Synthesis and X-ray Crystal Structure of a Dimethyltin(IV) Dithiocyanate Bihydrate Adduct with a Crown Ether

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Growing interest has been devoted recently to the interactions between macrocyclic polyethers and tin(II) or tin(IV) compounds. Solid state studies concerning the inorganic tin(II) [1, 2] complexes suggest for the adducts with 18-crown-6 and 15-crown-5 the existence of strong interactions between the tin(II) atom and two or three ethereal oxygen atoms. Some recent papers dealing with tin(IV) adducts with various crown ethers have been published [3–7] describing several compounds which always contain two or four water molecules. For two of these complexes, the crystal structure is also reported, showing that the molecule of the macrocyclic polyether is not directly bonded to the metal center, but acts as a second sphere ligand, interacting with the tin atom via hydrogen bondings to the coordinated water molecules. In this respect, the tin(IV) behaviour towards these ligands is similar to the one of the transition metals, which generally form aqua and ammine complexes [8], while it is very different from the one of the alkali and alkaline-earth metals [9] and of lantanoids and attinoids [10]. In this note we report the crystal structure of $Me_2Sn(NCS)_2(OH_2)_2 \cdot$ 18-crown-6, which represents the first structural determination of a bihydrated organotin(IV) complex with a cyclic polyether. In fact, the two other similar compounds already reported [5, 6] contain four water molecules per tin atom, every one of which plays an important role in the stability of the structure and in the conformation of the crown ether, even if the tin coordination geometry is substantially the same in all the complexes.

The compound was obtained by slow evaporation of a methanolic solution of an equimolar mixture of $Me_2Sn(NCS)_2$ and 18-crown-6; the white crystals so obtained were filtered off, washed, and dried under vacuum. All preparative work was performed in air, with the solvent not previously dehydrated: the use of perfectly anhydrous conditions prevents the formation of any complex. The elemental analysis agrees with the formula $Me_2Sn(NCS)_2(OH_2)_2 \cdot$ 18-crown-6 (*Anal.* Found: C, 34.59; H, 6.08; N, 4.95; Sn, 20.66; H_2O, 6.71. $C_{16}H_{34}N_2O_8S_2Sn$ calcd.: C, 34.00; H, 6.06; N, 4.96; Sn, 21.00; H_2O, 6.37%).

The crystals are monoclinic with $a = 12.532(4)$, $b = 12.804(5)$, $c = 8.106(3)$ Å, $\beta = 101.9(4)°$, $Z = 2$; $U = 1272.7$ Å^3, $D_o = 1.46$, $D_c = 1.47$ g cm^{-3}; $F(000) = 580$; $\mu R = 0.1$; space group $P2_{1/n}$. Intensity data were collected using a four-cycle Philips PW 1100 diffractometer with graphite-monochromated MoKα radiation ($\lambda = 0.7107$ Å) in the range $4 \leqslant 2\theta \leqslant 50$ by using the $\theta - 2\theta$ scan mode. Lorentz and polarization corrections were applied. The structure was solved by Fourier synthesis with the tin atom in the special position 1. A least-squares refinement on F was computed. The unitary weighting scheme was used because it presented the best convergence. The SHELX 76 program and the scattering factors there reported were used in the refinement [11]. All the non-hydrogen atoms, but not an oxygen one which presents a positional disorder, were refined anisotropically, while the positions of the hydrogen atoms were calculated. The positions of the carbon and oxygen atoms in the crown ether molecule were assigned on the basis of structural considerations and of the best refinement. The final R value was 0.058. The thermal parameters are nearly spherical for tin atom, while the thermal ellipsoids are strongly anysotropic for the other atoms. Bond distances and angles are reported in Table I. A view of the crystal structure of the complex in the solid state is reported in Fig. 1, together with the atomic labeling scheme.

The compound is formed by alternating $Me_2Sn(NCS)_2(OH_2)_2$ and 18-crown-6 moieties linked by hydrogen bonds, so that a linear polymer is constructed along the c axis. The polyhedron around the tin atom is a nearly regular octahedron with an all *trans* geometry, because the presence of the tin at a center of symmetry imposes 180° bond angles for the ligands. The Sn–C bond distance (2.066(14) Å) is practically identical with the one of the parent compound $Me_2Sn(NCS)_2$ (2.089 Å) [12], and is slightly shorter than in the other $Me_2SnX_2 \cdot 2L$ complexes (2.12 Å) [13]. On the contrary, the Sn–N and Sn–O bond distances (2.270 and 2.278 Å respectively) are a little longer than in the parent compound (2.139 Å) [12] and in the inorganic tin(IV) crown ether adducts (2.10–2.16 Å) [5, 6]. Thus a considerable rearrangement occurs in the $Me_2Sn(NCS)_2$ molecule when the coordination polyhedron is

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TABLE I. Bond Distances (Å) and Angles (°) for $Me_2Sn(NCS)_2(OH_2)_2 \cdot$18-crown-6.

