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Diorganotin(IV) complexes of D-galacturonic acid: solid-state and solution-phase structural study

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Three diorganotin(IV) complexes of D-galacturonic acid (H_2GalA; R = Me, *n*-Bu, Ph), two of which are new derivatives (R = Me, Ph), have been synthesized and their solid-state and solution-phase investigated by IR, Mössbauer, ^{1}H, ^{13}C and ^{119}Sn NMR spectroscopy. The FTIR data suggest that H_2GalA, in the dialkyltin derivatives, behaves as a dianionic ligand, coordinating the tin(IV) atom through an ester-type carboxylate and deprotonated alcoholic hydroxo groups, whereas a bridging carboxylate occurs in the diphenyltin(IV) complex. Octahedral and trigonal bipyramidal local geometries on tin(IV) atoms are proposed for dialkyltin(IV)GalA and diphenyltin(IV)GalA complexes respectively on the basis of Mössbauer spectroscopy. In D_2O solution, R_2Sn(IV) moieties seem to be mainly coordinated by the GalA^{2-} in the β-furanosidic (β-GalfA^{2-}) form, involving the β-furanosidic ring in rotational equilibrium. However, the α-furanosidic (α-GalfA^{2-}), α-pyranosidic (α-GalpA^{2-}) and the β-pyranosidic (β-GalpA^{2-}) isomers are also involved in the coordination upon the tin atom to a minor extent. In DMSO-d_6 solution, R_2Sn(IV) moieties are coordinated almost entirely by the GalA^{2-} in the β-furanosidic form. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: diorganotin; Mössbauer; NMR

INTRODUCTION

The interaction between carbohydrates and metallic cations has been the subject of a number of papers since 1980 because of its relevance in many fields of wide interest, such as health science, pharmacology and biology.[1–3]

Of the studies, organotin(IV) carbohydrate derivatives have been investigated mainly to focus the regioselective directing power of the organometallic moieties towards the reactivity of the sugar substrate, and to verify the modification of the biological activity when coordinated to the sugar, topics recently widely reviewed.[4] Among the acidic carbohydrate derivatives, D-galacturonic acid (H_2GalA, Fig. 1) is a molecule of biological relevance. In fact, it is present in plants as pectin (polygalacturonic acid), which is the main component of cell walls, as well as in some exopolysaccharides localized in plant roots, where it acts as a chelating agent towards metal ions.[5–8]

Derivatives of pectin have recently been tested as potential anticancer drugs.[9]

In aqueous solution, H_2GalA undergoes to the equilibrium reported in Fig. 1.

Although the synthesis and solid-state characterization of diethyltin(IV) and dibutyltin(IV) complexes of H_2GalA have been already reported,[10–12] in this paper we report the structural characterization, both in the solid state and solution phase, of complexes obtained from the reaction of dimethyltin(IV), dibutyltin(IV) and diphenyltin(IV)oxide with H_2GalA.

EXPERIMENTAL

All complexes were synthesized from R_2SnO, freshly prepared by hydrolysis of the parent R_2SnCl_2 (R = Me,

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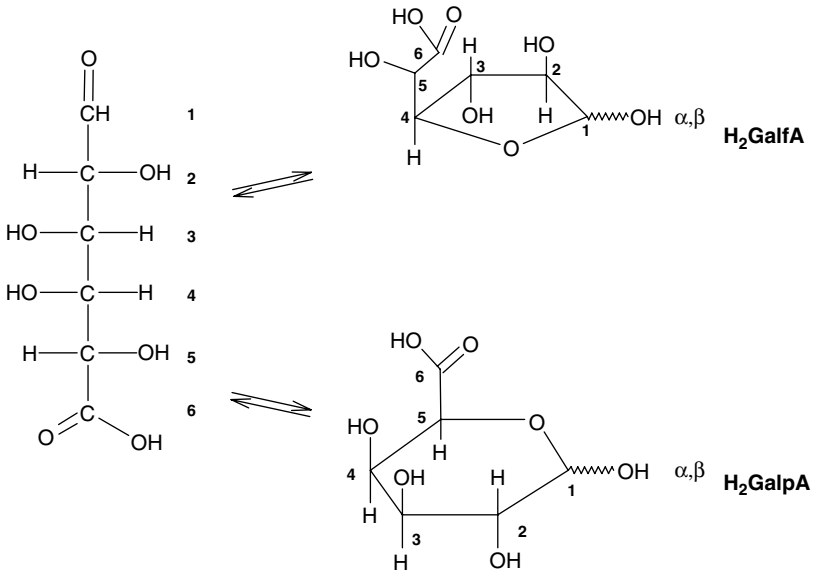

Figure 1. Isomeric equilibria in solution of H_2Gala. H_2GalfA is the furanosidic form of D-galacturonic acid; H_2GalpA is the pyranosidic form of D-galacturonic acid.

n-Bu, Ph; gifts from Witco GmbH, Bergkamen, Germany) and $H_2GalA{\cdot}H_2O$ (99% purity, Fluka, Buchs), used without further purification, in 1:1 molar ratio according to the following procedures.

