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SYNTHESIS AND CHEMICO-PHYSICAL CHARACTERIZATION OF TIN(IV) COMPLEXES WITH SOME CROWN ETHERS

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Summary

Some neutral adducts of diorganotin(IV) perchlorates and thiocyanates with three crown-ethers have been synthesised; they are of the type $Me_2SnX_2L_m \cdot nH_2O$ where $m = 1$ or 2, $n = 2$ or 4, X = ClO_4 or NCS, and L = 18-crown-6, 15-crown-5, and 12-crown-4. The values for m and n have been correlated with the coordinating ability of the two anions and with the steric hindrance by the crown ether molecules. From infrared and Mössbauer data, an octahedral coordination geometry is proposed for all the complexes. The Mössbauer parameters are discussed in terms of the electronegativity of the ligands on the tin(IV) center and of the distortions produced in the coordination polyhedra by the various crown-ether molecules. Preliminary DTG results suggest that it may be possible to obtain anhydrous complexes.

Introduction

Among the many reasons for the recent great interest in the complexometric abilities of the crown ethers their behavior in solution is one of the most important. This behaviour is so strongly affected by the solvent properties that the ethereal ring may form either a lipophobic or a lipophilic cavity depending on the polar characteristics of the solvent [1]. This is because the great flexibility of the crown ether molecules allows inversion of the relative positions of the carbon and oxygen atoms with respect to the ideal ring of the crown ether molecule.

Most research on these ligands has been performed with the cavity in the hydrophilic configuration, which gives rise to a great ability to bind positively charged groups. One of the most interesting consequences of this ability is the possibility of carrying cationic charges through liquid membranes [2]; as a result

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many metal complexes have been studied as models for the ionic transfer through cell membranes and this subject has become one of the most important aspects of inorganic biochemistry.

There have been papers on crown ether complexes, both in solution and in the solid state, mainly with alkali and alkaline earth metals, but also with the transition elements, especially lanthanides and actinides, and recently with some non-transition metals [3].

However only a few accounts have appeared on the interaction between the crown ethers and tin(II) [4] and tin(IV) [5–12]. With Sn^{II} there has been no crystal structure determination, but Mössbauer and infrared spectra have been interpreted in terms of direct bonding between the ethereal oxygens and the tin(II) center. Such bonding is not present in the tin(IV) complexes, in which the metal-crown ether interaction is provided by one or more water molecules as confirmed by several X-ray structural studies [8–10,12]. The role of the water molecules is so important that it is not possible to obtain a complex under rigorously anhydrous conditions.

We have examined some new complexes between dimethyltin diperchlorate and dithiocyanate and various crown ethers in order to provide new information about their electronic and structural properties. A preliminary study has been made of their thermal stability to throw light on the role of the water molecules. With this in mind, two different anions have been used, one with good donor properties toward the tin(IV) ion and the other with practically no coordination ability.

Experimental

The crown ethers were used as purchased. The yields of the complexes were always ca. 70%.

$Me_2Sn(NCS)_2$ was prepared as previously described [13]. $Me_2Sn(ClO_4)_2$ was prepared by dissolving a weighed amount of Me_2SnO in the stoicheiometric quantity of 1 *M* $HClO_4$, and the solution was then used without isolation of the solid.

TABLE 1

ANALYTICAL DATA FOR COMPLEXES OF TIN(IV) COMPOUNDS WITH CROWN-ETHERS

Complex	Analysis (Found (calc) (%))			
	C	H	N	H_2O
$Me_2Sn(ClO_4)_2(12-4)_2 \cdot 4H_2O$ (I)	27.18	5.42	–	9.65
	(28.00)	(6.00)		(9.33)
$Me_2Sn(ClO_4)_2(15-5)_2 \cdot 4H_2O$ (II)	29.51	6.12	–	8.05
	(30.71)	(6.33)		(8.38)
$Me_2Sn(ClO_4)_2(18-6) \cdot 4H_2O$ (III)	23.71	5.57	–	10.97
	(24.58)	(5.60)		(10.53)
$Me_2Sn(NCS)_2(12-4)_2 \cdot 2H_2O$ (IV)	36.28	6.37	4.24	5.12
	(36.76)	(6.48)	(4.29)	(5.51)
$Me_2Sn(NCS)_2(15-5)_2 \cdot 2H_2O$ (V)	38.56	6.68	3.91	4.65
	(38.88)	(6.80)	(3.78)	(4.86)
$Me_2Sn(NCS)_2(18-6) \cdot 2H_2O$ (VI)	34.38	6.21	5.07	6.61
	(34.10)	(6.06)	(4.95)	(6.37)