Sn–N(1)	2.270(10)	Sn–C(2)	2.066(14)
Sn–OW	2.278(7)		
N(1)–C(1)	1.118(15)	C(1)–S(1)	1.628(14)
O(1)–C(3)	1.447(17)	C(3)–C(4)	1.551(28)
C(4)–O(2)	1.438(23)	O(2)–C(5)	1.297(20)
C(5)–C(6)	1.375(26)	C(6)'–O(3)	1.448(24)
O(3)–C(7)	1.384(24)	C(7)–C(8)	1.532(27)
C(8)–O(1)	1.575(24)		
N1–Sn–C2	91.0(1.1)	N(1)–Sn–OW	89.0(3)
OW–Sn–C2	86.2(8)		
Sn–N(1)–C(1)	163.7(2.5)	N(1)–C(1)–S(1)	158.2(2.7)
O(1)–C(3)–C4	104.3(1.5)	C(3)–C(4)–O(2)	113.0(1.2)
C(4)–O(2)–C(5)	121.2(1.7)	O(2)–C(5)–C(6)	113.2(2.4)
C(5)–C(6)–O(3)'	155.2(2.4)	C(6)'–O(3)–C(7)	102.9(1.8)
C(8)–C(7)–O(3)	110.9(1.7)	C(8)–O(1)–C(3)	100.2(1.8)
O(1)–C(8)–C(7)	85.3(1.4)		

Symmetry code: ' = $x, y, 1 - z$

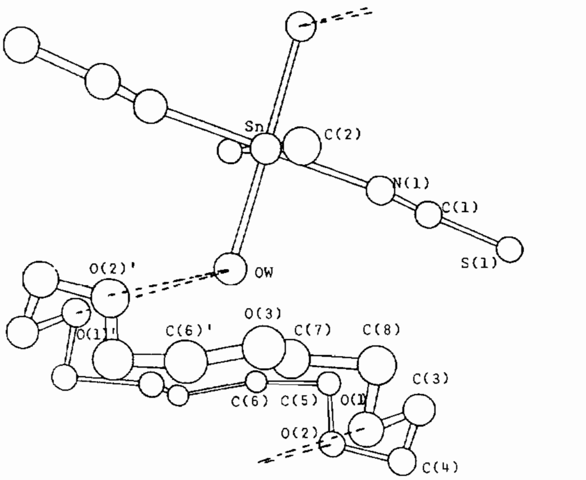

Fig. 1. View of the crystal structure of the $Me_2Sn(NCS)_2(OH_2)_2 \cdot$18-crown-6 compound along the y plane together with the asymmetric unity labeling scheme.

transformed from tetrahedral to octahedral, due to the bonding of two water molecules.

The thiocyanate group, is also considerably bent at the N(1)–C(1)–S(1) angle (158.2°) if compared with the parent compound (179.3°) [12], is N-bonded, as demonstrated by the infrared spectrum. In fact, it presents a strong, sharp ν(N–CS) band at 2030 cm^{-1} (2088 vs and 2062 vs cm^{-1} in the $Me_2Sn(NCS)_2$, a weak ν(NC–S) band at 782 cm^{-1} and a (NCS) at 478 cm^{-1} (487 sh and 483 m cm^{-1}) [14].

The crown ether molecule is quite distorted from the regular geometry and shows a considerable positional disorder in the O(3) atom, probably because it is the only oxygen not involved in the net of hydrogen bondings.

The coordinated water molecule is linked by two hydrogen bonds to the O(1) (3.03 Å) and O(2) atoms (2.80 Å) and, due to the presence of the inversion centre, these bonds propagate the polymeric chain. Moreover, this water molecule is very near the C(7) atom (2.78 Å) of the crown ether. The short distance OW–C(7), rahter than being due to the formation of an improbable hydrogen bond, seems to be imputable to a compromise among the repulsion of the coordinated water molecule toward the weakly hydrophobic methylene group and the steric and bonding requirements of the crown ether molecule. The two highly distorted bond angles O(3)'–C(6)–C(5) (155°) and C(7)–C(8)–O(1) (87°) seem to give support to this hypothesis; it is also worth noting that the X-ray analysis in this part of the crown ether molecule shows large thermal motions.

On this and other complexes of the same series structural and chemico-physical studies are in progress.

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