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S. Natarajan^{c*}^aDepartment of Physics, Saraswathi Narayanan College, Madurai 625 022, India, ^bDepartment of Physics, Thiagarajar College, Madurai 625 009, India, and ^cDepartment of Physics, Madurai Kamaraj University, Madurai 625 021, IndiaCorrespondence e-mail:
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Key indicators

Single-crystal X-ray study
 $T = 293\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.037
 wR factor = 0.113
Data-to-parameter ratio = 11.4For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Pyridinium oxalate(1⁻) oxalic acid dihydrate

In the title compound, $\text{C}_5\text{H}_6\text{N}^+\cdot\text{C}_2\text{HO}_4^-\cdot\text{C}_2\text{H}_2\text{O}_4\cdot 2\text{H}_2\text{O}$, the pyridine molecule exists as a cation and the oxalic acid molecules as an oxalate(1⁻) ion and a neutral oxalic acid. The structure is stabilized by $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds in addition to carbonyl-carbonyl $\text{O}\cdots\text{C}$ short contacts and van der Waals interactions. The water molecules are also found to mediate interactions between oxalate ions and oxalic acid molecules through a number of $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds. Pairs of pyridinium cations related by a center of inversion are surrounded by semi-oxalate anions and oxalic acid molecules, and the complex may be described as an inclusion compound.

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Comment

The present study reports the crystal structure of pyridinium oxalate(1⁻) oxalic acid dihydrate, (I), as part of a series of investigations being carried out to observe conformational changes in carboxylic acid molecules and characteristic hydrogen-bonding patterns in their crystal structures.

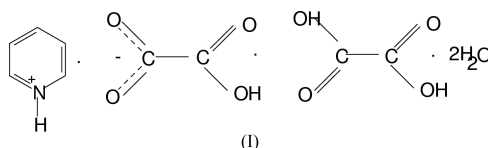


Fig. 1 shows the molecular structure of (I) with the atom-numbering scheme. The pyridine molecule exists in the cationic form with a protonated ring N atom. One of the oxalic acid molecules is in the mono-ionized state, while the other molecule is in the unionized state. The oxalic acid molecule is more nearly planar [the largest displacements from the plane are 0.012 (2) Å for O1 and 0.011 (1) Å for O4, both on the same side] than the oxalate(1⁻) ion [the largest displacements

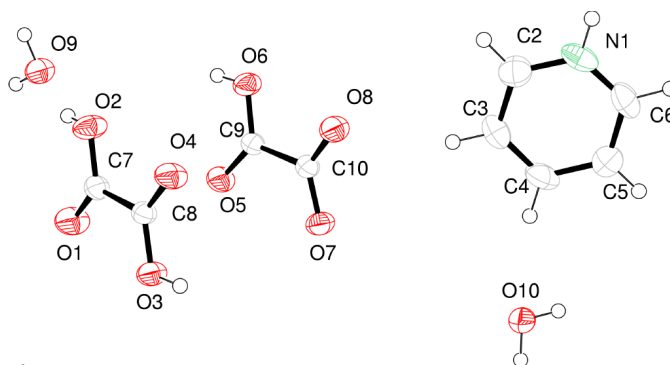


Figure 1

The molecular structure of (I), with the atom-numbering scheme and ellipsoids at the 50% probability level.

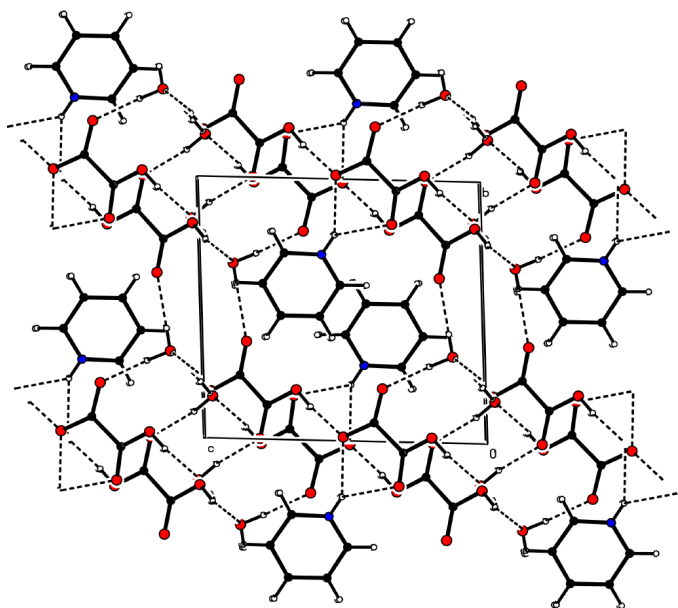


Figure 2
The packing of (I), viewed down the *a* axis.

