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Structures of Sodium Hydrogen L-Tartrate Monohydrate and Potassium Hydrogen L-Tartrate

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Crystals of sodium hydrogen L-tartrate monohydrate ($NaHC_4H_4O_6 \cdot H_2O$) were grown from the aqueous solution, while potassium hydrogen L-tartrate ($KHC_4H_4O_6$) crystallized as anhydrate. Their crystal structures were determined by X-ray diffraction method. The hydrogen bonds between the carboxyl and carboxylate groups in these crystals are rather long; O···O 2.533(3) and 2.531(1) Å for the sodium and potassium compounds, respectively. The sodium and potassium ions are coordinated by eight O atoms at the corners of distorted square antiprism, $Na^+ \cdots O$ 2.404(2)—2.826(3) Å and $K^+ \cdots O$ 2.718(1)—3.059(1) Å. The crystal and molecular structures have been compared with those of the corresponding rubidium, caesium, and ammonium salts, and discussed with the aid of semiempirical and ab initio MO methods.

Very short hydrogen bonds in crystals of acidic salts of carboxylic acids have been extensively studied by many investigators owing to an interest in nature of hydrogen bond.[1—9] Concerning the nature of hydrogen bond, we have intended to study the crystallographically asymmetric hydrogen bonds, that is, the hydrogen bonds which have no symmetry in crystals, because the geometries can be determined more precisely than those for crystallographically symmetric hydrogen bonds, that is, the hydrogen bonds which have a symmetry such as an inversion center or two fold axis, and are often suffered from disordering.[1,3,4] The lower limit in the O···O lengths observed by X-ray or neutron diffraction is around 2.43 Å for both crystallographically symmetric and asymmetric hydrogen bonds.[1,3] Thus, as the first step to characterize the potential function for the hydrogen atom participating in the hydrogen bond, we have determined the crystal structures of the title compounds at room temperature. A comparative study of the crystal structures has also been undertaken with particular reference to those of rubidium, caesium and ammonium hydrogen L-tartrates.[10—12] The crystal and molecular structures have been discussed based on the results of semiempirical and ab initio MO calculations.

Experimental

The samples (Tokyo Kasei; GR for L-tartaric acid, Ishidzu Seiyaku; EP for NaOH and KOH) were used without further purification. The crystals were prepared by slow evaporation from the NaOH or KOH aqueous solution containing an equimolar quantity of L-tartaric acid.

X-Ray Structure Analysis. Experimental details and crystal data are listed in Table 1.

The intensities were measured on a Rigaku AFC-5R diffractometer with graphite monochromated Mo $K\alpha$ radiation (λ=0.71073 Å, 40 kV, 200 mA, 295 K) at the X-Ray Laboratory of Okayama University. The unit cell dimensions were determined from 25 reflections (2θ range; 19 to 22° for $NaHC_4H_4O_6 \cdot H_2O$; 21 to 22° for $KHC_4H_4O_6$). The intensities were collected by ω–2θ scan method [scan width $(1.31+0.30 \tan\theta)^\circ$ for $NaHC_4H_4O_6 \cdot H_2O$; $(1.15+0.30 \tan\theta)^\circ$ for $KHC_4H_4O_6$, scan speed: 6° min^{-1} in ω]. Three standard reflections were measured after every 97 reflections. The intensities were corrected for Lorentz and polarization effects.

The structure of $NaHC_4H_4O_6 \cdot H_2O$ was solved by direct method using MULTAN84[13] and refined by block-diagonal least-squares method anisotropically for non-H atoms. The isotropic thermal parameters for H atoms were fixed to the equivalent thermal parameters, B_{eq}, of the non-H atoms to which the H-atoms are attached; $\Sigma w(|F_o|-|F_c|)^2$ was minimized with $w=(\sigma^2(F_o)+p|F_o|+q|F_o|^2)^{-1}$. The values of p and q are listed in Table 1.

The structure of $KHC_4H_4O_6$ was refined based on the atomic parameters of $RbHC_4H_4O_6$[10] by block-diagonal least-squares method in the same way as applied for $NaHC_4H_4O_6 \cdot H_2O$, but the anomalous-dispersion terms were taken into account for K and O. The correction for secondary extinction effect was made by $I_{corr}=I_{obs}(1+gI_c)$, where $g=1.76\times10^{-5}$ for $NaHC_4H_4O_6 \cdot H_2O$ and 1.15×10^{-5} for $KHC_4H_4O_6$.

Atomic scattering factors and anomalous-dispersion terms were taken from International Tables for X-Ray Crystallography.[14] The programs used: HBLS-V and DAPH,[15] MOLCON[16] and ORTEP.[17] Calculations were carried out at the Okayama University Computer Center.

