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Structure data at 150 K for diammonium oxalate monohydrate, $[\text{NH}_4]_2[\text{C}_2\text{O}_4][\text{H}_2\text{O}]$

Abstract

The single crystals of perfectly quality of the diammonium oxalate monohydrate, $[\text{NH}_4]_2[\text{C}_2\text{O}_4][\text{H}_2\text{O}]$, were obtained by the improved methods of crystal growth from solution. The crystal structure of title compound was studied at 150 K using modern X-ray equipment. At this temperature, as well as at room temperature, this compound crystallizes in the orthorhombic symmetry with $P2_12_12$ space group. The unit cell of the title compound is formed by four ammonium cations, two oxalate anions and water molecules, with a 2:1:1 cation-anion-water ratio. At 150 K oxalate ion is twisted by $26.9 (1)^\circ$. The similar twist angle ($26.6 (4)^\circ$) was observed at the room temperature. Central carbon-carbon bond in oxalate ion is insignificantly longer (1.568 \AA) in comparing with this bond at room temperature (1.559 \AA).

Keywords: oxalates; crystal structure; X-ray diffraction

Introduction

The first data about the crystallographic structure of ammonium oxalate (AO) monohydrate crystals $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$ were given by Groth,^[1] while the first X-ray analysis of AO structure was conducted by Hendricks and Jefferson.^[2] The results of more precise measurements of the AO crystallographic structure were reported later by Jeffrey and Parry,^[3] Robertson^[4] and Cadene and Fournel.^[5] At room temperature AO crystallizes in the orthorhombic system (space group $P2_12_12$) and has lattice parameters $a = 8.035 \text{ \AA}$, $b = 10.309 \text{ \AA}$ and $c = 3.795 \text{ \AA}$.^[6]

In recent years several papers have been published on ammonium oxalate monohydrate crystals obtained from pure aqueous solutions^[7,8] and from solutions containing impurities: Cu(II),^[9] Fe(III),^[10] Cr(III),^[11] Mn(II),^[12] Co(II) and Ni(II).^[13] These papers have been devoted to growth kinetics, crystal surface morphology and habit, and impurity segregation.^[14] It was found that the growth kinetics of AO crystals and segregation coeffi-

cient of different impurities in the crystals obtained from aqueous solutions differ enormously. Impurities responsible for inducing changes in crystal growth kinetics simultaneously build into the crystal structure. This phenomenon is known as impurity segregation. Supersaturation used for growth and growth temperature are the factors which influence growth kinetics and impurity segregation. This means that there is a relationship between processes responsible for changes in morphology and the value of segregation coefficient.

Experimental

Computing details

Data collection: *CrysAlis PRO* (Agilent Technologies, 2011);^[15] cell refinement: *CrysAlis PRO* (Agilent Technologies, 2011);^[15] data reduction: *CrysAlis PRO* (Agilent Technologies, 2011);^[15] program used to solve structure: *SHELXS97* (Sheldrick, 1990);^[16] program used to refine structure: *SHELXL97* (Sheldrick, 1997);^[16] molecular graphics: *DIAMOND* (Brandenburg, 2006).^[17]

Crystal growth

The experimental procedure for the growth of ammonium oxalate monohydrate crystals has been described in detail in our earlier studies.^[7,13] They were grown on seeds from solutions of known supersaturation (s), at a temperature of 30 °C (stabilization ± 0.02 °C) in 1 liter round-bottomed flasks containing supersaturated solutions surrounded by a water jacket. A glass stirrer and a hanging seed, tied by a polyacryl thread to the stirrer blade, were first dipped in distilled water heated to a temperature of about 5-10 °C above the growth temperature for a few seconds and then inserted in the solution. The stirrer and the mounted seed were connected to an auxiliary mechanism which enabled growth with stirring. The solutions were prepared from doubly-distilled water and analytically pure $[(\text{NH}_4)_2\text{C}_2\text{O}_4 \cdot \text{H}_2\text{O}]$. The solution supersaturation s was calculated from the solubility data,^[18] using the relation $s = (c - c_0)/c_0$ where c_0 is the equilibrium solubility and c is the actual solubility at the growth temperature 30 °C. The supersaturation (s) used for growth was 4 %.

Results and discussion

Since the last X-ray analyses of the AO crystal structure date back to 1977 and these crystals are still being investigated, it was thought worthwhile to carry out a structure refinement for ammonium oxalate monohydrate crystals at 150 K. This is the aim of the present communication.

