen and one of the chlorine atoms occupying the apical positions, whereas in **2** six-coordination at tin is created *via* dimer formation through bridging chlorine atoms. For the 1:2 adducts **3** and **4**, the structure determinations revealed all-*trans*-octahedral and crystallographically centrosymmetric complex molecules.

We describe here the first authenticated 1:4 complex formed between a diorganyltin(IV) salt and an aromatic amine *N*-oxide and, concomitantly, the first member in this class of coordination compounds that displays an *ionic* crystal structure.

Results and Discussion

The title complex (**5**) was discovered adventitiously. In previous work [8] we had shown that the dimeric hydroxide $[Me_2Sn(A)(\mu\text{-}OH)]_2$ (**6**), where A^- is di(methanesulfonyl)amide, readily forms novel 1:2 complexes with selected monodentate *O*-donor ligands according to the following equation:

$$[Me_2Sn(A)(\mu\text{-}OH)]_2 + 2\ L \rightarrow [Me_2Sn(A)(L)(\mu\text{-}OH)]_2 \qquad (1)$$

$A^- = (MeSO_2)_2N^-$; L = Ph_3PO, Ph_3AsO, $(Me_2N)_3PO$

In view of the fact that the amide species A^- is of considerable utility as a non-coordinating counter-ion for mono- and polynuclear organotin complex cations [9], we attempted to generate a

dinuclear dication of the hitherto unreported type $[R_2Sn(L)_2(\mu\text{-}OH)]_2^{2+}$ by treating **6** with four equivalents of monodentate *O*-donor ligands. Whereas the primary goal was not (yet) attained, we observed in the course of these studies (i) that **6** does not react with more than two equivalents of the bulky ligands shown in eq. (1), and (ii) that four equivalents of the sterically less demanding *O*-donors pyridine-1-oxide (*pyO*) and dimethyl sulfoxide (*dmso*) induce degradation of the central $[SnO(H)]_2$ four-membered ring of **6** to produce dimethyltin oxide, water and the mononuclear and ionic 1:4 complexes shown below:

$$[Me_2Sn(A)(\mu\text{-}OH)]_2 + 4\ L \rightarrow [Me_2Sn(L)_4]^{2+} \bullet 2\ A^- + Me_2SnO + H_2O \qquad (2)$$

$A^- = (MeSO_2)_2N^-$; L = *pyO*, *dmso*

The dimethyl sulfoxide complex formed according to eq. (2) was previously prepared by direct complexation of $Me_2Sn(A)_2$ with *dmso* and structurally characterized by X-ray diffraction and multinuclear CP/MAS NMR spectroscopy [10]. Its pyridine-1-oxide analogue crystallized from acetonitrile as the disolvate $[Me_2Sn(pyO)_4]^{2+} \bullet 2\ A^- \bullet 2$ MeCN (**5**), which was subjected to low-temperature X-ray structural analysis.

As shown in Fig. 1, the crystal consists of *trans*-octahedral $[Me_2Sn(pyO)_4]^{2+}$ cations, non-coordinating $(MeSO_2)_2N^-$ anions and non-coordinating MeCN molecules. The tin atom occupies a crystallographic centre of inversion. Selected geometric parameters for the ionic moieties are given in Table 1.

