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Characterization of complexes formed between $[Me_2Sn(IV)]^{2+}$ and carboxymethylcelluloses

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Abstract—Complexes formed between carboxymethylcellulose (CMC) and the $[Me_2Sn(IV)]^{2+}$ cation have been prepared in the solid state and characterized by FTIR and Mössbauer spectroscopy. The complexes contained CMC with varying molar weight and degree of carboxylation, and the complexes were isolated both from acidic and from neutral solutions at varying metal-to-ligand ratios. The characteristic vibration bands of the ligands were identified from their pH-dependent FTIR spectra. In the organotin(IV) complexes obtained at pH ~2, the $–COO^-$ moieties were found to be coordinated in a monodentate manner, and the band characteristic of the protonated (unbound) $–COO^-$ group(s) was also identified. The broad –OH band can be interpreted as the sum of the contributions of the alcoholic –OH groups of the anhydroglucose units and the mixed organotin aqua complexes. In complexes obtained at pH ~7, the broad –OH band significantly sharpens, which is probably due to the metal-ion induced deprotonation and subsequent coordination of the alcoholic –OH groups. At the same time, $–COO^-$ groups are also involved in the coordination of the metal ions, resulting in a complicated network that forms through inter- and intramolecular bridges. Quadrupole splitting ($|\Delta_{exp}|$) values observed by Mössbauer spectroscopy revealed that the valence state of tin is four in all of the complexes. The $|\Delta_{exp}|$ values were compared with the calculated ones, obtained from the pqs theory. From these data, trigonal bipyramidal (Tbp) and octahedral (O_h) geometries have been suggested for the complexes obtained. It has also been concluded that the structure of the complexes prepared depends mainly on the pH of the solution, and it is relatively insensitive to the other parameters, like molar mass or degree of carboxylation of the ligand, or the metal-to-ligand ratio in the reaction mixture.

Keywords: Carboxymethylcellulose; Sn(IV); Structure; Infrared spectra; Mössbauer spectra

1. Introduction

Organotin(IV) compounds are widely used in industry (e.g., PVC stabilizing agents), agriculture (e.g., wood preservatives and fungicides), etc. The rapid rise in the number of their applications during the last decades has led to their accumulation in the environment, and in biological systems, and their presence is now detected even in the human nutrition chain.[1]

The biological activity of organotin(IV) compounds is well known.[2,3] Most organotin compounds are generally very toxic, even at low concentration. Their biological activity is essentially determined by the number and nature of the organic groups bound by an Sn–C bond to the central atom, while the nature of the anionic group is only of secondary importance.

The strong interaction between organotin(IV) cations and sugar-type ligands is well documented in the literature.[4–7] The utilization of organotin(IV) derivatives of (poly)alcohols in regioselective manipulations[8,9] and the application of organotin(IV)-containing

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intermediates in carbohydrate chemistry are also well known.[10] Organotin(IV) carbohydrate derivatives are especially important for agricultural and clinical use. Several carbohydrate complexes have already been introduced into agriculture due to their fungotoxicity,[11] and conjugates between the $[Ar_3Sn(IV)]^+$ cation and D-saccharose have been demonstrated to be effective in marine antifouling paints.[12] The complexes formed between $[R_2Sn(IV)]^{2+}$ and various carbohydrates have also been investigated as possible antitumour agents.[13] The wood preservation properties of $[Bu_3Sn(IV)]^+$ are strongly related to the interactions between cellulose (polysaccharides) and the organotin(IV) cation and are based on the good antifungal activity and low mammalian toxicity of these complexes. $(Bu_3Sn)_2O$-treated wood is effectively preserved for up to 25 years, although there is some concern as to the long-term stability of the organotin(IV) with respect to less effective $[R_2Sn(IV)]^{2+}$ compounds.[14] Some fungi, which colonize wood, for example, are capable of causing a dealkylation process.[15,16]

Some types of polysaccharides exhibit extraordinary complexing ability towards cations, in particular transition-metal ions;[17] however, relatively little is known about the structure and equilibria of such 'complexes'. There are two main approaches in the literature for the description of their structure. The first (a site-binding model) assumes that metal ions are bound to the individual binding sites of the polymers and form spatially separated metal centres along the polymeric backbone. The second (a colloidal model) suggests that a metal-hydroxide precipitate is formed in these systems, which is covered by a polysaccharide layer that inhibits the aggregation of the nanometric-sized precipitate particles; in this model non-specific interactions are believed to be responsible for the observed high apparent solubility of the metal hydroxides. In the combination of these two, the donor groups of the polysaccharide act as nucleation sites for the metal ions, which then bind further metal ions through hydroxide bridges. Such interactions result in 'nanostructures' with shape and size that depend on the type of polysaccharide and the solution properties like pH, temperature and metal-to-ligand ratio.[18]

The fundamental aspects of polysaccharide–organotin(IV) interactions are largely unexplored. Formation of complexes with very high equilibrium stability constants is expected in aqueous systems containing $[R_2Sn(IV)]^{2+}$ cations and water-soluble extracellular glycosaminoglycans (GAGs), such as chondroitin sulfates, hyaluronan and heparin. GAGs differ in their structure, binding sites and charge density; therefore, characterization and comparison of the structure of their metal complexes is always very complicated. Carboxymethylcellulose (CMC) derivatives (Fig. 1) can be considered as suitable model compounds for GAGs. CMC might contain both negatively charged (carboxylate and alcoholate) and neutral (alcoholic and etheral oxygen) donor groups, and the potential coordinating atom is always oxygen. (In principle, coordination of the deprotonated acetamido nitrogen in GAG metal complexes is possible[18] and was ruled out even in the case of Cu(II)-hyaluronate complexes.[19]) A further important piece of information on CMC is that the average degree of carboxymethylation (DC), which is the average number of $–CH_2–COO^-$ groups per anhydroglucose unit, can be varied with the preparative conditions. This gives the opportunity of 'tailoring' both the average distance between the coordinating carboxylate groups (an important parameter governing the site-binding ability of CMC) and, at the same time, the charge density along the polymeric backbone (a factor, which is responsible for the electrostatic interactions between the cations and anionic polymers).

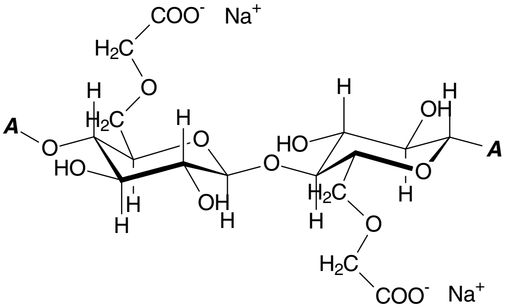

Figure 1. Structural formula of two adjacent monomeric units of a carboxymethylcellulose, sodium salt. ***A*** represents the continuation of the polymeric chain.

The aim of the present work is the preparation, IR- and Mössbauer spectroscopic characterization of a range of CMC derivatives and the $[Me_2Sn(IV)]^{2+}$ cation. During the preparation, CMCs with various DCs and average molecular mass were employed. The effect of pH and the metal-to-ligand ratio on the structure of the complexes have also been explored.

2. Experimental

2.1. Materials and method of preparation

All solutions were prepared from high-purity water (Millipore Milli-Q system). Analytical reagent grade Me_2SnCl_2 was purchased from Fluka. Four different CMC samples (all purchased from Sigma–Aldrich) were used for the experiments. The average degree of carboxymethylation (DC) values and average molar masses were determined by the supplier. DC values were checked by using a Na-flame-photometric technique, and were found to agree with the data of the supplier within 5%. Throughout this paper, the polymer samples