from the plane are 0.017 (2) Å for O6 and 0.123 (2) Å for O8, on opposite sides]. The geometric parameters of the pyridinium ion are in agreement with those of pyridinium ions in other structures, *e.g.* bithiourea pyridinium bromide (Truter & Vickery, 1972) and pyridinium dichloroiodide (Tucker & Kroon, 1973). The C—C bond lengths of the oxalic acid molecule and the oxalate(1[−]) ion [C7—C8 = 1.539 (2) Å and C9—C10 = 1.544 (2) Å] are longer than accepted values. Perhaps the abnormally long C—C distance found in the oxalic acid molecule and oxalate ion can be justified by intramolecular O···O steric hindrance, shown by the following contacts: O1···O3 = 2.682 (2), O2···O4 = 2.626 (2), O5···O7 = 2.691 (2) and O6···O8 = 2.666 (2) Å, all significantly shorter than the sum of the van der Waals radii of 3.04 Å (Bondi, 1964). This steric interaction not only causes an enlargement of about 0.04 Å of the C—C central bond in both oxalic acid residues, but also some twisting of the two carboxylic acid groups about it; this twisting is significant only in the anion, as shown by the values of the torsion angles O1—C7—C8—O3 = −0.5 (2)° and O5—C9—C10—O7 = 12.1 (2)°. However, such large deviations in bond lengths are also observed in the case of oxalic acid dihydrate, with C—C = 1.537 Å (Ahmed & Cruickshank, 1953), and in the crystal structures of anhydrous α - and β -oxalic acids, both with values of 1.537 (1) Å (Derrissen & Smith, 1974). A slight increase in the C10—O7 bond length [1.264 (2) Å] compared to C10—O8 [1.231 (2) Å] may be attributed to the participation of O7 in two hydrogen bonds and O8 in only one hydrogen bond in the structure. The other geometrical parameters of the oxalic acid molecules are found to be in agreement with those of other similar structures (oxalic acid dihydrate, anhydrous α - and β -oxalic acids, *etc.*).

Fig. 2 shows the packing pattern of (I), viewed down the *a* axis. The oxalate(1[−]) and oxalic acid residues and their inversion-related equivalents are linked along the diagonal of the *ac* plane. Pyridinium ions link the oxalate ion layers through bifurcated N—H···O hydrogen bonds, leading to a characteristic three-dimensional aggregation pattern. One of the water molecules, O10 acting as donor, mediates O—H···O interactions with the oxalic acid residue. It is also involved in a short C···O contact, *viz.* C8···O10(−*x*, −*y*, 1 − *z*) = 3.002(3) Å. The other water molecule (O9) links the neutral oxalic acid molecules and the oxalate ions through O—H···O hydrogen bonds. Short carbonyl—carbonyl contacts [C7···O5 = 3.004 (4) Å, C8···O5 = 2.995 (3) Å and C8···O10(−*x*, −*y*, −*z* + 1) = 2.995 (3) Å] are also observed (Allen *et al.*, 1998). Thus the structure is stabilized by O—H···O and N—H···O hydrogen bonds in addition to short contacts and van der Waals interactions. The complex can be described as an inclusion compound with the oxalate(1[−]) ion and oxalic acid molecule as hosts and the pyridinium ion as the guest.

Experimental

Colorless prismatic single crystals of (I) were obtained during an attempt to grow the complex of L-proline with oxalic acid, in the presence of a few drops of pyridine, from a saturated aqueous solution containing proline and oxalic acid in a 1:1 stoichiometric ratio. Unexpectedly, instead of L-proline oxalate, only the title compound, (I), was obtained.

Crystal data

C₅H₆N⁺·C₂H₂O₄[−]·C₂H₂O₄·2H₂O
M_r = 295.20
 Triclinic, *P*1̄
a = 6.992 (7) Å
b = 9.539 (2) Å
c = 10.098 (2) Å
 α = 84.36 (2)°
 β = 79.54 (4)°
 γ = 74.71 (6)°
V = 638.0 (7) Å³
Z = 2
D_x = 1.537 Mg m^{−3}