TABLE 2

MÖSSBAUER EFFECT PARAMETERS FOR THE CROWN-ETHERS ADDUCTS

Complex	IS [a]	ΔE_q [a]	$\Gamma_{av.}$ [b]
$Me_2Sn(ClO_4)_2(12-4)_2 \cdot 4H_2O$ (I)	1.30	4.52	0.83
$Me_2Sn(ClO_4)_2(15-5)_2 \cdot 4H_2O$ (II)	1.31	4.42	0.83
$Me_2Sn(ClO_4)_2(18-6) \cdot 4H_2O$ (III)	1.27	4.14	0.89
$Me_2Sn(NCS)_2(12-4)_2 \cdot 2H_2O$ (IV)	1.35	4.22	0.88
$Me_2Sn(NCS)_2(15-5)_2 \cdot 2H_2O$ (V)	1.28	4.07	0.91
$Me_2Sn(NCS)_2(18-6) \cdot 2H_2O$ (VI)	1.34	4.37	0.85

[a] Isomer shift at r.t. $Ca^{119}SnO_3$, and nuclear quadrupole splitting at liquid nitrogen temperature. [b] Full width half height resonance peaks; sample thicknesses were about 0.5 mg of $^{119}Sn/cm^2$; the data are expressed in mm s^{-1}; the standard deviations are 0.02 mm s^{-1} for all data.

$Me_2Sn(NCS_2)$ complexes: These were prepared by dissolving 0.5 g (1.89 mmol) of $Me_2Sn(NCS)_2$ in MeOH (10 ml) and adding to the pink solution so obtained 2 mmol of the crown ether. The resulting solution was refluxed for 2 h until it became colourless, then slowly evaporated to give a pink microcrystalline powder. The complexes were filtered off, washed with n-hexane, and dried over P_2O_5.

$Me_2Sn(ClO_4)_2$ complexes: 20 ml of a 0.1 *M* solution of $Me_2Sn(ClO_4)_2$ (2 mmol) were slowly added to 3 mmol of the ligand in ethanol (ca. 10 ml). The resulting solution was refluxed for 2 h and the solvent then evaporated off. The white microcrystalline powder obtained was filtered off, washed with n-hexane, and dried under vacuum.

The analyses are reported in Table 1. The infrared spectra were recorded with Nujol mulls on a Perkin–Elmer 983 spectrophotometer. The Mössbauer spectra were obtained with a 5 mC $Ba^{119}SnO_3$ source at room temperature by previously described procedures [14]. The results are shown in Table 2. Thermal gravimetric analysis (TGA) and differential thermal gravimetry (DTG) were carried out with a Mettler TA 3000 instrument under a stream of dry nitrogen at a heating rate of 20 °C/min.