Me_2SnGalA (**1**): 1 mmol (0.1648 g) of Me_2SnO and 1 mmol of H_2GalA (0.1941 g), in 40 cm^3 of methanol, were refluxed under continuous stirring at room temperature for 4 days. A white precipitate was obtained, which was filtered, washed with methanol and dried under vacuum in the presence of P_4O_{10}. Anal. Found (calc.): C = 28.19% (28.29%); H = 4.21% (4.15%); Sn = 33.97% (34.83%).

Bu_2SnGalA (**2**): 1 mmol (0.2489 g) of *n*-Bu_2SnO and 1 mmol of H_2GalA (0.1941 g), in 40 cm^3 of methanol, were refluxed under continuous stirring at room temperature for 10 days. The volume of the clear solution obtained was reduced in a rotatory evaporator to just 10 cm^3. After 1 day in a refrigerator, a white precipitate was formed, which was filtered, washed with methanol and dried under vacuum in the presence of P_4O_{10}. Anal. Found (calc.): C = 39.00% (39.37%); H = 6.14% (6.62%); Sn = 26.88% (27.80%).

Ph_2SnGalA (**3**): 1 mmol (0.2889 g) of Ph_2SnO and 1 mmol of H_2GalA (0.1941 g), in 40 cm^3 of methanol, were refluxed under continuous stirring at room temperature for 15 days. A white precipitate was obtained, which was filtered, washed with methanol and dried under vacuum in the presence of P_4O_{10}. Anal. Found (calc.): C = 47.35% (46.49%); H = 3.90% (3.91%); Sn = 24.56% (25.53%).

All the complexes obtained were analysed for their carbon and hydrogen content at the laboratory of the Dipartimento di Chimica Inorganica, Metallorganica e Analitica, University of Padova.

The tin content was determined in our laboratory, gravimetrically as SnO_2, according to Neumann's method.[13]

FTIR spectra of organotin(IV) complexes were recorded, both as Nujol and hexachlorobutadiene mulls, on a Perkin–Elmer model Spectrum 1 FT-IR, in CsI windows, with eight scans at 4 cm^{-1} resolution.

The ^{119}Sn Mössbauer spectra were recorded with a model 269 TAKES (Ponteranica, Bergamo, Italy) multichannel analyser (4096 channels) and the following MWE (München Wissenschaftilche Elektronik, GmbH, Starnberg, Germany) apparatus: MR250 driving unit, FG2 digital function generator and MA250 velocity transducer, moving at linear velocity and constant acceleration in a triangular waveform. A cryostat (Mod. NDR 1673 MB, Cryo Instruments, USA) with an ITC-2 Oxford Instruments temperature controller was used to maintain the absorber samples (absorber thickness, $[^{119}Sn] = 0.50–0.60$ mg cm^{-2}) at the temperature investigated (77.3 K). The temperature control was better than ±0.1 K. The multichannel calibration was performed with an enriched iron foil (^{57}Fe = 95.2%, thickness 0.06 mm) at room temperature using a ^{57}Co (10 mCi) source (New England Nuclear, Amersham), while the zero point of the Doppler velocity scale was determined at room temperature through the absorption spectrum of natural $CaSnO_3$ ($[^{119}Sn] =$ 0.50 mg cm^{-2}) as source.

The thermal behaviour of the complexes was studied by differential thermogravimetry (DTG) on a Mettler TA 4000 thermal analyser in the 25–800 °C range under a nitrogen stream.

^{1}H and ^{13}C and ^{119}Sn NMR spectra were recorded on a Bruker 300 ARX NMR spectrometer, at 300.13 MHz, 75.47 MHz and 111.92 MHz respectively. In D_2O, ^{1}H and ^{13}C resonances were calibrated using 2,2-dimethylsilapentane-5-sulfonic acid (DSS) as external standard. In dimethylsulfoxide (DMSO) the signals of the solvent were used as internal

standard (DMSO-d_6, $\delta = 2.49$, ^{1}H, and $\delta = 39.5$, ^{13}C). ^{119}Sn δ are reported in absolute frequency assuming external DSS (D_2O) or tetramethylsilane (TMS) (DMSO) = 100 MHz. Positive chemical shifts are, for all nuclei, to higher frequency of the reference. An inverse gated pulse sequence was used to record ^{119}Sn{^{1}H} spectra. In both D_2O and DMSO, unimportant δ variations were detected within the 0.1–0.01 M concentration range for **1** and **2**.

