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Creatininium dipicolinate monohydrate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.048
wR factor = 0.162
Data-to-parameter ratio = 22.3

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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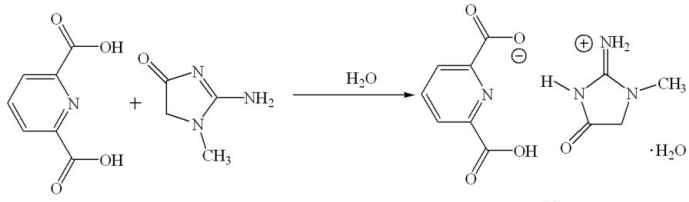
The title compound, $(creatH)^+(pydcH)^-\cdot H_2O$ or $C_4H_8N_3O^+\cdot C_7H_4NO_4^-\cdot H_2O$, was obtained by the reaction of 2,6-pyridinedicarboxylic acid (dipicolinic acid, $pydcH_2$) with creatinine (creat). A single proton from the dicarboxylic acid is transferred to the endocyclic imine N atom of creatinine. The cations and anions lie on a crystallographic mirror plane, across which the water molecule is disordered. The interactions among cations, anions and water molecules consist of ion-pairing, hydrogen bonding and π–π stacking.

Comment

Proton transfer in molecular associations between carboxylic acids and Lewis bases confers considerable stability in the structure-forming process, resulting generally in more hydrogen-bonding associations, particularly involving the protonated amine groups (Smith *et al.*, 1999). In order to study the role of the proton-acceptor compounds in the construction of the three-dimensional structure of the resulting proton-transfer compounds, we have already reported a number of novel proton-transfer compounds, using 2,6-pyridinedicarboxylic acid ($pydcH_2$) and 1,10-phenanthroline-2,9-dicarboxylic acid ($phendcH_2$) as proton donors and 2,6-pyridinediamine (pyda) and guanidine (G) as proton acceptors (Moghimi, Ranjbar, Aghabozorg, Jalali, Shamsipur, Yap & Rahbarnoohi, 2002; Moghimi *et al.*, 2003, 2004). The dicarboxylic acids in all of these cases are suitable ligands in the synthesis of metal complexes (Moghimi *et al.*, 2002*a*,*b*; Ranjbar, Moghimi *et al.*, 2001; Ranjbar, Aghabozorg & Moghimi, 2002; Ranjbar, Taghavipur *et al.*, 2002; Ranjbar, Moghimi *et al.*, 2002; Ranjbar, Aghabozorg *et al.*, 2001, Ranjbar *et al.*, 2003), leaving protonated acceptors as cationic counter-ions in the complexes. Reasoning that similar phenomena could be observed with biologically important acceptors having a number of functional groups suitable for hydrogen bonding, we undertook the synthesis of a novel creatinine-containing proton-transfer compound.



(I)

Creatinine as a proton acceptor has previously been used in the synthesis of some proton-transfer compounds such as those with nitrobenzoic acids, 3,5-dinitrobenzoic acid, 5-nitrosalicyclic acid, 3,5-dinitrosalicyclic acid and pyrazine-2,3-

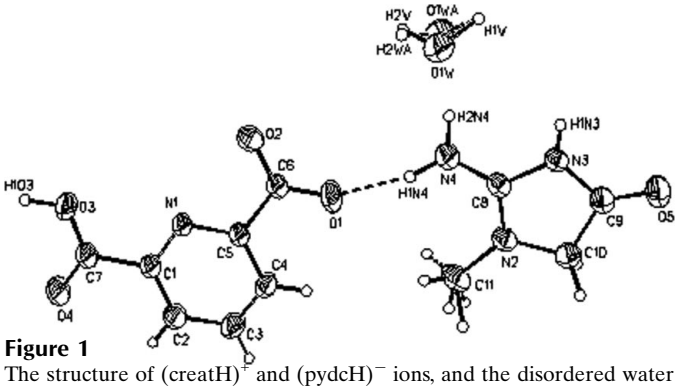


Figure 1
The structure of $(creatH)^+$ and $(pydcH)^-$ ions, and the disordered water molecule. Displacement ellipsoids are drawn at the 50% probability level. The dashed line indicates a hydrogen bond.

