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Sugar interaction with metal ions. FT-IR study on the structure of crystalline galactaric acid and its K^+, NH_4^+, Ca^{2+}, Ba^{2+}, and La^{3+} complexes

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Abstract

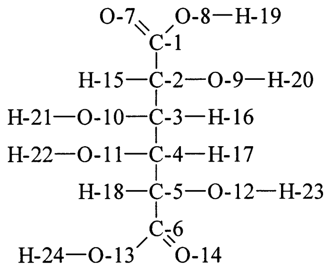
The FT-IR spectra of galactaric acid and its K^+, NH_4^+, Ca^{2+}, Ba^{2+}, and La^{3+} salts have been recorded and interpreted. Spectroscopic evidence shows that the dimeric carboxylic groups of the free acid are dissociated upon formation of the salt, and the asymmetric and symmetric stretching vibrations of the anionic COO^- group in these salts are observed at about 1600 and 1400 cm^{-1}, respectively. The two carboxylic groups of the galactarate coordinate with Ca^{2+} ions in a monodentate form. One of the carboxylic groups in the Ba^{2+} salt coordinates in a monodentate state; another group interacts with three cations in a tetradentate form. In the K^+, NH_4^+, and La^{3+} salts, the COO^- groups coordinate in a polydentate manner with the cations. By comparison of the spectra of the salts with that of the free acid, it is concluded that the hydroxyl groups of the galactarate skeleton take part in metal–oxygen interaction, and the hydrogen-bonding network is rearranged upon sugar metalation. The degree of participation of the sugar OH groups in metal–galactarate interaction is varied from the K^+ and NH_4^+ salts to the Ca^{2+}, Ba^{2+}, and La^{3+} salts. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: FT-IR; Galactaric acid; Potassium galactarate; Ammonium galactarate; Calcium galactarate tetrahydrate; Barium galactarate monohydrate; Lanthanum galactarate 6.5 hydrate

1. Introduction

Research on the bonding in carbohydrate–metal ion complexes, especially on the coordination of hydroxyl groups and changes of hydrogen-bonding networks, has been the subject of intensive studies by NMR, IR and Raman spectroscopies and by theoretical calculations [1–9].

Galactaric acid is a polyhydroxyl dibasic acid where atomic arrangement and numbering are given as follows:



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Galactaric acid, as a polyhydroxylated carboxylic acid, can provide valuable information on the interaction between a carbohydrate molecule and metal ions by studies on the structure of its coordination compounds. The crystal structures of galactaric acid and its K^+, NH_4^+, Ca^{2+}, Ba^{2+}, and La^{3+} salts have been determined recently [10–16], and some vibrational spectra were reported and briefly discussed [11,13,16]. However, band assignments and the correlation between structural information and the spectral properties for these compounds are still lacking. In the present work, five galactarates as well as the crystalline free acid were prepared and their infrared spectra have been measured, assigned, and interpreted in correlation with the crystal structures.

2. Results and discussion

Elemental analysis.—The results recorded in Table 1 show good agreement with theoretical values.

X-ray powder diagrams.—The X-ray powder patterns of the free acid and its K^+ and Ba^{2+} complexes confirm that the materials used for FT-IR spectral measurements have the same structures as the corresponding crystal structures [12,15]. The crystal structure of the Ca^{2+} salt was the same as that reported in Ref. [15].

FT-IR spectra.—To enhance the resolution of the FT-IR spectrum, the secondary derivative technique was used in order to make the ν_{OH}, ν_{CH}, and $\nu_{C=O}$ vibrations observable.

