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Sugar complexes with metal^{2+} ions: thermodynamic parameters of associations of Ca^{2+}, Mg^{2+} and Zn^{2+} with galactaric acid

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Abstract

A solution study on the complex ability of galactaric acid ($GalaH_2$) for complexation with Ca^{2+}, Mg^{2+} and Zn^{2+} ions is reported. The stability constants of the complex species are determined by means of potentiometric measurements. From the dependence of stability constants on temperature, the $\Delta H°$ and $\Delta S°$ values are also determined. The formation of the complex species is an endothermic process and $\Delta H°$ and $\Delta S°$ values suggest a chelate coordination mode of galactaric acid involving carboxylic oxygen and α-hydroxylic group. The prevailing species at acidic or neutral pH is [MGala] ($M = Ca^{2+}$, Mg^{2+}, Zn^{2+}) which is also isolated in the solid state and characterised by means of IR spectroscopy. On increasing pH, the $[MGalaH_{-1}]^-$ species is also formed, where the coordinated OH group undergoes deprotonation. © 2001 Elsevier Science Ltd. All rights reserved.

Keywords: Galactaric acid; Acid sugars; Metal complexes; Thermodynamic study

1. Introduction

Carbohydrate complexes with metal ions generally have a very low stability in aqueous solution, owing to the poor donor ability of hydroxylic oxygen atoms. Introduction of an anchoring group into a sugar molecule as a primary coordination site may promote the coordination and deprotonation of the alcoholic hydroxylic groups of the carbohydrate moiety. The complex forming ability is enhanced by several orders of magnitude, even in acidic or neutral solutions.[1] Among carbohydrate derivatives, sugar acids are of great interest because their metal ions complexes are largely present in biological media.[2] Zinc saccharide complexes have been shown to influence the activity of some Zn^{2+} enzymes and were investigated as preventive agents against lead intoxication in rats,[3] while Zn^{2+}-hyaluronic acid complex has been patented and used as a medicine for treatment of ulcers.[4] The ability of Ca^{2+} to form strong gels in the presence of alginic acid is related to the interaction of calcium ions with the α-glucuronic residues of alginic acid.[5]

Many structural studies have demonstrated that, in the solid state, the interaction of sugar acids with metal ions involves both the carboxylic oxygen and the α-hydroxylic group. The crystal and molecular structure of Ca^{2+} and Mg^{2+}-galactarate,[6,7] Ca^{2+}-glucarate,[8] Ca^{2+}-lactobionate and gluconate[9] has been reported. The structure of Zn^{2+}-hyaluronate

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Table 1
Protonation constants of $GalaH_2$ at different temperatures (°C) and thermodynamics quantities $\Delta H°$ and $\Delta S°$

	15°C	25°C	35°C	45°C	$\Delta H°$ (kcal mol^{-1})	$\Delta S°$ (cal mol^{-1} K^{-1})
Log K_1	3.07(2)	3.05(2)	2.96(3)	2.92(3)	−1.5(4)	9(1)
Log K_2	4.08(2)	4.04(2)	3.97(2)	3.95(2)	−1.9(4)	12(2)

was also obtained by EXAFS[10] and shown to give a tetracoordination of Zn^{2+} ion involving the carboxylic oxygen and the pyranosidic oxygen. However the existence of such crystalline adducts does not constitute evidence that complex formation occurs also in solution. A large number of solution studies on transition metal ions complexation by sugar acids are reported,[1] while few data regarding Mg^{2+}, Ca^{2+} and Zn^{2+} are available. Group II metals were widely studied interacting with simple sugars,[11] although the stability constants of the complex species were small and their accurate determination difficult.