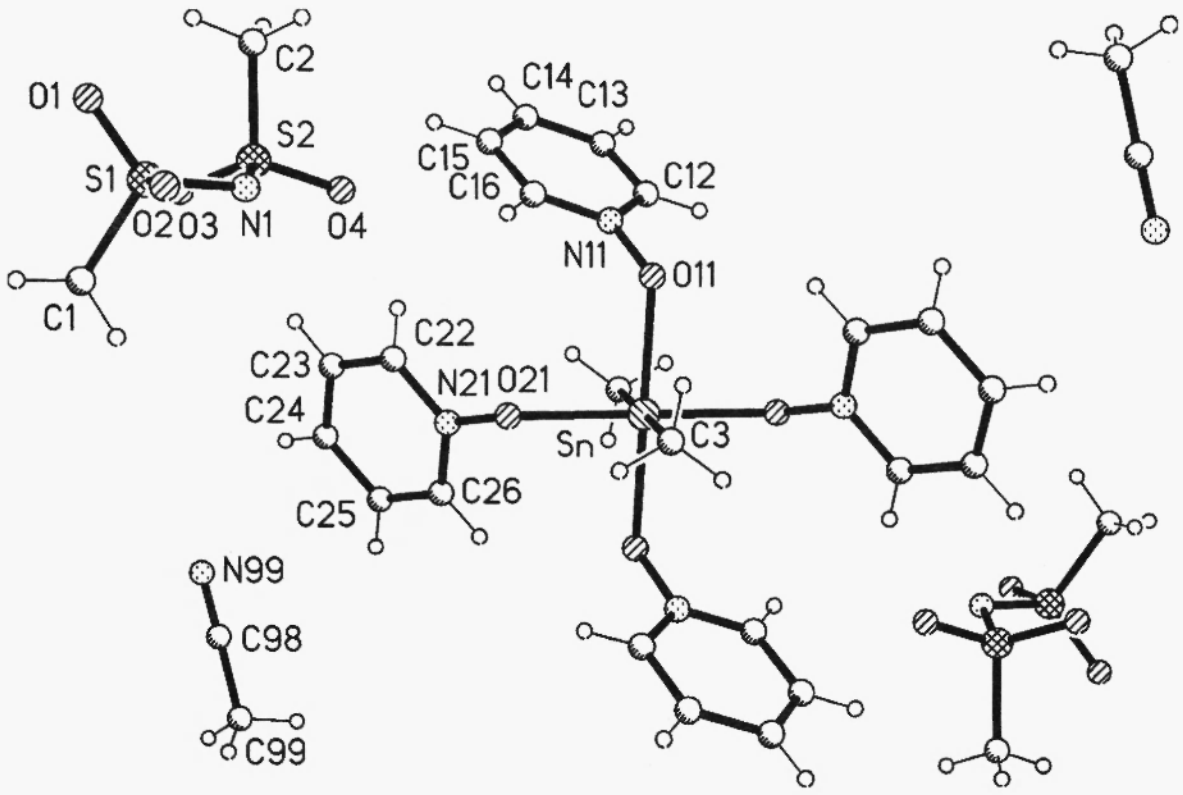

Fig. 1. The centrosymmetric formula unit of **5** showing the atomic labelling. Radii are arbitrary.

The coordination polyhedron around tin is similar to that found in the aforementioned *dmso* analogue. The Sn-O bond lengths (av. 221.1 pm) compare well with the Sn-O distance in **4** (222.0 pm), but they are markedly shorter than in **1** (229.0 pm), **2** (228.9 pm) or **3** (225 pm). The *cis*-angles

at tin lie in the range 90 ± 4.5°. The O-N distances (av. 134.7 pm), the Sn-O-N angles (av. 121.4°, reflecting sp^2 hybridization at the coordinating oxygen atoms), and the angles of twist between the mean planes of the aromatic rings and the corresponding Sn-O-N planes (84.5 and 64.5°) fall in the same ranges as the related parameters in **1-4** and in a large variety of transition metal complexes with pyridine-1-oxide (for a detailed discussion and a literature survey *cf.* Ref. [5]).

Table 1. Selected bond lengths (pm), bond angles (°) and dihedral angles (°) for **5** [a] [b]

Sn-C(3)	211.6(2)	N(11)-C(12)	134.7(2)
Sn-O(11)	223.14(12)	N(11)-C(16)	134.8(2)
Sn-O(21)	221.02(12)	N(21)-C(22)	134.6(2)
O(11)-N(11)	134.5(2)	N(21)-C(26)	134.9(2)
O(21)-N(21)	134.8(2)	N(1)-S(1)	158.99(14)
		N(1)-S(2)	159.4(2)
O(11)-Sn-O(21)	90.20(5)	N(11)-O(11)-Sn-O(21)	-67.4(1)
C(3)-Sn-O(11)	85.58(6)	N(21)-O(21)-Sn-O(11')	-69.3(1)
C(3)-Sn-O(21)	86.72(6)	φ_{11}	84.5(1)
Sn-O(11)-N(11)	119.28(9)	φ_{21}	64.5(1)
Sn-O(21)-N(21)	123.54(10)	O(1)-S(1)-N(1)-S(2)	-37.1(1)
O(11)-N(11)-C(12)	119.54(14)	O(2)-S(1)-N(1)-S(2)	-165.0(1)
O(11)-N(11)-C(16)	118.46(14)	C(1)-S(1)-N(1)-S(2)	81.6(1)
C(12)-N(11)-C(16)	122.0(2)	O(3)-S(2)-N(1)-S(1)	-42.4(1)
O(21)-N(21)-C(22)	118.20(14)	O(4)-S(2)-N(1)-S(1)	-170.3(1)
O(21)-N(21)-C(26)	120.18(14)	C(2)-S(2)-N(1)-S(1)	75.9(1)
C(22)-N(21)-C(26)	121.51(14)		
S(1)-N(1)-S(2)	121.33(9)		

[a] Symmetry code: (i) -*x*+1, -*y*, -*z*+1. [b] φ_n are the tilt angles between the Sn-O(*n*)-N(*n*) planes and the respective aromatic N(*n*)C_5 rings.

