

Original Research Article

Crystal Structure and Thermal Properties of Racemic $\text{BaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ Single Crystals

ABSTRACT

Single crystals of racemic barium tartrate monohydrate, $\text{BaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$, were grown at 308 K by a gel method using silica gel as the growth medium. Differential scanning calorimetry, thermogravimetric-differential thermal analysis, and X-ray diffraction measurements were performed on the single crystals. The space group symmetry (monoclinic $P2_1/c$) and structural parameters were determined at room temperature. The crystal structure consisted of BaO_9 and BaO_{10} polyhedra, two independent $\text{C}_4\text{H}_4\text{O}_6$ molecules, and $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds between adjacent H_2O or $\text{C}_4\text{H}_4\text{O}_6$ molecules. Weight losses due to thermal decomposition of racemic $\text{BaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ were found to occur in the temperature range of 300–1550 K. We suggested that the weight losses were caused by the evaporation of bound water molecules and the evolution of H_2CO , H_2 , CO , and O_2 gases from the two $\text{C}_4\text{H}_4\text{O}_6$ molecules, and that the residual chalky white and black substances that remained as a mixture in the vessel after decomposition were barium oxide (BaO) and barium monocarbide (BaC), respectively.

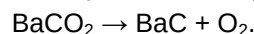
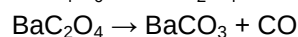
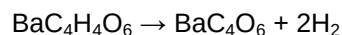
Keywords: racemic $\text{BaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$; crystal structure; thermal decomposition; TG-DTA; X-ray diffraction.

1. INTRODUCTION

Many tartrate compounds are formed by reacting tartaric acid (chemical formula: $\text{C}_4\text{H}_6\text{O}_6$; systematic name: 2,3-dihydroxybutanedioic acid) with compounds containing positive ions (two monovalent cations or one divalent cation) [1–6]. Tartaric acid has two chiral carbon atoms in its structure, which provides the possibility for four possible different forms of chiral, racemic, and achiral isomers: L(+)-tartaric, D(–)-tartaric, racemic (DL-) tartaric, and meso-tartaric acid [6–8]. Some of these compounds are of interest due to their physical properties, particularly their excellent dielectric, ferroelectric, piezoelectric, and nonlinear optical properties [1,9–11]. Moreover, they are used in numerous industrial applications, for example, as transducers and in linear and non-linear mechanical devices [1,4,11].

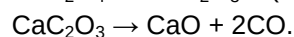
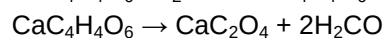
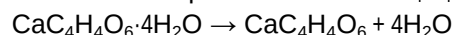
Silgo et al. have published the crystal structure of barium L-tartrate, $\text{BaC}_4\text{H}_4\text{O}_6$, as determined at room temperature by means of single-crystal X-ray diffraction [12]. The crystal structure was orthorhombic with space group $P2_12_12_1$, and consisted of BaO_9 polyhedra, $\text{C}_4\text{H}_4\text{O}_6$ molecules, and $\text{O}-\text{H} \cdots \text{O}$ hydrogen bonds between adjacent molecules. The positions of hydrogen atoms were calculated based on geometric criteria ($\text{O}-\text{H}$ and $\text{C}-\text{H}$ distances of 0.82 and 0.98 Å, respectively), and the atoms were refined with fixed positional and isotropic displacement parameters. Recently, we have determined a more accurate crystal structure in which the positional and thermal parameters of all the atoms including hydrogen atoms were refined, and reported the existence of zig-zag hydrogen-bonded chains along the *a*- and *c*-axes linked by $\text{O}-\text{H} \cdots \text{O}$ and $\text{C}-\text{H} \cdots \text{O}$ hydrogen bonds between

adjacent $C_4H_4O_6$ molecules [5]. Moreover, the chemical reactions occurring during the thermal decomposition of $L-BaC_4H_4O_6$ in the temperature range of 450–1530 K were found to be:



Thus, the weight losses due to the thermal decomposition were confirmed to be caused by the evolution of H_2 , CO , and O_2 gases, and the resulting black substance in the vessel after decomposition was barium monocarbide BaC [5].

DL-tartaric compounds have been synthesized with divalent cations by using DL-tartaric acid as a crystallization reagent instead of L(+)-tartaric acid [2,13]. We have grown single crystals of racemic calcium tartrate tetrahydrate, $DL-CaC_4H_4O_6 \cdot 4H_2O$, by the gel method and have determined the crystal structure at room temperature (triclinic with space group $P\bar{1}$) [13]. Moreover, it was found that a phase transition derived from intramolecular proton transfer between three possible sites occurred at around 310 K. The chemical reactions during the thermal decomposition of $DL-CaC_4H_4O_6 \cdot 4H_2O$ were found to be:



Moreover, single crystals of racemic strontium tartrate tetrahydrate, $DL-SrC_4H_4O_6 \cdot 4H_2O$, were also grown by the gel method, and their structural and thermal properties were found to be very similar to those of DL-calcium tartrate [14]. However, investigations of the crystal growth and physical properties of DL-tartaric compounds other than those of $DL-CaC_4H_4O_6 \cdot 4H_2O$ and $DL-SrC_4H_4O_6 \cdot 4H_2O$ have not been carried out yet [13,14].

