



Study on the coordination of the hydroxyl group: crystal structure and FT-IR spectra of potassium hydrogen galactarate

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Abstract—Potassium hydrogen galactarate monohydrate was prepared for the first time. X-ray diffraction analysis showed that the K^+ ion in this complex is hepta-coordinated, and two of the four hydroxyl groups are coordinated to the K^+ ion. The complex forms a hydrogen bonding network. The results of the FT-IR spectra measurement are in agreement with the conclusion of X-ray crystal structural study. © 1997 Elsevier Science Ltd. All rights reserved.

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Galactaric acid as a poly-hydroxylic dibasic acid has found wide application in analytical chemistry [1], biomedical studies [2], and also agricultural production [3]. As discussed in a previous paper [4], metal salts of galactarate have been studied widely in order to get detailed information about the coordination of hydroxyl group with the metal ion. The crystal structure of the free acid was determined by Jeffrey *et al.* [5] in 1982. It is rather interesting to note that two types of crystal structures of its metal complexes have been studied recently. (1) Yang *et al.* [6] determined the first crystal structure of a metal salt of galactarate, a lanthanum salt, in which two hydroxyl groups of one galactarate ion were coordinated to La^{3+} ions. Sheldrick *et al.* found in the barium and calcium salts that the four hydroxyl groups were coordinated to metal ions [7], and in the magnesium salt, two of the hydroxyl groups were coordinated to magnesium ions [8]. On the other hand, Taga *et al.* [9] have reported the crystal structures of the sodium and potassium salts. In both crystals, the four hydroxyl groups joined in the coordination to metal ions. (2) Benetollo *et al.* [4] studied the crystal structure of ammonium galactarate, revealing that the entirely three-dimensional

network in a layer structure was formed with hydrogen bonding, in which the four OH groups served simultaneously as donator and acceptor.

Complexes of galactarate acid-salt are comparatively difficult to prepare, and are scarcely reported in the literature. In the present investigation the crystal structure of potassium hydrogen galactarate monohydrate was determined. It indicates that a new and much-complicated hydrogen bonding network is formed, the K^+ ion is hepta-coordinated, and two of the four hydroxyl groups are coordinated to the K^+ ion. In addition, the mid- and far-IR spectra of this complex were measured and discussed.

RESULTS AND DISCUSSION

X-ray crystal structure

In Fig. 1 and Fig. 2, the crystal structure of potassium hydrogen galactarate monohydrate is seen to be an extensive three-dimensional network, which may be visualized as the accumulation of two-dimensional layers parallel to the *bc* plane, and within the layer the galactarate radicals are connected with the hydrogen bonds and through the coordination with K^+ ion. Neighboring layers are connected by $K-O(7)-K1$ links along the direction of the *a* axis.

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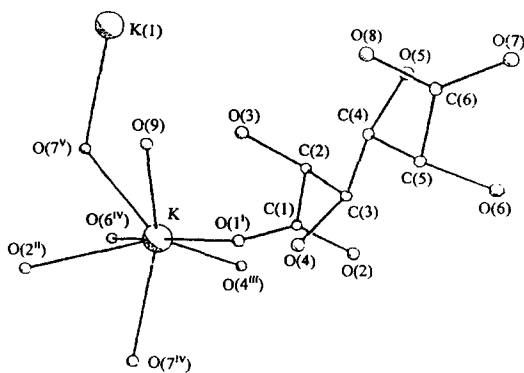


Fig. 1. The crystal structure with atom numbering.

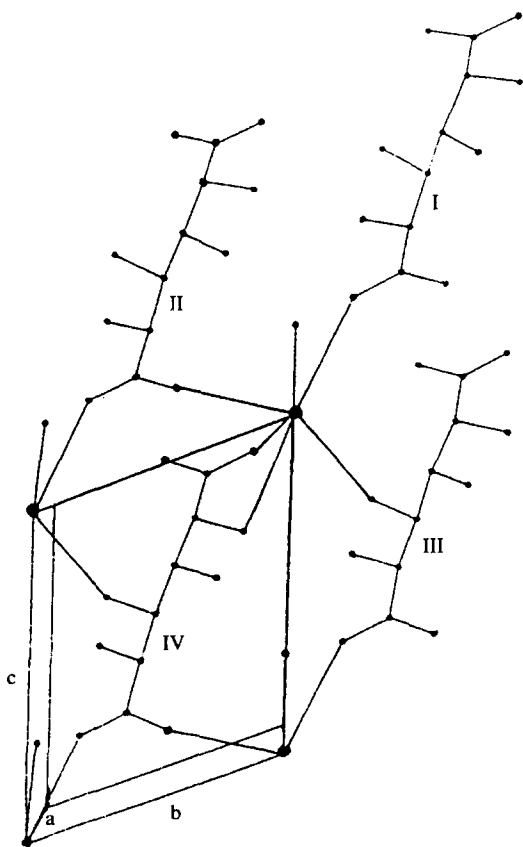


Fig. 2. The projection of the crystal cell along the direction of the *a* axis.