D_m = 1.55 Mg m^{−3}
D_m measured by flotation in a mixture of xylene and bromoform
 Mo *K* α radiation
 Cell parameters from 25 reflections
 θ = 2.0–25.0°
 μ = 0.14 mm^{−1}
T = 293 (2) K
 Prism, colourless
 0.40 × 0.35 × 0.17 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
 ω –2 θ scans
 Absorption correction: ψ scan (North *et al.*, 1968)
T_{min} = 0.948, *T_{max}* = 0.971
 2451 measured reflections
 2250 independent reflections
 1946 reflections with *I* > 2 σ (*I*)

R_{int} = 0.006
 θ_{max} = 25.0°
h = 0 → 8
k = −10 → 11
l = −11 → 11
 2 standard reflections every 200 reflections
 intensity decay: <1%

Refinement

Refinement on *F*²
R[*F*² > 2 σ (*F*²)] = 0.037
wR(*F*²) = 0.113
S = 1.09
 2250 reflections
 198 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0645P)^2 + 0.1652P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} < 0.001$
 $\Delta\rho_{\text{max}} = 0.26 \text{ e \AA}^{-3}$
 $\Delta\rho_{\text{min}} = -0.21 \text{ e \AA}^{-3}$
 Extinction correction: *SHELXL97*
 Extinction coefficient: 0.017 (5)

Table 1
Selected geometric parameters (Å, °).

| | | | |
|-------------|-----------|--------------|------------|
| O1—C7 | 1.201 (2) | O8—C10 | 1.231 (2) |
| O2—C7 | 1.294 (2) | N1—C6 | 1.315 (2) |
| O3—C8 | 1.283 (2) | N1—C2 | 1.336 (2) |
| O4—C8 | 1.212 (2) | C2—C3 | 1.365 (3) |
| O5—C9 | 1.209 (2) | C3—C4 | 1.365 (3) |
| O6—C9 | 1.297 (2) | C4—C5 | 1.380 (3) |
| O7—C10 | 1.264 (2) | | |
| | | | |
| C6—N1—C2 | 122.9 (2) | O3—C8—C7 | 112.7 (1) |
| N1—C2—C3 | 119.2 (2) | O5—C9—O6 | 125.8 (1) |
| O1—C7—O2 | 126.3 (1) | O5—C9—C10 | 121.3 (1) |
| O1—C7—C8 | 122.4 (1) | O6—C9—C10 | 112.8 (1) |
| O2—C7—C8 | 111.3 (1) | O8—C10—O7 | 127.0 (1) |
| O4—C8—O3 | 127.0 (1) | O8—C10—C9 | 119.4 (1) |
| O4—C8—C7 | 120.3 (1) | O7—C10—C9 | 113.6 (1) |
| | | | |
| C6—N1—C2—C3 | 0.3 (3) | O2—C7—C8—O3 | −179.7 (1) |
| N1—C2—C3—C4 | −0.6 (3) | O5—C9—C10—O8 | −167.5 (2) |
| O1—C7—C8—O4 | 178.0 (2) | O6—C9—C10—O8 | 11.9 (2) |
| O2—C7—C8—O4 | −1.3 (2) | O5—C9—C10—O7 | 12.1 (2) |
| O1—C7—C8—O3 | −0.5 (2) | O6—C9—C10—O7 | −168.5 (1) |

Table 2
Hydrogen-bonding 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—H2A...O9 | 0.82 | 1.80 | 2.592 (3) | 161 |
| O3—H3A...O7 ⁱ | 0.82 | 1.67 | 2.486 (2) | 174 |
| O6—H6A...O10 ⁱⁱ | 0.82 | 1.82 | 2.626 (2) | 166 |
| O9—H7...O8 ⁱⁱⁱ | 0.88 (2) | 1.85 (2) | 2.735 (2) | 176 (2) |
| O9—H8...O1 ^{iv} | 0.81 (3) | 1.99 (3) | 2.802 (2) | 179 (3) |
| O10—H9...O4 ^v | 0.90 (2) | 1.92 (2) | 2.811 (2) | 171 (2) |
| O10—H10...O9 ⁱⁱ | 0.83 (3) | 2.07 (3) | 2.897 (2) | 173 (2) |
| N1—H1...O7 ^{vi} | 0.86 | 2.13 | 2.889 (2) | 147 |
| N1—H1...O5 ^{vi} | 0.86 | 2.25 | 2.934 (2) | 137 |

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

All the H atoms, except those of the water molecules, were positioned geometrically and were allowed to ride on their respective parent atoms. The water H atoms were located in a difference Fourier map and allowed to refine isotropically.

Data collection: *CAD-4 Software* (Enraf-Nonius, 1989); cell refinement: *CAD-4 Software*; data reduction: *CAD-4 Software*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 1999); software used to prepare material for publication: *SHELXL97*.

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