Table 1
Results of elemental analysis of the compounds

Galactarate	Found (%)		Calculated (%)	
	C	H	C	H
Potassium galactarate	25.3	2.8	25.2	2.8
Ammonium galactarate	29.7	6.6	29.5	6.6
Calcium galactarate tetrahydrate	22.3	5.0	22.5	5.0
Barium galactarate monohydrate	19.9	2.8	19.8	2.8
Lanthanum galactarate 6.5 hydrate	21.5	3.7	21.7	3.7

Stretching vibrations of hydroxyl groups and the interaction between hydroxy groups and the metal ion.—From the crystal structure data [10], there are four distinct pairs of hydrogen bonds in free galactaric acid because of the existence of a symmetrical center. The very strong band in the 3800–2300 cm^{-1} region of the IR spectrum of the free acid was centered at 3288 cm^{-1} (see Fig. 1 and Tables 2 and 3). The OH stretching vibrations were assigned to the H-bonds formed between the hydroxyl groups (see Tables 2 and 3) [17–25]. The band for O-14···H-19–O-8, one of the two H-bonds of the carboxylic acid dimer, was in the 2500–3200 cm^{-1} region because of the strong hydrogen bonding with O-14 of another molecule and the ionizing tendency of the carboxylic group.

In the K^+ salt [12], all oxygen atoms of the galactarate coordinate with K^+ ions, and four oxygen atoms of the hydroxyl groups interact with one individual K^+ ion. The galactarate skeleton has a symmetrical center. Four pairs of intermolecular H-bonds are formed and the vibrational spectrum exhibits strong ν_{OH} bands centered at 3289 and 3154 cm^{-1}. From secondary derivative analysis, the bands at 3445, 3350, 3289, and 3154 cm^{-1} were observed in the region of 4000–3000 cm^{-1} and assigned as given in Tables 2 and 3.

The ammonium salt crystal is assembled by hydrogen bonds that involve all of the functional groups, and the anion skeleton possesses a symmetrical center [13]. Three pairs of O···O H-bonds and seven pairs of N···O H-bonds are formed in the crystal [13]. The OH and NH stretching vibrations of the ammonium salt exhibited band broadening and shifting toward lower frequency, centered at 3196 and 3058 cm^{-1} (see Fig. 1), due to new H-bonds being formed. The bands at 3259 and 3196 cm^{-1} were assigned to O-9–H-20···O-8 (2.764 Å) and O-10–H-21···O-7 (2.730 Å), respectively. The N–H-6···O-10 and N–H-7···O-9 vibrations were located at 3129 and 3058 cm^{-1} (see Tables 2 and 3). [23].

The H-bond system for the Ca^{2+} salt is not given in Ref. [15]. The band at 3443 cm^{-1} was primarily assigned to vibration of the water molecules. The hydroxyl groups not only coordinate with the Ca^{2+} ions but also form