Here we report a thermodynamic solution study on the ability of galactaric acid ($GalaH_2$) for complexation with Ca^{2+}, Mg^{2+} and Zn^{2+} ions. Previous investigations on coordination behaviour of $GalaH_2$ towards Cu^{2+} ascertained the involvement of α-hydroxylic oxygen in metal coordination also in aqueous solution, on the basis of thermodynamic and spectroscopic data.[12]

2. Results and discussion

The protonation constants of the ligand at different temperature are reported in Table 1 together with the $\Delta H°$ and $\Delta S°$ values, calculated from the dependence of protonation constants on temperature, according to the integrated van't Hoff equation.[13]

$$\text{Log}\,\beta = -\frac{\Delta H°}{2.3RT} + \frac{\Delta S°}{2.3R}$$

The protonation reaction of carboxylic acids is usually an endothermic process, owing to ionic species desolvation upon protonation; on the contrary, the formation of intra-molecular hydrogen bonds involving hydroxylic groups makes the protonation reaction of hydroxycarboxylic acids an exothermic process,[14] as it is shown from the negative $\Delta H°$ of $GalaH_2$. The positive $\Delta S°$ value, which denotes an increased disorder of the system, is attributed to the desolvation of the carboxylic anion upon protonation. Our values are similar to those found for tartaric acid[15] and other hydroxycarboxylic acids.[14]

The pH–metric titration curves of the M^{2+}-containing systems (Fig. 1), in all metal to ligand molar ratios investigated, showed two equivalent points and the amount of NaOH spent to reach each equivalent point is represented by the equations:

$$m_{\text{NaOH}} = 2m_{\text{L}}$$

$$m_{\text{NaOH}} = 2m_{\text{L}} + m_{\text{M}}$$

where m is the number of moles, L is $GalaH_2$ and M is the metal ion. The first equivalent point (pH ∼6) is consistent with the formation of the neutral [MGala] species, while the second (pH ∼8) is attributed to the formation of $[MGalaH_{-1}]^-$ species. The stability constants of the complexes are reported in Table 2 together with the calculated thermo-

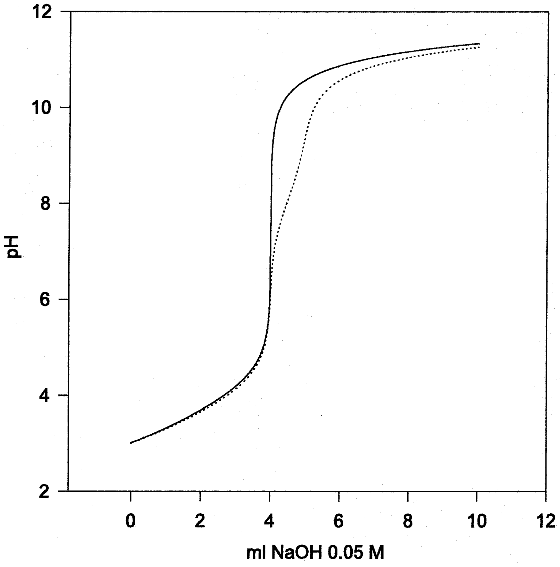


Fig. 1. Potentiometric titration at 25 °C and $I = 0.1$ with $NaNO_3$: (—) $GalaH_2$; (...) Ca–$GalaH_2$ in 1:2 molar ratio; $GalaH_2 = 0.1$ m mol.

Table 2
Logarithms of the stability constants of the complex species at 25 °C and thermodynamic parameters $\Delta H°$ (Kcal mol^{-1}) and $\Delta S°$ (cal mol^{-1} K^{-1}) [a]

	Log β			$\Delta H°$ (kcal mol^{-1})			$\Delta S°$ (cal mol^{-1} K^{-1})		
	Ca^{2+}	Mg^{2+}	Zn^{2+}	Ca^{2+}	Mg^{2+}	Zn^{2+}	Ca^{2+}	Mg^{2+}	Zn^{2+}
[MGala]	2.45	2.32	3.04	4.9	4.2	3.8	27	25	26
$[MGalaH_{-1}]^-$	−5.93	−5.28	5.08	22.2	20.5	19.6	47	45	42
$[M(Gala)_2]^{2-}$	4.37	4.17		15.1	15.9		70	72	
$[M(Gala)_2H_{-1}]^{3-}$	−1.73	−2.53		36.2	32.9		114	100	

[a] Average errors: $\beta \pm 0.03$; $\Delta H° \pm 0.5$; $\Delta S° \pm 3$.

