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SYNTHESIS AND MÖSSBAUER STUDIES OF SOME AQUO COMPLEXES OF TIN(IV) WITH CROWN ETHERS

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Summary

The preparation, characterization, and ^{119}Sn Mössbauer spectra of a number of tin(IV) complexes with cyclic polyethers are presented. With tin(IV) chloride and methyltin(IV) trichloride, 1 : 1 and 2 : 1 metal-to-crown-ether complexes are formed, while dimethyltin(IV) dichloride forms only 2 : 1 complexes; in every case, two water molecules are present in the solid state structure. An octahedral coordination geometry around the tin(IV) center is proposed on the basis of Mössbauer and IR spectra.

Introduction

In recent years interest has been growing concerning the preparation and the electronic and structural characterization of complexes formed between tin(II) or tin(IV) and crown-ethers [1–5], due to their possible applications as biological models. Although direct bonding between the metal center and the crown-ether oxygens has been shown to occur in the tin(II) compounds [1,2], such bonding may not be present in the tin(IV) complexes [3–5]. In fact, in the latter complexes, the metal coordination sphere may be completed either by the crown-ether, or by the two water molecules linked by hydrogen bonding to the crown-ether. This latter type of interaction has been shown by X-ray diffraction studies to occur in the complex $[SnCl_4(H_2O)] \cdot 18\text{-crown-6} \cdot 2H_2O$ [5], in which a complex network of hydrogen bonding connects the metal atom coordination octahedron to the crown-ether and to the two water molecules of hydration.

In the present note we report on five new inorganic and organometallic tin(IV) 1 : 1 and 2 : 1 complexes with 18-crown-6, dibenzo-18-crown-6 (Ph_2-18-crown-6), and

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TABLE 1

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

Complex	M.p. (°C)	Analysis (found (calcd.) (%))			
		C	H	Cl	H_2O
1 $SnCl_4 \cdot$18-crown-6$\cdot 2H_2O$ [a]	175–180	26.18	5.18	24.92	6.81
		(25.70)	(5.03)	(25.28)	(6.42)
2 $(SnCl_4)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	152–157	25.45	4.47	25.78	4.12
		(25.84)	(4.34)	(25.84)	(3.88)
3 $SnCl_4 \cdot Ph_2$-18-crown-6$\cdot 2H_2O$	161–165	36.22	4.23	21.43	5.82
		(36.57)	(4.30)	(21.59)	(5.48)
4 $MeSnCl_3 \cdot$18-crown-6$\cdot 2H_2O$	115–117	28.62	5.43	19.94	7.03
		(28.89)	(5.59)	(19.68)	(6.67)
5 $(MeSnCl_3)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	102–108	29.46	5.11	23.69	4.57
		(29.73)	(5.22)	(23.94)	(4.40)
6 $(Me_2SnCl_2)_2 \cdot$18-crown-6$\cdot 2H_2O$ [b]	98–101	32.06	6.76	13.85	7.32
		(32.34)	(6.59)	(13.64)	(6.93)
7 $(Me_2SnCl_2)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	107–108	41.85	7.22	11.14	6.05
		(42.06)	(7.38)	(11.29)	(5.74)

[a] See ref. 3. [b] See ref. 4.

dicyclohexano-18-crown-6 (Chx_2-18-crown-6). In all of these complexes two water molecules per metal atom are also present in the solid state structure.

Experimental

The complexes were prepared by mixing solutions of the tin(IV) chloride and of the crown-ether in the same solvent (methylene chloride for the tin tetrachloride adducts, and diisopropyl ether in the other syntheses,) which resulted in the slow formation of a microcrystalline white solid. The complexes were repeatedly recrystallized to yield products of reproducible stoichiometry. All operations were carried out, using commercially available reactants, under a nitrogen atmosphere.

Analytical, IR, and ^{119}Sn Mössbauer data for these compounds are reported in Tables 1–3, together with published values for the complexes $SnCl_4 \cdot$ 18-crown-6.$2H_2O$ [3] and $(Me_2SnCl_2)_2 \cdot$ 18-crown-6 $\cdot\ 2H_2O$ [4], for comparison purposes.

TABLE 2

INFRARED DATA FOR TIN(IV) COMPLEXES OF CROWN-ETHERS

Complex	ν(C–O–C) (cm^{-1})	ν(Sn–Cl) (cm^{-1})	ν(Sn–C) (cm^{-1})
1 $SnCl_4 \cdot$18-crown-6$\cdot 2H_2O$ [a]	1097s	345s–327s–306sh–298w	–
2 $(SnCl_4)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	1060s	363s–334s–307sh–295w	–
3 $SnCl_4 \cdot Ph_2$-18-crown-6$\cdot 2H_2O$	1130s–1121s	330s–283s	–
4 $MeSnCl_3 \cdot$18-crown-6$\cdot 2H_2O$	1101s	303s–278s–241m	536m
5 $(MeSnCl_3)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	1098s–1085s	298m–255m	542m
6 $(Me_2SnCl_2)_2 \cdot$18-crown-6$\cdot 2H_2O$ [b]	1101s	244s	575m–524w
7 $(Me_2SnCl_2)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	1100s–1081s	279s	572m–512w

[a] See ref. 3. [b] See ref. 4.

