

Hydrogen Bonds in the Structure of $\text{BaC}_2\text{O}_4 \cdot \text{D}_2\text{O}$

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The hydrogen bonds in the crystal structure of $\text{BaC}_2\text{O}_4 \cdot \text{D}_2\text{O}$ were investigated from profile refinement of neutron powder diffraction data. The structure is monoclinic, space group $C2/m$ (No. 12) with the lattice parameters $a = 10.0648(3)$, $b = 7.9350(2)$, $c = 6.8503(2)$ Å, $\beta = 122.35(2)^\circ$ and $Z = 4$. The barium atom in the structure is coordinated with ten oxygen atoms, the oxalate ion is planar, and the OD–O hydrogen-bond length is $2.762(5)$ Å.

The crystal structure of lead oxalate¹ was recently investigated by powder diffraction methods, and this study created an interest in an investigation of the structures of barium oxalates. A number of hydrates have been reported for barium oxalate, $\text{BaC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$,² $\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$,^{2,4} $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}^{2.5}$ and $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$,⁶ as well as two modifications of the anhydrous compound BaC_2O_4 .² The crystal structure of $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ has earlier been studied by the single-crystal X-ray film technique using Mo $K\alpha$ radiation.⁵ However, the hydrogen bonding of the structure was not described. In this paper investigation of the hydrogen bonding using neutron powder diffraction data and a deuterated sample of $\text{BaC}_2\text{O}_4 \cdot \text{D}_2\text{O}$ is reported.

Experimental

Preparation of barium oxalate hydrates. The compounds were made from CO_2 -free solutions of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ (Merck p.a.) and $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ (Merck p.a.). The purity of the hydrates was investigated with Guinier photographs which were taken with a Nonius Guinier camera using Cu $K\alpha_1$ radiation ($\lambda = 1.540598$ Å) and silicon as internal standard ($a_{\text{Si}} = 5.43050$ Å). The positions and intensities of the Bragg reflections of a powder pattern

were measured on a photometer and compared with the respective JCPDS data cards (Table 1).

(i) $\text{BaC}_2\text{O}_4 \cdot 3.5 \text{H}_2\text{O}$ and $\text{BaC}_2\text{O}_4 \cdot 0.5 \text{H}_2\text{O}$. 50 ml of a 0.05 M solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were added dropwise to 250 ml of a 0.07 M solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The white crystalline precipitate was $\text{BaC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$. 500 ml of a 0.20 M solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$ were added dropwise to 500 ml of a 0.20 M solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$. The precipitated barium oxalate was washed by decanting, filtered and dried on the filter at room temperature. The white crystalline product was $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$.

(ii) $\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$ and $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$. 300 ml of a 0.133 M solution of $(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ was added dropwise to 50 ml of a 0.80 M solution of $\text{BaCl}_2 \cdot 2\text{H}_2\text{O}$. The precipitate was filtered and washed on the filter and had the composition $\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$. After drying at room temperature the composition of the white crystalline product was $\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$.

(iii) $\text{BaC}_2\text{O}_4 \cdot \text{D}_2\text{O}$. When the barium chloride solution was added dropwise to the ammonium oxalate solution, the final crystalline product, after drying at room temperature, was the hemihydrate of barium oxalate, $\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$. When the ammonium oxalate solution was added dropwise to the barium chloride solution, the final crystalline prod-

Table 1. Results from DTA and TGA of the conversion of barium oxalate hydrates into barium oxalate.

Compound	JCPDS card no.	Endothermic transition maxima/ $^\circ\text{C}$		Mass of barium oxalate after dehydration of 100 mg hydrate/mg		
		This work	Ref. 2 ^a	This work	Ref. 2	Calculated values
$\text{BaC}_2\text{O}_4 \cdot 0.5\text{H}_2\text{O}$	20–134	118	140	96.3	96	96.2
$\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$	20–135	155	165	95.3	92.7	92.6
$\text{BaC}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$	20–136	69, 99, 130	100, 110, 160	87	86.3	86.2
$\text{BaC}_2\text{O}_4 \cdot 3.5\text{H}_2\text{O}$	20–137	95, 108, 150	75, 105, 165	84	78.0	78.1

^aHeating rate 150°C h^{-1} .

