Synthesis and X-Ray Crystal Structure of a Tin(IV) Tetrahalide Adduct with a Crown Ether

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The polymeric structure of the complex, [$SnCl_4(H_2O)_2$]18-crown-6·$2H_2O$, prepared by the addition of a solution of $SnCl_4$ to 18-crown-6, has been determined by X-ray analysis. The structure has been solved by three-dimensional Patterson-Fourier synthesis to a conventional R-factor of 0.13, by using 1394 reflections with $I > 3\sigma(I)$. The crystals are monoclinic, with $a = 15.753(3)$, $b = 15.072(3)$, $c = 12.209(4)$, $\beta = 97.77°(1.0)$, $z = 4$, and space group $P2_1/a$. The tin atom is octahedrally coordinated to four chlorine atoms and two water molecules in cis *positions. A very complex network of hydrogen bonding links together the tin coordination octahedron, the two water hydration molecules, and the two crystallographically-different half crown-ethers.*

Introduction

Since their discovery in 1967, crown-ethers have been widely used as ligands, normally with alkali and alkaline-earth elements [1] and with the f-block metals [2]. Many papers have also been published dealing with complexes formed with transition metals such as cobalt [3], nickel [4], and manganese [5], as well as with non-transition metals such as aluminium [6] and copper [7]. Only recently have complexes between crown-ethers and tin been described in the literature.

Tin(II) is reported to form 1:1 and 1:2 ligand-to-metal complexes with 18-crown-6 and 2:3 and 2:1 complexes with the smaller 15-crown-5 [8, 9]. A tin(IV) complex with dibenzo-24-crown-8 was postulated in benzene solution [10], while the tin(IV) complexes with 18-crown-6, 15-crown-5, and 12-crown-4 have recently been studied in the solid state [11, 12]. They form 1:1 and 1:2 ligand-to-metal complexes with two water molecules; different structures are proposed for these complexes on the basis of their infrared and Mössbauer spectral properties. In only one complex are the water molecules proposed to be coordinated directly to the tin(IV) ion.

In this paper we report the preparation of the unusual compound, [$SnCl_4(H_2O)_2$]18-crown-6·$2H_2O$, in which the crown-ether is hydrogen-bonded to four water molecules in two [$SnCl_4(H_2O)_2$] moieties to form a linear polymeric structure. We also present the X-ray crystal structure of this adduct, which is, to the best of our knowledge, the first published structure of this type.

Experimental

The complex [$SnCl_4(H_2O)_2$]18-crown-6·$2H_2O$ was prepared by adding tin(IV) chloride dissolved in chloroform to a solution of 18-crown-6 in the same solvent at room temperature; the compound precipitated on addition of hexane. 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 and no solid compound is obtained. In this case a white powder is formed nearly immediately on addition of a drop of water. The essential role of water in the stabilization of the adduct is supported by the impossibility of dehydration of the adduct without its decomposition. Moreover, preliminary thermodynamic studies in anhydrous CH_3CN solutions of the $SnCl_4$ and 18-crown-6 demonstrate the absence of any bonding interaction between $SnCl_4$ and the crown-ether. The precipitate was recrystallized by slow evaporation of its methanolic solution in air. The analytical results give C = 23.81, H = 5.3, Cl = 23.95, Sn = 20.12%, whereas the calculated values for $C_{12}H_{32}O_{10}SnCl_4$ are C = 24.15, H = 5.4, Cl = 23.76, Sn = 19.88%. M.P. = 175–80° under vacuum. The infrared spectrum was recorded on a Perkin-Elmer 580 B instrument in a KBr pellet. The conductivity value, determined in a 10^{-3} M solution in $MeNO_2$ on a LKB bridge at 25°, is far below the

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range suggested for 1:1 electrolyte complexes [13]. The water content, as determined by Karl-Fisher titration, is 12.5 (calcd. 12.1%).

Intensity data were collected using a Philips PW 1100 four-circle diffractometer, in the range $2 < \theta < 45°$ with graphite monochromatized Cu-K_α radiation ($\lambda = 1.5418$ Å). By using the criterion $I > 3\sigma(I)$, 1394 of the 2441 unique reflections were deemed independent and observable. The structure was solved by using three-dimensional Patterson–Fourier synthesis and locating first the Sn, Cl, and O atoms, and then the C atoms. A block-diagonal least-squares refinement on F was computed and the function $\Sigma w[|Fo| - |Fc|]^2$, in which w is 1, was minimized. The SHELX-76 program and the usual scattering factors were used in the refinement [14]. All the non-carbon atoms were refined anisotropically. The final R-factor is 0.13: this high value is due to the slow decomposition of the crystal under the X-ray beam, probably as a consequence of the loss of the water molecules. The Fourier difference map points out that, without any question, all atoms heavier than hydrogen were found in the structure refinement.

The white crystals are monoclinic, space group $P2_1/a$ $a = 15.753(3)$, $b = 15.072(3)$, $c = 12.209(4)$ Å, $\beta = 97.7°(1.0)$, $Dc = 1.375$ g cm^{-3}, $z = 4$, $U = 2873$ Å^3, and $F(000) = 1208$.