TABLE 3

^{119m}Sn MÖSSBAUER PARAMETERS FOR TIN(IV) COMPLEXES WITH CROWN-ETHERS

	δ^a (mm s^{-1})	$\Delta E_Q{}^b$ (mm s^{-1})	$\Gamma_{av}{}^c$ (mm s^{-1})
1 $SnCl_4 \cdot$18-crown-6$\cdot 2H_2O$[d]	0.34	0.49	0.89
2 $(SnCl_4)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	0.51	0.80	0.97
3 $SnCl_4 \cdot Ph_2$-18-crown-6$\cdot 2H_2O$	0.43	0.63	0.91
4 $MeSnCl_3 \cdot$18-crown-6$\cdot 2H_2O$	0.78	2.21	0.96
5 $(MeSnCl_3)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	1.05	2.06	1.04
6 $(Me_2SnCl_2)_2 \cdot$18-crown-6$\cdot 2H_2O$[e]	1.48	3.93	0.92
7 $(Me_2SnCl_2)_2 \cdot Chx_2$-18-crown-6$\cdot 2H_2O$	1.37	3.46	0.92

[a] Isomer shift with respect to RT $CaSnO_3$. [b] Nuclear quadrupole splitting. [a,b] Parameters measured at liquid N_2 temperature. Errors in δ and ΔE_Q ± 0.01 mm s^{-1}. [c] Full width at half height of the resonance peaks, average; sample thickness was from 0.5 to 1.0 mg ^{119}Sn/cm^2. [d] Ref. 3: $\delta = 0.29$, $\Delta E_Q = 0.82$ mm s^{-1}. [e] Ref. 4: $\delta = 1.43$, $\Delta E_Q = 3.94$ mm s^{-1}.

Results and discussion

On the basis of the ^{119}Sn Mössbauer spectroscopic data (vide infra) the tin(IV) atoms in all of the complexes prepared in the present study appear to be hexa-coordinated. Moreover, in each compound the chloride atoms are covalently bonded to tin(IV), as indicated by the very low molar conductances (compared with the values expected for ionic species), and by the presence in the far IR spectra of bands attributable to the Sn–Cl stretch (see Table 2). However, from the available data, it is not possible to tell which ligand, water or crown-ether, occupies the other two available positions in the coordination octahedron about tin(IV). Support for the hypothesis that direct coordination of the water molecules is involved is given by preliminary thermogravimetric measurements. In fact, these complexes decompose to yield, ultimately, tin(IV) dioxide without any indication of intermediate compound formation.

The far IR spectra of Nujol mull samples of the tin(IV) tetrachloride complexes indicate a *cis*-configuration for the ligand atoms, other than halide, around the tin(IV) center. In fact, in the region where ν(Sn–Cl) is expected, various bands attributable to this mode are usually detected, although there is probably strong coupling with ν(Sn–O) (see Table 2). This pattern is typical for a *cis*-O_2 environment. The Mössbauer spectra of the compounds (see Table 3) show the occurrence, albeit small, of a quadrupole splitting, which may be attributed to the fact that donor interactions Sn ← O are weaker than Sn ← Cl [6]. The weak nature of these bonds may arise from steric hindrance.

The values of quadrupole splitting for the $MeSnCl_3$ derivatives (see Table 3) are comparable to that of 2.0 mm s^{-1} reported for octahedral complexes of the $RSnCl_3 \cdot 2L$ type [7,8]. These complexes have been assigned octahedral structures with meridional $SnCl_3$ skeletons; a similar geometry is now proposed for the alkyl tin(IV) complexes of the crown ethers, with the methyl group occupying the fourth position in the equatorial plane of the coordination octahedron. This hypothesis is also supported by the pattern of bands, assigned to the Sn–Cl and Sn–C stretches, in the far IR region of the vibrational spectra (see Table 2).

The dimethyltin dichloride derivatives show (see Table 2) strong bands due to Sn–C and Sn–Cl asymmetric stretching vibrations in the far IR spectra, while only very weak bands attributable to the Sn–C symmetric stretches are observable. This appears to indicate that the adducts present an all-*trans* octahedral geometry around the tin(IV) atom, in which the C–Sn–C bond angle shows a significant departure from 180°. The Mössbauer parameters (see Table 3) further support these suggested structures: the values of the quadrupole splittings seem to indicate C–Sn–C angles of about 140 and 160° for the $\mathrm{Chx_2}$-18-crown-6 and 18-crown-6 complexes, respectively [9].

For all the complexes, the ^{119}Sn Mössbauer isomer shift values are lower than those observed in the parent tin(IV) compounds, and cover a fairly wide range, the highest values being those of the 2 : 1 complexes. In all cases, they do not conflict with the assumed geometries.

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