Theoretical Calculations. The geometrical optimizations were carried out by the MNDO method in MOPAC Ver. 5.02 available from JCPE.[18—20] The geometries obtained by the X-ray structure analyses were adopted for the optimization. The calculations were performed at the Okayama University Computer Center. The Gaussian 88 program[21] accessible at the Computer Center of Kyushu University was used for the ab initio calculations at STO-3G, 3-21G, and 6-31G levels.

Results and Discussion

The final atomic parameters are listed in Table 2.[22] The thermal ellipsoids of the molecules are shown in Fig. 1 with atomic numbering. The bond lengths and angles are listed in Table 3. The selected torsion angles, τ's, are listed in Table 4 along with those calculated by the MNDO method. Geometries of hydrogen bonds are summarized in Table 5. The crystal structures are shown in Fig. 2.

Table 1. Experimental Details and Crystal Data

	$NaHC_4H_4O_6 \cdot H_2O$	$KHC_4H_4O_6$
M_r	190.08	188.18
Morphology	Prismatic	Prismatic
Size of specimen (l/mm)	0.25×0.25×0.45	0.25×0.13×0.25
Crystal system	Orthorhombic	Orthorhombic
Space group	$P2_12_12_1$	$P2_12_12_1$
a/Å	8.663(1)	7.782(2)
b/Å	10.583(2)	10.643(2)
c/Å	7.228(1)	7.6084(8)
V/Å^3	662.7(2)	630.2(2)
D_x/Mg m^{-3}	1.905	1.983
Z	4	4
$F(000)$	392	384
μ/mm^{-1}	0.25	0.82
Radiation	Mo $K\alpha$	Mo $K\alpha$
$2\theta_{max}$/°	50.0	55.0
Range of h,k,l	$0 \leq h \leq 10$	$0 \leq h \leq 10$
	$0 \leq k \leq 12$	$0 \leq k \leq 13$
	$-1 \leq l \leq 8$	$-1 \leq l \leq 9$
Fluctuation of standard reflections/%	1.1	1.6
R_{int}	0.043	0.024
Number of unique	617	822
Reflections used	$\|F_o\|>2\sigma(F_o)$	$\|F_o\|>2\sigma(F_o)$
Number of parameters	138	121
R	0.033	0.024
wR	0.054	0.029
S	1.52	1.20
Constants for w		
p	−0.0024	−0.0062
q	0.0015	0.0007
$(\Delta/\sigma)_{max}$	0.7	0.7
ρ_{max}/e Å^{-3}	0.3	0.2
ρ_{min}/e Å^{-3}	−0.3	−0.2

Description of the Structures. The corresponding bond lengths and angles of the hydrogen tartrate anions in $NaHC_4H_4O_6 \cdot H_2O$ and $KHC_4H_4O_6$ are substantially the same. The bond O(3)–C(2) in both crystals are significantly longer than O(4)–C(3). This tendency is also seen in $RbHC_4H_4O_6$, $CsHC_4H_4O_6$, and $NH_4HC_4H_4O_6$. The difference in bond lengths between those bonds is reproduced by MNDO-optimization. The chain of four C atoms in the anion has a planar zig-zag conformation in both crystals (see, τ_4 in Table 4).

In the crystals of $NaHC_4H_4O_6 \cdot H_2O$, the asymmetric O–H···O hydrogen bond is formed between the carboxyl and carboxylate groups of the anions related by a c translation (Table 5). Each water molecule forms one hydrogen bond, O(W)···H–O, and two hydrogen bonds, O(W)–H···O, to form a three-dimensional network.

The crystals of $KHC_4H_4O_6$ are isomorphous with those of $RbHC_4H_4O_6$, $CsHC_4H_4O_6$, and $NH_4HC_4H_4O_6$. In the crystals, the similar asymmetric hydrogen bonds as found in $NaHC_4H_4O_6 \cdot H_2O$ are formed between the carboxyl and carboxylate groups of the anions related by the c translation. The hydroxyl groups O(3)–H and O(4)–H act as hydrogen bond donors (Table 5).

The Asymmetric Hydrogen Bond. The O···O distances of asymmetric hydrogen bonds between the carboxyl and carboxylate groups are rather long: 2.533(3) Å for $NaHC_4H_4O_6 \cdot H_2O$, 2.531(1) Å for $KHC_4H_4O_6$. The O···O distances increase with an increase in the ionic radii of metal ions in the isomorphous crystals: 2.559(3) Å for $RbHC_4H_4O_6$, 2.575(3) Å for $CsHC_4H_4O_6$. The values of the cell constant c also increase with an increase in the ionic radius. The chains of the anions connected by hydrogen bonds are formed along the c axis. Thus, the O···O distances are affected with the packing effect.

