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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.

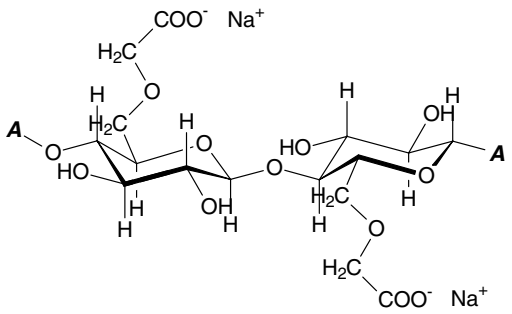

Figure 1. Structural formula of two adjacent monomeric units of a carboxymethylcellulose, sodium salt. ***A*** represents the continuation of the polymeric chain.

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).

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

will be denoted as A (DC 0.7 and M_r 90,000 D), B (DC 0.7 and M_r 250,000 D), C (DC 0.9 and M_r 250,000 D) and D (DC 1.2 and M_r 250,000 D). The chemical formulae of the CMC ligand is shown in Figure 1.

As $[Me_2Sn(IV)]^{2+}$ complexes with carboxylate containing ligands are known to be stable (i.e., withstand to hydrolytic decomposition) over a wide pH range (i.e., even in strongly acidic solutions).[1–3] However, the local structure of Sn(IV) often depends on the pH of the reaction mixture.[3] Therefore, syntheses were carried out both in acidic (pH 2) and in approximately neutral solutions. Accordingly, the complexes of the ligands were prepared as follows. A calculated amount of the polymer was dissolved in 100 mL of doubly distilled water, and the pH of the solution was set to pH 2 with standard HCl. A 50 mL aliquot of a standard aqueous Me_2SnCl_2 solution with a concentration of 0.57 M and pH ~2 was then added to the reaction mixture, in which the metal-to-ligand ratio (M:L, where L denotes a carboxylated anhydroglucose unit of the polymer) was 1:1, 1:2 and 1:5. The reactants were thoroughly mixed and then the pH was adjusted to pH ~2 or to pH ~7. For the pH adjustment, standard HCl and NaOH solutions (~1 M) were used, and the pH was monitored by a calibrated digital pH-meter, equipped with a combination glass electrode.

In acidic solutions at pH ~2, at any M:L, the solutions were free of precipitate. Upon slow evaporation (performed at room temperature in an evaporating dish loosely covered with a filter paper), a readily sedimenting white precipitate appeared in the systems. As control experiments (performed with ligand only and Me_2SnCl_2 only solutions) resulted in no formation of precipitate under identical experimental conditions, we suppose that in these systems the slow formation of a sparingly soluble complex took place. When the pH of the solution was raised to pH ~7, rapid precipitation of a gelatinous, sticky substance was observed with each of the ligands and at any of the M:L ratios. The solvent water was evaporated as above. The dry product was powdered in a mortar and then kept in a vacuum desiccator. The data of the complexes prepared are reported in Table 1.

To explore the effect of pH on the IR spectra of CMC, the acidic forms of the ligands were prepared. The pH of a 0.2 m/m% ligand solution was adjusted to pH 2 with HCl, and the solution was quickfrozen and then freezedried.

2.2. Characterization of CMC–organotin complexes

FTIR spectra were recorded on a Bio-Rad Digilab Division FTS-65A/869 Fourier-transform infrared (FTIR) spectrometer in KBr pellets between 4000 and 400 cm^{-1}. It was assumed that the samples remained intact during the preparation of the pellets. The spectrometer was equipped with a DTGS detector. The spectral resolution was 2 cm^{-1}, and 128 scans were averaged. Data were processed by using the software GRAMS 386.3 (Galactic Corporation).

Table 1. Analytical data of the complexes prepared

Specimen code in text	M_r[a]	DC[b]	pH	M:L[c]
1A	90,000	0.70	≈7	1:1
1B	250,000	0.70	≈7	1:1
1C	250,000	0.90	≈7	1:1
1D	250,000	1.20	≈7	1:1
2A2	90,000	0.70	≈7	1:2
2A5	90,000	0.70	≈7	1:5
3A	90,000	0.70	2–3	1:1
3B	250,000	0.70	2–3	1:1
3C	250,000	0.90	2–3	1:1
3D	250,000	1.20	2–3	1:1
4A2	90,000	0.70	2–3	1:2
4A5	90,000	0.70	2–3	1:5

[a] Molar mass of the ligand.
[b] Average degree of carboxymethylation.
[c] Metal-to-ligand ratio or the number of Sn(IV) atoms divided by the number of carboxylate groups present in the reaction mixture (i.e., the ligand concentration is expressed in terms of the concentration of $-COO^-$ of the CMC).