As mentioned above, it is expected that a racemic barium tartrate compound can be synthesized using a Ba^{2+} ion as a divalent cation and DL-tartaric acid. In this paper, we report the synthesis of single crystals of racemic barium tartrate monohydrate, $BaC_4H_4O_6 \cdot H_2O$, using the gel method, and determine their crystal structure at room temperature using X-ray diffraction. Moreover, the thermal properties of the DL-barium salt are studied by means of differential scanning calorimetry (DSC) and thermogravimetric-differential thermal analysis (TG-DTA).

2. EXPERIMENTAL

2.1 Crystal Growth

Single crystals of $DL-BaC_4H_4O_6 \cdot H_2O$ were grown in a silica gel medium at 308 K using the single test tube diffusion method. The gels were prepared in test tubes (length of 200 mm, and diameter of 30 mm) using aqueous solutions of Na_2SiO_3 (25 ml of 1 M), $DL-C_4H_6O_6$ (25 ml of 1 M), and CH_3COOH (25 ml of 1 M), and aged for six days. A solution of $Ba(NO_3)_2$ (30 ml of 0.25 M) was then gently poured on top of the gel. The crystals were harvested after six months. Samples used for measurements were cut from transparent areas on the tips of the crystals.

83 **Table 1. Crystal data, intensity data collection, and structure refinement for DL-**
 84 **BaC₄H₄O₆·H₂O**
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Compound, M_r	BaO ₇ C ₄ H ₆ , 303.42
Crystal color	Colorless
Measurement temperature	299 K
Crystal system, space group	Monoclinic, $P2_1/c$
Lattice constants	$a = 9.3805(3) \text{ \AA}$, $b = 7.8957(3) \text{ \AA}$, $c = 19.0742(7) \text{ \AA}$, $\beta = 91.202(1)^\circ$
V , Z	$1412.43(9) \text{ \AA}^3$, 8
$D(\text{cal.})$, $\mu(\text{Mo } K_\alpha)$, $F(000)$	2.854 Mg m^{-3} , 5.623 mm^{-1} , 1136
Crystal size	$0.14 \times 0.26 \times 0.30 \text{ mm}$
θ range for data collection	$2.14\text{--}38.00^\circ$
Index ranges	$-15 \leq h \leq 15$, $-13 \leq k \leq 13$, $-32 \leq l \leq 32$
Reflections collected, unique	39522, 7446 [$R(\text{int}) = 0.0330$]
Completeness to θ_{max}	96.7 %
Absorption correction type	Numerical
Transmission factor $T_{\text{min}}\text{--}T_{\text{max}}$	0.2647–0.4996
Date, parameter	6669 [$I > 2\sigma(I)$], 266
Final R indices	$R_1 = 0.0288$, $wR_2 = 0.0498$
R indices (all data)	$R_1 = 0.0355$, $wR_2 = 0.0531$
Weighting scheme	$w = 1/[\sigma^2(F_o^2) + (0.016P)^2 + 1.257P]$ $P = (F_o^2 + 2F_c^2)/3$
Goodness-of-fit on F^2	1.162
Extinction coefficient	0.0015(1)
Largest diff. peak and hole	1.916 and $-1.556 \text{ e \AA}^{-3}$

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88 2.2 Structure Determination

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90 The X-ray diffraction measurements were carried out using a Rigaku Saturn CCD X-ray
 91 diffractometer with graphite-monochromated Mo K_α radiation ($\lambda = 0.71073 \text{ \AA}$). The diffraction
 92 data were collected at 299 K using an ω scan mode with a crystal-to-detector distance of 40
 93 mm, and processed using the CrystalClear software package. The intensity data were
 94 corrected for Lorentz polarization and absorption effects. The structure was solved by direct
 95 methods using the SIR2011 program and refined on F^2 by full-matrix least-squares methods
 96 using the SHELXL-2013 program in the WinGX package [15–17].

97 2.3 Thermal Measurements

98 DSC and TG-DTA measurements were carried out in the temperature ranges of 100–490 K
 99 and 300–1550 K, respectively, using DSC7020 and TG-DTA7300 systems from Seiko
 100 Instruments Inc. Aluminium (for DSC) and platinum (for TG-DTA) open pans with no pan
 101 cover were used as measuring vessels and reference pans. Fine powder samples, prepared
 102 by grinding some transparent areas of the crystals, were used for the measurements. The
 103 sample amount varied between 3.02 and 5.22 mg, and the heating rates were 5 or 10 K min⁻¹
 104 under a dry nitrogen gas flow.