Distances and angles between the atoms involved in the octahedron around the tin(IV) ion and the lengths of the contacts between oxygen atoms are reported in Tables I and II. The fractional atomic coordinates and the observed and calculated structure factors can be obtained from the authors. A perspective view of the structure along the X-axis is reported in Fig. 1.

TABLE I. Bond Distances (Å) and Angles (°) for the $[SnCl_4(H_2O)_2]$ Octahedron with Standard Deviation in Parentheses.

Sn–Cl(1)	2.37(1)	Sn–Cl(4)	2.38(2)
Sn–Cl(2)	2.37(2)	Sn–OH(1)	2.16(4)
Sn–Cl(3)	2.40(1)	Sn–OH(2)	2.10(4)
Cl(1)–Sn–Cl(2)	171.1(5)	Cl(2)–Sn–OH(2)	89.1(1.1)
Cl(1)–Sn–Cl(3)	94.0(6)	Cl(3)–Sn–Cl(4)	96.3(6)
Cl(1)–Sn–Cl(4)	92.6(6)	Cl(3)–Sn–OH(1)	88.9(1.1)
Cl(1)–Sn–OH(1)	87.0(1.2)	Cl(3)–Sn–OH(2)	170.8(1.1)
Cl(1)–Sn–OH(2)	83.5(1.1)	Cl(4)–Sn–OH(1)	174.8(1.1)
Cl(2)–Sn–Cl(3)	92.5(6)	Cl(4)–Sn–OH(2)	92.7(1.1)
Cl(2)–Sn–Cl(4)	92.7(6)	OH(1)–Sn–OH(2)	82.1(1.4)
Cl(2)–Sn–OH(1)	87.1(1.2)		

TABLE II. Contact Distances (Å) for the $[SnCl_4(H_2O)_2]$18-crown-6·$2H_2O$ Complex with Standard Deviation in Parentheses.

OH(1)–OH(2)	2.51(3)	OH(2)–OH(4)	2.48(3)
OH(1)–O(1)	2.68(4)	OH(2)–O(5)	2.76(4)
OH(3)–O(1)	3.01(4)	OH(4)–O(4)	2.93(3)
OH(3)–O(2)	2.83(3)	OH(4)–O(5)	3.04(4)
OH(3)–O(3)	2.89(4)	OH(4)–O(6)	2.86(3)

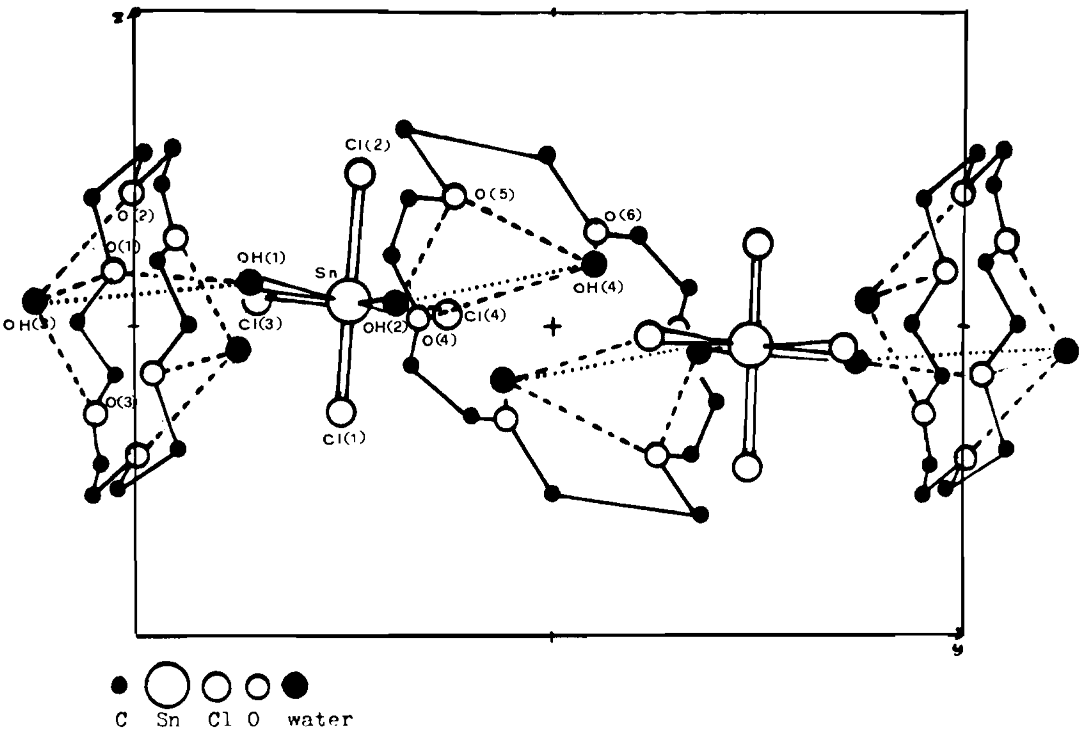

Fig. 1. Perspective view of the $[SnCl_4(H_2O)_2]$18-crown-6·$2H_2O$ complex with the atom numbering scheme.

