

Morpholinium dihydrogen citrate hydrate

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Key indicators

Single-crystal X-ray study
 $T = 298\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.003\text{ \AA}$
 R factor = 0.055
 wR factor = 0.143
Data-to-parameter ratio = 11.0For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

In the crystal structure of the title compound, $[\text{O}(\text{CH}_2\text{CH}_2)_2\text{NH}_2][\text{C}_6\text{H}_7\text{O}_7]\cdot\text{H}_2\text{O}$, the cation interacts with the negatively charged carboxylate group of adjacent anions $[\text{N}\cdots\text{O} 2.847(3)$ and $2.942(3)\text{ \AA}]$, forming a linear chain running along the b axis of the crystal. Adjacent chains are linked through the carboxylic $-\text{CO}_2\text{H}$ groups and the water molecule into a layer structure.

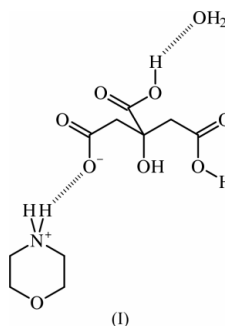
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Comment

A previous report described the dicyclohexylammonium salts of monocarboxylic and dicarboxylic acids (Ng, 2003). For some of the acids, their reaction with dicyclohexylamine afforded the corresponding ammonium carboxylate as a hydrate (Ng, 1992; Yang *et al.*, 2002). On the other hand, others reacted with an excess of this secondary amine to yield only the mono(ammonium) salt, *e.g.*, dicyclohexylammonium hydrogen oxalate (Ng, 1994). The reaction with the tribasic acid, citric acid, gave a compound that rapidly turned opaque when the crystals were removed from its solution in ethanol; on the other hand, the use of diisopropylamine in place of dicyclohexylamine led to a syrupy material after the solvent had evaporated. A cursory check through the Cambridge Structural Database (Allen, 2002) on the *sec*-ammonium derivatives of carboxylic acids suggested the use of morpholine, as this amine furnishes a large number of isolable carboxylates, such as chloronitrobenzoates (Ishida *et al.*, 2001*a,b,c*) and morpholinoformate (Brown & Gray, 1982). Citric acid has also been characterized as an *N*-substituted piperidinium salt (Peeters *et al.*, 1979). In the present study, the reaction of citric acid with either one or two molar equivalents of morpholine gave the air-stable title compound, (I) (Fig. 1).



In the crystal structure of (I), the cation interacts with the carboxyl O atoms of two citrate anions $[\text{N}\cdots\text{O} 2.847(3)$ and $2.942(3)\text{ \AA}]$, resulting in the formation of a linear chain running along the b axis of the crystal. Such a hydrogen-bonded motif has previously been noted in dicyclohexylammonium trifluoroacetate (Ng, 1999). Adjacent chains are

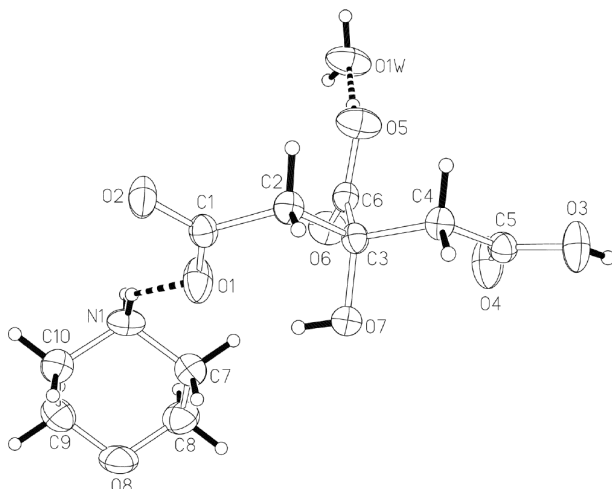


Figure 1
ORTEPII (Johnson, 1976) plot of (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are drawn as spheres of arbitrary radii.

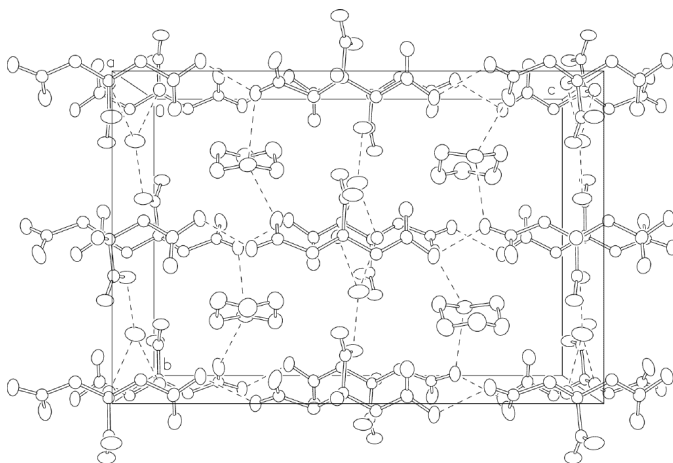


Figure 2
ORTEPII (Johnson, 1976) plot, illustrating the hydrogen-bonded layer structure. H atoms are omitted.

linked through the carboxylic $-\text{CO}_2\text{H}$ groups and water molecule into a layer structure (Fig. 2 and Table 2).