dynamic parameters $\Delta H°$ and $\Delta S°$. In the [MGala] species, it is suggested that the metal ion is coordinated by carboxylic and alpha-hydroxylic oxygens, as observed in the crystal structure of Ca- and Mg-galactarate.[6,7] The existence of a chelate complex also in solution is supported by thermodynamic considerations:

1. From a comparison of the stability constants of various M^{2+}-carboxylate and M^{2+}-hydroxocarboxylate complexes reported in Table 3, it can be seen that the stability constant of the complex species is lower if the ligand is monodentate like **1**, **2** and **3**, and is higher if the ligand is a bidentate chelate like **4**–**7**; the value found for galactaric acid is nearer to those of the second type of ligands, suggesting a chelate coordination mode for galactaric acid.
2. Also the $\Delta H°$ value is in line with this coordination behaviour. The complexation reaction is usually an endothermic process, but when the ligand acts as a bidentate chelate, a diminution in the $\Delta H°$ value is observed.[17,18] In fact the $\Delta H°$ value for Zn^{2+}-acetate (5.26 kcal mol^{-1}) is greater than that of Zn^{2+}-malonate (3.10 kcal mol^{-1}),[13] where the dicarboxylic acid chelates the Zn^{2+} ion. The $\Delta H°$ value of Zn^{2+}-galactarate (3.8 kcal mol^{-1}) is in line with the formation of a chelate complex.
3. Positive values of $\Delta S°$ are associated with an increased disorder because of solvent removal from ionic species. These values increase on metal chelation and, in our case, are nearer to those found for M^{2+}-malonate complexes ($M = Mg$, $\Delta S° = 24$ cal mol^{-1} K^{-1},[16] $M = Zn^{2+}$, $\Delta S° = 28$ cal mol^{-1} K^{-1}[13]), therefore suggesting for $GalaH_2$ the involvement of a hydroxylic group in metal chelation in aqueous solution.

A comparison of ligating ability of galactaric acid toward Ca^{2+} with respect to other sugars is reported in Table 4. The results show that the [CaGala] species is more stable than the corresponding $[CaL]^+$ complex where L is an aldonic acid such as gluconic or lactic, despite the higher acidity of $GalaH_2$ ($\log K_1 = 3.05(2)$) with respect to gluconic acid ($\log K_1 = 3.47$).[23] This difference may be attributed to the electroneutrality of the complex and to the ability of $GalaH_2$ to form polymeric structures, as observed in the crystal structure of the $[CuGala(bpy)]_n \cdot 2n\ H_2O$ complex.[12] The [CaGala] species was also more stable than $[CaL]^+$, with L = alduronic acid; in fact these acids were found to coordinate the metal ion through the ethereal oxygen, as their cyclic structure disfavours the

Table 3
Comparison of stability constants of various M^{2+} carboxylate and hydroxycarboxylate complexes, literature values taken from Ref. 16

Acid	Log β [a]		
	Ca^{2+}	Mg^{2+}	Zn^{2+}
Acetic (**1**)	0.57	0.51	1.0
Succinic (**2**)	1.16	1.18	1.6
Glutaric (**3**)	1.06	1.08	1.6
Malonic (**4**)	1.51	2.11	2.96
Tartronic (**5**)	2.27	2.17	3.22
Malic (**6**)	1.96	1.70	2.93
Tartaric (**7**)	1.80	1.36	2.68
Galactaric (**8**)	2.45	2.37	3.04

[a] Log β for [ML] species, charges are omitted for clarity.

Table 4
Stability constants of Ca^{2+} carbohydrate complexes

	Log β_{110}	Log $\beta_{11\text{-}1}$	Log β_{120}	Δ log K [a]	Ref.
Galactaric acid	2.45(1)	−5.93(5)	4.37(2)	1.92	
Gluconic acid	1.05(10)		1.88(8)	0.83	19
Lactic acid	0.90(10)		1.62(8)	0.72	19
Galacturonic acid	1.79(2)	−10.15			20
Glucuronic acid	1.49(1)	−10.40			20
Ribose	1.9(1)				21,22

[a] $\Delta \log K = \log \beta_{120} - \log \beta_{110}$.