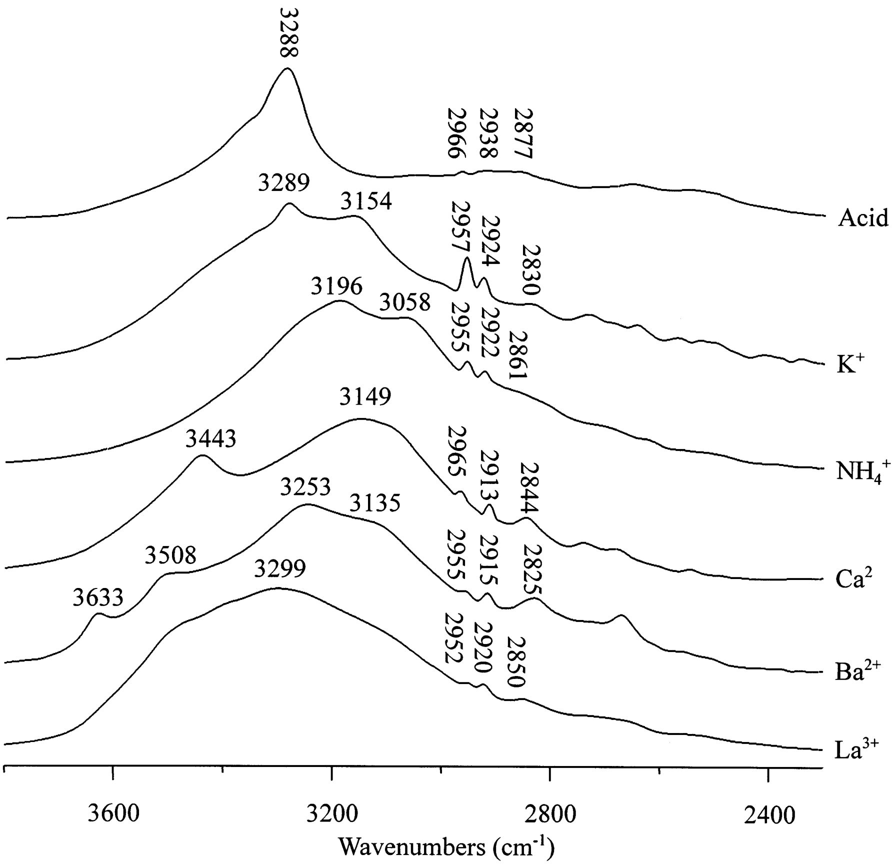


Fig. 1. The FT-IR spectra of galactaric acid and its K^+, NH_4^+, Ca^{2+}, Ba^{2+}, and La^{3+} salts in the region 3800–2300 cm^{-1}.

H-bonds. The ν_{OH} of the hydroxyl groups appeared at about 3149 cm^{-1}. The hydrate in the Ba^{2+} salt does not take part in coordination with the Ba^{2+} ions [15]. The new bands at 3633 and 3512 cm^{-1} in the spectrum of the Ba^{2+} salt were assigned to the hydrate. All of the hydroxyl groups of the galactarate skeleton are involved in the coordination with the Ba^{2+} ions [15], and the ν_{OH} of the hydroxyl groups were observed at 3253 and 3113 cm^{-1}, as given in Tables 2 and 3. For the La^{3+} salt, the bands at 3610, 3562, 3508, 3474, 3414, and 3392 cm^{-1} were related to the ν_{OH} of the 6.5 hydrate molecules, and the bands at lower frequencies, related to the ν_{OH} of the hydroxyl groups (see Tables 2 and 3).

In the case of the stretching vibration of the C–H group (ν_{CH}), the free acid exhibited three bands at 2966, 2938 and 2877 cm^{-1}. The bands shifted toward lower frequency upon salt formation, and the intensities of each of these bands became much stronger than those of the corresponding bands of the free acid [17–29] (see Fig. 1 and Table 2).

The carbonyl stretching vibrations and the binding of metal ions with the functional group [21–25].—The very strong band at 1724 cm^{-1} was assigned to the C=O stretching vibration ($\nu_{C=O}$) of galactaric acid, as shown in Fig. 2 and Table 2. When the galactarates coordinated with metal ions, the $\nu_{C=O}$ shifted toward lower frequency and split into two bands at ~1600 and 1400 cm^{-1}. The two absorption bands in the spectra of the galactarates are related to the asymmetric and symmetric stretching vibrations (denoted as ν_{as}COO and ν_sCOO, respectively) of the anion COO groups, respectively. The number, shape, and intensity of the ν_{as}COO band at ~1600 cm^{-1} was rather different in each individual metal salt.

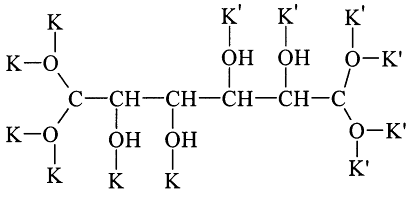
In the crystal structure of the K^+ galactarate [12], the carboxylate groups are strongly involved in K–sugar binding. Each oxygen atom of one carboxylate group coordinates with two K^+ ions, and thus each COO^- group coordinates with four K^+ ions. The ν_{as}COO and ν_sCOO in the spectrum of the K^+

Table 2
The FT-IR absorption bands of galactaric acid and its K^+, NH_4^+, Ca^{2+}, Ba^{2+}, and La^{3+} complexes in the region of 4000–400 cm^{-1} with a tentative assignment [a]

