

Equilibrium studies, co-ordination isomers and local structure of organotin(IV) complexes formed with carbohydrates

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INTRODUCTION

Interaction of organotin(IV) compounds with biologically active ligands -among them carbohydrates and their derivatives - have attracted considerable interest, because the presence of these ligands modifies the biological properties (even anticancer activity) of the organotin(IV) cations. In spite of this, the species distribution, the chemical and electronic structure, bond distances of the reaction products remained largely unexplored. This communication is dealing with these problems.

RESULTS AND DISCUSSION

Complex formation equilibrium of diethyltin(IV) cation with six 2-polyhydroxyalkyl-thiazolidine-4-carboxylic acid (PHTAc) [1] and five *N*-D-gluconylamino acids [2] in aqueous solution ($I = 0.1 \text{ M}$, NaClO_4) were studied and the stabilities of the species were determined by potentiometric titrations. Both type of ligands are effective complexing agents in physiological pH range where the mixed hydroxo species (MLOH in the former system and MLOH_2 in the latter one) are predominant parallel with the formation of hydrolysis product of diethyltin(IV) cation. The polyhydroxyalkyl substituents on the PHTAc ligands do not show direct co-ordination to dialkyltin(IV), they exert only sterical effects on the process. In the *N*-D- α -amino acid complexes the ligand is co-ordinated through its deprotonated carboxylate oxygen, amide nitrogen and C(2)-hydroxy group, while for the soluble *N*-D-gluconyl- β -alanine complex the ligand is co-ordinated *via* the deprotonated carboxylate and C(3)-, C(4)-, C(5)-hydroxy groups. Mössbauer measurements reflected the geometry of the complexes formed.

A series of diethyltin(IV)-, [3] dibutyltin(IV)- [4] and dibenzyltin(IV) [5] complexes formed with 19 different carbohydrates (aldoses, polyalcohols, aldonic acids, amino-sugars, di-, and

trisaccharides) were prepared. The composition of the complexes were determined by standard analytical methods. The results showed that complexes formed containing the dialkyltin(IV) moiety and the carbohydrate ligand in 1:1 ratio. The IR data are also consistent with the formation of well-defined compounds with composition R_2SnL by replacement of the oxygen atom in R_2SnO by carbohydrate ligands. The most characteristic spectral changes occurred in the spectral regions 1200-1000 and 600-400 cm^{-1} .

1., Vibrational bands characteristic of Sn-C (at 520-600 cm^{-1}) and Sn-O (at 410-470 cm^{-1}) bonds appeared.

2., The changeover from the C-O vibrations of the COH groups in the ligands to those of COSn groups in the complexes caused alterations in the region 1000-1200 cm^{-1} . In the complexes formed with aldonic acids the differences in carboxylate symmetric and asymmetric vibration frequency (~ 210 cm^{-1}) indicate the co-ordination of the carboxylate group to the central tin(IV) atom.

Comparison of the Mössbauer experimental Quadrupole Splitting (Q.S) values with those calculated on the basis of a simple but general molecular orbital model according to the Partial Quadrupole Splitting, P.Q.S. concept, revealed that the complexes are of three types:

- 1., with the central tin(IV) atoms surrounded by donor atoms in a purely trigonal bipyramidal,
- 2., in a purely octahedral,

3., or in both trigonal bipyramidal and octahedral arrangements in different molar ratio. This procedure also distinguished between the different structural isomers of both trigonal bipyramidal and octahedral complexes. Conclusion could therefore be drawn as to the factors determining which of the isomers are formed in the systems. The changes in the room temperature Debye-Waller factors and the integral intensities of the Mössbauer doublets assigned to the tin(IV) in different surroundings reflected the oligomerization in the systems.

These complexes are amorphous. The local structure of several selected $Et_2Sn(IV)L$ complexes have been determined by Extended X-ray Absorption Fine Structure (EXAFS) measurements in solid state [6]. The curve fitting analysis have been performed by using multi-shell (5) model. The results showed that the dioxastannolane units are associated into an infinite chain polymer, in which the tin(IV) is bound by two carbon atoms (Sn-C distance is 213 pm) and three or four oxygen atoms. The symmetries are in agreement with those suggested on the basis of the Mössbauer data. The Sn-O average bond lengths in the first shell are in the range of 206-210 pm. These values are in consistent with values observed for Sn-O bonds by X-ray diffraction method for 2,2-dibutyl-1,3,2-dioxastannolane (197-212 pm), or for methyl-4,6-O-benzylidene-2,3-O-dibutyl-stannilene- α -D-

mannopyranoside (203 and 214 pm). The intermolecular Sn-O distances show a somewhat larger variation compared with intramolecular ones: 246-255 pm.

The average Sn...C and Sn...Sn distances in the fourth and fifth shells agreed well with the literature values obtained by X-ray diffraction of diorganotin(IV) complexes formed with protected carbohydrates.

CONCLUSION

The combined application of equilibrium and spectroscopic methods has made possible the full structural characterisation of the species formed in equilibrium reactions. This is very important one to understand the biological effect of complexes in question.

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