The O···O distances for these hydrogen tartrates are larger than 2.43 Å found in crystallographically symmetric hydrogen bonds in sodium and rubidium hydrogen succinates.[8,9] Such a phenomenon has been observed in potassium hydrogen *meso*-tartrate ($P\overline{1}$, $Z=4$), which contains a longer asymmetric hydrogen bond [O···O 2.521(5) Å] and two shorter symmetric ones [O···O 2.440(8) and 2.474(8) Å].[23] It is noted that the electrostatic interactions in the hydrogen bonds in the hydrogen tartrates are weaker than in the hydrogen succinates as indicated from the MNDO net atomic charges, q's on the atoms participating in the hydrogen bonds: q[O(5)] for $NaHC_4H_4O_6 \cdot H_2O$ and q[O(6)]

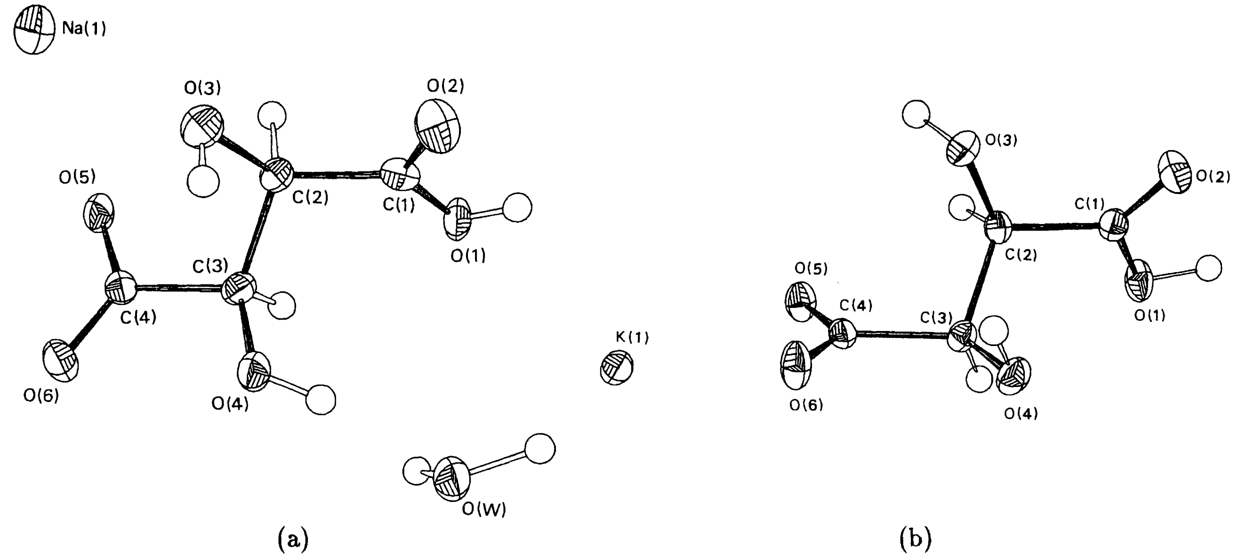


Fig. 1. The thermal ellipsoids and atomic numbering for non-H atoms for (a) $NaHC_4H_4O_6{\cdot}H_2O$ and (b) $KHC_4H_4O_6$. The thermal ellipsoids are drawn at 50% probability. The H atoms are represented as spheres equivalent to $B=1.0$ Å^2.

Table 2. Fractional Atomic Coordinates and Equivalent Thermal Parameters B_{eq} with Their esd's in Parentheses

$$B_{\mathrm{eq}} = (4/3)\sum_i \beta_{ii} a_i^2.$$

Atom	x	y	z	B_{eq}/Å^2
$NaHC_4H_4O_6{\cdot}H_2O$				
Na	0.2926(1)	0.9268(1)	−0.0897(2)	2.12(5)
O(W)	−0.0244(2)	0.4912(2)	0.5983(3)	2.26(9)
O(1)	0.2823(2)	0.6590(2)	0.5852(2)	1.88(7)
O(2)	0.1875(2)	0.8548(2)	0.5891(3)	2.30(8)
O(3)	0.1677(2)	0.8663(2)	0.2189(3)	2.23(8)
O(4)	0.0056(2)	0.6290(2)	0.2866(3)	1.99(8)
O(5)	0.2857(2)	0.6604(2)	−0.0644(2)	2.03(8)
O(6)	0.0357(2)	0.6109(2)	−0.0677(3)	2.12(8)
C(1)	0.2314(3)	0.7622(3)	0.5073(4)	1.6(1)
C(2)	0.2365(3)	0.7557(2)	0.2973(4)	1.5(1)
C(3)	0.1585(3)	0.6367(2)	0.2238(4)	1.5(1)
C(4)	0.1562(3)	0.6355(2)	0.0122(4)	1.4(1)
$KHC_4H_4O_6$				
K	0.32843(5)	0.03262(4)	0.16602(6)	1.84(1)
O(1)	0.6188(2)	−0.1360(1)	1.0495(2)	1.92(5)
O(2)	0.7070(2)	−0.3347(1)	1.0225(2)	1.97(5)
O(3)	0.5806(2)	−0.3498(1)	0.6888(2)	1.55(5)
O(4)	0.8666(2)	−0.1688(1)	0.6857(2)	1.65(5)
O(5)	0.4703(2)	−0.1024(1)	0.4618(2)	1.77(5)
O(6)	0.7299(2)	−0.1530(1)	0.3613(2)	1.94(5)
C(1)	0.6414(2)	−0.2412(2)	0.9627(2)	1.39(7)
C(2)	0.5784(2)	−0.2305(2)	0.7736(3)	1.24(6)
C(3)	0.6909(2)	−0.1368(2)	0.6736(2)	1.25(6)
C(4)	0.3248(2)	−0.1289(2)	0.4839(2)	1.23(6)