3. RESULTS AND DISCUSSION

3.1 Crystal Structure

The crystal structure of DL-BaC₄H₄O₆·H₂O was determined by the single-crystal X-ray diffraction method at room temperature. The lattice parameters calculated from all observed reflections showed that the crystal belongs to the monoclinic system. The intensity statistics and systematic extinctions of the observed reflections revealed that the crystal structure has a centric space group of *P*2₁/*c*. Thus, the space group of DL-BaC₄H₄O₆·H₂O was determined to be monoclinic *P*2₁/*c* with cell parameters *a* = 9.3805(3) Å, *b* = 7.8957(3) Å, *c* = 19.0742(7) Å, and β = 91.202(1)°. The atomic coordinates and thermal parameters of all the atoms including hydrogen atoms were refined. A final *R*-factor of 2.88 % was calculated for 6669 unique observed reflections. The relevant crystal data, and a summary of the intensity data collection and structure refinement parameters are given in Table 1. Figure 1 shows a projected view of the DL-BaC₄H₄O₆·H₂O crystal structure along the *b*-axis. The positional parameters in fractions of the unit cell and the thermal parameters are listed in Table 2. Selected bond lengths and angles are given in Table 3, and the hydrogen-bond geometry is presented in Table 4.

The lattice constants observed along the *a*- and *b*-axes are similar to those previously reported for L-BaC₄H₄O₆, but the value of the *c*-axis is approximately twice as large [5]. Thus, the volume of the unit cell (1412.43(9) Å³) is more than twice that of L-BaC₄H₄O₆ (621.79(3) Å³). Moreover, the calculated density of 2.854 Mg m⁻³ is lower than that of L-BaC₄H₄O₆, which is 3.049 Mg m⁻³. Eight water molecules are present in the unit cell of the observed structure, which were taken from the solution used for crystallization, while there are no water molecules in the L-BaC₄H₄O₆ crystal [5]. This difference is probably strongly related to the difference in the density. The observed structure of DL-BaC₄H₄O₆·H₂O consists of BaO₉ and BaO₁₀ polyhedra, two independent C₄H₄O₆ and H₂O molecules, and O—H···O and C—H···O hydrogen bonds between adjacent C₄H₄O₆ or H₂O molecules. Each Ba atom in the unit cell is surrounded by nine or ten O atoms forming BaO₉ or BaO₁₀ polyhedra, as listed in Table 3. The lengths of the Ba—O bonds are in the range of 2.705(2)–3.128(2) Å, and the average Ba—O distances in the BaO₉ and BaO₁₀ polyhedra are 2.861 and 2.871 Å, respectively. These values are larger than that of the BaO₉ polyhedra in L-BaC₄H₄O₆ (2.818 Å) [5]. This is also considered to be related to the difference in the densities of the crystals.

Table 2. Atomic coordinates and thermal parameters (×10⁴ Å²) for DL-BaC₄H₄O₆·H₂O at room temperature, with standard deviations in brackets. The anisotropic thermal parameters are defined as $\exp[-2\pi^2(U_{11}a^{*2}h^2 + U_{22}b^{*2}k^2 + U_{33}c^{*2}l^2 + 2U_{23}b^*c^*kl + 2U_{13}a^*c^*hl + 2U_{12}a^*b^*hk)]$. The isotropic thermal parameters (Å²) for H atoms are listed under *U*₁₁

Atom	<i>X</i>	<i>Y</i>	<i>Z</i>	<i>U</i> ₁₁	<i>U</i> ₂₂	<i>U</i> ₃₃	<i>U</i> ₂₃	<i>U</i> ₁₃	<i>U</i> ₁₂
Ba(1)	0.47015(2)	0.42311(2)	0.15686(2)	185.8(5)	201.8(6)	181.9(5)	-16.9(4)	37.0(4)	-16.1(4)
Ba(2)	0.03597(2)	0.01576(2)	0.37406(2)	159.8(5)	164.8(5)	186.7(5)	3.2(4)	20.7(3)	14.8(4)
C(1)	0.8607(2)	0.6564(3)	0.2994(1)	227(8)	152(8)	182(8)	22(6)	-9(6)	-10(6)
C(2)	0.7808(2)	0.4880(2)	0.3087(1)	190(8)	139(7)	171(7)	-9(6)	2(6)	-5(6)
C(3)	0.8140(2)	0.4175(2)	0.3825(1)	156(7)	133(7)	171(7)	-7(6)	21(6)	-3(6)
C(4)	0.7183(2)	0.2665(2)	0.3985(1)	143(7)	160(8)	210(8)	28(6)	1(6)	-5(6)
C(5)	0.3495(2)	0.2793(2)	0.3222(1)	183(8)	144(8)	201(8)	-9(6)	8(6)	19(6)
C(6)	0.2848(2)	0.4560(3)	0.3291(1)	156(7)	163(8)	205(8)	16(6)	47(6)	19(6)
C(7)	0.3264(2)	0.5328(2)	0.4013(1)	156(7)	145(8)	220(8)	8(6)	24(6)	14(6)
C(8)	0.2295(2)	0.6826(3)	0.4164(1)	168(7)	179(8)	198(8)	-21(6)	21(6)	30(6)