The $(MeSO_2)_2N^-$ anion in **5** adopts an extended conformation approximating to C_2 symmetry (*cf.* torsion angles in Table 1). This geometry, with short N-S bond lengths of *ca.* 160 pm and an S-N-S angle of *ca.* 120°, is persistent for the non-coordinating species in question and has been observed in numerous ionic di(methanesulfonyl)amides including, among others, organotin complexes and onium salts [9, 11-13].

In the crystal packing (Fig. 2), one MeCN hydrogen atom is directed towards the nitrogen atom of an adjacent anion, and the resulting intermolecular sequence may be viewed as a C-H···N^- hydrogen bond. The geometric data are as follows: C(99)-H(99C) 98, H(99C)···N(1') 251, C(99)···N(1') 338.6(3) pm, angle at H(99C) 150(1)° [symmetry code for N(1'): -*x*+1, -*y*+1, -*z*+1].

Experimental

The dimeric hydroxide **6** was prepared according to a published procedure [8].

[*trans-Dimethyltetrakis(dimethyl sulfoxide)tin(IV)] Bis[di(methanesulfonyl)amide*]

A MeCN solution (20 mL) of Me_2SO (5.93 mmol, 0.463 g) was added to a suspension of **6** (1.48 mmol, 1.00 g) in the same solvent (30 mL). The mixture was stirred for 6 h at reflux temperature of the solvent. Me_2SnO was removed by filtration. Removal of the volatiles from the filtrate under reduced pressure afforded a solid residue that was recrystallized from MeCN (15 mL; 80 °C → -20 °C); large colourless crystals; yield 52% (0.62 g); m.p. 88-92 °C (reported m.p. [10]: 95-98 °C). Analysis: found C 20.85, H 5.26, N 3.48%; $C_{14}H_{42}N_2O_{12}S_8Sn$ (805.72 g mol^{-1}) requires C

20.87, H 5.25, N 3.48%. ^{1}H NMR (CD_3CN, 200 MHz): δ = 0.53 (s, 6H, MeSn), $^2J(^{117}Sn\text{-}^1H)$ = 105.1 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 110.9 Hz; 2.65 (s, 24H, Me_2SO); 3.01 (s, 12H, MeS).