Table 3. Bond Lengths and Angles

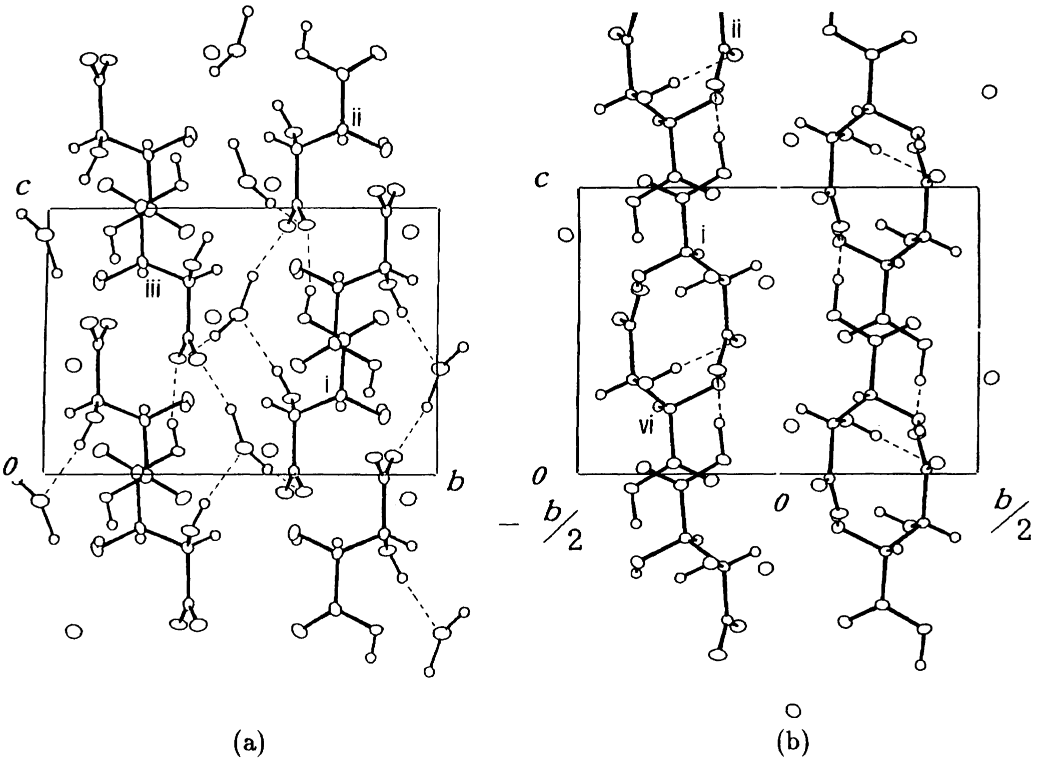
	$NaHC_4H_4O_6{\cdot}H_2O$	$KHC_4H_4O_6$
	l/Å	l/Å
O(1)-C(1)	1.305(4)	1.311(2)
O(2)-C(1)	1.206(4)	1.210(2)
O(3)-C(2)	1.431(4)	1.423(2)
O(4)-C(3)	1.403(3)	1.411(1)
O(5)-C(4)	1.278(4)	1.242(2)
O(6)-C(4)	1.221(4)	1.270(2)
C(1)-C(2)	1.520(4)	1.526(3)
C(2)-C(3)	1.525(4)	1.532(2)
C(3)-C(4)	1.530(4)	1.535(2)
	ϕ/°	ϕ/°
O(1)-C(1)-O(2)	125.1(3)	124.7(2)
O(1)-C(1)-C(2)	112.5(2)	111.7(2)
O(2)-C(1)-C(2)	122.4(3)	123.6(2)
C(1)-C(2)-O(3)	110.3(2)	111.0(2)
C(1)-C(2)-C(3)	111.9(2)	109.2(2)
O(3)-C(2)-C(3)	110.7(2)	110.3(1)
C(2)-C(3)-O(4)	110.7(2)	111.6(1)
C(2)-C(3)-C(4)	111.2(2)	108.0(1)
O(4)-C(3)-C(4)	108.1(2)	113.8(1)
C(3)-C(4)-O(5)	114.8(2)	117.8(2)
C(3)-C(4)-O(6)	119.1(3)	117.3(2)
O(5)-C(4)-O(6)	126.1(3)	124.9(2)

for $KHC_4H_4O_6$ are lower negative than −0.8697 for corresponding O atom in sodium hydrogen succinate; q[H(5)]'s for $NaHC_4H_4O_6{\cdot}H_2O$ and $KHC_4H_4O_6$ are lower positive than 0.2384 for sodium hydrogen succinate (Table 7).