RESULTS AND DISCUSSION

The analytical data clearly indicated that organotin(IV) moieties reacted with $GalA^{2-}$ in 1 : 1 stoichiometric ratio, and that $GalA^{2-}$ acted as a dianionic ligand in all the complexes.

Solid state

Thermal decomposition

DTG shows that the thermal decomposition takes place in two steps for all the compounds. The first stage corresponds roughly to the loss of half a ligand unit, and the second half of the ligand is lost together with the organic groups bonded to the tin atom, leaving an Sn/SnO mixture as a residue in the case of the dialkyltin(IV) derivatives and SnO_2 in the case of the diphenyl complex. Analogous thermal decomposition patterns have already been reported for several organotin(IV) carbohydrates derivatives.[10,14]

IR spectra

The more relevant IR absorption bands of the free and coordinated $H_2GalA{\cdot}H_2O$ are reported in Table 1.

Evidence of the change in the structural arrangement of the hydrogen bond network in the complexes obtained with respect to the free $H_2GalA{\cdot}H_2O$[15] was obtained through the variation of the ν(OH) vibrations, which were present in the range 3450–3300 cm^{-1} in the free ligand, whereas in the complexes synthesized they occurred in the 3260–3000 cm^{-1} range (Table 1). In the free ligand, the –C=O stretching vibrations of the carboxylic group were observed at 1713 cm^{-1}. In the spectra of all the complexes these bands were shifted towards lower wavenumbers and were observed in the 1652–1565 cm^{-1} and in the 1386–1350 cm^{-1} ranges (Table 1). These two sets of absorption are assigned, respectively, to the asymmetric and symmetric stretching vibrations of the carboxylate group of the coordinated $GalA^{2-}$ (Table 1). The $\Delta\nu$(COO) [$= \nu_a(COO^-) - \nu_s(COO^-)$] values for both the dimethyltin(IV) and the dibutyltin(IV) GalA derivatives are characteristic of the values found for coordinated ester-type carboxylate groups, and the value found for the diphenyltin(IV)GalA complex was in the range of a bidentate bridging carboxylate. Bands attributable to $\nu_a(SnC_2)$ and $\nu_s(SnC_2)$ were present in the IR spectrum of the dimethyltin(IV) at 590 cm^{-1} and 526 cm^{-1} respectively. Finally, in the diphenyltin(V)GalA complex, the characteristic Y-mode of the phenyl group band was present at 450 cm^{-1}.

Table 1. Assignment of more relevant absorption bands of diorganotin(IV)–GalA derivatives in the 4000–250 cm^{-1} region[a]

$H_2GalA{\cdot}H_2O$	Me_2 SnGalA	*n*-Bu_2 SnGalA	Ph_2 SnGalA	Band assignment
3440s	3406s	3386s	3320s	ν(OH)
3360s			3260s	
3320s				
1713s				ν(COOH)
	1652s	1633s	1565s	$\nu_a(OCO^-)$
1640m				$\delta(H_2O)$
	1350s	1376s	1386s	$\nu_s(OCO^-)$
	590w			$\nu_a(SnC_2)$
	526w			$\nu_s(SnC_2)$
			449w	Y-mode Sn–Ph
	302	257	179	$\Delta\nu$

[a] H_2GalA = D-galacturonic acid; IR spectra taken as Nujol and hexachlorobutadiene mulls; s = strong, m = medium, w = weak.

^{119}Sn Mössbauer spectra

The Mössbauer data are given in Table 2. The compounds have fairly large nuclear quadrupole splitting ($|\Delta_{exp}|$) values; calculations based on the simple point charge treatment of Sham and Bancroft,[16] which assumes the splitting to be due solely to the disposition of the Sn–C bonds, would give C–Sn –C bond angles of about 155° and 135° for the dialkyltin(IV) and the diphenyltin(VI) units, respectively.

Table 2 also gives the quadrupole splitting values calculated (Δ_{calcd}) according to the point charge model formalism[17–19] for the idealized steric arrangements of Fig. 2, where the six-coordinated structure in Fig. 2a applies to the dialkyltin(IV) compounds with the fifth and sixth tin coordination sites occupied, through intramolecular interactions, by alcoholic hydroxy oxygen atoms, and

Table 2. ^{119}Sn Mössbauer data[a]

Compound[b]	δ (mm s^{-1})	$\lvert\Delta_{exp}\rvert$ (mm s^{-1})	Δ_{calcd}[c] (mm s^{-1})	Figure
$Me_2SnGalA$	1.34	3.86	+4.03	2a
n-$Bu_2SnGalA$	1.44	3.81	+4.03	2a
$Ph_2SnGalA$	1.12	3.01	−2.81	2b

[a] Experimental Mössbauer parameters measured at liquid nitrogen temperature; isomer shift, $\delta \pm 0.02$, with respect to room temperature $Ca^{119}SnO_3$; nuclear quadrupole splitting, $|\Delta_{exp}| \pm 0.03$.

