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Crystal Structure of Potassium Hydrogen Terephthalate: Symmetric Hydrogen Bond in One-Dimensional Chain

Keisuke MIYAKUBO,* Sadamu TAKEDA,* and Nobuo NAKAMURA
Department of Chemistry, Faculty of Science, Osaka University, Toyonaka, Osaka 560

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Synopsis. Crystal structure of potassium hydrogen terephthalate was determined by X-ray diffraction. Crystals have monoclinic unit cells with $C2/c$, a=18.776(6), b=3.761(3), c=11.150(4) Å, β=94.72(3)°, V=784.6(6) Å^3, and Z=4. Acid anions form a one-dimensional chain linked by short ($R_{\mathrm{O}\cdots\mathrm{O}}$=2.459(3) Å) and symmetric hydrogen bonds. The acidic hydrogen was distributed at two equivalent sites in the hydrogen bond.

In the crystals of half-hydrogenated dicarboxylate such as potassium hydrogen acetylenedicarboxylate (KHADC), KH(C_4O_4),[1] and ammonium hydrogen terephthalate (AHTP), (NH_4)H($C_8H_4O_4$),[2] a one-dimensional hydrogen bonded chain is formed by successive linking of single hydrogen bonds. In such a case, the translational motion of hydrogen atoms in the chain is expected to be correlated, because a local independent motion of a single hydrogen atom in the chain would bring about very high energy state. For a correlated motion of hydrogen atoms, the soliton-like mechanism has been proposed.[3,4]

In the course of a series of study of correlated protonic motion in one-dimensional hydrogen bonded chains, we investigated the crystal structure of potassium hydrogen terephthalate (KHTP), $C_8H_5O_4K$, which is a typical example of a half-hydrogenated dicarboxylate.

Experimental

Material: Potassium hydrogen terephthalate (KHTP) was synthesized by a method similar to that for AHTP.[2] KOH was dissolved in mixed solvent of H_2O and *N*,*N*-dimethylformamide (DMF). The solution of KOH was poured slowly into a DMF solution of the stoichiometric amount of terephthalic acid (TPA). White powders were precipitated immediately. Recrystallization from the 1 : 1 mixed solvent of H_2O and DMF by slow cooling from ca. 80 °C brought about colorless needle like crystals. Chemical analysis Found: C, 47.17; H, 2.56%. Calcd for $C_8H_5O_4K$: C, 47.05; H, 2.47%.

X-Ray Data Collection: A single crystal of KHTP with dimensions 0.7×0.3×0.05 mm was used for the X-ray diffraction experiment. X-Ray measurements were made at room temperature using a full-automated four-circle diffractometer (Rigaku Co., Ltd., model AFC5R) with graphite-monochromated Mo $K\alpha$ radiation at the X-ray Diffraction Service of the Department of Chemistry, Faculty of Science, Osaka University. The intensity data were collected with the ω–2θ scan technique. The scan rate and width were 8° min^{-1} in ω-axis and $\Delta\omega$=1.37°+0.35° tan θ, respectively. The number of independent reflections is 1320 in the range 3.0°≤2θ≤60.1°. The data were corrected for Lorentz and polarization effects. An empirical absorption correction and a liner correction to a decrease of the intensity through the measurement (0.2%) were also applied. The cell dimensions and the crystal orientation were refined using 25 reflections in the range 28.21°≤2θ≤29.92°.

Structure Determination: The structure was solved by the direct method using DIRDIF.[5] All calculations were performed using crystallographic software package teXsan.[6]

The systematic absence of reflections of hkl: $h+k\neq 2n$, $h0l$: $l\neq 2n$, revealed the space group of Cc or $C2/c$. The space group of $C2/c$ was deduced from a statistical analysis of the intensities of the observed reflections. This was confirmed by a structure solution and a least-squares refinement.

Firstly, the structure without acidic hydrogen atom was determined. Thermal parameters were refined anisotropically for non-hydrogen atoms and isotropically for hydrogen atoms. The differential Fourier map obtained in this step gave two clearly separated maxima for the acidic hydrogen atom which are related to each other by the center of inversion at the center of the hydrogen bond. Thus the half-hydrogen model for the hydrogen bond was used. The final full-matrix least-squares refinement was carried out using 72 variables and 958 reflections with $I>3.0\sigma(I)$, and resulted in R=0.034, R_w=0.053, S=2.40, and $(\Delta/\sigma)_\mathrm{max}$=0.0002. The final positional parameters are listed in Table 1. The numbering scheme is given in Fig. 1, which represents the crystal structure viewed along the b-axis. The bond distances and the bond angles are recorded in Table 2. The complete list of the anisotropic temperature factors and the structure factors was deposited as Document No. 67041 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Table 1. Atomic Coordinate and Equivalent Isotropic Thermal Parameters

$$B_\mathrm{eq}=\frac{8\pi^2}{3}\sum_{i=1}^{3}\sum_{j=1}^{3}U_{ij}a_i^*a_j^*\vec{a}_i\vec{a}_j$$

Atom	x	y	z	B_eq/Å^2
K	0	0.1555(2)	0.75	3.21(2)
O(1)	0.08697(6)	0.6794(4)	0.6573(1)	2.59(3)
O(2)	0.05997(7)	0.5410(5)	0.4654(1)	3.34(3)
C(1)	0.10415(8)	0.6395(5)	0.5536(1)	1.96(3)
C(2)	0.17939(7)	0.6982(4)	0.5244(1)	1.60(3)
C(3)	0.22829(8)	0.8414(5)	0.6114(1)	1.83(3)
C(4)	0.20141(8)	0.6069(5)	0.4120(1)	1.88(3)
H(1)	0.214(1)	0.900(6)	0.687(2)	2.9(5)
H(2)	0.169(1)	0.498(7)	0.353(2)	2.5(4)
H(3)[a]	0.024(2)	0.50(1)	0.492(4)	3(1)

[a] The population of H(3) is 0.5.