Results and discussion

The complexes previously described between tin(IV) compounds and 18-crown-6 ether have been shown to have various stoicheiometric formulae, but all contained at least two water molecules [5–12]. The composition of the complex seems to depend on the preparative conditions, the organic groups bonded to the tin atom, and the binding ability of the anions; the substituents on the ethereal ring also appear to be important. Thus five different stoicheiometries have been proposed for the ca. twentyfive complexes reported in the literature. For some of these complexes X-ray studies revealed the existence of a distorted octahedral coordination geometry around the tin atom, and closely related coordination geometries have been proposed for the others on the basis of the infrared and Mössbauer spectra. In no case was a direct interaction between the metal and the crown-ether observed. In particular, the coordination sphere of the $Me_2Sn(NCS)_2$ complex with 18-crown-6 ether [12] consists of two methyl groups, two thiocyanate ions, and two water molecules, all in *trans* dispositions with respect to the tin atom. Hydrogen bonds between the water molecules and the crown-ether give rise to a linear polymeric chain. The two other thiocyanate derivatives are assumed to have a closely related structure on the basis of their infrared spectra. These are identical for the three complexes, and show that the thiocyanate ions are *N*-bonded to the tin(IV) atom as indicated by the appearance of the asymmetric CN band at ca. 2050 cm^{-1} and the δ(NCS) band at 479 cm^{-1}; there is no $\nu(CN)_s$ band, and this indicates a *trans* arrangement for the anion. Similarly, the two methyl groups must be in *trans* disposition because there is only the $\nu(Sn{-}C)_{as}$ at ca. 580 cm^{-1}. A broad band at about 3450 cm^{-1} confirms the presence of water in all these compounds. The structure of the perchlorate complexes may be related to that of the thiocyanate adducts by replacement of the two anions with two water molecules, which are assumed to be coordinated to the metal because they are better ligands than the crown-ether. The infrared spectra help to elucidate the structure of these compounds. Thus only one band due to (ClO_4) is found at 628 cm^{-1} (the band expected at 1110 cm^{-1} due to $\nu(ClO_4)_{as}$ overlaps the $\nu(COC)_{as}$ found at roughly the same frequency). This single band is typical of ionic ClO_4^- with T_d symmetry; any anion to metal coordination would lower the symmetry to C_{2v} or C_{3v} and consequently split the absorption band. Thus there is probably no coordination of perchlorate to the tin center. As regards the Me_2Sn moiety, there is only the asymmetric stretching present at 628 cm^{-1} associated with the (ClO_4), and a normal *trans* geometry is proposed. The four water molecules are assumed to be coordinated to the tin atom in the square plane of the octahedron and to be hydrogen bonded to the ethereal oxygens; in agreement with this the $(COC)_{as}$ band is slightly shifted to lower wavenumbers. Thus an almost normal regular octahedral geometry is proposed for these complexes; the anions and the crown ether molecules are possibly connected to one another and the coordinated water molecules by a network of hydrogen bonds.

The dimensions of the crown-ether molecules are important in determining the stoicheiometry of the compounds: thus only one large 18-crown-6 can be accommodated in the crystal lattice, whereas there is room for two molecules of the smaller 15-crown-5 and 12-crown-4 ethers. The different stoicheiometric ratios do not seem to affect the coordination at the metal center. With the two smaller ethers the polymeric chain is probably broken because every tin coordination polyhedron can be surrounded by two crown-ether molecules.

Other structural and electronic information may be obtained from the Mössbauer effect spectra of these complexes at 78 K (see Table 2). They all consist of a single quadrupole-split doublet with a narrow line width indicating the presence of a single tin(IV) site. The ΔE_q values range from 4.07 to 4.52 mm s^{-1} and are typical of *trans* octahedral geometry around the tin(IV) atom with oxygen donor ligands. The isomer shifts for the thiocyanate derivatives are lower than that for the parent compound (*IS* 1.48 mm s^{-1}) [15] which has a distorted octahedral coordination with the thiocyanate groups bridging two tin(IV) ions through the nitrogen and sulfur atoms. Upon replacement of the two sulfur atoms by two water molecules, the electronic density at the tin nucleus decreases along with the isomer shift values. The diphenyl derivative gives values (1.10 mm s^{-1}) [11] much lower than the dimethyl compounds, reflecting the difference in the electronegativity between aryl and alkyl groups. Conversely, the dichloride complex has a higher value (1.43 mm s^{-1}) [8] than the isothiocyanate, in line with the higher electronegativity of the chloride than of the isothiocyanate substituent. The number of crown-ether molecules present in these complexes seems to influence the symmetry at the tin center of the thiocyanate and of the perchlorate adducts in opposite directions. Thus complex III of Table 2 gives an ΔE_q that is much lower than those of complexes I and II, while compound VI gives a higher value than compounds IV and V. This seems to indicate that the hydrogen bond networks in the two series of complexes are completely different, and that the removal of one molecule of crown-ether causes a decrease in the symmetry of the thiocyanate compound and an increase in that of the perchlorate one. No effect was observed in the isomer shift values.

Preliminary studies on the thermal behavior of these compounds seem to indicate that even the complexes from the perchlorate are fairly stable, and at temperatures < 100 °C probably only the water molecules are lost. The residue does not seem to be simply a mixture of the tin(IV) salt and crown ether, at least in the case of the (18 – 6)-complex with $Me_2Sn(NCS)_2$ because the decomposition temperature of the residue is much higher than either of the two components in the pure state. For example, the 18-crown-6 ether decomposes on its own at ca. 200 °C, and the metal salt at 223 °C whereas the complex decomposes at ca. 250 °C. Thus some interaction must remain between the two components when the water is lost. Work is in progress to elucidate the nature of these interactions and their effects at the tin atom.

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