

Redetermination of ammonium oxalate
oxalic acid dihydrateGustavo Portalone* and
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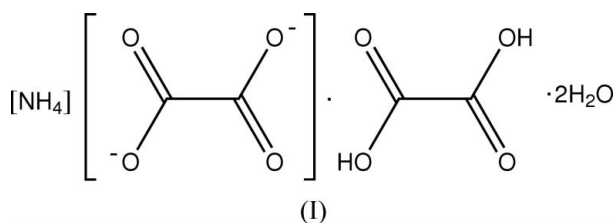
Key indicators

Single-crystal X-ray study
 $T = 298$ K
Mean $\sigma(\text{C}-\text{C}) = 0.001$ Å
 R factor = 0.043
 wR factor = 0.132
Data-to-parameter ratio = 34.9For details of how these key indicators were
automatically derived from the article, see
<http://journals.iucr.org/e>.

The crystal structure of the triclinic form of the title compound, $\text{NH}_4^+ \cdot \text{C}_2\text{HO}_4^- \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$, has been redetermined, providing a significant increase in the precision of the derived geometric parameters. The asymmetric unit comprises an ammonium cation, an oxalate anion, half each of two oxalic acid molecules, each disposed about a centre of inversion, and two water molecules of crystallization.

Comment

For some time now, we have studied co-crystals of DNA/RNA pyrimidine bases with amino derivatives of aromatic N-heterocycles *via* multiple hydrogen bonds (Brunetti *et al.*, 2000, 2002; Portalone *et al.*, 1999, 2002; Portalone & Colapietro, 2004*a,b*) as examples of supramolecular structures. Recently, attention has been devoted to polymorphic compounds as useful co-crystallizing agents (Bernstein, 2002; Portalone & Colapietro, 2004*b*). Since oxalic acid and oxalates are known to exist in different crystalline forms, we have been interested in the study of tetroxalates, *i.e.* the superacid salts of general formula $M\text{H}_3(\text{C}_2\text{O}_4)_2 \cdot 2\text{H}_2\text{O}$, with $M = \text{NH}_4, \text{K}, \text{Rb}, \text{Cs}$, or Tl , which are isomorphous in the triclinic crystal system. Despite numerous crystal-growth experiments involving slow evaporation and liquid or vapour diffusion using a number of solvents, we were only able to isolate single crystals of ammonium tetraoxalate (atoxal), (I).



The crystal structure of (I) was originally determined by neutron diffraction some 40 years ago (Currie *et al.*, 1967). That work was of remarkable precision for the time: 1731 independent reflections (1226 of these having values significantly above background) were measured and used in the refinement. The final block-diagonal least-squares refinement gave $R = 0.089$ for 180 refined parameters. The current re-investigation confirms and amplifies Currie's work, providing a much lower R value and a significant increase in the precision of the geometric parameters, *viz.* $\sigma(\text{C}-\text{C}) = 0.0007$ – 0.0011 Å in the present work, compared with 0.006 – 0.010 Å in the earlier work.

The asymmetric unit of (I) comprises a planar oxalate anion, two half-molecules of oxalic acid, each disposed about a