[b] $GalA^{2-}$ = D-galacturonate^{2-}.

[c] The regular structures octahedral *trans*-Alk_2 (Fig. 2a) and trigonal bipyramidal eq-Ph_2 (Fig. 2b) were assumed to calculate the nuclear quadrupole splitting value according to the point charge model formalism[17–19]; the partial quadrupole splitting values (mm s^{-1}) employed were: $\{Alk\}^{Oct} = -1.03$, Ref. 19; $\{COO^-_{unid}\}^{Oct} = -0.11$ (calculated from $\{COO_{unid}\}^{Tet}$, Ref. 19); $\{RO^-\}^{Oct} = -0.32$ (calculated from $\{RO^-\}^{Tba}$, Ref. 20); $\{ROH\}^{Oct} = 0.16$ (see text); $Ph^{Tbe} = -0.98$, Ref. 18; $\{COO^-_{bridg}\}^{Tba} = 0.075$, Ref.18; $\{RO^-\}^{Tbe} = -0.19$, Ref. 20.

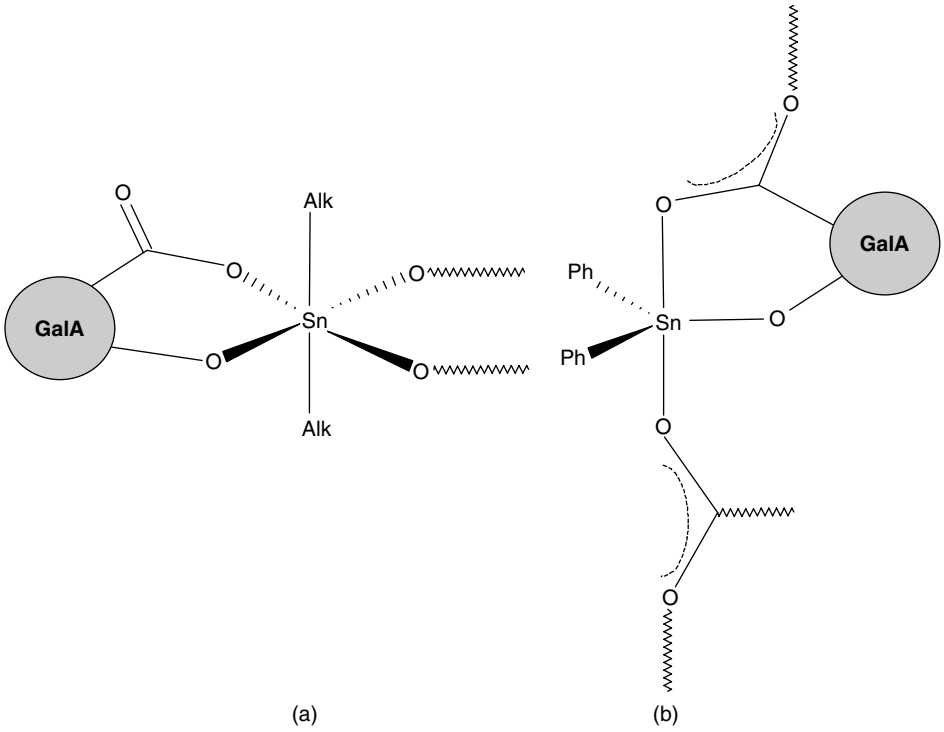

Figure 2. Proposed solid-state structures for (a) $R_2SnGalA$ (R = Me, *n*-Bu) and (b) $Ph_2SnGalA$. $GalA^{2-}$ = D-galacturonate^{2-}.

the five-coordinated structure in Fig. 2b considers the presence of bridging carboxylate in the diphenyltin(VI)GalA complex.

Consider, however, the Δ_{calcd} value reported for structure in Fig. 2a as just indicative, since it has been calculated in spite of the lack of a reliable partial quadrupole splitting value for an ROH coordinating group, which, in turn, derives from the lack of suitable derivatives with a known structure.