Obtained single-crystal data show that the title compound at 150 K crystallizes with the orthorhombic space group $P2_12_12$. Only $h00 : h = 2n$; $0k0 : k = 2n$ (for general) and $hk0 : h+k = 2n$ (for special) reflections were observed in the recorded data set, clearly indicating that this crystal structure possesses a P -orthorhombic unit cell. Possible space

groups for the title compound were $P2_12_12$ (№ 18) and $P2_12_12_1$ (№ 19). The test of statistical distribution of intensities $|E^2-1|$ gives 0.736 with strong indication of non-centrosymmetrical character. In fact the adequate structural model was deduced from an automatic interpretation of direct methods with the *SHELX-97* package programs in the non-centrosymmetric $P2_12_12$ space group; this model is also associated with the lowest combined figure of merit. Crystal refinement and data collection for $[\text{NH}_4]_2[\text{C}_2\text{O}_4][\text{H}_2\text{O}]$ are given in Table 1.

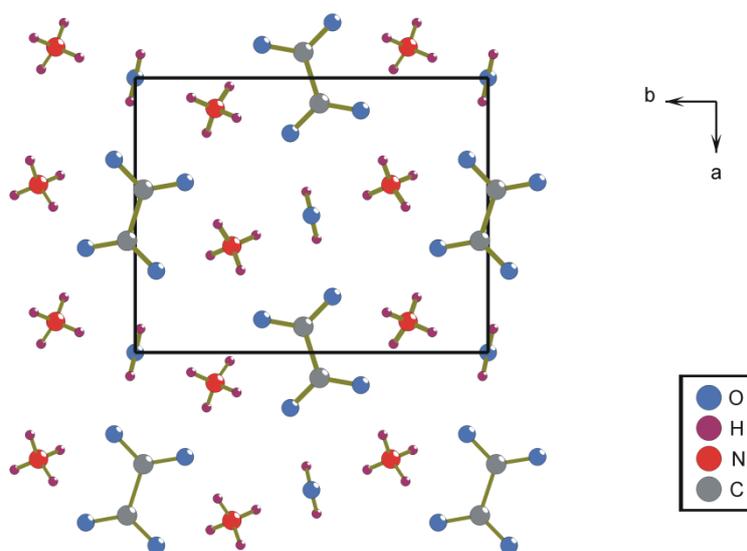
Table 1. Crystal refinement and data collection for $[\text{NH}_4]_2[\text{C}_2\text{O}_4][\text{H}_2\text{O}]$.

Crystal data	
$[\text{NH}_4]_2[\text{C}_2\text{O}_4][\text{H}_2\text{O}]$	$F(000) = 152$
$M_r = 142.12$	$D_x = 1.513 \text{ Mg m}^{-3}$
Orthorhombic, $P2_12_12$	Mo $K\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$
Hall symbol: P 2 2ab	Cell parameters from 468 reflections
$a = 8.0320 (2) \text{ \AA}$	$\theta = 3.2\text{-}27.9^\circ$
$b = 10.3110 (4) \text{ \AA}$	$\mu = 0.15 \text{ mm}^{-1}$
$c = 3.7663 (1) \text{ \AA}$	$T = 150 \text{ K}$
$V = 311.92 (2) \text{ \AA}^3$	Prismatic platelet, colourless
$Z = 2$	$0.09 \times 0.06 \times 0.02 \text{ mm}$
Data collection	
Xcalibur, Eos, Gemini ultra diffractometer	468 independent reflections
Radiation source: Enhance (Mo) X-ray Source	462 reflections with $I > 2\sigma(I)$
graphite	$R_{\text{int}} = 0.014$
ω scans	$\theta_{\text{max}} = 27.9^\circ$, $\theta_{\text{min}} = 3.2^\circ$
Absorption correction: multi-scan <i>CrysAlis PRO</i> (Agilent Technologies, 2011)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.984$, $T_{\text{max}} = 0.999$	$k = -13 \rightarrow 12$
3647 measured reflections	$l = -4 \rightarrow 4$
Refinement	
Refinement on F^2	Hydrogen site location: structure-invariant direct methods
Least-squares matrix: full	All H-atom parameters refined
$R[F^2 > 2\sigma(F^2)] = 0.023$	$w = 1/[\sigma^2(F_o^2) + (0.0405P)^2 + 0.0192P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.066$	$(\Delta/\sigma)_{\text{max}} = 0.001$
$S = 1.29$	$\Delta_{\text{max}} = 0.30 \text{ e \AA}^{-3}$
468 reflections	$\Delta_{\text{min}} = -0.13 \text{ e \AA}^{-3}$

Table 1. (cont.).