Conformations of the Anion and Optimized Geometry. The conformations of the hydrogen tartrate anion in $KHC_4H_4O_6$ are substantially the same as those found in the isomorphous crystals of $RbHC_4H_4O_6$, $CsHC_4H_4O_6$, and $NH_4HC_4H_4O_6$, as well as in $NaHC_4H_4O_6{\cdot}H_2O$. In all these crystals the carboxyl and carboxylate groups of the anion take *gauche*

Table 4. Torsion Angles of Tartrate Anions Obtained from X-Ray Structure Analyses and by MNDO Method

X-Ray data	$NaHC_4H_4O_6 \cdot H_2O$ $\tau/°$		$KHC_4H_4O_6$ $\tau/°$
τ_1[O(1)-C(1)-C(2)-O(3)]	175.1(2)		−171.6(2)
τ_2[O(2)-C(1)-C(2)-C(3)]	−129.9(3)		−112.3(3)
τ_3[O(3)-C(2)-C(3)-O(4)]	−66.9(3)		−68.2(3)
τ_4[C(1)-C(2)-C(3)-C(4)]	176.6(2)		179.7(2)
τ_5[O(5)-C(4)-C(3)-O(4)]	170.3(2)		179.3(2)
τ_6[O(6)-C(4)-C(3)-C(2)]	−131.9(3)		−123.1(2)
MNDO method	$NaHC_4H_4O_6 \cdot H_2O$ $\tau/°$	$NaHC_4H_4O_6$ $\tau/°$	$KHC_4H_4O_6$ $\tau/°$
τ_1	179.8	−164.6	−169.2
τ_2	−128.7	−113.0	−114.3
τ_3	−65.2	−70.0	−69.1
τ_4	−174.7	−179.1	−177.7
τ_5	165.2	170.1	−169.0
τ_6	−137.8	−132.4	−119.5



(a) (b)

Fig. 2. Projections of the crystal structures along the *a* axes. (a) $NaHC_4H_4O_6 \cdot H_2O$ and (b) $KHC_4H_4O_6$. Broken lines show hydrogen bonds. The symmetry codes are given in Table 6.

conformations relative to the carbon framework as seen from τ_2 and τ_6 in Table 4. However, it should be noted that τ_2 in $NaHC_4H_4O_6 \cdot H_2O$ is different by ca. 13° from that in $KHC_4H_4O_6$.

The conformations of the anion were optimized by MNDO. The calculations were made for asymmetric units ($Na^+HC_4H_4O_6^- \cdot H_2O$), ($Na^+HC_4H_4O_6^-$) and ($K^+HC_4H_4O_6^-$) which were chosen as given in Table 2 and Fig. 1. Although the effect of intermolecular hydrogen bonds is neglected in the calculation, the conformations optimized for ($K^+HC_4H_4O_6^-$) are in agreement within 10° except for τ_5 with those found in the crystals of $KHC_4H_4O_6$ (Table 4).

The conformations optimized for ($Na^+HC_4H_4O_6^-$) well reproduce the conformations at the carboxylate side (τ_5, τ_6 in Table 4) of the anion in the crystals of $NaHC_4H_4O_6 \cdot H_2O$, but exhibit some deviations at the carboxyl side (τ_1, τ_2). On the other hand, the conformations optimized for ($Na^+HC_4H_4O_6^- \cdot H_2O$) better reproduce the observed conformations than those op-