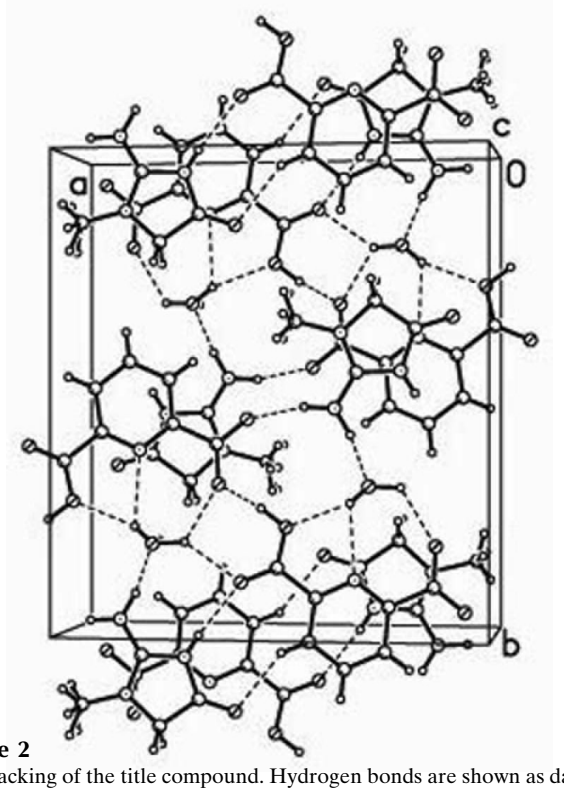


Figure 2
The packing of the title compound. Hydrogen bonds are shown as dashed lines.

dicarboxylic acid (Smith & White, 2001). Among these 1:1 proton-transfer compounds obtained from creatinine, the one obtained with pyrazine has been the single case for which a crystal structure has been determined and reported (Smith & White, 2001). We report here the crystal structure of a 1:1 proton-transfer compound, $(creatH)^+(pydcH)^-\cdot H_2O$, (creat = creatinine, $pydcH_2$ = 2,6-pyridinedicarboxylic acid), (I), as a new example of a creatinine-containing proton-transfer compound.

The structure consists of $(creatH)^+$ and $(pydcH)^-$ ions and a disordered water molecule (Fig. 1), all lying on a crystallographic mirror plane. As is clear from Figs. 2 and 3, the intermolecular interactions among these three fragments consist of ion-pairing, hydrogen bonding and π–π stacking. Fig. 3 also shows the parallel-layered packing pattern, with an

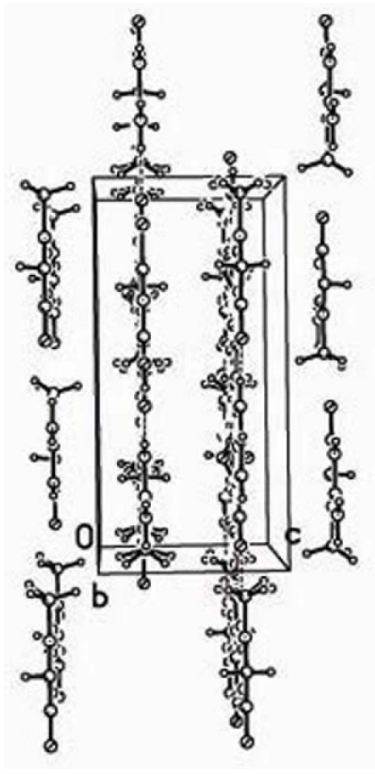


Figure 3
Layers of ions and molecules.