We attempted to overcome this difficulty by taking the value $\Delta_{av} = 0.65$ mm s^{-1} measured for $SnCl_4 \cdot 2ROH$ (R = Me, Et, *n*-Pr, i-Pr)[21] as the possible estimator of the missing parameter, which would give 0.16 or 0.32 mm s^{-1} for the absolute (algebraic) value of $\{ROH\}^{Oct}$, depending on whether these addition complexes might actually be considered *trans*- or *cis*-ROH octahedral tin species. The value employed in the calculation, 0.16 mm s^{-1}, has then been crudely selected by discharging the negative values, as they would indicate a charge donating power of ROH consistently higher than that of Cl^- and, at the same time, choosing a value that is close to $\{H_2O\}^{Tba} = 0.18$ mm s^{-1}.[18]

Solution phase

^1H and ^{13}C NMR spectra

The solution-phase investigation was carried out by NMR spectroscopy. Dimethyltin(IV)GalA (**1**) complex was monitored both in D_2O and DMSO-d_6 solutions, whereas dibutyltin(IV)GalA (**2**) and diphenyl(IV)GalA (**3**), owing to their low solubility in water, were monitored only in DMSO-d_6 solution (Tables 3–8).

Table 3. ^1H NMR data data for H_2GalA and its $R_2Sn(IV)GalA$ complexes (R = Me) in D_2O solution at 298 K and, for the complexes, at pD 7 (δ, ppm from TMS)[a]

Compound	H-1	H-2	H-3	H-4	H-5	CH_3
α-H_2GalpA	5.29	3.82	3.91	4.28	4.40	—
β-H_2GalpA	4.57	3.50	3.69	4.21	4.05	—
α-H_2GalfA	5.24	4.05	4.32	4.10	n.d.	—
β-H_2GalfA	5.20	4.00	4.16	n.d.	n.d.	—
α-[$Me_2SnGalpA$]	5.31	3.82	3.93	4.28	4.52	0.84
β-[$Me_2SnGalpA$]	4.59	3.52	3.71	4.24	4.17	0.84
α-[$Me_2SnGalfA$]	5.29	4.08	4.30	4.08	4.33	0.84
β-[$Me_2SnGalfA$]	5.26	4.00	4.30	4.41	4.36	0.84

[a] n.d. = not determined; H_2GalpA = pyranosidic form of D-galacturonic acid; H_2GalfA = furanosidic form of D-galacturonic acid; $GalpA^{2-}$ = pyranosidic form of D-galacturonate^{2-}; $GalfA^{2-}$ = furanosidic form of D-galacturonate^{2-}.

$Me_2Sn(IV)$–GalA in D_2O

In aqueous solution, D-galacturonic acid (H_2GalA) exists as $\alpha + \beta$ pyranose (about 90%) and $\alpha + \beta$ furanose forms (about 10%).

^1H and ^{13}C assignments and the percentages of the isomers present in D_2O solution are reported in Tables 3–5. These values are in substantially good agreement with literature

Table 4. ^{13}C NMR data for H_2GalA and its $R_2Sn(IV)GalA$ complexes (R = Me) in D_2O solution at 298 K and, for the complexes, at pD 7 (δ, ppm from TMS)[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	CH_3
α-H_2GalpA	92.11	68.00	69.30	70.75	71.30	175.95	—
β-H_2GalpA	95.97	71.55	72.85	70.25	75.46	175.08	—
α-H_2GalfA	94.62	76.00	n.d.	82.27	n.d.	n.d.	—
β-H_2GalfA	100.88	81.16	n.d.	83.34	n.d.	n.d.	—
α-[$Me_2SnGalpA$]	92.18	67.92	69.04	70.54	70.99	n.d.	n.d.
β-[$Me_2SnGalpA$]	96.04	71.43	72.64	70.06	74.99	n.d.	n.d.
α-[$Me_2SnGalfA$]	95.25	75.41	73.64	82.79	n.d.	n.d.	n.d.
β-[$Me_2SnGalfA$]	101.78	80.22	75.71	85.87	71.94	n.d.	n.d.

[a] n.d. = not determined; H_2GalpA = pyranosidic form of D-galacturonic acid; H_2GalfA = furanosidic form of D-galacturonic acid; $GalpA^{2-}$ = pyranosidic form of D-galacturonate^{2-}; $GalfA^{2-}$ = furanosidic form of D-galacturonate^{2-}.

Table 5. Percentages of D-galacturonic system stereoisomers in D_2O solution of H_2GalA and its $Me_2Sn(IV)GalA$ complex at 298 K and pD 7[a]

Compound	Percentage (%)
α-H_2GalpA	36
β-H_2GalpA	55
α-H_2GalfA	4
β-H_2GalfA	5
α-[$Me_2SnGalpA$]	16
β-[$Me_2SnGalpA$]	23
α-[$Me_2SnGalfA$]	14
β-[$Me_2SnGalfA$]	47

[a] H_2GalpA = pyranosidic form of D-galacturonic acid; H_2GalfA = furanosidic form of D-galacturonic acid; $GalpA^{2-}$ = pyranosidic form of D-galacturonate^{2-}; $GalfA^{2-}$ = furanosidic form of D-galacturonate^{2-}.

data.[22] Small discrepancies could be due to pD differences in the media.

