

A novel proton-transfer compound:
piperazinium oxalate monohydrateHossein Aghabozorg,^{a*}
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Key indicators

Single-crystal X-ray study
 $T = 120\text{ K}$
Mean $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$
 R factor = 0.071
 wR factor = 0.168
Data-to-parameter ratio = 13.5For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

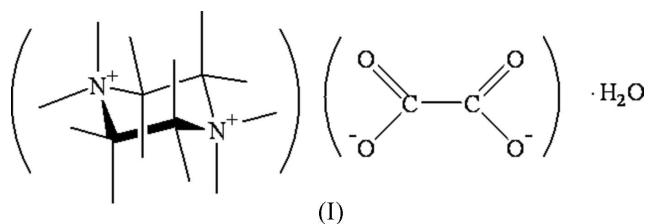
The asymmetric unit of the title compound, $\text{C}_4\text{H}_{12}\text{N}_2^{2+} \cdot \text{C}_2\text{O}_4^{2-} \cdot \text{H}_2\text{O}$, contains one water molecule, one anion and two half-cations, both cations having chair conformations. The crystal structure is stabilized by intra- and intermolecular $\text{O}-\text{H} \cdots \text{O}$ and $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonds, linking the molecules into a three-dimensional framework, which results in the formation of a supramolecular structure based on a hydrogen-bonded network.

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Comment

The preparation and characterization of self-associated proton-transfer systems have been considered by chemists in recent years. There has been a wide range of studies of different aspects of proton-transfer systems. There have also been several attempts to employ proton transfer from carboxylic acids to amines. In connection with such self-associated proton-transfer systems that are soluble in polar solvents, we have previously reported some self-associated proton-transfer systems using pyridine-2,6-dicarboxylic acid (pydcH_2) and 1,10-phenanthroline-2,9-dicarboxylic acid (phendcH_2) as proton donors and pyridine-2,6-diamine (pyda), creatinine (creat), 1,10-phenanthroline (phen), guanidine (G) and $\text{N,N}'$ -diethyl-2-amino-6-methyl-4-pyrimidinol (pyrim) as proton acceptors; these formed the proton-transfer compounds (creatH)(pydcH) (Moghimi, Sharif & Aghabozorg, 2004), (creatH)(phendcH) (Soleimannejad *et al.*, 2005), (pydaH)(pydcH) (Aghabozorg, Akbari Saei & Ramezanipour, 2005), (pydaH_2)(phendc) (Moghimi *et al.*, 2003), (phenH)₂(pydc) (Moghimi, Sheshmani *et al.*, 2005), (GH)₂(pydc) (Moghimi, Sheshmani *et al.*, 2004) and (pyrimH){ $\text{H}(\text{Hpydc})_2$ } (Aghabozorg, Soleimannejad *et al.*, 2005). Some complexes of these systems have been synthesized and their X-ray crystal structures have been reported (Aghabozorg, Ramezanipour *et al.*, 2006; Aghabozorg, Nakhjavan *et al.*, 2006; Moghimi, Sheshmani *et al.*, 2005; Moghimi, Sharif *et al.*, 2005).



Here, the synthesis and crystal structure of the title self-associated system, (I), (pipzH_2)(oxa)- H_2O (pipz is piperazine and oxaH_2 is oxalic acid), is reported. This system arises from ion-pairing and hydrogen bonding.

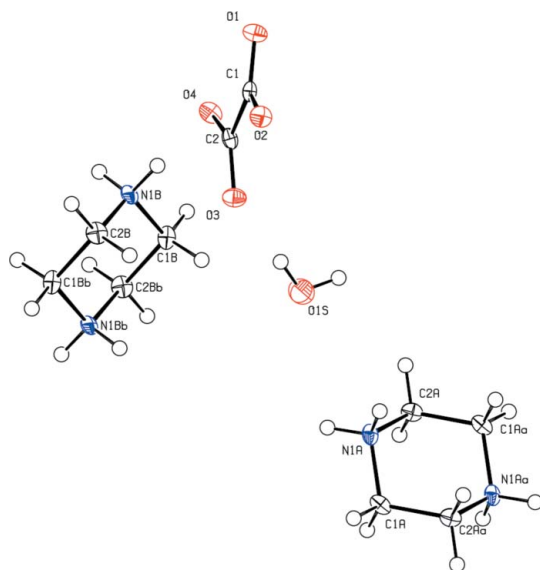


Figure 1
A drawing of the components of the title structure with the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. Atoms labelled with the suffix a or b are generated by the symmetry operators $(-x, -y, -z)$ or $(1-x, 1-y, 1-z)$, respectively.