α-hydroxylic oxygen.[18,24] Neutral sugars, such as arabinose or ribose, were found to form complexes with Ca^{2+} of low stability whilst with Mg^{2+}, these sugars give rise to very weak non-specific interactions.[21,22] The order of stability of [MGala] complexes is

$$Cu^{2+} > Zn^{2+} > Ca^{2+} \geq Mg^{2+}$$

(similar to glucuronic and galacturonic acids for Cu^{2+} [12] and Ca^{2+} [23]). Other authors have previously observed a diminution in pH by adding bivalent metal ions to an alginic acid containing solution, finding the order of metal^{2+} affinity Pb > Cu > Cd > Ba > Sr > Ca > Co, Ni, Zn, Mn > Mg.[25]

The species distribution curves for Mg^{2+} and Zn^{2+} complexes are reported in Fig. 2 (Scheme 1). The prevailing species at acidic pH were [MGala] ($M = Zn^{2+}$ or Mg^{2+}) and $[Mg(Gala)_2]^{2-}$ while the formation of the corresponding Zn^{2+} complex was prevented by the lower coordination number (usually four) of Zn^{2+} complexes[26–28] with respect to Mg^{2+} and Ca^{2+} which were found to coordinate six or eight oxygen atoms, respectively, in the crystal structure of galactaric salts.[6,7]

The formation of the $[MGalaH_{-1}]^-$ species, on increasing pH, may be explained by two different hypothesis: (1) deprotonation of the coordinated α-OH group; (2) substitution of the sugar OH group by a hydroxide ion, resulting in the formation of mixed-hydroxo complexes. The carbohydrate and their derivatives are very weak acids; the first protonation constant lies in the range log $K = 12-14$,[29] but in presence of metal ions, sugars become more acids. The presence of copper ion was found to lower the pK value of the coordinated α-hydroxylic group deprotonation to form stable chelate (COO^-, O^-) complexes with galactaric acid[12] and with other sugar acids[30] or amine sugars.[31]

The positive $\Delta H°$ value found for the reaction

$$M^{2+} + Gala^{2-} \rightleftarrows [MGalaH_{-1}]^- + H^+$$

suggested the dissociation of coordinated α-hydroxylic group, rather than the metal coordination of OH^- group which is always an exothermic process.[16]

The solid complexes [MGala]·x H_2O ($x = 2$ with $M = Ca^{2+}$ or Mg^{2+}, $x = 4$ with $M = Zn^{2+}$) were synthesised and characterised by means of elemental analysis and IR spectroscopy. The more relevant IR bands and their tentative assignment are reported in Table 5. In the IR spectrum of the free galactaric acid, a very strong band is present at 3287 cm^{-1} which was assigned to the strongly hydrogen bonded OH groups,[32] as shown in the crystal structure of $GalaH_2$[12] (O···O distance 2.747(4) Å). Upon metal complexation, the OH stretching vibration showed shifting

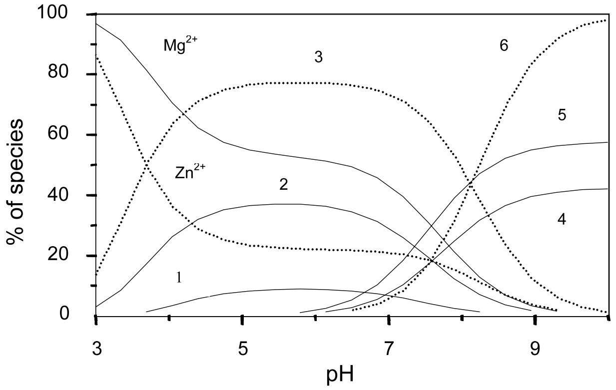
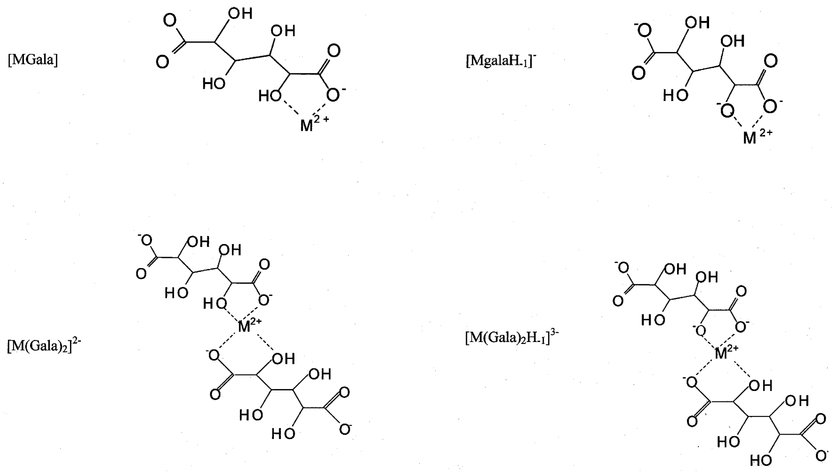