Experimental

Morpholine (0.87 g, 10 mmol) and citric acid monohydrate (0.21 g, 10 mol) were heated in a small volume of ethanol (25 ml); a few drops of water were added to dissolve the acid completely. Slow evaporation of the solvent yielded the title compound. The use of twice the quantity of the amine gave the identical compound. Elemental analysis, found (calc. for $\text{C}_{10}\text{H}_{19}\text{O}_9\text{N}$): C 40.8 (40.4); H 6.5 (6.4); N 4.5% (4.7%). IR (KBr pellet): ν_{COOH} 1717, $\nu_{\text{as(COO)}}$ 1414, $\nu_{\text{s(COO)}}$ 1414, 1396; $\nu_{\text{C=N}}$ 1107 cm^{-1} .

Crystal data

$\text{C}_4\text{H}_{10}\text{NO}^+ \cdot \text{C}_6\text{H}_7\text{O}_7^- \cdot \text{H}_2\text{O}$
 $M_r = 297.26$
 Orthorhombic, $Pbca$
 $a = 11.3774$ (6) Å
 $b = 12.4823$ (7) Å
 $c = 18.437$ (1) Å
 $V = 2618.3$ (2) Å³
 $Z = 8$
 $D_x = 1.508$ Mg m⁻³

Mo $K\alpha$ radiation
 Cell parameters from 4726 reflections
 $\theta = 2.4\text{--}27.3^\circ$
 $\mu = 0.13$ mm⁻¹
 $T = 298$ (2) K
 Block, colorless
 $0.28 \times 0.18 \times 0.18$ mm

Data collection

Bruker AXS area-detector diffractometer
 φ and ω scans
 Absorption correction: none
 12407 measured reflections
 2305 independent reflections

2103 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.028$
 $\theta_{\text{max}} = 25.0^\circ$
 $h = -13 \rightarrow 13$
 $k = -14 \rightarrow 10$
 $l = -20 \rightarrow 21$

Refinement

Refinement on F^2
 $R[F^2 > 2\sigma(F^2)] = 0.055$
 $wR(F^2) = 0.143$
 $S = 1.15$
 2305 reflections
 209 parameters
 H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0711P)^2 + 1.4573P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\text{max}} = 0.001$
 $\Delta\rho_{\text{max}} = 0.29$ e Å⁻³
 $\Delta\rho_{\text{min}} = -0.19$ e Å⁻³

Table 1

Selected geometric parameters (Å, °).

O1—C1	1.243 (3)	N1—C7	1.482 (3)
O2—C1	1.253 (3)	N1—C10	1.484 (3)
O3—C5	1.304 (3)	C1—C2	1.524 (3)
O4—C5	1.207 (3)	C2—C3	1.536 (3)
O5—C6	1.316 (3)	C3—C4	1.525 (3)
O6—C6	1.203 (3)	C3—C6	1.536 (3)
O7—C3	1.421 (3)	C4—C5	1.505 (3)
O8—C8	1.418 (3)	C7—C8	1.489 (4)
O8—C9	1.421 (3)	C9—C10	1.496 (4)
C8—O8—C9	109.9 (2)	C3—C4—C5	113.6 (2)
O1—C1—O2	124.2 (2)	O3—C5—O4	123.1 (2)
O1—C1—C2	118.7 (2)	O3—C5—C4	112.8 (2)
O2—C1—C2	117.2 (2)	O4—C5—C4	124.1 (2)
C1—C2—C3	114.6 (2)	O5—C6—O6	124.4 (2)
O7—C3—C2	109.6 (2)	O5—C6—C3	111.1 (2)
O7—C3—C4	107.7 (2)	O6—C6—C3	124.4 (2)
C2—C3—C4	110.9 (2)	N1—C7—C8	109.8 (2)
O7—C3—C6	109.4 (2)	O8—C8—C7	111.1 (2)
C2—C3—C6	109.0 (2)	O8—C9—C10	111.4 (2)
C4—C3—C6	110.3 (2)	N1—C10—C9	109.0 (2)

Table 2

Hydrogen-bonding geometry (Å, °).

$D\text{—}H\cdots A$	$D\text{—}H$	$H\cdots A$	$D\cdots A$	$D\text{—}H\cdots A$
O3—H3o ⁱ ⋯O2 ⁱ	0.85 (1)	1.76 (1)	2.612 (2)	176 (4)
O5—H5o ⁱ ⋯O1w	0.86 (1)	1.68 (1)	2.529 (3)	172 (4)
O7—H7o ⁱ ⋯O1	0.85 (1)	1.89 (2)	2.625 (2)	144 (3)
N1—H1n2 ⁱ ⋯O1	0.85 (1)	2.13 (2)	2.847 (3)	143 (3)
N1—H1n1 ⁱ ⋯O2 ⁱⁱ	0.85 (1)	2.12 (2)	2.942 (3)	162 (3)
O1w—H1w1 ⁱ ⋯O6 ⁱⁱⁱ	0.85 (1)	2.16 (2)	2.932 (3)	152 (3)
O1w—H1w2 ⁱ ⋯O7 ⁱⁱ	0.85 (1)	1.93 (1)	2.782 (3)	175 (4)

Symmetry codes: (i) $\frac{1}{2} - x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, z$; (iii) $\frac{1}{2} + x, \frac{1}{2} - y, 1 - z$.

The water, hydroxyl and ammonium H atoms were located and refined. The aliphatic H atoms were positioned geometrically (C—H 0.97 Å), and were included in the refinement in the riding model approximation; the displacement factors were set to 1.5 (methyl) or 1.2 (other H atoms) times U_{eq} of the parent atom.

The diffraction measurements were performed up to a 2θ angle of 56° ; however, as the inclusion of reflections above 50° led to an R factor greater than 7%, these were excluded from the refinement.

Data collection: SMART (Bruker, 2001); cell refinement: SAINT (Bruker, 2001); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEPII* (Johnson, 1976); software used to prepare material for publication: *SHELXL97*.

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