The equilibria of complexation reported here have been studied at pD 7.0. Complexation of D-galacturonate ($GalA^{2-}$) to tin(IV) is evidenced by the fast complete solubilization of the poorly soluble Me_2SnO in H_2O after addition of equimolar amounts of H_2GalA. The '*in situ*' mixture of reactants at pD 7.0 leads slowly to spectra superimposable to those of the preparative solid dissolved in D_2O. On the basis of the poor influence exerted by the concentration on the NMR signal frequencies, monomeric structures should be assigned in solution to **1**.

$^{119}Sn\{^1H\}$ NMR of **1** in D_2O at 298 K shows a broad signal ($\delta = -131$ ppm, linewidth lw = 800 Hz).

At 275 K, the ^{119}Sn resonance is split into two sharper signals of about 1:3 intensity ratio, centred respectively at -125 ppm (lw = 600 Hz) and -134 ppm (lw = 450 Hz). We attribute the splitting of the ^{119}Sn NMR signals at 275 K to a lowered rate of the exchange reported in the Fig. 3 where at least one molecule of the solvent is involved (*vide infra*).

^1H and $^{13}C\{^1H\}$ NMR galacturonate resonances after coordination to Me_2Sn^{2+} showed very low frequency differences (Tables 3 and 4). $GalA^{2-}$ coordination, however, can be argued by the strong relative intensity variation of the NMR spectra upon metal addition. Indeed, complexation can be regarded as a molecular recognition of furanosate anion (especially the β form), whose concentration is about eight

Table 6. ^1H NMR data for H_2GalA and its $R_2Sn(IV)GalA$ complexes (R = Me, *n*-Bu, Ph) in DMSO-d_6 solution at 298 K (δ, ppm from TMS)[a]

Compound	H-1	H-2	H-3	H-4	H-5	1-OH	2-OH	3-OH	α-CH_2	β-CH_2	γ-CH_2	CH_3	Ph
α-H_2GalpA	4.98	3.51	3.60	3.96	4.31	6.30	n.d.	n.d.	—	—	—	—	—
β-H_2GalpA	4.25	3.23	3.32	3.89	4.03	n.d.	n.d.	n.d.	—	—	—	—	—
α-H_2GalfA	4.94	3.66	3.86	4.00	4.00	n.d.	n.d.	n.d.	—	—	—	—	—
β-H_2GalfA	4.87	3.64	3.89	3.98	4.00	6.25	n.d.	n.d.	—	—	—	—	—
β-[$Me_2SnGalfA$]	4.82	3.65	3.94	4.02	3.98	6.08	5.31	5.05	—	—	—	0.52	—
β-[n-$Bu_2SnGalfA$]	4.84	3.66	3.96	4.03	3.98	6.04	5.24	5.03	1.21	1.52	1.29	0.86	—
β-[$Ph_2SnGalfA$]	4.72	3.70	4.04	4.20	4.15	6.04	5.22	5.13	1.21	1.52	1.29	0.86	4.67, 7.43

[a] n.d. = not determined; H_2GalpA = pyranosidic form of D-galacturonic acid; H_2GalfA = furanosidic form of D-galacturonic acid; $GalpA^{2-}$ = pyranosidic form of D-galacturonate^{2-}; $GalfA^{2-}$ = furanosidic form of D-galacturonate^{2-}.

Table 7. ^{13}C NMR data for H_2GalA and its $R_2Sn(IV)GalA$ complexes (R = Me, *n*-Bu, Ph) in DMSO-d_6 solution at 298 K. (δ, ppm from TMS)[a]

Compound	C-1	C-2	C-3	C-4	C-5	C-6	α-CH_2	β-CH_2	γ-CH_2	CH_3	Ph
α-H_2GalpA	93.15	68.53	69.39	70.98	70.27	171.13	—	—	—	—	—
β-H_2GalpA	97.54	71.86	73.36	70.39	73.90	170.55	—	—	—	—	—
α-H_2GalfA	95.64	77.62	83.50	74.22	69.74	174.20	—	—	—	—	—
β-H_2GalfA	102.03	82.71	75.56	82.53	69.11	174.57	—	—	—	—	—
β-[Me_2SnGalfA]	102.29	82.11	76.34	84.67	71.99	n.d.	—	—	—	3.46	—
β-[n-Bu_2SnGalfA]	102.27	82.26	76.27	84.35	71.91	n.d.	22.12	26.55	25.94	13.54	—
β-[Ph_2SnGalfA]	102.14	82.26	76.51	84.06	71.76	n.d.	22.12	26.55	25.94	13.54	135.8, 129.38

[a] n.d. = not determined; H_2GalpA = pyranosidic form of D-galacturonic acid; H_2GalfA = furanosidic form of D-galacturonic acid; $GalpA^{2-}$ = pyranosidic form of D-galacturonate^{2-}; $GalfA^{2-}$ = furanosidic from of D-galacturonate^{2-}.