O(1)	0.8185(2)	0.7781(2)	0.33543(9)	296(8)	154(7)	343(8)	-52(6)	6(6)	-3(6)
O(2)	0.9629(2)	0.6596(2)	0.25779(9)	352(9)	303(9)	250(7)	4(6)	110(7)	-108(7)
O(3)	0.8126(2)	0.3694(2)	0.25521(8)	293(8)	177(7)	200(6)	-45(5)	11(6)	9(6)
O(4)	0.9588(2)	0.3644(2)	0.38705(9)	147(6)	168(6)	298(7)	1(6)	-8(5)	-14(5)
O(5)	0.7628(2)	0.1215(2)	0.3847(1)	222(7)	147(7)	478(10)	-26(7)	66(7)	-22(5)
O(6)	0.5987(2)	0.2963(2)	0.4234(1)	172(7)	296(9)	456(10)	106(8)	105(7)	39(6)
O(7)	0.3009(2)	0.1666(2)	0.3617(1)	236(7)	164(7)	404(9)	63(6)	46(6)	-18(6)
O(8)	0.4459(2)	0.2543(2)	0.27943(9)	340(9)	271(8)	255(7)	35(6)	117(6)	144(7)
O(9)	0.3337(2)	0.5598(2)	0.27432(9)	361(9)	216(7)	261(8)	88(6)	125(7)	85(7)
O(10)	0.4697(2)	0.5877(2)	0.4030(1)	144(6)	207(7)	435(10)	-35(7)	-7(6)	29(5)
O(11)	0.2781(2)	0.8294(2)	0.41464(9)	234(7)	155(6)	349(8)	31(6)	41(6)	31(5)
O(12)	0.1004(2)	0.6479(2)	0.4268(1)	168(7)	306(9)	548(11)	-182(8)	99(7)	-21(6)
O(13)	0.0955(2)	0.3458(3)	0.00649(9)	267(8)	318(9)	249(8)	47(7)	-1(6)	-37(7)
O(14)	0.3939(2)	0.3617(4)	0.0163(1)	338(10)	829(18)	256(9)	-101(11)	-11(8)	155(11)
H(1)	0.890(4)	0.329(4)	0.262(2)	0.038(9)					
H(2)	0.002(4)	0.447(5)	0.402(2)	0.06(1)					
H(3)	0.682(3)	0.514(3)	0.306(1)	0.017(6)					
H(4)	0.797(3)	0.501(3)	0.416(2)	0.020(7)					
H(5)	0.276(5)	0.628(6)	0.265(2)	0.07(1)					
H(6)	0.518(4)	0.509(5)	0.408(2)	0.05(1)					
H(7)	0.181(3)	0.439(4)	0.329(2)	0.021(7)					
H(8)	0.312(3)	0.446(4)	0.435(2)	0.025(7)					
H(9)	0.046(5)	0.265(6)	0.016(2)	0.07(1)					
H(10)	0.170(4)	0.328(5)	0.013(2)	0.04(1)					
H(11)	0.371(6)	0.422(8)	-0.016(3)	0.16(2)					
H(12)	0.449(6)	0.300(7)	-0.001(3)	0.10(2)					

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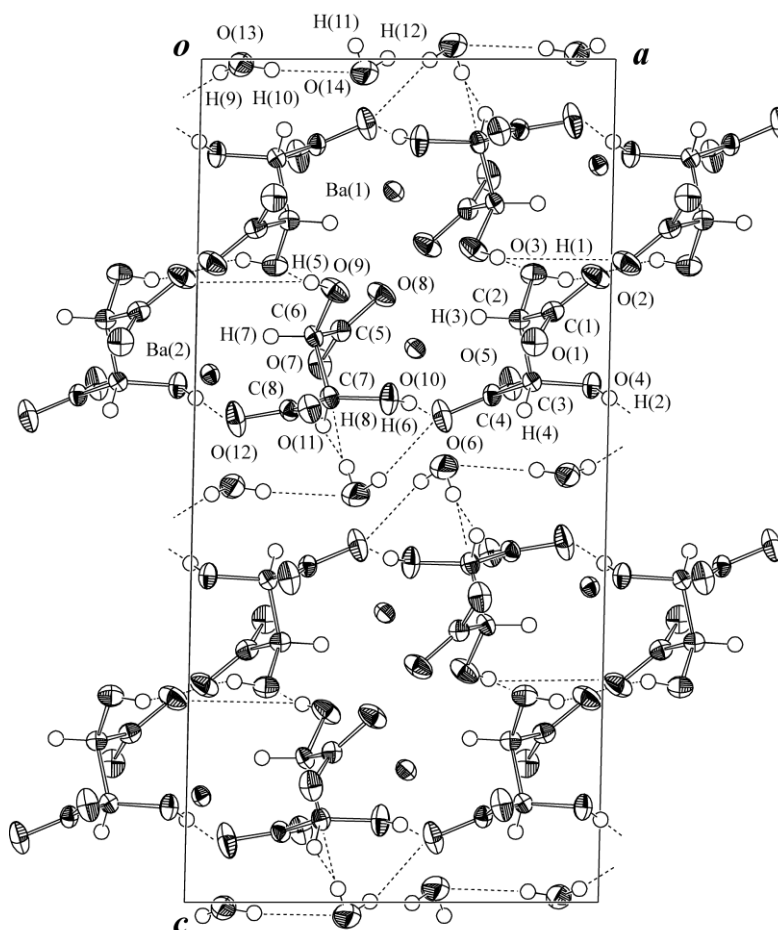


Fig. 1. Projection of the crystal structure of DL-BaC₄H₄O₆·H₂O along the *b*-axis at room temperature with 60% probability-displacement thermal ellipsoids. The solid and dashed short lines indicate O—H···O hydrogen bonds, as shown in Table 4.