Results and Discussion

The asymmetric unit of the $[SnCl_4(H_2O)_2]$18-crown-6·$2H_2O$ is composed of a tin(IV) center coordinated to four chlorine atoms and two water molecules, two water molecules of hydration, and two half crown-ethers in special position $\bar{1}$; all these parts are connected by a very complex network of hydrogen bonding.

The $[SnCl_4(H_2O)_2]$ moiety forms a slightly distorted octahedron around the tin(IV) ion with the oxygens from the water ligands in *cis* positions; the average bond lengths and angles are: Sn–Cl, 2.38 Å; Sn–O, 2.13 Å; Cl–Sn–Cl, 93.6°; Cl–Sn–O, 88.1°; O–Sn–O, 82.1°. All these values are typical for octahedral tin(IV) complexes. The covalent nature of the Sn–Cl bonds agrees with the very low value of the conductivity, whereas the *cis* arrangement is supported by the far infrared spectrum. In fact, the compound exhibits three of the four absorptions, 353sh, 321s, and 298sh cm^{-1}, due to ν(Sn–Cl) required by a *cis*-octahedral coordination geometry. In the analogous *trans* complex, only one band should be infrared active. The four water molecules are all involved in different bonding (see Fig. 1), as shown by the very broad infrared absorptions centered at 3275 and 1620 cm^{-1}. Each of the two water molecules bonded to the tin(IV) ion is also bonded to an ethereal oxygen and to another water molecule on the other side of the crown-ether plane. This bond (2.50 Å) is much shorter than the typical water–water hydrogen bond: for instance, in the complex $[SnCl_4(H_2O)_2]\cdot 3H_2O$ [15], the length of a similar hydrogen bond between the coordinated and the uncoordinated water molecules is within the normal range (2.75 Å). This bond is practically identical to the one found in the diaquo-hydrogen ion ($H_5O_2^+$) that is also 2.50 Å [16]. One of the hydration water molecules is at a distance typical for hydrogen bonding from three adjacent crown-ether oxygens. Because of the centrosymmetric nature of the structure, the second hydration water molecule is linked in the same way to the other three oxygens of the crown-ether. In this way, a roughly linear polymeric chain is formed along the crystallographic y-direction (see Fig. 1). The ν_{as}(C–O–C) infrared band, which is sensitive to the coordination of the crown-ether molecule, is split and shifted from 1110 cm^{-1} in the free ligand to 1101 and 1095 cm^{-1} in the complex, suggesting the presence of at least two differently bonded types of ethereal oxygen atoms.

There are many similar compounds in which the crown-ether is not directly bonded to a transition metal center. In fact, in the complex between 18-crown-6 and manganese perchlorate [5], the metal is surrounded by six water molecules in a distorted octahedral geometry and these are hydrogen-bonded to the crown-ether oxygens. The complex between the same ligand and manganese nitrate [5] shows the manganese(II) ion octahedrally coordinated to five water molecules and a monodentate nitrate ligand. A complex network of hydrogen bonds links the complex cation, the crown-ether, the other nitrate group, and a sixth water molecule. Again cobalt chloride [3] forms a hexaaquo ion coordinated to the crown-ether via hydrogen bonds. More complex is the adduct between nickel chloride and 18-crown-6: it forms a chain structure in which $[Ni_2Cl_2(H_2O)_8]^{2+}$ and 18-crown-6 groups are bonded by hydrogen bonds [4].

In all of these complexes the interactions between the crown-ether and the metal occur through a water molecule by the formation of a network of hydrogen bonds (2.73–3.11 Å), in such a way that polymeric chains are always formed.

Other examples are known in tin(IV) coordination chemistry in which the ligand is not bound to the tin atom at all, but is hydrogen-bonded to a coordinated water molecule. The 2,2′,6′,2″-terpyridyl moiety in the complexes with triphenyl tin chloride and thiocyanate is bonded by two hydrogen bonds to one water molecule coordinated to the tin(IV) ion [17]. In a similar way, the cyclic ethers, 1,4-dioxan and 1,8-cineole [15] are hydrogen bonded to the water molecules in the coordination sphere of the octahedron of the tin(IV) ion.

Our compound seems to be unique in that a second water molecule is hydrogen bonded between the $[SnCl_4(H_2O)_2]$ moiety and the crown-ether. The extremely strong bond formed between these two water molecules (2.50 Å) across the crown-ether stabilizes this unusual polymeric chain. In our structure the presence of the additional water of hydration, OH(3), serves to lock the crown-ether into an unusual conformation because it is hydrogen-bonded both to the crown-ether and the tin(IV) coordinated water molecule OH(1). The centrosymmetric nature of the structure propagates this unusual conformation through the two symmetry related water molecules to the next tin(IV) ion in the polymeric chain. It will be interesting to compare this structure with the dihydrated compound [11] which we are currently studying.

Acknowledgements

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