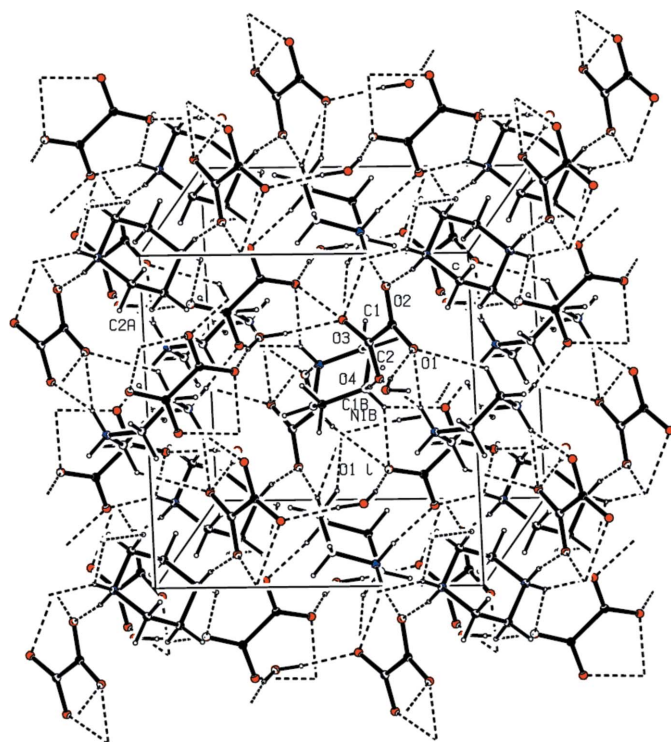


Figure 2
A packing diagram for (I). Hydrogen bonds are shown as dashed lines. [Symmetry code: (i) $-x, -y + 1, z - \frac{1}{2}$]

In the structure of compound (I) (Fig. 1), the bond lengths and angles are within normal ranges (Allen *et al.*, 1987). The asymmetric unit contains one water molecule, one one anion and two half-cations.

The rings *A* [N1A/N1Aa/C1A/C1Aa/C2A/C2Aa; atoms labelled with the suffix *a* are generated by the symmetry

operator $(-x, -y, -z)$ and *B* [N1B/N1Bb/C1B/C1Bb/C2B/C2Bb; atoms labelled with the suffix *b* are generated by the symmetry operator $(1-x, 1-y, 1-z)$ are not planar, having total puckering amplitudes $Q_T = 1.446$ (3) and 1.456 (4) Å, respectively, and chair conformations [$\varphi = 160.6$ (2)° and $\theta = 0.0$ (3)°, and $\varphi = 88.0$ (2)° and $\theta = 0.0$ (3)°, respectively] (Cremer & Pople, 1975).

As can be seen from the packing diagram (Fig. 2), intra- and intermolecular O—H...O and N—H...O hydrogen bonds (Table 1) link the components into a three-dimensional framework, which results in the formation of a supramolecular structure based on a hydrogen-bonded network.

Experimental

The title compound, (I), was synthesized by a reaction between oxalic acid (oxaH₂) and piperazine (pipz) in a 1:1 molar ratio. To a solution of oxaH₂ (450 mg, 5 mmol) in tetrahydrofuran (30 ml) was added a solution of pipz (430 mg, 5 mmol) in tetrahydrofuran (30 ml). The resulting powder was dissolved in water to give colourless crystals of (I) (yield 80%; decomposition at 423 K).

Crystal data

C₄H₁₂N₂²⁺·C₂O₄²⁻·H₂O
M_r = 194.19
 Monoclinic, *P*2₁/*c*
a = 11.983 (3) Å
b = 6.4802 (18) Å
c = 11.256 (3) Å
 β = 96.858 (6)°
V = 867.8 (4) Å³

Z = 4
D_x = 1.486 Mg m⁻³
 Mo *K*α radiation
 μ = 0.13 mm⁻¹
T = 120 (2) K
 Cube, colourless
 0.02 × 0.02 × 0.02 mm

Data collection

Bruker Smart 1000 CCD area-detector diffractometer
 φ and ω scans
 Absorption correction: multi-scan (SADABS; Sheldrick, 1998)
T_{min} = 0.998, *T_{max}* = 0.998

4334 measured reflections
 1591 independent reflections
 930 reflections with *I* > 2σ(*I*)
R_{int} = 0.065
 θ_{\max} = 26.0°

Refinement

Refinement on *F*²
R [*F*² > 2σ(*F*²)] = 0.071
wR (*F*²) = 0.168
S = 0.93
 1591 reflections
 118 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0845P)]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.46 \text{ e \AA}^{-3}$
 $\Delta\rho_{\min} = -0.32 \text{ e \AA}^{-3}$

Table 1
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>
N1B—H1BA...O4	0.92	1.79	2.707 (4)	175
N1A—H1AA...O2 ⁱ	0.92	1.96	2.818 (4)	154
N1A—H1AA...O3 ⁱ	0.92	2.27	2.902 (4)	125
N1A—H1AB...O2 ⁱⁱ	0.92	1.83	2.735 (4)	167
N1B—H1BB...O1 ⁱⁱⁱ	0.92	2.18	2.958 (4)	142
N1B—H1BB...O4 ⁱⁱⁱ	0.92	2.04	2.794 (4)	138
O1S—H1SA...O3	0.85	1.94	2.789 (4)	175
O1S—H1SB...O1 ^{iv}	0.85	1.98	2.805 (4)	165

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

The crystal was a non-merohedral twin; data were collected from both components, and some partially overlapped reflections were discarded. H atoms were positioned geometrically, with N–H = 0.92 Å, O–H = 0.85 Å and C–H = 0.99 Å, and constrained to ride on their parent atoms, with $U_{\text{iso}}(\text{H}) = xU_{\text{eq}}(\text{C,N,O})$, where $x = 1.5$ for water H and $x = 1.2$ for all other H.

Data collection: *SMART* (Bruker, 1998) and *GEMINI* (Bruker, 2000); cell refinement: *SAINT-Plus* (Bruker, 1998); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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