Table 8. Percentage of D-galacturonic system stereoisomers in DMSO solution at 298 K of H_2GalA and its $R_2Sn(IV)GalA$ complexes (R = Me, *n*-Bu, ph)[a]

Compound	Percentage (%)
α-H_2GalpA	22
β-H_2GalpA	23
α-H_2GalfA	11
β-H_2GalfA	44
α-[Me_2SnGalfA]	3
β-[Me_2SnGalfA]	97
β-[nBu_2SnGalfA]	>99
β-[Ph_2SnGalfA]	>99

[a] H_2GalpA = pyranosidic form of D-galacturonic acid; H_2GalfA = furanosidic form of D-galacturonic acid; $GalpA^{2-}$ = pyranosidic form of D-galacturonate^{2-}; $GalfA^{2-}$ = furanosidic form of D-galacturonate^{2-}.

times enhanced by the Me_2Sn^{2+} cation. This result is in agreement with the suggestion of Ramos *et al.*,[22] that furanosate, owing to O-5 coordination availability, forms more stable metal chelates. Coordination of $GalA^{2-}$ is definitively proved by the interligand positive nuclear Overhauser enhancement (NOE) between tin-methyl groups and galacturonate H-1. This spatial connection can only take place by either O-4 or O-1 complexation. Thus, NOE effects can be taken as a measure of O-1 or O-4 involvement in coordination. Remarkably, H-1 is the only $GalA^{2-}$ proton showing interligand spatial connection. The most clear and striking NOE (+2%) concerns the β-furanosate complex, where the metal is placed, opposite to O-1, by carboxylate and O-5 chelation. As a consequence, the spatial tin-methyl–H-1 connectivity can only be established through O-4 coordination (Fig. 3, **1b**).

Consistently, $^{13}C\{^1H\}$ NMR show for the β-furanosate C-4 the highest metal-induced $\Delta\delta$ (+2.5 ppm). In the analogous

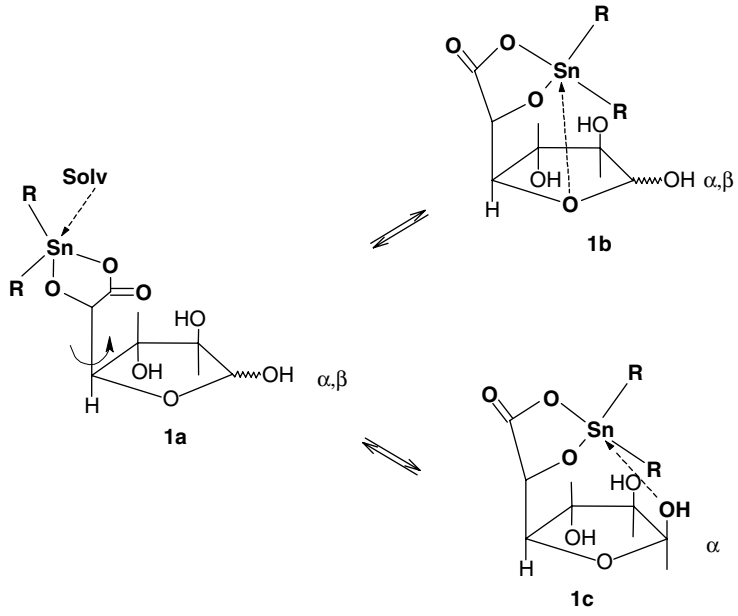

Figure 3. Rotational equilibrium of α,β-$R_2SnGalfA$ (R_2 = Me, *n*-Bu, Ph) in solution. $GalfA^{2-}$ = D-galacturonate^{2-} furanosidic form.

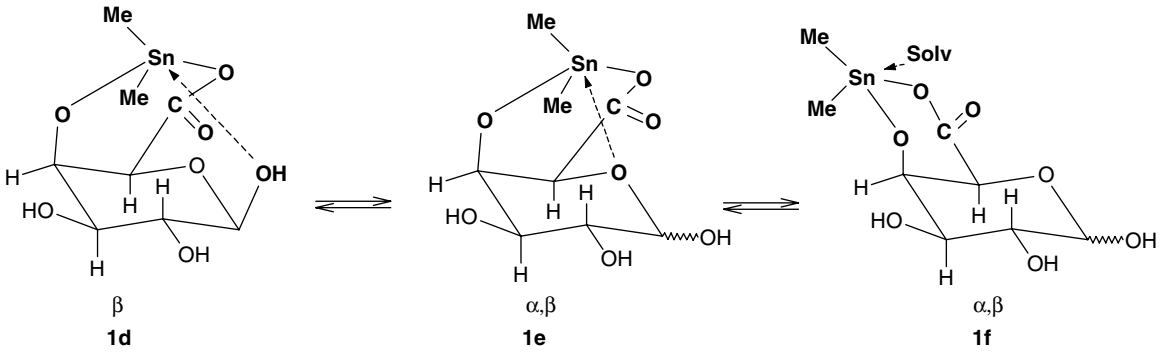

Figure 4. Equilibria in D_2O solution of α,β-$Me_2SnGalpA$. $GalpA^{2-}$ = D-galacturonate^{2-} pyranosidic form.