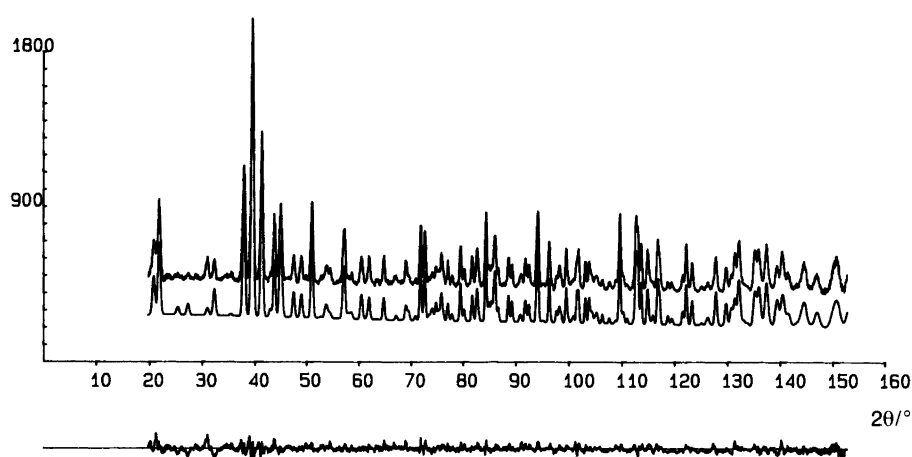


Fig. 1. Neutron diffraction powder pattern of BaC₂O₄ · D₂O. The upper and lower curves represent the observed and calculated profiles, respectively, with the difference shown in the lower part of the figure. The intensities (on the ordinate) are on an arbitrary scale.

uct, after drying at room temperature, was the monohydrate of barium oxalate, BaC₂O₄ · H₂O. These findings were used in the preparation of a deuterated sample of barium oxalate monohydrate. 150 ml of a 0.333 M solution of (NH₄)₂C₂O₄ · H₂O in D₂O (Norsk Hydro, 99.9%) were added dropwise to 50 ml of a 1.00 M solution of BaCl₂ · 2H₂O in D₂O. The precipitated barium oxalate was filtered and dried in an evacuated desiccator over silica gel at room temperature. The white crystalline product was pure BaC₂O₄ · D₂O.

Physical characterization. Differential thermal analysis and thermogravimetric analysis were made of the barium oxalate hydrates, and the results are listed in Table 1. A Stanton Redcroft TG-DTA simultaneous thermal analyser STA 1000/1500 was used in the measurements, and a heating rate of 600 °C h⁻¹ was applied. The results obtained are comparable with the data reported in Ref. 2. However, the maxima of the endothermic transitions in this work are observed at lower temperatures than in Ref. 2, and the loss in weight of BaC₂O₄ · 3.5H₂O to BaC₂O₄ was found to be less than in Ref. 2.

The infrared spectrum of BaC₂O₄ · H₂O was measured on a Nicolet Analytical Instrument MX5 spectrometer using a pellet of 2% BaC₂O₄ · H₂O in KBr. The spectrum had an absorption band at 3450 cm⁻¹, corresponding to a weak hydrogen bond.

Neutron powder diffraction. A neutron diffraction powder pattern of BaC₂O₄ · D₂O was measured at room temperature on the multidetector diffractometer D1A at the Institut Laue-Langevin, Grenoble, using 1.909 Å neutrons. The pattern was measured in the 2θ range 20.00–153.00° in steps of 0.05°. The sample was housed in a 12 mm diameter vanadium container.

Structural analysis and discussion

The coordinates of the atoms of the structure found in the X-ray investigation⁵ are listed in brackets in Table 2. Pack-

ing considerations suggest that the oxygen atom O3 of the water molecule is hydrogen bonded to the oxygen atom O1 of the oxalate ion, and that the coordinates of the hydrogen/deuterium atom are close to (0.41, 0.09, 0.13). This model was used in a profile refinement⁸ with the neutron powder diffraction data using the program EDINP⁹ and nuclear scattering contributions from Ref. 10. The following parameters were refined: a scale factor, a zero point of the diffractometer, four profile parameters, four unit-cell parameters, 16 positional parameters of the model and six isotropic temperature factor parameters for the atoms. Values for the refined parameters are listed in Table 2, and Fig. 1 displays the observed and calculated neutron diffraction powder pattern with a difference plot. A projection of the structure along *c** of BaC₂O₄ · D₂O is shown in Fig. 2.

The crystal structure of BaC₂O₄ · D₂O has one independent barium atom, one independent C₂O₄²⁻ ion and one

Table 2. Refined parameters^a for the structure of BaC₂O₄ · D₂O, space group *C2/m* (No. 12). Atomic coordinates from the single-crystal X-ray analysis⁵ in brackets.