The lengths of twelve O—C bonds in the two independent C₄H₄O₆ molecules are in the range of 1.246(2)–1.422(2) Å, as listed in Table 3. The variation in O—C distances is probably related to differences in bond type, as the upper and lower values match the typical lengths of single and double O—C bonds in organic molecules (around 1.43 and 1.22 Å, respectively). Thus, the O(3)—C(2), O(4)—C(3), O(9)—C(6), and O(10)—C(7) bonds on the hydroxyl groups have single-bond character (with lengths of about 1.42 Å), while the remaining eight bonds have double-bond character (with lengths of about 1.25 Å). Moreover, the lengths of six C—C bonds are in the range of 1.523(3)–1.547(3) Å. Since typical C—C single bonds in organic molecules are around 1.54 Å, these six bonds have single-bond character. The angles between the two least-squares planes of atoms in the two C₄H₄O₆ molecules, [O(1)O(2)O(3)C(1)C(2) and O(4)O(5)O(6)C(3)C(4)], and [O(7)O(8)O(9)C(5)C(6) and O(10)O(11)O(12)C(7)C(8)], were calculated to be 30.2(1)° and 42.12(8)°, respectively. These calculated angles are much smaller than that of L-BaC₄H₄O₆ (67.17(8)°), indicating that the C₄H₄O₆ molecules are more planar [5]. Although they do not have completely identical molecular structures due to differences in the occlusal plane angles and in interatomic distances and angles (Table 3), it can be seen that the two independent C₄H₄O₆

196 molecules are related to each other by a mirror plane, and also that the chemically
197 equivalent molecules possessing an inversion center in the unit cell are mirror images of
198 each other. Therefore, it is believed that the $C_4H_4O_6$ molecules in $DL\text{-}BaC_4H_4O_6 \cdot H_2O$ have
199 racemic characters.

200 **Table 3. Selected interatomic distances (in Å) and angles (in degrees) for $DL\text{-}$**
201 **$BaC_4H_4O_6 \cdot H_2O$**

Ba(1)–O(1) ¹	2.946(2)	Ba(1)–O(5) ²	2.790(2)
Ba(1)–O(7) ²	2.909(2)	Ba(1)–O(8) ²	2.982(2)
Ba(1)–O(8)	2.705(2)	Ba(1)–O(9)	2.819(2)
Ba(1)–O(10) ¹	2.943(2)	Ba(1)–O(11) ¹	2.849(2)
Ba(1)–O(14)	2.802(2)	Ba(1)–C(4) ²	3.393(2)
Ba(1)–C(5) ²	3.302(2)	Ba(2)–O(1) ³	2.857(2)
Ba(2)–O(2) ¹	2.760(2)	Ba(2)–O(3) ¹	3.095(2)
Ba(2)–O(4) ⁴	2.858(2)	Ba(2)–O(5) ⁴	2.706(2)
Ba(2)–O(7)	2.771(2)	Ba(2)–O(11) ⁵	2.802(2)
Ba(2)–O(12) ⁵	3.128(2)	Ba(2)–O(13) ⁶	2.798(2)
Ba(2)–O(13) ⁷	2.938(2)	Ba(2)–C(8) ⁵	3.287(2)
O(1)–C(1)	1.251(3)	O(2)–C(1)	1.258(3)
O(3)–C(2)	1.421(2)	O(4)–C(3)	1.422(2)
O(5)–C(4)	1.249(3)	O(6)–C(4)	1.249(2)
O(7)–C(5)	1.257(2)	O(8)–C(5)	1.246(2)
O(9)–C(6)	1.412(2)	O(10)–C(7)	1.413(2)
O(11)–C(8)	1.247(3)	O(12)–C(8)	1.261(2)
C(1)–C(2)	1.538(3)	C(2)–C(3)	1.540(3)
C(3)–C(4)	1.528(3)	C(5)–C(6)	1.528(3)
C(6)–C(7)	1.547(3)	C(7)–C(8)	1.523(3)
O(1)–C(1)–O(2)	125.9(2)	O(1)–C(1)–C(2)	116.1(2)
O(2)–C(1)–C(2)	118.0(2)	O(3)–C(2)–C(1)	112.2(2)
O(3)–C(2)–C(3)	112.1(2)	O(4)–C(3)–C(2)	109.7(2)
O(4)–C(3)–C(4)	108.8(2)	O(5)–C(4)–O(6)	124.1(2)
O(5)–C(4)–C(3)	118.2(2)	O(6)–C(4)–C(3)	117.7(2)
O(7)–C(5)–O(8)	123.9(2)	O(7)–C(5)–C(6)	116.4(2)
O(8)–C(5)–C(6)	119.7(2)	O(9)–C(6)–C(5)	109.3(2)
O(9)–C(6)–C(7)	110.6(2)	O(10)–C(7)–C(6)	111.2(2)
O(10)–C(7)–C(8)	109.3(2)	O(11)–C(8)–O(12)	124.0(2)
O(11)–C(8)–C(7)	119.8(2)	O(12)–C(8)–C(7)	116.1(2)
C(1)–C(2)–C(3)	109.2(2)	C(2)–C(3)–C(4)	110.9(2)
C(5)–C(6)–C(7)	110.0(2)	C(6)–C(7)–C(8)	109.4(2)