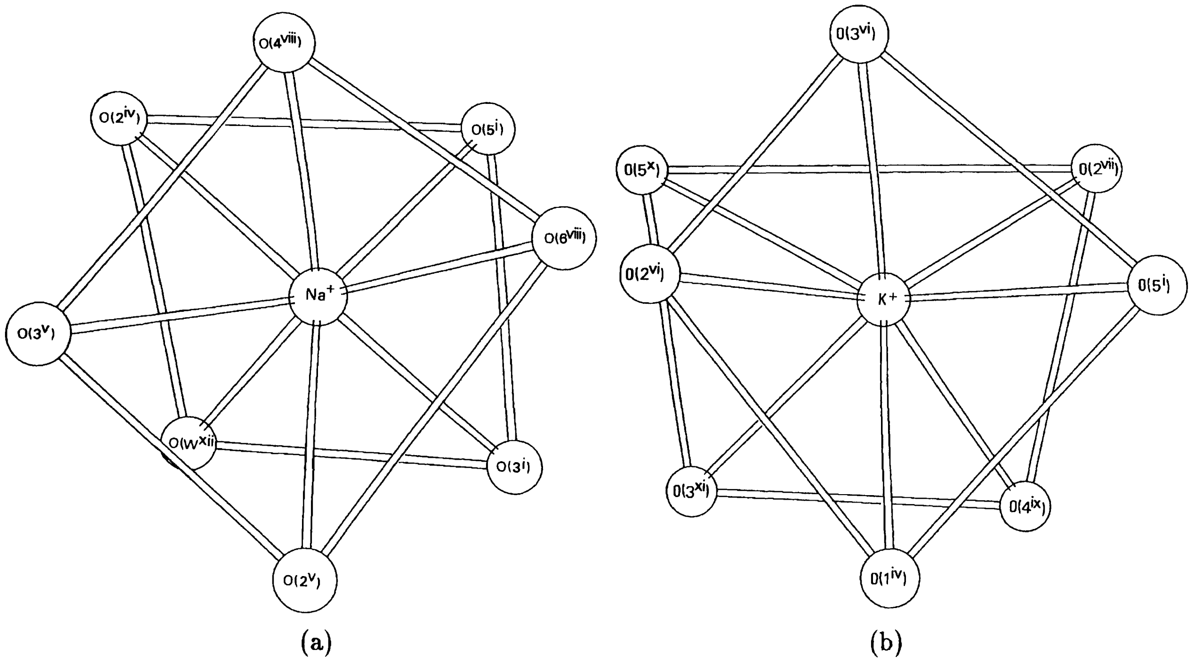


Fig. 3. Coordination geometry of eight O atoms to a metal ion. (a) $NaHC_4H_4O_6 \cdot H_2O$ and (b) $KHC_4H_4O_6$. The symmetry codes are given in Table 6.

Table 5. Geometries of Hydrogen Bonds[a)]

Donor(D) Acceptor(A)	D···A l/Å	H···A l/Å	D–H···A ϕ/°
$NaHC_4H_4O_6 \cdot H_2O$			
$O(1^{i}) \cdots O(5^{ii})$	2.533(3)	1.78(4)	165(4)
$O(4^{i}) \cdots O(W^{i})$	2.696(3)	1.86(4)	170(4)
$O(W^{i}) \cdots O(5^{iii})$	2.869(3)	1.84(5)	165(5)
$O(W^{i}) \cdots O(6^{ii})$	2.776(3)	1.67(6)	165(5)
$KHC_4H_4O_6$			
$O(1^{i}) \cdots O(6^{ii})$	2.531(1)	1.60(2)	165(2)
$O(3^{i}) \cdots O(6^{vi})$	2.756(1)	1.89(2)	161(2)
$O(4^{vi}) \cdots O(5^{i})$	2.800(1)	1.95(2)	163(2)

a) Symmetry codes are given in Table 6.

timized for $Na^+HC_4H_4O_6^-$. The MNDO calculation suggests that the conformations at the carboxylate side near Na^+ is determined by the electrostatic interactions with Na^+, and those at the carboxyl side are affected by the inclusion of the water molecule.

Coordination of O Atoms around the Metal Ions and Electronic Property of the Anion. In the crystals of $NaHC_4H_4O_6 \cdot H_2O$ and $KHC_4H_4O_6$ each metal ion is coordinated by eight O atoms at the corners of a distorted square antiprism as shown in Fig. 3. The coordination distances M···O and angles M···O–X (X=C or H) are given in Table 6. The distances range from 2.404(2) to 2.826(3) Å for $NaHC_4H_4O_6 \cdot H_2O$ and 2.718(1) to 3.059(1) Å for $KHC_4H_4O_6$. The angles range from 104.6(2) to 124.3(2)° for $NaHC_4H_4O_6 \cdot H_2O$ and 115.2(1) to 140.1(1)° for $KHC_4H_4O_6$. In $NaHC_4H_4O_6 \cdot H_2O$ the M···O–X angles involving the sp^3 O atoms close to the sp^3 angle and those involving the sp^2 O atoms close to the sp^2 angles. However, $M \cdots O(1^{i})–C(1^{i})$, $M \cdots O(4^{ix})–(3^{ix})$, and $M \cdots O(3^{xi})–C(2^{xi})$ angles in $KHC_4H_4O_6$ are largely widened from the sp^3 angle because of the hydrogen bond formation. The features of the coordination in the isomorphous crystals of $RbHC_4H_4O_6$, $CsHC_4H_4O_6$, and $NH_4HC_4H_4O_6$ are the same as those in $KHC_4H_4O_6$.