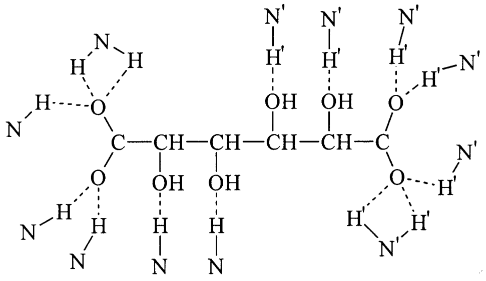
Acid	K^+ salt	NH_4^+ salt	Ca^{2+} salt	Ba^{2+} salt	La^{3+} salt	Assignment [17–28]
Band (cm^{-1})	Band (cm^{-1})	Band (cm^{-1})	Band (cm^{-1})	Band (cm^{-1})	Band (cm^{-1})	
3288(vs)	3289(vs)	3196(vs)	3443(m)	3633(w)	3299(vs)	ν_{OH}
	3154(vs)	3058(vs)	3149(vs)	3253(s)		
2966(w)	2957(w)	2955(w)	2965(w)	2955(w)	2952(w)	
2938(w)	2924(w)	2922(w)	2913(w)	2915(w)	2920(w)	ν_{CH}
2877(w)	2830(sh)	2861(sh)	2844(w)	2825(w)	2850(sh)	
1724(vs)						$\nu_{C=O}$
	1597(vs)	1692(w)	1627(sh)	1573(vs)	1589(vs)	$\nu_{as}COO^-$
	1570(sh)	1609(vs)	1591(vs)			
1453(m)	1434(m)	1464(sh)	1432(s)	1447(m)	1433(s)	ν_{CC}, δ_{COH}, δ_{CCH}
	1406(m)	1428(sh)	1378(sh)	1392(m)	1404(sh)	ν_sCOO
1420(m)		1399(m)				
1375(w)	1366(m)	1352(m)			1347(m)	δ_{COH}, δ_{CCH}
1317(sh)	1313(m)	1304(m)		1314(m)	1308(m)	δ_{COH}, δ_{CCH}
1295(m)			1291(s)	1284(m)		
1270(sh)	1280(m)	1272(m)			1277(w)	δ_{COH}, δ_{CCH}
1240(m)	1243(m)	1239(m)	1248(s)	1254(m)	1249(w)	δ_{COH}, δ_{CCH}
1207(w)	1196(m)	1196(m)	1212(m)	1217(w)	1209(m)	δ_{COH}, δ_{CCH}
1120(s)	1111(s)	1108(vs)	1091(s)	1089(s)	1094(s)	ν_{CO}, ν_{CC}
1061(s)	1048(vs)	1049(vs)	1039(s)	1038(s)	1038(s)	ν_{CO}, ν_{CC}
965(w)	969(m)	967(m)	974(w)	968(w)	975(m)	ν_{CO}, ν_{CC}
920(m)						τ_{COOH}
861(m)	872(m)	872(m)	902(m)	885(w)	880(m)	τ_{OCCC}, ν_{CC}
827(w)	843(m)	839(m)	851(m)	838(m)	827(m)	τ_{OCCO}, τ_{OCCC}
799(m)	766(m)	772(m)	768(m)	722(m)	696(m)	τ_{OCCO}, τ_{OCCC}
699(m)			715(w)			τ_{OCCO}, τ_{OCCC}
667(m)	669(s)	667(s)	656(m)	679(m)	644(m)	τ_{OCCO}, τ_{OCCC}
				644(m)		
631(m)	633(s)	633(m)	609(sh)			τ_{OCCC}, δ_{CCO}
	571(sh)					
509(m)	523(s)	524(s)	511(m)	505(w)	512(m)	τ_{OCCO}, δ_{CCO}
461(w)	475(s)	476(m)	462(m)	472(m)	470(m)	δ_{CCO}, τ_{OCCO}

[a] ν, denotes stretching vibration; δ, bending vibration; τ, torsion vibration; vs, very strong band; s, strong; m, medium; w, weak; sh, shoulder band.

salt appeared at 1597 and 1406 cm^{-1}, respectively, with a difference (denoted as $\Delta\nu_{COO}$) of 191 cm^{-1}.