Mössbauer spectroscopic measurements were performed as described previously.[20] In order to determine the steric arrangement of the coordination sphere, the experimental quadrupole splitting values ($|\Delta_{exp}|$) were compared with those calculated (Δ_{calcd}) for different possible tetra-, penta- and hexacoordinated symmetries of the Sn(IV) centres, according to point-charge model formalism [partial quadrupole splitting (pqs) concept].[21] On the basis of these calculations, the most probable stereochemistry of a given complex can be suggested. The pqs values of the different functional groups in question were taken in part from the relevant literature.[22,23]

3. Results and discussion

3.1. FTIR spectroscopic characterization

The coordination sites of the ligands in the complexes were determined by means of FTIR spectroscopy. The assignments have been performed according to Refs. 24–26. The coordination mode of the carboxylate groups was established on the basis of the difference between the position of the ν_{sym} and ν_{as} vibrations of the $-COO^-$ group, as described in.[27] For comparison, the FTIR spectra of the uncomplexed ligands (both in Na^+ salt and in acid form) and that of the Me_2SnCl_2 were recorded.

An intense and broad band is seen on the spectra of the uncomplexed ligands between 3700 and 2700 cm^{-1}, which can be attributed to the valence modes of the

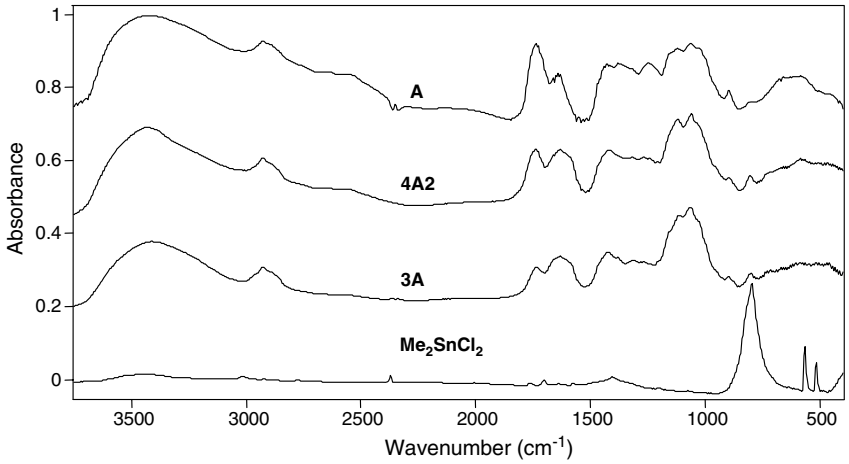

Figure 2. FTIR spectra of Me_2SnCl_2, ligand A (in protonated form) and complexes 3A and 4A2 (see Table 1), prepared at pH ~2–3.

alcoholic hydroxyl groups (Fig. 2). Similar bands can be identified in the spectrum of anhydroglucose unit. The band maximum is seen at 3390–3415 cm^{-1}. The broadening is likely to be associated with the complex H-bonding system between the –OH groups and the high lifetime of these interactions. The band appearing at 2922 cm^{-1} (well separated from the envelope of the ν_{OH} vibrations) is the asymmetric $–CH_2–$ valence mode, accompanied with a shoulder at 2873 cm^{-1}, attributable to the symmetric valence mode of the same group. The behaviour of the carboxylate group is of great importance in understanding the structure of the complexes formed. The valence modes of the $–COO^-$ appear at 1600 (ν_{sym}) and 1423 (ν_{as}) cm^{-1}. A deformation mode of the –OH groups is seen at 1327 cm^{-1}, and a shoulder at 1657 cm^{-1} is likely to be the deformation mode of water present in the samples. From the spectra of the ligands isolated in acidic form (Fig. 3), the valence modes of the $–COO^-$ group disappear, while a new band is present at 1735 cm^{-1}, associated with the symmetric stretching vibration of the –C=O moiety of –COOH group. A further set of bands are seen in the 1200–400 cm^{-1} region (at 1115, 1060, 900, 710, 585 and 480 cm^{-1}), and are likely to be the combination of valence and deformation of groups like –C–C–O, –C=O and –C–H. Because of broadening effects, minor bands at <700 cm^{-1} cannot be unambiguously identified.

In the FTIR spectrum of the Me_2SnCl_2, three dominant bands are seen. The most intense at 796 cm^{-1} is associated with the motion of the $–CH_3$ groups attached to the {Sn} central atom. The asymmetric and symmetric modes of the Sn–C bond are seen at 563 and 514 cm^{-1}, respectively.