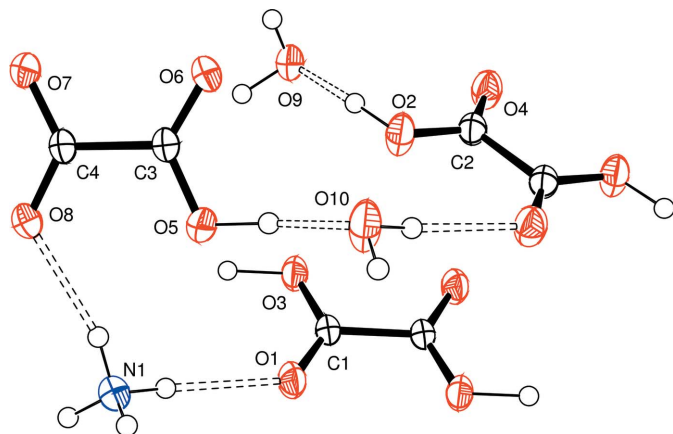


Figure 1

The asymmetric unit of (I), together with additional atoms to complete the two oxalic acid molecules. Displacement ellipsoids are drawn at the 50% probability level. Dashed lines indicate hydrogen bonds. Unlabelled atoms in the C1 molecule are related to labelled atoms by the symmetry operator $(-x + 1, -y + 1, -z + 1)$. Unlabelled atoms in the C2 molecule are related to labelled atoms by the symmetry operator $(-x + 1, -y, -z + 1)$.

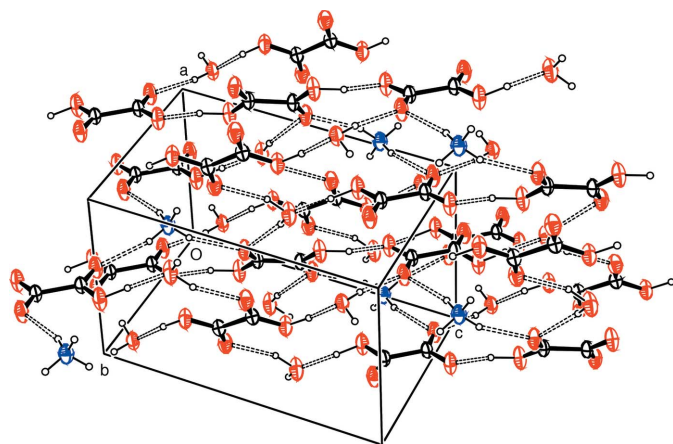


Figure 2

The packing of (I), showing the hydrogen-bonding scheme projected normal to (100). Displacement ellipsoids are at the 50% probability level. Dashed lines indicate hydrogen bonds.

centre of inversion, an ammonium cation and two water molecules (Fig. 1). The corresponding bond lengths and angles of the independent molecules in the asymmetric unit show small differences, which can be attributed to different hydrogen-bonding configurations (Table 1).

Consistent with the earlier study (Currie *et al.*, 1967), in the crystal structure of (I) the intricate three-dimensional network (Fig. 2) is sustained by seven medium to strong hydrogen bonds between O atoms, with O...O distances in the range 2.4731 (8)–2.8959 (9) Å. Four intermolecular N—H...O interactions complete the hydrogen-bonding system.

Subunits of the oxalic acid molecules, one oxalate anion and two water molecules form infinite chains running along the [011] direction via O—H...O hydrogen bonds. These chains are connected transversely by the two independent water molecules and the ammonium cation through O—H...O and

N—H...O hydrogen bonds. The three very strong O—H...O hydrogen bonds all have carboxyl groups as H-atom donors, and the two independent water molecules participate as H-atom acceptors. The corresponding H...O distances range in length from 1.46 (2) to 1.52 (2) Å [1.399 (7)–1.493 (9) Å in Currie's neutron diffraction work). Considering the hydrogen bonding as an incipient H-atom transfer reaction (Jeffrey, 1997; Steiner, 2002), the stage of H-atom transfer in (I) is quite advanced. The remaining four, weaker, O—H...O hydrogen bonds have the two independent water molecules as H-atom donors.

Experimental

Compound (I) (Fluka; 99% purity) was recrystallized from water by slow evaporation.

Crystal data

$\text{NH}_4^+ \cdot \text{C}_2\text{HO}_4^- \cdot \text{C}_2\text{H}_2\text{O}_4 \cdot 2\text{H}_2\text{O}$
 $M_r = 233.14$
 Triclinic, $P\bar{1}$
 $a = 6.3387$ (8) Å
 $b = 7.2227$ (9) Å
 $c = 10.5527$ (11) Å
 $\alpha = 94.172$ (10)°
 $\beta = 100.274$ (10)°
 $\gamma = 97.704$ (10)°