Table 2. Relevant Bond Distances (Å) and Bond Angles (deg.) in KHTP

	Anion geometry		
C(1)–O(1)	1.235(2)	O(1)–C(1)–O(2)	123.3(1)
C(1)–O(2)	1.288(2)	O(1)–C(1)–C(2)	120.8(1)
C(1)–C(2)	1.492(2)	O(2)–C(1)–C(2)	116.0(1)
C(2)–C(3)	1.389(2)	C(1)–C(2)–C(3)	119.2(1)
C(2)–C(4)	1.394(2)	C(1)–C(2)–O(4)	121.1(1)
C(3)–C(4*)	1.380(2)	C(3)–C(2)–C(4)	119.7(1)
C(3)–H(1)	0.94(2)	C(2)–C(3)–C(4*)	120.6(1)
C(4)–H(2)	0.95(2)	C(2)–C(4)–C(3*)	119.7(1)
	Coordination around K^+		
K–O(1)	2.810(2)	O(1)–K–O(1†)	86.32(6)
K–O(1†)	2.687(2)	O(1)–K–O(2‡)	66.73(5)
K–O(2‡)	2.809(2)	O(1†)–K–O(2‡)	98.94(5)
	Hydrogen bond		
O(2)···O(2‡)	2.459(3)	O(2)–H···O(2‡)	171(6)
O(2)–H(3)	0.77(4)	C(1)–O(2)–H(3)	107(4)
O(2)···H(3‡)	1.69(4)	C(1)–O(2)···H(3‡)	112(2)
H(3)···O(3‡)	0.94(9)	O(2)–H(3)···H(3‡)	163(10)

Equivalent positions mean as $(1/2-x,\ 3/2-y,\ 1-z)^*$, $(x,\ -1+y,\ z)^\dagger$, and $(-x,\ 1-y,\ 1-z)^\ddagger$.

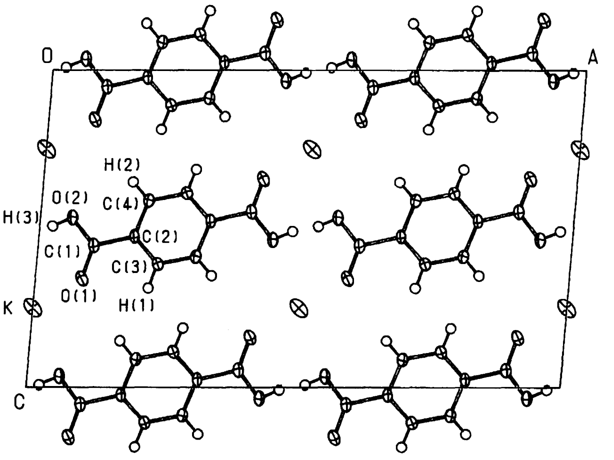

Fig. 1. ORTEP[7)]-plot of *b*-axis projection of KHTP.

Results and Discussion

KHTP crystallizes in a monoclinic $C2/c$ unit cell in which terephthalic acid anions are linked by symmetric and very short hydrogen bonds. The center of symmetry is located at the middle of the symmetric hydrogen bond and at the center of the acid anion. The potassium ion lies on the two fold symmetry axis and is surrounded by six oxygen atoms of the six nearby carboxyl groups. For a carboxyl group, the bond lengths C=O and C–O differ significantly from each other, as can be seen in the mono hydrogen salts of other dicarboxylic acids. The planar carboxyl groups are tilted by 8.0° from the plane of the benzene ring.

There is inversion symmetry at the center of the hydrogen bond, as mentioned above. The geometry of the symmetric hydrogen bond is also summarized in Table 2. The distance between two oxygen atoms ($R_{O\cdots O}$) is 2.459(3) Å. This is one of the shortest hydrogen bond distances ever reported.[8)]

It is interesting to compare the nature of the hydrogen bond in KHTP with that in AHTP, which is isomorphous to KHTP. AHTP also contains a similar kind of hydrogen bond to that of KHTP.[2)] The distance between the two oxygen atoms is also very short ($R_{O\cdots O}=2.51$ Å). However, the acidic hydrogen atom in AHTP was refined as located at the center of the hydrogen bond (inversion center). An important difference between the hydrogen bonds in KHTP and AHTP is that the hydrogen bonding in KHTP is localized in the O–H···O system, whereas both oxygens in the carboxyl group in AHTP participate in the formation of N–H···O hydrogen bonds with the ammonium ions. In AHTP, therefore, the single minimum hydrogen bond may be brought about as a result of a subtle balance of these complex hydrogen-bond networks. It is noted that the value of the R factor, 0.076, in the case of AHTP seems to be significantly large.

Numerous efforts have been made to distinguish the single-minimum hydrogen bond from the usual double minimum ones. Sometimes this point was discussed in relation to anisotropic vibration of the acidic hydrogen[9,10)] and to its anomalous thermal parameter.[11—14)] The clear distinction between a single and double minimum potentials for the hydrogen atom has been very difficult even by means of X-ray or neutron diffraction methods; many old works assigned "so-called" short hydrogen bond to single minimum hydrogen bond. A recent X-ray diffraction experiment revealed that the very short hydrogen bond ($R_{O\cdots O}=2.493$ Å at room temperature) in $K_3H(SO_4)_2$ has two distinct hydrogen atom positions.[15)] In the case of KHTP, present work revealed two stable sites for the acidic hydrogen in the hydrogen bond. This fact suggests that the acidic hydrogen is in a dynamic equilibrium and moving between two sites.

An NMR study of the dynamics of the hydrogen atom is in progress.

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