203 (Symmetry codes: (1) $-x+1, y-1/2, -z+1/2$; (2) $-x+1, y+1/2, -z+1/2$; (3) $x-1, y-1, z$; (4) $x-1, y, z$; (5)
204 $x, y-1, z$; (6) $x, y+1/2, z+1/2$; (7) $-x, y-1/2, -z+1/2$.)

205 The H_2O molecules are interstitially intercalated between the $C_4H_4O_6$ molecules, leaving
206 them at intervals of one-half of the c -axis distance, as shown in Fig. 1. The $O-H\cdots O$ and $C-$
207 $H\cdots O$ hydrogen bonds, which are formed between adjacent H_2O or $C_4H_4O_6$ molecules, build

hydrogen-bonding networks in the *bc*-plane. The structures formed by the networks in DL-BaC₄H₄O₆·H₂O differ significantly from that formed by the zig-zag hydrogen-bonding networks along the *a*- and *c*-axes in L-BaC₄H₄O₆ [5]. The lengths of the O—H···O bonds are in the range of 2.695(2)–3.286(3) Å, while of the C—H···O bonds are in the range of 3.353(2)–3.855(3) Å, as shown in Table 4. The C—H···O bonds are longer than the O—H···O bonds. Thus, the bonding strength of the C—H···O bonds is weaker than that of the O—H···O bonds since the magnitude of bonding strength is mainly reflected in the bond length.

Table 4. Hydrogen bond distances (in Å) and angles (in degrees)

D—H···A	D—H	H···A	D···A	<D—H···A
O(3)—H(1)···O(2) ¹	0.80(3)	1.96(3)	2.695(2)	152(3)
O(4)—H(2)···O(12) ²	0.81(4)	1.89(4)	2.704(2)	174(4)
O(9)—H(5)···O(3) ³	0.78(5)	2.11(4)	2.853(2)	159(4)
O(10)—H(6)···O(6)	0.78(4)	1.86(4)	2.625(2)	168(4)
O(13)—H(9)···O(12) ⁴	0.81(5)	1.99(4)	2.745(2)	153(4)
O(13)—H(10)···O(14)	0.72(4)	2.12(4)	2.804(3)	160(4)
O(14)—H(11)···O(7) ⁵	0.80(6)	2.52(6)	3.066(3)	127(5)
O(14)—H(11)···O(11) ⁶	0.80(6)	2.51(6)	3.286(3)	162(6)
O(14)—H(12)···O(6) ⁵	0.79(5)	2.17(5)	2.921(3)	159(5)
C(2)—H(3)···O(8) ³	0.95(3)	2.75(3)	3.408(3)	126(2)
C(2)—H(3)···O(8)	0.95(3)	3.05(3)	3.676(3)	125(2)
C(2)—H(3)···O(10)	0.95(3)	2.81(3)	3.548(3)	135(2)
C(3)—H(4)	0.94(3)			
C(6)—H(7)···O(4) ⁷	0.99(3)	2.45(3)	3.353(2)	152(2)
C(7)—H(8)···O(14) ⁸	0.95(3)	2.98(3)	3.855(3)	154(2)

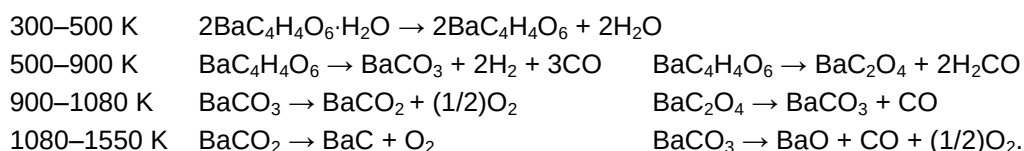
(Symmetry codes: (1) $-x+2, y-1/2, -z+1/2$; (2) $x+1, y, z$; (3) $-x+1, y+1/2, -z+1/2$; (4) $-x, y-1/2, -z+1/2$; (5) $x, -y+1/2, z-1/2$; (6) $x, -y+3/2, z-1/2$; (7) $x-1, y, z$; (8) $x, -y+1/2, z+1/2$.)