The FTIR spectra of the complexes differ significantly from those of the uncomplexed ligands (Figs. 2 and 3). In the FTIR spectra of the ligands in their acidic form, the bands related to the asymmetric and symmetric vibrations of hydroxyl groups are broad, due to the multiple hydrogen-bonding system and to the presence of the physically bound water molecules. In the spectra of the complexes, the shape of the alcoholic –OH bands is slightly shifted, which is a likely indication of the de-

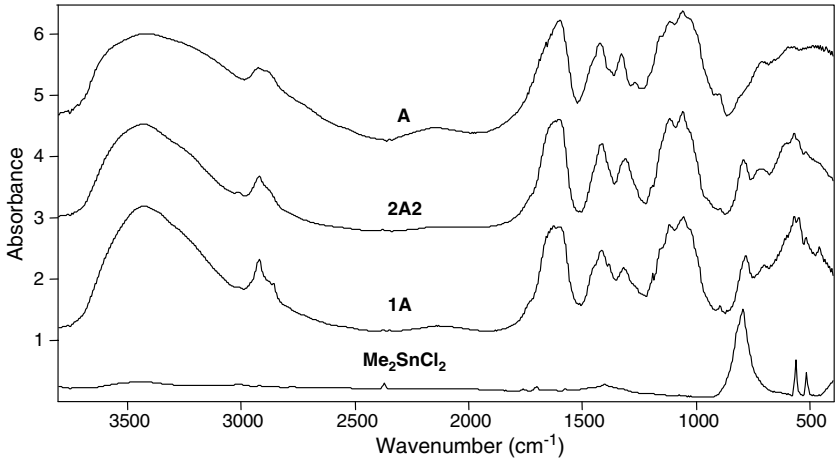

Figure 3. FTIR spectra of Me_2SnCl_2, the Na^+ salt of ligand A and complexes 1A and 2A2 (see Table 1), prepared at pH ~7.

creased ordering of the hydrogen-bonding system. As a result of this, the average lifetime of such interactions decreases, resulting in sharper absorption bands. The coordination of H_2O is confirmed by the presence of a shoulder at ca. 1650 cm^{-1}, assigned to a δH_2O band of a water molecule. A sharp band at 796 ± 10 cm^{-1} is found on the spectra of all complexes, confirming the presence of the $[Me_2Sn(IV)]^{2+}$ cation in the solid samples. However, the Sn–C asymmetric and symmetric modes of the organotin(IV) cation are obscured by the bands of the ligand in the spectra of the complexes; therefore, information regarding the bond angle of the C–Sn–C bond cannot be extracted from the FTIR spectra.

The position of the bands of the carboxyl(ate) group appeared to depend on the preparation of pH and the metal-to-ligand ratio. In the spectra of the complexes prepared at pH ~2 (Fig. 2), the intensity of the $\nu_{sym}(COO^-)$ band decreases (only a shoulder is seen on the spectra), and its position is shifted to ca. 1400 cm^{-1} (Fig. 2). The broad band in the spectral region of 1660–1600 cm^{-1} is likely to be a combination of two bands, the first of them corresponding to the δH_2O band of the coordinated H_2O molecule, and the latter to the $\nu_{as}(COO^-)$ band of the monodentately bonded carboxylate group of the anhydroglucose unit. The appearance of the symmetric stretching vibration of the C=O at 1735 cm^{-1} indicates that in these complexes a fraction of the carboxylate groups is protonated and thus not coordinated to the organotin cation. With ligand A, complexes were prepared at various metal-to-ligand ratios and at pH ~2. From the spectra it can be seen that with the increasing ligand excess, the intensity of the $\nu_{as}(COOH)$ band at 1735 cm^{-1} increases relative to that of the $\nu_{as}(COO^-)$. This means that an increasing fraction of the $-COO^-$ groups remains protonated in the complexes. This suggests that under the preparative conditions employed, the microenvironment of the organotin(IV) centre in the complexes is independent of the metal-to-ligand ratio. This will be further corroborated by the Mössbauer spectroscopic results (see below).