The main chain of the galactarate ion is in the (110) plane.

All the K^+ ions are equivalent. The K^+ ion has the coordination number of 7 (see Fig. 1), and is located in the center of seven O atoms, among which one comes from the water molecule. Five galactaric skeletons are involved in the coordination of one potassium ion: i.e., two skeletons (I and II) each supplying one O atom from COO^- group; one skeleton (III) supplying one O atom from hydroxyl group on C(3); one (IV) supplying two O atoms from OH

group on C(5) and carboxylic group ($CO(OH)$) respectively, and the other one (V) supplying one O atom from carboxylic group ($CO(OH)$), where such an O atom serves as a bridge to coordinate with two K^+ ions. All of the bond lengths of $K-O$ vary considerably from 2.747 to 3.161 Å (shown in Table 1), and the average bond length is 2.907 Å. Furthermore, the $O-K-O$ angles differ considerably from one another, and the heptahedron formed by the seven O atoms is utterly non-symmetrical.

In contrast to that in the free acid molecule [5], the galactaric skeleton in the molecule of potassium hydrogen galactarate monohydrate has no more symmetrical center. Though the entire galactaric radical keeps a zigzag form, the two carboxyl groups at the end positions are different in structure, one is $CO(OH)$, the other a COO^- group. Under different coordinated conditions, the two O atoms of the COO^- group are in a non-equivalent environment. Therefore, the free acid structure is a *meso*-dibasic acid [5]. On the other hand, the crystal structure of potassium hydrogen galactarate monohydrate is no longer in a *meso*-form because the space group is *P1*, and the coordinations between the two carboxyl groups and the K^+ ions are different.

In the case of hydroxyl groups, two of the four OH groups are coordinated to K^+ ion, whereas the others do not enter into coordination.

Furthermore, there exist many hydrogen bonds as shown in Table 2. The four hydroxyl groups all join in hydrogen bonding to form a hydrogen-bonded network together with the water molecule and the two terminal function groups of galactaric moiety. This hydrogen-bond system is different from that in the ammonium galactarate molecule [4]. The OH(8) group furnishes the proton to form a very strong hydrogen bond ($O \cdots O$ distance 2.476 Å) with carboxylic O(2) in potassium hydrogen galactarate molecule. And this bond is much stronger than the corresponding hydrogen bond ($O-O$ distance 2.68 Å) in the galactaric acid [5]. The O atom of the water molecule is not only coordinated with K^+ ion but also accepts a proton from HO(5) group to form a hydrogen bond.

FT-IR spectra study

Comparing the IR spectra of potassium hydrogen galactarate with that of galactaric acid [4], the $\nu_{C=O}$ band of $COOH$ group shifted 30 cm^{-1} , from 1724 cm^{-1} to 1754 cm^{-1} , toward higher wavenumber, and two new bands assigned to $\nu_{as}(COO^-)$ and $\nu_{s}(COO^-)$ appeared at 1629 and 1411 cm^{-1} , respectively (Fig. 3). It should be noted that the $\nu_{C=O}$ at a higher wavenumber position in the acid-salt has been observed elsewhere [10]. The varieties of the absorption bands indicate that the dimer of galactaric acid was dissociated, and its potassium hydrogen salt formed. Furthermore, the band at 189 cm^{-1} as shown in Fig.

Table 1. Some selected bond lengths (Å) and bond angles (°)

K—O(9)	2.833(5)	O(1)—C(1)—O(2)	124.7(6)
K—O(1 ^I)	3.155(6)	O(1)—C(1)—C(2)	120.8(5)
K—O(2 ^{II})	2.797(4)	O(2)—C(1)—C(2)	114.5(6)
K—O(4 ^{III})	2.808(4)	O(7)—C(6)—O(8)	123.1(6)
K—O(6 ^{IV})	3.161(6)	O(7)—C(6)—C(5)	124.1(6)
K—O(7 ^{IV})	2.747(6)	O(8)—C(6)—C(5)	112.8(6)
K—O(7 ^V)	2.751(5)		

Symmetry code: I: $x - 1, y, z$; II: $x - 1, y - 1, z$; III: $x - 1, y, z - 1$; IV: $x - 1, y - 1, z - 1$; V: $x, y - 1, z - 1$.

Table 2. The O...O distances (Å) of hydrogen bonds

O(3)...O(1)	2.741	O(4)...O(3)	2.866
O(6)...O(5)	2.916	O(7)...O(6)	2.687
O(9)...O(1 ^I)	2.754	O(9)...O(3 ^I)	3.048
O(8)...O(2 ^{VI})	2.476	O(9)...O(1 ^{VII})	2.786
O(9)...O(5 ^{VIII})	2.667	O(6)...O(5 ^{IX})	2.743
O(4)...O(3 ^{IX})	2.797	O(6)...O(3 ^X)	2.876

Symmetry code: VI: $x - 1, y, z + 1$; VII: $x - 2, y, z$; VIII: $x - 1, y - 1, z$; IX (=V - 1): $x + 1, y, z$; X (=III - 1): $x, y + 1, z$.