$V = 468.77$ (10) Å³
 $Z = 2$
 $D_x = 1.652$ Mg m⁻³
 Mo $K\alpha$ radiation
 $\mu = 0.17$ mm⁻¹
 $T = 298$ (2) K
 Block, colourless
 0.30 × 0.20 × 0.20 mm

Data collection

Huber CS four-circle diffractometer
 ω scans
 Absorption correction: none
 6934 measured reflections
 6283 independent reflections
 5265 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.021$
 $\theta_{\text{max}} = 42.0^\circ$
 3 standard reflections
 every 97 reflections
 intensity decay: 1%

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.043$
 $wR(F^2) = 0.132$
 $S = 1.04$
 6283 reflections
 180 parameters
 All H-atom parameters refined

$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 0.0474P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.44$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.31$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.2219 (7)	O7—C4	1.2586 (8)
O2—C2	1.2912 (8)	O8—C4	1.2392 (7)
O3—C1	1.2867 (8)	C1—C1 ⁱ	1.5464 (10)
O4—C2	1.2155 (8)	C2—C2 ⁱⁱ	1.5386 (11)
O5—C3	1.2970 (8)	C3—C4	1.5483 (7)
O6—C3	1.2150 (7)		
O1—C1—O3	126.54 (5)	O6—C3—O5	125.20 (5)
O1—C1—C1 ⁱ	120.29 (7)	O6—C3—C4	121.59 (5)
O3—C1—C1 ⁱ	113.16 (6)	O5—C3—C4	113.21 (5)
O4—C2—O2	126.72 (6)	O8—C4—O7	127.69 (5)
O4—C2—C2 ⁱⁱ	120.98 (7)	O8—C4—C3	117.30 (5)
O2—C2—C2 ⁱⁱ	112.30 (6)	O7—C4—C3	115.00 (5)

Symmetry codes: (i) $-x + 1, -y + 1, -z + 1$; (ii) $-x + 1, -y, -z + 1$.

Table 2
Hydrogen-bond geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
O2—H6···O9	1.016 (18)	1.459 (18)	2.4731 (8)	175.7 (17)
O3—H7···O7 ⁱⁱⁱ	1.042 (19)	1.463 (19)	2.4974 (7)	171.3 (18)
O5—H5···O10	0.995 (16)	1.517 (16)	2.5120 (8)	177.4 (14)
O9—H2···O6 ^{iv}	0.838 (16)	1.913 (17)	2.7476 (9)	173.4 (15)
O9—H1···O8 ⁱⁱⁱ	0.89 (2)	1.85 (2)	2.7231 (8)	166.7 (18)
O10—H4···O1 ^v	0.879 (19)	2.06 (2)	2.8959 (9)	158.3 (16)
O10—H3···O4 ⁱⁱ	0.94 (2)	1.92 (2)	2.8311 (8)	162 (2)
N1—H8···O1	0.90 (2)	2.079 (19)	2.9466 (8)	162.0 (17)
N1—H9···O4 ^{vi}	0.866 (18)	2.101 (18)	2.9359 (9)	161.6 (15)
N1—H10···O6 ^{vii}	0.89 (2)	2.09 (2)	2.9671 (8)	166 (2)
N1—H11···O8	0.903 (16)	2.058 (16)	2.9275 (9)	161.2 (14)

Symmetry codes: (ii) $-x + 1, -y, -z + 1$; (iii) $-x + 1, -y + 1, -z$; (iv) $-x + 1, -y, -z$; (v) $-x + 2, -y + 1, -z + 1$; (vi) $x + 1, y + 1, z$; (vii) $x, y + 1, z$.

All H atoms were found in a difference map and refined freely; O—H = 1.00 (2)–1.04 (2) Å for oxalic acid and 0.84 (2)–0.94 (2) Å for water, and N—H = 0.87 (2)–0.90 (2) Å.

Data collection: *XCS* (Colapietro *et al.*, 1992); cell refinement: *XCS*; data reduction: *XCS*; program(s) used to solve structure: *SIR97* (Altomare *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3*

(Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

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