3.2 Thermal Analysis

Figure 2 shows the DTA, TG, and differential TG (DTG) curves of the DL-BaC₄H₄O₆·H₂O crystal in the temperature range of 300–1550 K. The sample weight (powder) used for the measurements was 5.22 mg, and the heating rate was 10 K min⁻¹ under a nitrogen gas flow of 300 ml min⁻¹. The DTA curve exhibits five endothermic peaks at 328.9, 523.3, 733.7, 1062.6, and 1283.3 K, including small peaks. Moreover, eight peaks at 328.4, 527.0, 541.2, 587.4, 632.5, 725.9, 1050.6, and 1276.4 K, including a small shoulder peak, are observed in the DTG curve. These DTA peaks correspond relatively closely to the respective DTG peaks. The DTG curve, which is the first derivative of TG curve, reveals the temperature dependence of the rate of weight loss. Thus, the DTA peaks are associated with the maximum rate of weight loss in the TG curve due to thermal decomposition of the sample.

DSC measurements on the powder sample of DL-BaC₄H₄O₆·H₂O were performed in the temperature range from 100 to 490 K at a heating rate of 5 K min⁻¹. No obvious endothermic or exothermic peaks were observed in the DSC curve, except for a weak broad endothermic peak at 322.7 K corresponding to that at 328.9 K in the DTA curve. In general, it is believed that a clear peak in DSC curve is attributed to a change in exchange energy at a phase transition. Thus, the obtained results indicate that there is no phase transition in the temperature range of 100–322 K for the DL-BaC₄H₄O₆·H₂O crystal.

The TG curve shows the temperature-dependent weight loss of the DL-BaC₄H₄O₆·H₂O crystal. After heating the sample up to 1550 K, a mixture of chalky white and black substances was found in the open vessel. In previous papers, we have reported that white oxide products remain in the vessel after TG-DTA measurements of L-SrC₄H₄O₆·4H₂O, DL-CaC₄H₄O₆·4H₂O, and DL-SrC₄H₄O₆·4H₂O, and that after the evolution of gases from L-BaC₄H₄O₆, barium monocarbide (BaC) remains on the inside surface of the vessel, which turns black in color [4,5,13,14]. There are two types of crystallographically independent C₄H₄O₆ molecules in the unit cell of DL-BaC₄H₄O₆·H₂O. Consequently, we consider that the white oxide and monocarbide products are each generated from one of the two C₄H₄O₆ molecules. The chemical reactions during the decompositions of L-BaC₄H₄O₆ and DL-CaC₄H₄O₆·4H₂O mentioned in the introduction allow us to assume that two reaction processes are involved in the decomposition of DL-BaC₄H₄O₆·H₂O, and that these can be represented as follows:



The experimental weight losses obtained from the TG analysis, the theoretical losses based on the chemical reactions above, and the molecular gases eliminated at various temperature ranges are summarized in Table 5. The theoretical losses calculated for each temperature range match closely with the experimental data. However, there is a difference of 1.8% between the theoretical and experimental losses in the temperature range of 300–500 K, as shown in Table 5. In general, there are many defects in the crystal structure, such as pores and cracks, and the aqueous solution used for crystal growth can infiltrate these defects. Thus, the difference in the range of 300–500 K is probably caused by the evaporation of the infiltrated solution from these defects, and this is also the cause of the slight difference between the experimental and theoretical total losses. The other slight differences between the experimental and theoretical values at each temperature range are probably a result of overlapping temperature ranges corresponding to the decomposition reactions. The residual chalky white and black substances remaining in the vessel after heating the sample up to 1550 K are barium oxide (BaO) and BaC, respectively, as suggested by the chemical equations as described above. If significant differences in the Ba–O or Ba–C distances exist, we can determine the corresponding relation between the evaporation products (BaO or BaC) and the two C₄H₄O₆ molecules. However, we could not find a relationship between the products and molecules because of the lack of the significant differences in these distances, as shown in Table 3.

Table 5. TG results for thermal decomposition of DL-BaC₄H₄O₆·H₂O

Temp. range [K]	Weight loss (obs.) [%]	Weight loss (cal.) [%]	Elimination molecules
300–500	7.7	5.9	2H ₂ O
500–900	25.4	24.4	2H ₂ + 3CO + 2H ₂ CO
900–1080	9.2	7.3	(1/2)O ₂ + CO
1080–1550	10.3	12.5	(3/2)O ₂ + CO
Total	52.6	50.1	