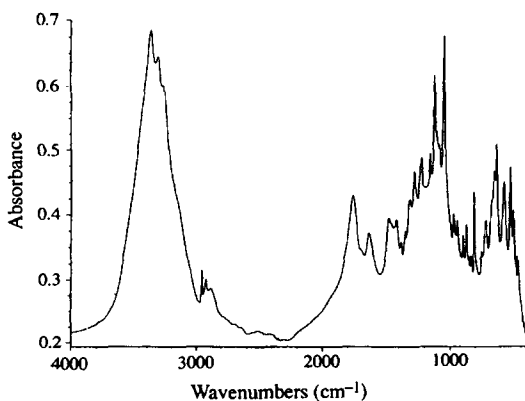


Fig. 3. The mid-IR spectrum of potassium hydrogen galactarate at room temperature.

4, assigned to $\nu_{\text{K-O}}$, shifted a little when the temperature was raised from 25 to 120°C. However, other bands changed significantly during such temperature

elevation. In the case of the absorption bands of hydroxyl group, the ν_{OH} band of CHO group and water became strong and broadened with four bands at 3365, 3308, 3259 and 3143 (shoulder) cm^{-1} . In addition, the band of ν_{OH} of COOH group in the range of 2500–3000 cm^{-1} were weaker obviously, and a very broad band appeared in the range of 400–2000 cm^{-1} with two centres at about 600 and 1200 cm^{-1} . These phenomena are typical and common in the IR spectra of acid-salts [11,12]. The changes indicate that the hydroxyl group of COOH took part in a very strong hydrogen bond, and a new hydrogen bonding network in the acid-salt molecule formed.

EXPERIMENTAL

Preparation of potassium hydrogen galactarate monohydrate, $\text{COOH}(\text{CHOH})_4\text{COOK} \cdot \text{H}_2\text{O}$

The acid salt was prepared by mixing an aqueous solution (20 cm^3) of pure galactaric acid (2.13 g) with

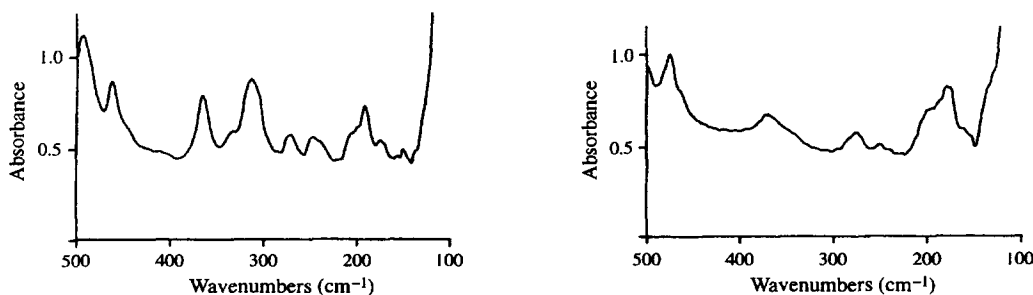


Fig. 4. The far IR spectra of potassium hydrogen galactarate at room temperature (A) and 120°C (B).

a solution of KOH (0.56 g, G.R.) in 5 cm³ distilled water at about 100°C. The resulting solution was refluxed for 30 min. After cooling, crystalline needles separated, were washed and dried. Three crops were collected, weighing 1.65 g KC₆H₉O₈ · H₂O. Yield 62%. The melting point was 205°C with decomposition. Found: C, 26.4; H, 4.2. Calc.: C, 27.1; H, 4.2%.

X-ray crystallography

A single crystal was mounted on a glass capillary, and data collection was made on a Nicolet R3 CAD-4F diffractometer with Mo-K_α radiation ($\lambda = 0.71069$ Å), using ω -2 θ scanning. The final cycle of full-matrix least squares refinement was based on 1171 observed reflections ($I > 2.5 \sigma(I)$). $R = 0.047$. Calculations were completed with a SHELX program package. The crystal structure is triclinic with $a = 4.798(1)$, $b = 6.752(1)$, $c = 8.304(1)$ Å; $\alpha = 66.66(1)^\circ$, $\beta = 86.63(1)^\circ$, $\gamma = 79.44(1)^\circ$. Space group = $P1$, $V = 242.81$ Å³, $Z = 1$. Figure 1 shows the crystal structure with atom numbering, whereas Fig. 2 shows the projection of the crystal cell along the direction of the a axis. Some selected bond lengths and bond angles are listed in Table 1, and the O...O distances of H-bonds, tabulated in Table 2. The supplementary data have been deposited in the Cambridge Crystallographic Centre.

FT-IR spectroscopy

The mid- and far-FT-IR spectra of potassium hydrogen galactarate monohydrate were measured with a Nicolet Magna 750 spectrometer with 4 cm⁻¹

resolution. The KBr and CsI pellet techniques were adopted. The results are shown in Figs 3 and 4. It should be noted that the mid and far FT-IR spectra of galactaric acid have been reported elsewhere [4].

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