α-anomer (NOE = +0.9%), the O-1 placed on the same side of the chelated metal hinders O-4 coordination and, eventually, may compete with it for the third coordination site (Fig. 3, **1c**).

Moreover, in the ^1H NMR spectra, the signal of the methyl groups also shows the satellites due to the two-bond coupling constant between $^{115,117,119}Sn$ and ^1H. The $^2J(^{119}Sn-^1H)$ value measured was 86.5 Hz, and on using this in the Lockhart equation[23] the calculated C–Sn–C angle was *ca* 139°. This angle is indicative of a local skew-octahedral geometry around the tin. This is possible because of water molecules present in the first sphere of coordination of the tin atom, so that a fast exchange with the solvent may occur. A slightly positive NOE between tin-methyl groups and water (*ca* 0.3%) seems to confirm this suggestion.

Previous experimental and computational studies for similar systems,[24,25] where the effects of the water as coordinating solvent were taken into account, enable us to guess that the experimental value of the chemical shift for the tin nucleus in compound **1** is in agreement with the presence of one coordinated solvent molecule. Clearly, owing to the continuum in the internuclear distances between tin(IV) and solvent molecules, the dynamics of the exchange process may give an averaged value of the chemical shift of the tin. As a consequence, it is even possible that two solvent molecules may be coordinated to the tin atom.

The pyranose anomers show very weak interligand NOE (*ca* +0.3%). The lack of strong spatial connections suggests the preference of this ligand for a looser bidentate coordination. Models show that the most stable pyranosate complexes are obtained upon coordination of carboxylate and O-4 as second coordination site of the complex **1e**, represented schematically in the Fig. 4. Occasional participation of O-1 and O-5 in coordination would lead to the rigid entropically disfavoured structures **1d** and **1f**, which could justify the weak interligand NOE experimentally observed.

We did not report in all the figures the $GalA^{2-}$ fast dissociation equilibrium (leading to small amounts of the solvated Me_2Sn^{2+} cation) suggested by the lack of ^{119}Sn coupling in the GalA proton and carbon resonance.

$R_2Sn(IV)$–GalA in DMSO-d_6

As dissolved in DMSO, D-galacturonic acid (H_2GalA) is exclusively in the α-pyranosidic form. At equilibrium, (after 3–4 h), the main stereoisomer is the β-furanose (Table 8).

Complexation of D-galacturonic acid to tin(IV) is evidenced by the complete solubilization of R_2SnO (R = Me or *n*-Bu) suspended in DMSO-d_6 after addition of equimolar amounts of H_2GalA. Complex **3**, instead, showed low solubility.

$R_2SnGalA$ complexes prepared according to the procedure reported in the Experimental section have been studied in DMSO-d_6 at 298 K.

$^{119}Sn\{^1H\}$ NMR spectra of **1** and **2** at 298 K show single resonances, at −100.3 ppm (lw = 48 Hz) at −126.1 ppm (lw = 18 Hz) respectively. These signals were much sharper than the analogous signals observed in D_2O. This means that $GalA^{2-}$ dissociation in DMSO-d_6 is much slower. Owing to the lower solubility of complex **3**, no appreciable $^{119}Sn\{^1H\}$ NMR signal was detected.

^1H and $^{13}C\{^1H\}$ NMR show that more than 95% of the total $GalA^{2-}$ is coordinated as β-furanosate (Table 8). Thus, in this solvent, the R_2Sn^{2+} cation is even more selective in the anion recognition. The H-1–tin-alkyl interligand spatial connection (NOE = +1%) for complexes **1** and **2** indicates β-furanosate O-4 coordination; for complex **3**, no appreciable NOE was detected. However, the ^1H and $^{13}C\{^1H\}$ NMR $GalA^{2-}$ signals for compounds **1**, **2** and **3** are very similar (Tables 6 and 7), and a shift towards higher frequency for the C-4 and C-5 $^{13}C\{^1H\}$ chemical shifts of greater than 2 ppm (Table 7) also supports the O-4 involvement as the third coordinating site of the ligand (Fig. 3).

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