The N–H groups form five H-bonds with one carboxylate group in the NH_4^+ crystal structure [13]. The $\nu_{as}COO$ vibration in the spectrum of NH_4^+ salt was overlapped by the N–H bending and the sugar O–H deformation modes [23]. As a result, a band centered at 1609 cm^{-1} was observed.



The carboxylate groups coordinate to Ca^{2+} ions as a monodentate ligand form in the crystal of calcium galactarate tetrahydrate [15]. In the IR spectrum, the $\nu_{as}COO$ and

Table 3
The vibrational bands observed with the secondary derivative technique in the region of 3800–3000 cm^{-1} and a tentative assignment

Galactaric acid		K$^+$ salt		NH$_4^+$ salt		Ca^{2+} salt [a]		Ba^{2+} salt [a]		La^{3+} salt [a]	
Band (cm^{-1})	Assignment [17–25]	Band (cm^{-1})	Assignment [17–25]	Band (cm^{-1})	Assignment [17–25]	Band (cm^{-1})	Assignment [17–25]	Band (cm^{-1})	Assignment [17-25]	Band (cm^{-1})	Assignment [17-25]
3381	O-10–H-21…O-7 [b]	3445	O-9–H-20…O-8	3483	O-10–H-21…O-8	3443	ν_{H_2O} [c]	3633	ν_{H_2O}	3610	ν_{H_2O}
3363	O-10–H-21…O-7	3350	O-10–H-21…O-7	3452	N–H-8…O-8	3159	ν_{OH} [d]	3512	ν_{H_2O}	3562	ν_{H_2O}
3318	O-10–H-21…O-9	3289	O-9–H-20…O-7	3418	N–H-5…O-8	3134	ν_{OH}	3253	ν_{OH}	3508	ν_{H_2O}
3303	O-10–H-21…O-9	3154	O-10–H-21…O-8	3382	N–H-6…O-8	3095	ν_{OH}	3113	ν_{OH}	3474	ν_{H_2O}
3283	O-9–H-20…O-10			3355	N–H-5…O-7					3414	ν_{H_2O}
3265	O-9–H-20…O-10			3289	N–H-8…O-7					3392	ν_{H_2O}
				3259	O-9–H-20…O-8					3313	ν_{OH}
				3196	O-10–H-21…O-7					3236	ν_{OH}
				3129	N–H-6…O-10					3114	ν_{OH}
				3058	N–H-7…O-9					3082	ν_{OH}
										3007	ν_{OH}

[a] Crystallographic data of H-bonds were not given in literature.

[b] The stretching vibration was related to the H-bond.

[c] ν_{H_2O} denotes stretching vibration related to water molecule.

[d] ν_{OH} denotes stretching vibration related to the hydroxyl groups of galactarate.