interlayer distance of half of the unit-cell parameter *c*. A single proton transfer occurs from one of the two carboxylic acid functional groups to the endocyclic imine N atom of creatinine. This results in the localization of the exocyclic C8—N4 double bond [1.300 (2) Å] and the adjacent single bond C8—N3 [1.369 (2) Å]. These values may be compared with the intermediate, delocalized values in the parent neutral creatinine molecule [1.320 (3) and 1.349 (3) Å, respectively; Smith & White, 2001]. The two carboxylic groups of the $(pydcH)^-$ anion adopt slightly different conformations, both being essentially coplanar with the pyridine ring. As shown in Figs. 2 and 3, as well as in Table 1, all of the N and O heteroatoms participate in extensive strong or weak hydrogen-bonding interactions, particularly the strong $O3\cdots O2^{i}$ interaction.

Experimental

The title compound was synthesized by the reaction between 2,6-pyrydinedicarboxylic acid and creatinine in a 1:1 molar ratio in water. Colorless crystals were obtained in 94% yield by the partial evaporation of the solvent at room temperature over 7 days.

Crystal data

$C_4H_8N_3O^+\cdot C_7H_4NO_4^-\cdot H_2O$
M_r = 298.26
Orthorhombic, *Pnam*
a = 13.485 (3) Å
b = 15.107 (3) Å
c = 6.5150 (13) Å
V = 1327.2 (5) Å^3
Z = 4
D_x = 1.493 Mg m^{-3}
Mo Kα radiation
Cell parameters from 24 reflections
θ = 10–11°
μ = 0.12 mm^{-1}
T = 293 (2) K
Block, colorless
0.45 × 0.30 × 0.25 mm

Data collection

Enraf–Nonius CAD-4 diffractometer	$\theta_{max} = 34.0^\circ$
$\theta/\frac{5}{3}\theta$ scans	$h = 0 \rightarrow 21$
3012 measured reflections	$k = 0 \rightarrow 23$
2898 independent reflections	$l = 0 \rightarrow 10$
1603 reflections with $I > 2\sigma(I)$	3 standard reflections
$R_{int} = 0.013$	every 97 reflections
	intensity decay: 2.5%

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0896P)^2 + 0.0618P]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)] = 0.048$	$(\Delta/\sigma)_{max} < 0.001$
$wR(F^2) = 0.162$	$\Delta\rho_{max} = 0.39$ e Å^{-3}
$S = 1.03$	$\Delta\rho_{min} = -0.29$ e Å^{-3}
2898 reflections	
130 parameters	
H-atom parameters constrained	

Table 1
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
O3—H1O3···O2^{i}	0.97	1.52	2.490 (2)	172
N3—H1N3···O4^{ii}	0.82	2.13	2.946 (2)	174
N4—H2N4···O1W	0.95	1.75	2.672 (3)	163
N4—H2N4···O1W^{iii}	0.95	1.75	2.672 (3)	163
N4—H1N4···O1	0.95	1.83	2.754 (2)	165
O1W—H1W···O2^{iv}	1.04	2.10	2.768 (2)	120
O1W—H1W···O4^{ii}	1.04	2.16	2.999 (3)	136
O1W—H2W···O3^{iv}	1.03	2.17	2.953 (2)	132
O1W—H2W···N1^{iv}	1.03	2.39	2.978 (3)	115

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

All H atoms were positioned geometrically or located in a difference synthesis, and were included in the refinement in a riding model, with U_{iso}(H) = 1.2U_{eq} of the carrier atom (U_{iso} = 1.5 U_{eq} for methyl H atoms). The H atoms of the C11 methyl group are disordered over two positions related by the mirror plane; their occupancy factors were set to 0.5. The water molecule is disordered over two positions across the mirror plane; the positions of one of the H atoms (H1W) for both components of disorder coincide. Bond distances are C—H 0.93, N—H 0.82–0.95, O—H 0.97–1.04 Å.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1984); cell refinement: *CAD*-4 *Software*; data reduction: *XCAD*4 (Harms, 1996); program(s) used to solve structure: *SHELXTL* (Sheldrick, 1998); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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