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>	<i>B/Å</i> ²
Ba	0.2183(10) [0.2175(1)]	0.0 0.0	0.3167(13) 0.3153(1)]	0.1(1)
C1	0.3612(6) [0.3615(18)]	0.3987(4) 0.4030(19)	0.2390(9) 0.2405(26)]	0.0(1)
O1	0.4140(5) [0.4133(12)]	0.3326(6) 0.3346(21)	0.1281(9) 0.1305(21)]	0.0(1)
O2	0.3114(6) [0.3102(13)]	0.3295(6) 0.3300(22)	0.3484(9) 0.3516(26)]	0.7(1)
O3	0.4756(10) [0.4712(18)]	0.0 0.0	0.2674(13) 0.2439(46)]	0.9(2)
D1	0.4639(7)	0.0938(8)	0.1789(12)	5.2(2)

^a Refined parameters: Scale factor = 0.103(1), zero point = 0.340(2), *U* = 0.195(7), *V* = -0.514(14), *W* = 0.453(9), *T* = 0.003(8). FWHM = (*U* tan² θ + *V* tan θ + *W*)^{1/2} + *T*/cos θ. *a* = 10.0648(3), *b* = 7.9350(2), *c* = 6.8503(2) Å, β = 122.35(2)°. *R*_p = 5.5%, *R*_{wp} = 6.4%, *R*_i = 10.1%, *R*_F = 8.4%, *R*_E = 4.7%. The definitions of the *R*-values are given in Refs. 1 and 7.

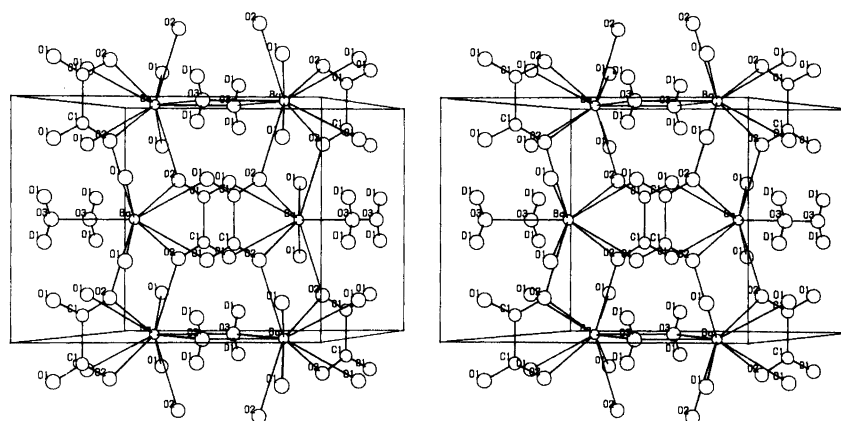


Fig. 2. Projection of the structure of $\text{BaC}_2\text{O}_4 \cdot \text{D}_2\text{O}$ along c^* . The a -axis is along the page.

Table 3. Interatomic distances (in Å) of $\text{BaC}_2\text{O}_4 \cdot \text{D}_2\text{O}$ and related compounds.

Atoms	Distances	Literature values	
Ba—O2×2	2.747(6)	BaSO_4 ¹¹	
Ba—O3	2.785(9)	Ba—O	2.768(4)—3.075(3)
Ba—O2×2	2.814(6)	$\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ⁵	
Ba—O3	2.866(9)	Ba—O	2.76(2)—2.99(2)
Ba—O1×2	2.912(9)		
Ba—O1×2	2.929(9)		
C1—O2	1.231(9)	PbC_2O_4 [†]	
C1—O1	1.252(9)	C—O	1.229(9)—1.275(9)
C1—C1	1.608(5)	C—C	1.561(8)—1.581(9)
O3—D1×2	0.927(9)	$\text{CaC}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ¹²	
O3—O1	2.762(5)	C—O	1.229(8)—1.253(4)
		C—C	1.530(8)—1.550(4)
O1—D1	1.943(9)	$\text{BaC}_2\text{O}_4 \cdot \text{H}_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}$ ¹³	
		C—O	1.21(6)—1.37(5)
		C—C	1.52(6)
		O—O	2.76(5)

independent water molecule. The barium atom is coordinated with ten oxygen atoms, eight oxygen atoms from oxalate ions and two oxygen atoms from the water molecules. The interatomic distances in this coordination polyhedron are listed in Table 3. The oxalate ion is planar and has distances comparable with the planar oxalate ions in the structure of lead oxalate.¹ The structure has hydrogen bonds, O3—D1...O1, and the distance of 2.762(5) Å corresponds to a weak hydrogen bond.

The precisions of the atomic coordinates found in this investigation are, except for the barium atom, higher than the precision found in Ref. 5. This shows that structures derived from single-crystal X-ray film data can be improved by neutron powder diffraction data measured on high-resolution powder diffractometers.

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