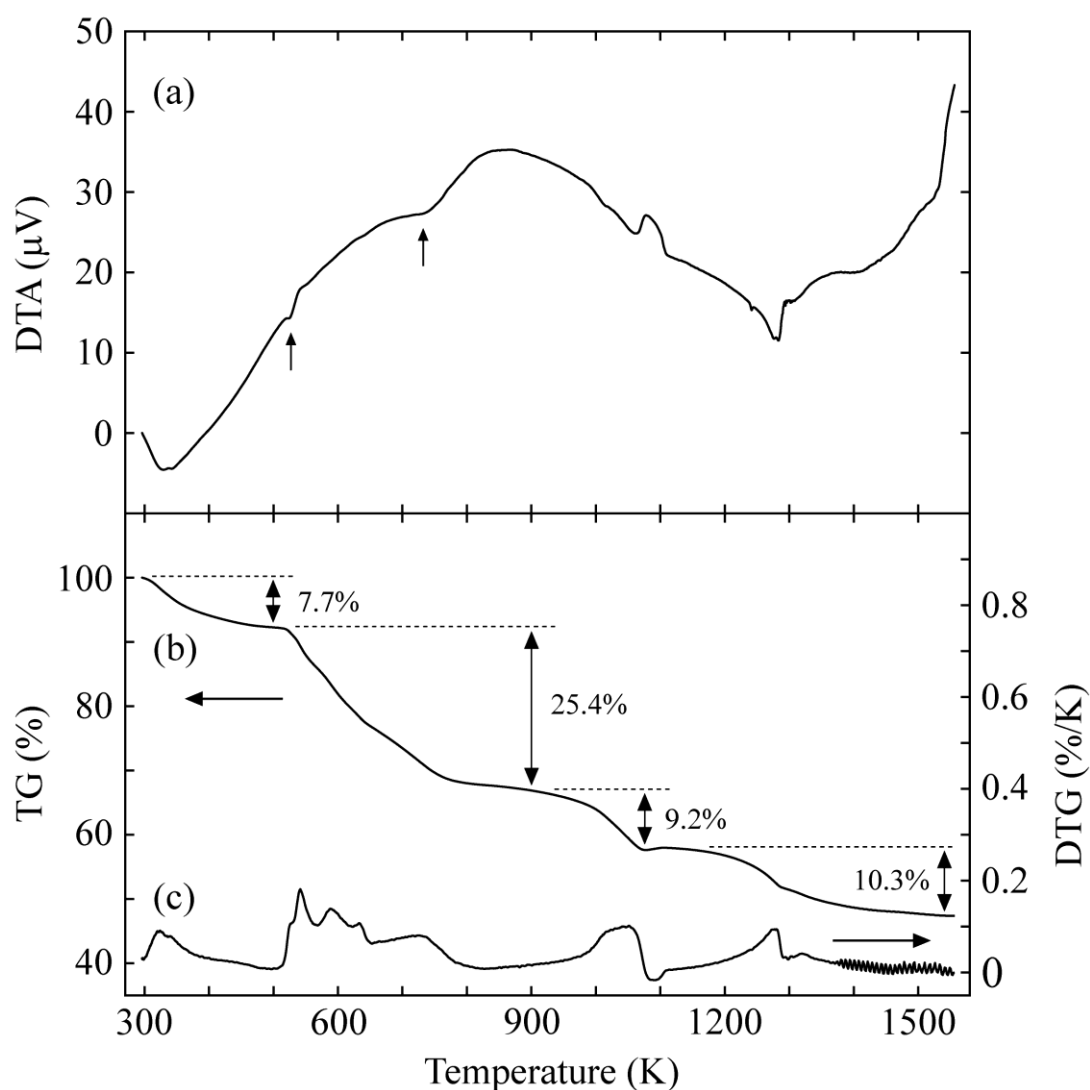


Fig. 2. TG, DTG, and DTA thermograms for DL-BaC₄H₄O₆·H₂O crystal on heating. The sample weight (powder) was 5.22 mg, and the heating rate was 10 K min⁻¹ under a dry N₂ flux of 300 ml min⁻¹

4. SUMMARY

Single crystals of DL-BaC₄H₄O₆·H₂O have been grown in silica gel medium at 308 K by the diffusion method. The thermal properties and crystal structure of the single crystals are studied by DSC, TG-DTA, and X-ray diffraction. The room temperature crystal structure, including the positional and thermal parameters of all the hydrogen atoms, is determined to be monoclinic with space group *P*2₁/*c* by means of single-crystal X-ray diffraction. We found that the structure consists of BaO₉ and BaO₁₀ polyhedra, two independent C₄H₄O₆ molecules, and O–H···O and C–H···O hydrogen bonds between adjacent H₂O or C₄H₄O₆ molecules. No phase transition was observed in the temperature range of 100–322 K, and weight losses due to the thermal decomposition of DL-BaC₄H₄O₆·H₂O were found to occur in

the temperature range of 300–1550 K. The chemical equations illustrating the decomposition reactions of $\text{DL-BaC}_4\text{H}_4\text{O}_6 \cdot \text{H}_2\text{O}$ are presented with the corresponding temperature ranges. We concluded that the weight losses are caused by the evaporation of two bound water molecules and the evolution of $2\text{H}_2\text{CO}$, 2H_2 , 5CO , and 2O_2 gases from the two independent $\text{C}_4\text{H}_4\text{O}_6$ molecules, and that the residual chalky white and black substances mixed together in the vessel after decomposition are BaO and BaC , respectively.

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