The square-antiprismatic arrangement is not generally found in inorganic ionic crystals but the cubic arrangement is found, because the square-antiprismatic arrangement is difficult to extend to three-dimensional directions in spite of the minimization of electrostatic repulsions.[24)] In the case of $NaHC_4H_4O_6 \cdot H_2O$, $KHC_4H_4O_6$, $RbHC_4H_4O_6$, $CsHC_4H_4O_6$, and $NH_4HC_4H_4O_6$, the minimization is preferential because the three-dimensional extension can be realized by the existence of multifunctional hydrogen tartrate ions.

Though the negative atomic charge on O(5) is very large, the Na···O(5) and K···O(5) distances are not so short in comparison with the others. On the other hand, the distance between Na and O(4) is the shortest. These facts are inconsistent with the strength of electrostatic attraction between these atoms. As can be seen from Table 7, the negative atomic charge on O(4) increases on going from STO-3G to 6-31G basis set. Nevertheless, it is smaller than that on O(5) even in 6-31G level. Thus, the distances between the metal ions and O atoms are not determined only by the electrostatic forces but also by the interatomic and intermolecular interactions such as hydrogen bonds.

The mean values of the M···O distances, $<r_{M-O}>$, for $M=Na^+$, K^+, Rb^+, and Cs^+ are collected in Table 8 together with the ionic radii of metal ions, r_{ion}'s,[25)] and

Table 6. The Coordination Distances between O Atoms and a Metal Ion, M, and Related Angles[a)]

M	Na l/Å	K l/Å
M···O(2^{iv})	2.608(2)	
M···O(2^{v})	2.654(2)	
M···O(2^{vi})		2.718(1)
M···O(2^{vii})		2.772(1)
M···O(4^{viii})	2.404(2)	
M···O(4^{ix})		2.785(1)
M···O(5^{i})	2.826(3)	2.889(1)
M···O(5^{x})		2.893(1)
M···O(1^{iv})		3.019(1)
M···O(3^{i})	2.560(2)	
M···O(3^{v})	2.613(2)	
M···O(3^{vi})		2.954(1)
M···O(3^{xi})		3.059(1)
M···O(6^{viii})	2.427(3)	
M···O($\mathrm{W}^{\mathrm{xii}}$)	2.422(3)	

	ϕ/°		ϕ/°
Na···O(3^{i})–C(2^{i})	111.9(2)	K···O(1^{i})–C(1^{i})	139.1(1)
Na···O(4^{viii})–C(3^{viii})	123.2(2)	K···O(5^{x})–C(4^{x})	139.5(1)
Na···O(3^{v})–C(2^{v})	114.9(2)	K···O(4^{ix})–C(3^{ix})	134.12(7)
Na···O($\mathrm{W}^{\mathrm{xii}}$)–H($\mathrm{W1}^{\mathrm{xii}}$)	114(3)	K···O(5^{ii})–C(4^{ii})	125.9(1)
Na···O($\mathrm{W}^{\mathrm{xii}}$)–H($\mathrm{W2}^{\mathrm{xii}}$)	105(3)	K···O(2^{vi})–C(1^{vi})	125.9(1)
Na–O(2^{v})–C(1^{V})	116.6(2)	K···O(3^{vi})–C(2^{vi})	115.2(1)
Na–O(2^{iv})–C(1^{iv})	124.3(2)	K···O(2^{vii})–C(1^{vii})	134.4(1)
Na···O(5^{i})–C(4^{i})	104.6(2)	K···O(3^{xi})–C(2^{xi})	140.1(1)
Na···O(6^{viii})–C(4^{viii})	123.7(2)		

a) Symmetry codes: (i) x,y,z, (ii) $x,y,1+z$, (iii) $1/2-x,1-y,1/2+z$, (iv) $x,y,-1+z$, (v) $1/2-x,2-y,-1/2+z$, (vi) $-1/2+x,-1/2-y,1-z$, (vii) $1-x,1/2+y,3/2-z$, (viii) $1/2+x,3/2-y,-z$, (ix) $3/2-x,-y,-1/2+z$, (x) $1/2-x,-y,-1/2+z$, (xi) $1-x,1/2+y,1/2-z$, (xii) $-x,1/2+y,1/2-z$.

Table 7. Net Atomic Charges for $NaHC_4H_4O_6{\cdot}H_2O$, $NaHC_4H_4O_6$, and $KHC_4H_4O_6$