Fig. 2. Species distribution curves for Zn^{2+} (…) and Mg^{2+} (—) containing systems: $[M^{2+}] = 10^{-3}$ M, M–Gala 1:4, (1) $[Mg(Gala)_2]^{2-}$; (2) [MgGala]; (3) [ZnGala]; (4) $[MgGalaH_{-1}]^-$, (5) $[Mg(Gala)_2H_{-1}]^{3-}$ (6) $[ZnGalaH_{-1}]^-$.



Scheme 1. Scheme of Gala coordination mode in metal complexes.

Table 5
More relevant IR bands and their tentative assignment

$GalaH_2$	$Ca(Gala)\cdot 2\ H_2O$	$Mg(Gala)\cdot 2\ H_2O$	$Zn(Gala)\cdot 4\ H_2O$	
	3447_{vs}	3427_{vs}	3412_{vs}	ν(OH) (weakly H-bonded)
		332_{vs}		
3287_{vs}	3171_{s}	3231_{vs}	3261_{vs}	ν(OH) (strongly H-bonded)
		3103_{vs}		
	1695_{s}	1691_{m}		$\delta(H_2O)$
1719_{vs}				$\nu(CO_2)$
	1596_{vs}	1603_{vs}	1623_{vs}	$\nu(OCO)_{asym}$
	1433_{vs}	1415_{vs}	1435_{vs}	$\nu(OCO)_{sym}$
1454_{s}	1384_{s}	1332_{s}	1384_{s}	$\delta(COH)+\delta(CCH)$
1420_{s}	1309_{m}	1294_{m}	1300_{m}	
1295_{vs}	1251_{m}	1276_{m}	1262_{w}	
1239_{vs}	1216_{m}	1215_{w}	1237_{w}	
1118_{vs}	1090_{s}	1117_{m}	1102_{m}	
1060_{vs}	1035_{m}	1037_{s}	1038_{s}	ν(CO)
918_{s}	900_{w}	881_{m}	886_{w}	

and broadening; this shift toward higher frequencies was due to the general weakening of the strong sugar hydrogen bond system upon acid metalation[33] as observed in the crystal structure of the Ca^{2+}- and Mg^{2+}-galactarate salts;[6,7] while the presence of an intense band below 3200 cm^{-1} is attributed to the OH stretching vibration of the bonded water molecules. Similarly a shoulder band around 1690 cm^{-1}, in the spectra of Ca^{2+} and Mg^{2+} salts, which is not present in the uncomplexed sugar and in the Zn^{2+} complex, is also assigned to the bending mode of the coordinate water molecules.

The carbonyl stretching vibration observed in $GalaH_2$ at 1719 cm^{-1} disappeared in the metal^{2+} complexes and two additional absorption bands were observed around 1600 and 1430 cm^{-1}, these bands were assigned to the antisymmetric and symmetric OCO^- stretching vibrations, respectively. The separation (188 cm^{-1}) of the two OCO^- components observed in the IR spectra of Zn^{2+} and Mg^{2+} complexes is indicative of a unidentate mode of carboxylic group, in agreement with the structural analysis of the Mg^{2+} salt;[6,7] while in the sodium and potassium galactarate, the carboxylic group acts as bridging bidentate.[34]