In the spectra of the complexes obtained at pH ~7 (Fig. 3), the $\nu_{as}(COOH)$ band at 1735 cm^{-1} completely disappears. A shoulder at 1650 cm^{-1} is also found in the spectra of these complexes, suggesting the presence of coordinated H_2O molecules. The dominant feature of the spectra is the $\nu_{as}(COO^-)$ band, corresponding to a monodentately coordinating carboxylate moiety. The position of the combination band observed at 1630 cm^{-1} for complexes obtained from acidic solutions is shifted towards the higher wavenumbers in complexes isolated from pH ~7 solutions. The width of the envelope corresponding to $\nu(OH)$ significantly decreases in comparison to those in the uncomplexed ligands. This suggests the rearrangement and restructuring of the H-bridging system. It is likely that at this pH region, the metal-ion-induced deprotonation of the alcoholic hydroxide groups and their coordination to the $[Me_2Sn(IV)]^{2+}$ ion take place.[20] Similar processes have already been observed for complexes formed between sugars and organotin(IV) derivatives in the same pH range.[26] The spectra of these complexes displayed systematic variations with the metal-to-ligand ratio: the uncomplexed and deprotonated carboxylate groups appear in the spectra as separate bands, clearly distinguished from those complexed with the organotin centre.

3.2. Mössbauer spectroscopic measurements

In order to gain further structural information on the solid complexes, Mössbauer spectra of the compounds were recorded and analyzed. As an example, the experimental Mössbauer spectrum of complex 1D is shown in Figure 4. The ^{119}Sn Mössbauer spectroscopic parameters are listed in Table 3.

The experimental quadrupole splitting values ($|\Delta_{exp}|$) obtained are characteristic of organotin(IV) complexes. All the spectra consist of asymmetric doublets, indicating that in the complexes prepared the Sn(IV) central atoms are present in two different geometric surroundings. The spectra were deconvoluted into two doublets. The deconvoluted spectra have an average half-width of 0.8–1.0 mm s^{-1}. From the peak areas of the deconvoluted spectra, it was possible to estimate the number of tin atoms found in these different geometric arrangements. In general, the ratio was found to be 1:1, but in cases of complexes 1A/2, 1D, 2A5 and 3B, they are 2:1, 2:3, 1:3 and 2:3, respectively.

The $|\Delta_{exp}|$ values were compared with the calculated ones on the basis of partial quadrupole splitting (pqs) theory. The pqs values used in these calculations are collected in Table 2. As coordination of alkoxy- or carboxylate groups of sugars is far more favoured than that of the etheral oxygen,[3] participation of the latter in binding to $[Me_2Sn(IV)]^{2+}$ was not taken into consideration during the calculations. A large number of possible

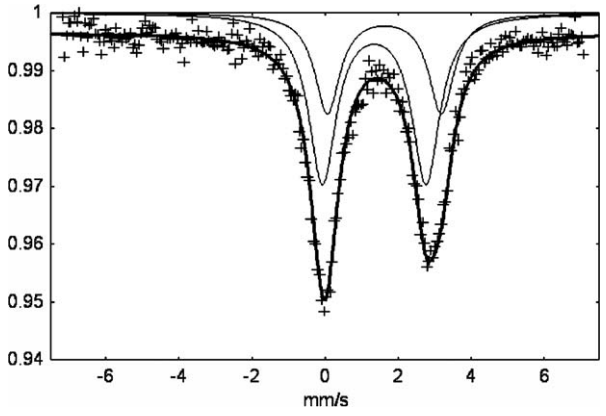

Figure 4. Mössbauer spectrum of complex 1D.

Table 2. pqs values employed in the calculations

Donor groups	Coordination geometry			
	T_h	Tbp_a	Tbp_e	O_h
$-CH_3$	−1.37	−0.94	−1.13	−1.01
$-O^-$ [a]	−0.37	−0.21	−0.09	−0.27
$-O^-_{bidentate}$	—	−0.10	−0.3; 0.02	−0.11
–OH	−0.40	−0.13	0.02[b]	−0.14[b]
H_2O	—	0.18	0.43	0.20[b]
–C=O	0.24	0.16	0.41[b]	0.177[b]
$-COO^-_{monodentate}$	−0.15	−0.10	0.06	−0.11
$-COO^-_{bidentate}$	0.114	0.075	0.293	0.083

T_h, Tbp_e, Tbp_a and O_h mean tetrahedral (T_h), trigonal bipyramidal equatorial (Tbp_e) or axial (Tbp_a) and octahedral (O_h) positions in the geometry, respectively.

[a] $-O^-$ denotes deprotonated, while –OH denotes a protonated alcoholic hydroxy group.