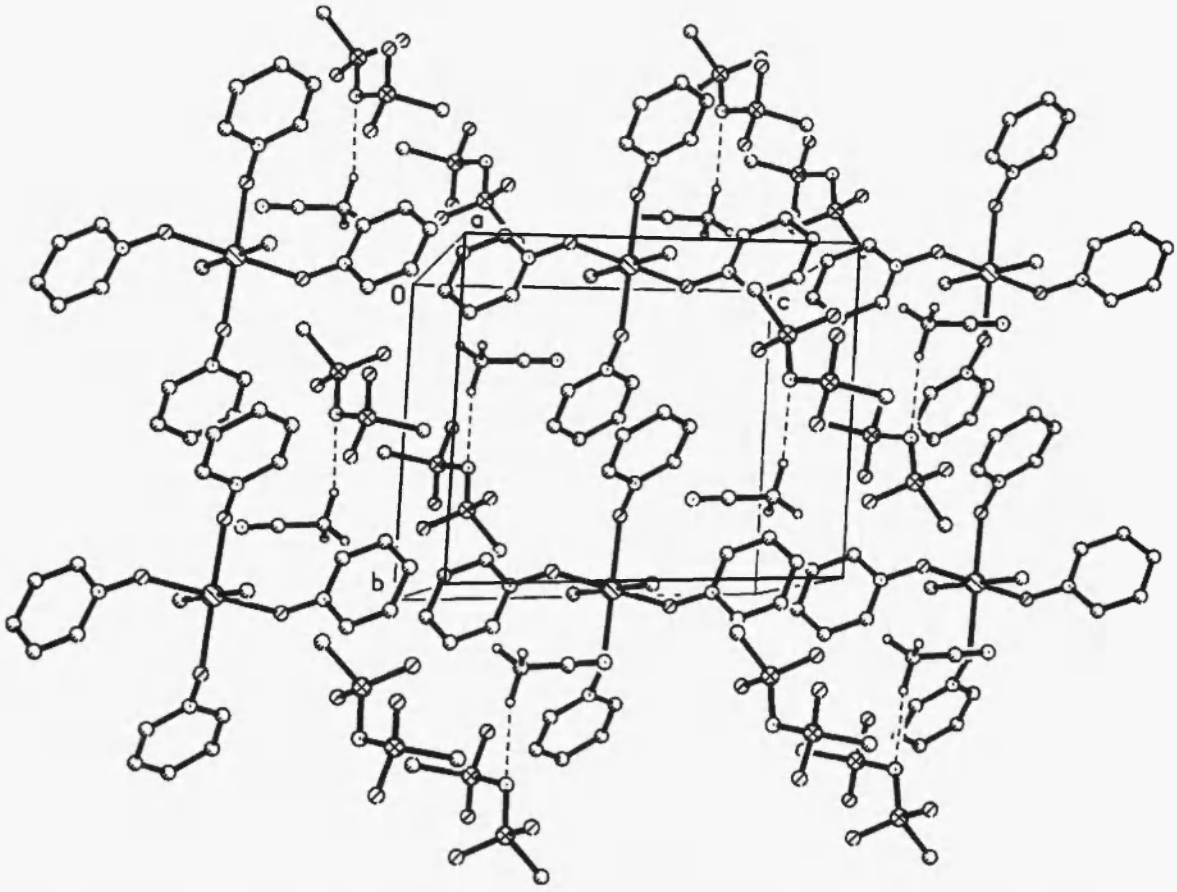

Fig. 2. Packing diagram of **5** viewed approximately parallel to the *x* axis. H atoms in the ions are omitted and the C-H···N^- interactions are indicated by broken lines.

*[trans-Dimethyltetrakis(pyridine-1-oxide)tin(IV)] Bis[di(methanesulfonyl)amide]-Acetonitrile (1/2) (**5**)*

Following the above procedure, **5** was obtained by treating **6** (2.96 mmol, 2.00 g, 30 mL of MeCN) with pyridine-1-oxide (11.9 mmol, 1.13 g, 20 mL of MeCN) for 4 days at 20 °C: The pale yellow raw product was recrystallized from MeCN (20 mL, 80 °C → -20 °C); large colourless crystals; yield 34% (0.97 g); dec. 83 °C. Analysis: found C 37.69, H 4.62, N 11.72, S 13.58%; $C_{30}H_{44}N_8O_{12}S_4Sn$ (955.66 g mol^{-1}) requires C 37.70, H 4.64, N 11.72, S 13.42%. ^{1}H NMR (CD_3CN, 200 MHz): δ = 0.53 (s, 6H, MeSn), $^2J(^{117}Sn\text{-}^1H)$ = 105.1 Hz, $^2J(^{119}Sn\text{-}^1H)$ = 110.9 Hz; 1.96 (s, 6H, MeCN); 2.86 (s, 12H, MeS); 7.63-7.77 (8H, ar. H_β); 7.82-7.95 (4H, ar. H_γ); 8.45-8.55 (8H, ar. H_α).

*X-ray crystal structure determination of **5***

Crystal data: triclinic, space group P$\bar{1}$, *a* = 914.50(8), *b* = 953.96(8), *c* = 1171.09(10) pm, α = 94.272(6), β = 95.757(6), γ = 92.467(6)°, *V* = 1.0124(2) nm^3, *Z* = 1, D_c = 1.568 Mg m^{-3}, *F*(000) = 490, λ(MoKα) = 71.073 pm, μ = 0.905 mm^{-1}, *T* = 173(2) K.

Data collection and reduction: A colourless prism of approximate dimensions 0.38 x 0.36 x 0.32 mm was mounted in inert oil and transferred to the cold gas stream of the diffractometer (Siemens R3 system with LT-2 low-temperature attachment). Intensities were measured with ω-

scans using monochromated MoKα radiation to $2\theta_{max}$ = 55°. Cell constants were refined from diffractometer angles of 59 reflections in the 2θ range 10-25°. The absorption correction (transmissions: 0.74-0.77) was based on ψ-scans. Of 4866 data, 4639 were unique (R_{int} = 0.011) and were used for all calculations.

Structure solution and refinement: The structure was solved by the heavy-atom method and refined anisotropically on F^2 using the program SHELXL-93 (*G.M. Sheldrick*, University of Göttingen). Hydrogen atoms were included with a riding model or as rigid methyl groups. The final *wR*2 was 0.054, with conventional *R*1 = 0.021, for 255 parameters. GOOF = 1.03; max. Δρ = 313 e nm^{-3}.

Full details of the structure determination (excluding structure factors) have been deposited at the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, and can be obtained on quoting the reference number CSD-408349.

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