Other absorption bands in the 1454–1118 cm^{-1} range, in the spectrum of the free sugar, relating mainly to the bending vibrations of the COH and CCH groups,[35] showed considerable intensity changes and shifting towards lower frequencies, upon sugar metalation. The changes observed for the COH bending vibrations are consistent with the participation of the sugar OH groups in metal–ligand bonding and the alteration of the sugar hydrogen bonds network. In the same way the stretching vibration of the C–O groups[36] which appears as strong absorption bands in the 1100–900 cm^{-1} region, exhibited spectral changes (shifting and diminishing in intensity) on sugar salts formation. The similarity in the IR spectra for the three ion complexes suggested for all the same coordination mode of galactaric acid was found in the crystal structure of Ca^{2+} and Mg^{2+} salts.[6,7]

It may be concluded that the binding mode of galactaric acid toward metal^{2+} ions is the same: it acted as a chelate ligand through the monodentate carboxylic group and the α-hydroxylic oxygen. This coordination mode was also maintained in aqueous solution and the complex species found were more stable with respect to those of aldonic or alduronic acids, owing to the great symmetry of galactaric acid molecule which allows the formation of polymeric species as observed in the crystal structure of the solid complexes.[6,7,12] On increasing the pH, the deprotonation of the coordinated α-hydroxylic group leads to the formation of stable complexes at a pH value (pH > 5 for Cu^{2+}, pH > 7 for Zn^{2+}, Ca^{2+} and Mg^{2+}) significantly lower than that of metal complexes with alduronic acids (pH > 10 for Ca^{2+}).[20]

3. Experimental

Potentiometry.—A $GalaH_2$ aqueous solution (3×10^{-3} M) was standardised by titration with NaOH and the protonation constants were determined at different temperatures (15, 25, 35 and 45 °C). The concentration of the stock solutions of M^{2+} nitrate hydrate (C. Erba) ($M^{2+} = Ca^{2+}, Mg^{2+}, Zn^{2+}$) was determined with EDTA. The starting solution for each titration was prepared by addition of known volumes of $M(NO_3)_2$ and $GalaH_2$ solutions in the 1:1, 1:2 and 1:4 metal–ligand molar ratios, the metal concentration was 5×10^{-4} M, the pH range investigated was 3–10. Potentiometric measurements were performed at 15, 25, 35 and 45 °C using a fully automated ORION 960 Autochemistry system, following the general procedures previously reported.[12] A constant ionic strength 0.1 M (solid $NaNO_3$) and an N_2 atmosphere were maintained in all experiments. The stability constants (β_{pqr}), which are defined by Eqs. (1) and (2), where M is the metal, L is the ligand in the dianionic form and H is the proton, were refined by least-squares calculations using computer program SUPERQUAD,[37] taking into account the presence of $M(OH)_2$ species:[15]

$$pM + rL + sH \leftrightarrow M_pL_rH_s \quad (1)$$

$$\beta_{prs} = [M_pL_rH_s]/[M]^p[L]^r[H]^s \quad (2)$$

Preparation of compounds.—[MGala]·x H_2O ($x = 4$ for $M = Zn^{2+}$; $x = 2$ for $M = Ca^{2+}$ and Mg^{2+}). An aqueous solution of M^{2+} acetate hydrate was added under continuous stirring to 50 mL of an hot aq solution (0.02 M) of galactaric acid at pH 4. The pH was kept constant by adding small amounts of concd aq NaOH. Solid compounds were rapidly separated.

[ZnGala]·4 H_2O: Anal. Calcd for $C_6H_{16}O_{12}Zn$ (345.5): C, 20.84; H, 4.67. Found C, 21.02; H, 4.37. Yield: 80%.

[MgGala]·2 H_2O: Anal. Calcd for $C_6H_{12}MgO_{10}$ (268.4): C, 26.82; H, 4.51. Found C, 26.21; H, 4.08. Yield: 60%.

[CaGala]·2 H_2O: Anal. Calcd For $C_6H_{12}CaO_{10}$ (284.2): C, 25.33; H, 4.24.Found C, 25.80; H, 4.01. Yield: 85%.

Physical measurements.—The infrared spectra of the solid compounds in KBr pellets were obtained by means of a Perkin–Elmer FT-IR 1600, in the 4000–400 cm^{-1} spectral range.

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