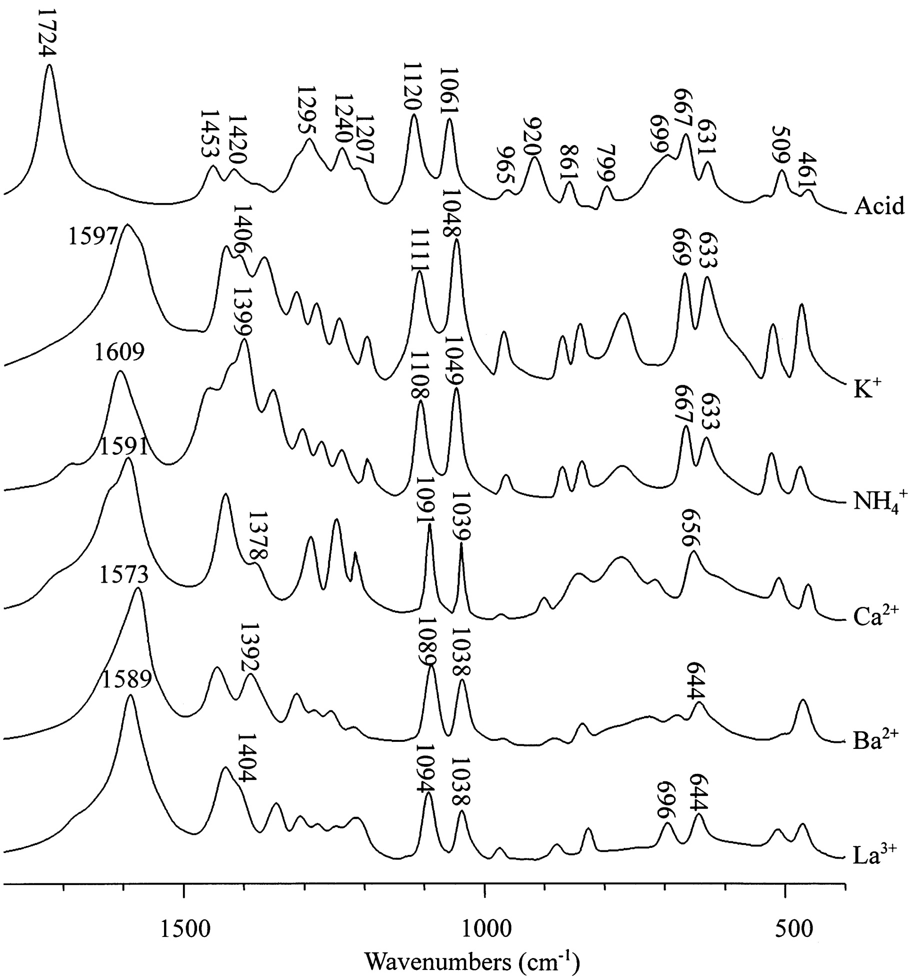
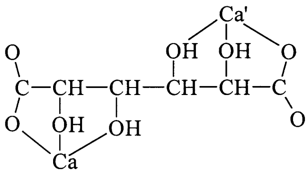
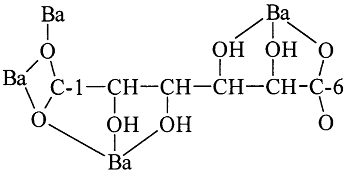


Fig. 2. The FT-IR spectra of galactaric acid and its K^+, NH_4^+, Ca^{2+}, Ba^{2+}, and La^{3+} salts in the region 1800–400 cm^{-1}.

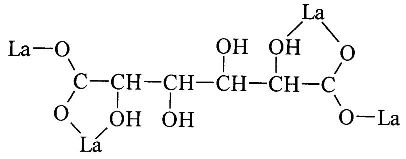
ν_sCOO bands were observed at 1591 and 1378 cm^{-1}, respectively. The $\Delta\nu_{COO}$ was 213 cm^{-1}. A shoulder band at 1627 cm^{-1} was also observed and assigned to the bending vibration of the water molecules.



The crystal structure of the Ba^{2+} salt shows the carboxylate group of C-1 coordinating with three Ba^{2+} ions as a tetradentate form, whereas the group of C-6 coordinates with one Ba^{2+} ion as a monodentate form [15]. The vibration spectrum of this compound showed three bands in the 1800–1500 cm^{-1} region. The bending mode of the water molecule appeared at 1637 cm^{-1}. The band at 1607 cm^{-1} was assigned to the ν_{as}COO of the monodentate coordination ($\Delta\nu_{COO} = 215$ cm^{-1}), and that at 1573 cm^{-1} was related to the ν_{as}COO of the tetradentate type ($\Delta\nu_{COO} =$ 181 cm^{-1}). The ν_sCOO appeared at 1392 cm^{-1}.



In the crystal of the La^{3+} complex, each of the two carboxylic groups of one galactarate coordinates with two La^{3+} ions [16]. In the spectrum of the La^{3+} salt, a major band at 1589 cm^{-1}, assigned to the ν_{as}COO band, and a shoulder one at 1404 cm^{-1}, assigned to the ν_sCOO, were indicative that the carboxylic groups coordinated with the La^{3+} ions in a bidentate form with $\Delta\nu_{COO} = 185$ cm^{-1}. The bending vibration of the water molecules appeared at 1648 cm^{-1}.