	$NaHC_4H_4O_6{\cdot}H_2O$	$NaHC_4H_4O_6$				$KHC_4H_4O_6$
	MNDO	MNDO	STO-3G	3-21G	6-31G	MNDO
H(5)	0.2038	0.2080	0.3253	0.3803	0.3565	0.2058
O(1)	−0.2452	−0.2403	−0.4207	−0.6556	−0.5726	−0.2727
O(2)	−0.3618	−0.3623	−0.2903	−0.5931	−0.5230	−0.3504
O(3)	−0.3802	−0.3791	−0.3715	−0.6988	−0.7753	−0.2809
O(4)	−0.3146	−0.3001	−0.3874	−0.6772	−0.6870	−0.3005
O(5)	−0.7091	−0.7048	−0.5483	−0.7819	−0.8060	−0.6981
O(6)	−0.4774	−0.4787	−0.4346	−0.6748	−0.6246	−0.5704

the sum of r_{ion} and van der Waals radius of O atom, r_{O}.[26)] The $<r_{\mathrm{M-O}}>$ in rubidium hydrogen succinate which exhibits a square antiprism formed by the eight O atoms, is determined to be 2.96 Å.[8)] The value is comparable with that in $RbHC_4H_4O_6$, 2.984 Å.[10)] On the other hand, the $<r_{\mathrm{M-O}}>$ in sodium hydrogen succinate, 2.45 Å,[8,9)] is shorter than that in $NaHC_4H_4O_6{\cdot}H_2O$, 2.564 Å, because the Na^+ in the crystals of sodium hydrogen succinate is coordinated by six O atoms.

Packing Coefficient. The packing coefficient, k is defined by $k=Z{\cdot}V_{\mathrm{o}}/V$, where Z is the number of molecules in the unit cell, V_{o} the molecular volume, and V the unit cell volume.[27)] In order to find the reason why anhydrate crystals of $NaHC_4H_4O_6$ were not formed, but only those of the monohydrate were formed, the packing coefficient, k, for hypothetical crystal of $NaHC_4H_4O_6$ has been evaluated from the V estimated by extrapolation of unit cell volumes V of isomorphous crystals of $KHC_4H_4O_6$, $RbHC_4H_4O_6$, and $CsHC_4H_4O_6$ vs. $(4/3)\pi r_{\mathrm{ion}}^3$ (Fig. 4) and the molecular volumes V_{o} estimated by using the van der Waals radii[26)] and r_{ion}.[25)] The value of k for $NaHC_4H_4O_6$ was estimated to be as high as 0.911, which implies that no anhydrate crystals with isomorphous structure could be

Table 8. The Experimental Mean-Values, $<r_{\mathrm{M-O}}>$, of Distances between O Atoms and a Metal Ion, M, with the Ionic Radii of Metal Ions, r_{ion}'s

M	$<r_{\mathrm{M-O}}>$/Å	$r_{\mathrm{ion}}$$^{a)}$/Å	$r_{\mathrm{ion}}+r_{\mathrm{O}}$$^{b)}$/Å
Na^+	2.564	1.32(1.18)	2.84(2.58)
K^+	2.886	1.65(1.51)	3.17(2.91)
Rb^+	2.984	1.75(1.61)	3.27(3.01)
Cs^+	3.131	1.88(1.74)	3.40(3.14)

a) Ref. 25. b) Ref. 26. Values in parentheses refer to r_{ion}'s given by Pauling.[28)]

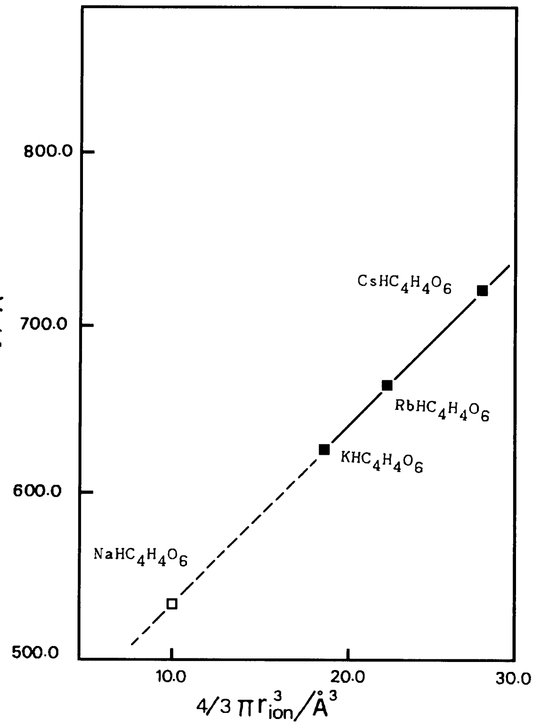


Fig. 4. Plots of the unit cell volume, V, vs. $(4/3)\pi r_{\mathrm{ion}}^3$. ■: experimental V, □: estimated V.

formed for $NaHC_4H_4O_6$.[27)] On the other hand, the k for $NaHC_4H_4O_6 \cdot H_2O$ is 0.845, which is close to 0.835 for $KHC_4H_4O_6$.

The ionic radius of NH_4^+ in crystals has not been determined clearly. We can assume that the ionic radius of NH_4^+ is 1.70 Å, because the V is well fitted to the relations of V vs. $(4/3)\pi r_{\mathrm{ion}}^3$ for the present isomorphous series. The estimated ionic radius of NH_4^+ is close to that of Rb^+, 1.75 Å.

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