[b] Calculated from the axial (Tbp_a) structure.

structures were taken into account during the calculations, and the most possible geometry of the complexes has been suggested. The experimental and calculated Mössbauer parameters and the corresponding suggested structures are summarized in Table 3. As it can be seen in Table 3, the experimental Mössbauer quadrupole splitting values for the complexes obtained, at a given pH, are close to each other and lie within 0.4 mm s^{-1} ($|\Delta_{1m}| = 3.92$–4.40 mm s^{-1}, $|\Delta_{2m}| = 3.38$–3.69 mm s^{-1} at pH ~2–3; $|\Delta_{1m}| = 3.58$–3.88 mm s^{-1}, $|\Delta_{2m}| = 2.83$–3.16 mm s^{-1} at pH ~7). According to the pqs calculation the complexes, CMC–$[Me_2Sn(IV)]^{2+}$, obtained at pH ~2–3 have O_h and Tbp structures. The complex with an O_h ($\Delta = 4.24$ mm s^{-1}) structure is most likely to be a hydrolysis product of the Me_2SnCl_2. In the equatorial plane, there are two water molecules (close to each other) and two OH^- ions from the hydrolysis, while the methyl groups occupy the axial positions. In the species with the Tbp structure, there are two methyl groups and one OH^- ion in the equatorial plane. The axial positions are occupied by one water molecule and one carboxylate group coordinated in a monodentate mode, and by this way mixed ligand species and hydrolysis products are simultaneously formed. In the complexes obtained from solution at pH ~7, the $[Me_2Sn(IV)]^{2+}$ cations are found in two different Tbp geometries. The only differences seen are between the C–Sn–C bond angles, namely $\Delta = 2.97$ or 3.68 mm s^{-1}; C–Sn–C α: 120° or 134°, respectively. The monodentately coordinated carboxylate group and the methyl groups are in equatorial position, while the axial positions are occupied by the deprotonated –OH group of the D-glucose monomers (or the carboxylate group of the doubly carboxymethylated anhydroglucose units with the ligand D, where such arrangement is most likely to occur) and one water molecule. The results of FTIR measurement supported the monodentate coordination mode of the carboxylate groups. The structures suggested are depicted in Figure 5.

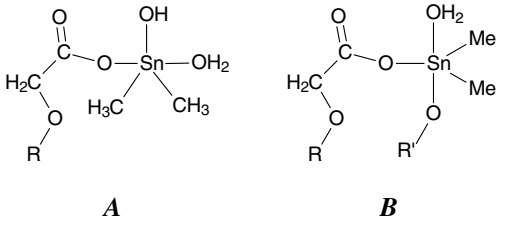

Figure 5. Suggested structure of the complexes prepared: (***A***) $Me_2Sn(IV)$–CMC complex obtained at pH ~2–3; (***B***) $Me_2Sn(IV)$–CMC complex obtained at pH ~7, where R and R′ represent different anhydroglucose units of the CMC molecule.

Table 3. Observed and calculated Mössbauer parameters (mm s^{-1}) and the suggested structures

	Component 1					Component 2				
	δ_1[a]	$\lvert\Delta_{1m}\rvert$[b]	%[c]	$\lvert\Delta_{1calcd}\rvert$[d]	Str.[e]	δ_2[a]	$\lvert\Delta_{2m}\rvert$[b]	%[c]	$\lvert\Delta_{2calcd}\rvert$[d]	Str.[e]
1A/2	1.25	3.65	66	3.68	Tbp	1.14	3.02	34	2.97	Tbp
1B/2	1.22	3.69	50	3.68	Tbp	1.15	2.95	50	2.97	Tbp
1C	1.18	3.58	44	3.68	Tbp	1.13	2.84	56	2.97	Tbp
1D	1.26	3.80	38	3.68	Tbp	1.15	3.06	62	2.97	Tbp
2A2	1.30	3.89	50	3.68	Tbp	1.16	3.17	50	2.97	Tbp
2A5	1.19	3.59	28	3.68	Tbp	1.11	2.88	72	2.97	Tbp
3A	1.15	3.92	50	3.82	Tbp	1.09	3.70	50	3.82	Tbp
3B	1.40	4.39	42	4.27	O_h	1.27	3.46	58	3.43	Tbp
3C	1.36	4.25	60	4.27	O_h	1.27	3.39	40	3.43	Tbp
3D	1.40	4.36	46	4.27	O_h	1.28	3.43	54	3.43	Tbp
4A2	1.37	4.40	50	4.27	O_h	1.28	3.43	50	3.43	Tbp
4A5	1.42	4.23	47	4.27	O_h	1.19	3.47	53	3.43	Tbp

Note that in the case of Tbp structures, the $|\Delta|$ values were calculated by changing the C–Sn–C bond angles according to the Sham–Bancroft equation.

[a] Experimental isomer shift in mm s^{-1}.

[b] Experimental quadrupole splitting in mm s^{-1}.

[c] Percentage contribution of the component to the total spectrum.

[d] Calculated quadrupole splitting in mm s^{-1}.

[e] Suggested structure.

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