The $\Delta\nu_{COO}$s of the monodentate coordination form were more than 210 cm^{-1}, for example, 213 cm^{-1} in the Ca^{2+} salt and 215 cm^{-1} in the Ba^{2+} salt. The $\Delta\nu_{COO}$s of the polydentate form were about 180 cm^{-1}, namely 181, 181, and 185 cm^{-1} in the NH$_4^+$, Ba^{2+}, and La^{3+} salts, respectively. The K$^+$ salt is considered to be a typical ionic compound. However, the $\Delta\nu_{COO}$ of the K$^+$ salt was 191 cm^{-1}, as one oxygen atom of the carboxylate group coordinated with two K$^+$ ions.

It is interesting to compare the bending modes of the hydrates. The bending vibration of the 6.5 water molecules in the La^{3+} salt appeared at a higher frequency (1648 cm^{-1}). The single water molecule of the Ba^{2+} salt involved in four H-bonds plays an important role in the hydrogen-bonding network [15]. Thus, the bending vibration of the water molecule shifted toward lower wavenumbers (1637 cm^{-1}). In the Ca^{2+} salt, the water molecules not only take part in H-bonds, but also coordinate to the Ca^{2+} ions [15]. These caused shifting of the bending vibrations of the water molecules at 1627 cm^{-1}, this being a much lower frequency than that of the Ba^{2+} salt.

Vibrational frequencies of the galactarate skeleton and its interaction with metal ions [17–28].—Eight absorption bands at 1453, 1420, 1375, 1317, 1295, 1270, 1240, and 1207 cm^{-1}, mainly assigned to the bending vibrations of the COH and CCH groups, were observed in the spectrum of galactaric acid (see Fig. 2 and Table 2). The bands of the COH bending vibrations of the complexes shifted toward lower frequencies upon salt formation. The C–O and C–C stretching vibrations of the free acid were observed as two strong bands at 1120 and 1061 cm^{-1} (see Fig. 2 and Table 2). After the salts were formed, the band shifts in this region were mainly caused by the changes of the C–O vibrations. The frequency differences for each of the two bands between the free acid and each of the salts were 9–13 cm^{-1} for the K$^+$ and NH$_4^+$ salts, and 22–31 cm^{-1} for the Ca^{2+}, Ba^{2+}, and La^{3+} salts, respectively. The skeletal deformations at about 900–400 cm^{-1} in the spectrum of the galactaric acid showed considerable changes on metalation. The broadened bands at 920 cm^{-1} disappeared upon salt formation (see Fig. 2 and Table 2).

These results indicated that (a) the hydroxyl groups of the galactarates took part in metal–oxygen interactions; (b) the hydrogen-bonding network was rearranged upon metalation of the sugar; (c) the degree of participation of the sugar OH groups in metal–galactarate interaction varied from the K$^+$ and NH$_4^+$ salts to the Ca^{2+}, Ba^{2+}, and La^{3+} salts; and (d) the conformation of the galactarate skeleton changed as a result of the formation.

3. Experimental

General.—Galactaric acid was purified by crystallization from aqueous solution. All other chemicals were analytically pure reagents and used without further purification. All of the samples for instrumental measurements were pure crystalline compounds.

Preparation of complexes.—The crystalline Ca^{2+}, Ba^{2+}, and La^{3+} complexes were prepared as described in the literature [15,16]. The K$^+$ salt was prepared from potassium hydroxide and galactaric acid in a 2:1 molar ratio, and the ammonium salt, from $NH_3 \cdot H_2O$ and the free acid in a 2:1 molar ratio.

Elemental analysis.—Carbon and hydrogen in the compounds were analyzed by an Elementar Vario EL instrument. The results were shown in Table 1.

X-ray powder diffractometer.—The X-ray powder diagrams were recorded on a Rigaku D/Max 2400 diffractometer with Cu K$_\alpha$ radiation and a LiF monochromator.

FT-IR spectroscopy.—The FT-IR spectra of the above-mentioned compounds were measured with a Nicolet Magna-IR 750 spectrometer with DTGS detector, 32 scans at 4 cm^{-1} resolution (OMNIC 3.1 software). The KBr pellet technique was used throughout.

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