Refinement	
64 parameters	Extinction correction: <i>SHELXL</i> , $F_c^* = kFc [1 + 0.001x Fc^2 \lambda^3/\sin(2\theta)]^{-1/4}$
0 restraints	Extinction coefficient: 0.15 (3)
Primary atom site location: structure-invariant direct methods	Absolute structure: Flack H. D., <i>Acta Cryst.</i> , 1983, A39, 876-881
Secondary atom site location: difference Fourier map	Flack parameter: 0 (10)

The projection of the unit cell is shown in Figure 1. The geometrical parameters are presented in Table 2. At 150 K oxalate ion is twisted by 26.9 (1)°, similar to that at room temperature (26.6 (4)°). Central carbon-carbon bond in oxalate ion is longer (1.568 Å) compared with that bond at room temperature (1.559 Å). This insignificant abnormal change in carbon-carbon bond probable is the result of the use of modern and more precision equipment.

**Figure 1.** The unit-cell contents viewed along *c* and cation-anion packing.**Table 2.** Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²).

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	U_{iso}^*/U_{eq}
O1A	0.0000	0.0000	0.1851 (4)	0.0241 (3)
H1A	0.427 (2)	0.342 (2)	0.537 (5)	0.032 (4)*

Table 2. (cont.).

Atoms	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$		
N1	0.38822 (13)	0.27426 (10)	0.4263 (3)	0.0212 (3)		
H1	0.469 (2)	0.2330 (16)	0.291 (5)	0.036 (5)*		
H2	0.3549 (18)	0.2126 (18)	0.581 (6)	0.030 (4)*		
H3	0.300 (2)	0.2980 (16)	0.286 (5)	0.024 (4)*		
H4	0.086 (2)	0.015 (2)	0.044 (5)	0.040 (5)*		
C1	0.09298 (14)	0.47680 (11)	0.0698 (3)	0.0190 (3)		
O1	0.11927 (10)	0.35935 (8)	0.0020 (3)	0.0239 (3)		
O2	0.20197 (10)	0.55974 (8)	0.1401 (3)	0.0249 (3)		
Atomic displacement parameters (\AA^2)						
Atoms	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1A	0.0183 (5)	0.0256 (6)	0.0285 (7)	-0.0003 (5)	0.000	0.000
N1	0.0219 (5)	0.0197 (5)	0.0220 (5)	0.0015 (4)	-0.0001 (4)	0.0002 (4)
C1	0.0178 (5)	0.0208 (6)	0.0184 (5)	0.0019 (4)	-0.0003 (4)	0.0010 (4)
O1	0.0214 (4)	0.0194 (5)	0.0310 (5)	0.0031 (3)	-0.0039 (4)	-0.0037 (4)
O2	0.0188 (4)	0.0231 (5)	0.0328 (5)	-0.0011 (3)	0.0001 (4)	-0.0054 (4)
Geometric parameters (\AA , $^\circ$)						
O1A—H4	0.886 (19)	N1—H3	0.919 (19)			
N1—H1A	0.87 (2)	C1—O2	1.2521 (14)			
N1—H1	0.926 (18)	C1—O1	1.2555 (14)			
N1—H2	0.902 (19)	C1—C1 ⁱ	1.568 (2)			
H1A—N1—H1	112.5 (15)	H2—N1—H3	109.2 (14)			
H1A—N1—H2	111.3 (18)	O2—C1—O1	125.75 (11)			
H1—N1—H2	103.7 (15)	O2—C1—C1 ⁱ	117.22 (12)			
H1A—N1—H3	109.7 (17)	O1—C1—C1 ⁱ	117.03 (12)			
H1—N1—H3	110.2 (18)					

Symmetry code: (i) -x, -y+1, z.

Conclusions

- 1) The single crystals of perfectly quality of the diammonium oxalate monohydrate, $[\text{NH}_4]_2[\text{C}_2\text{O}_4][\text{H}_2\text{O}]$ growth from solution.
- 2) The crystal structure the diammonium oxalate monohydrate was studied at 150 K using modern X-ray equipment.
- 3) At 150 K oxalate ion is twisted by 26.9 (1) $^\circ$. Central carbon-carbon bond in oxalate ion is longer at 150 K compare to room temperature.

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