Propane-1,3-diaminium bis(pyridine-4-carboxylate) monohydrate

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The asymmetric unit of the title compound, $C_3H_{12}N_2^{2+} \cdot 2C_6H_4NO_2^- \cdot H_2O$, consists of half of a doubly protonated propane-1,3-diammonium dication, a pyridine-4-carboxylate anion and half of a solvent water molecule; the dication and the solvent water are located on a twofold rotation axis which passes through the central C atom of the dication and the water O atom. The carboxylate group of the anion appears to be delocalized on the basis of the C—O bond lengths. In the crystal, the components are linked by intermolecular N—H···O, N—H···N and O—H···O hydrogen bonds.

Related literature

For related compounds with a propane-1,3- diammonium dication which exhibit an all-*trans* zigzag conformation, see: Turner & Batten (2010); Aghabozorg *et al.*, (2011). For the preparation of the flexible ligand, see: Brito *et al.* (2010, 2011).
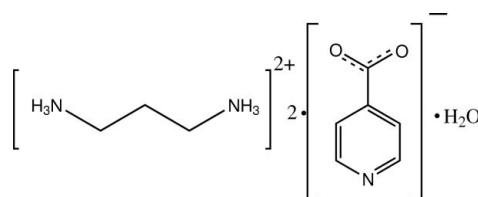
Experimental

Crystal data

$C_3H_{12}N_2^{2+} \cdot 2C_6H_4NO_2^- \cdot H_2O$	$a = 15.360\ (3)$ Å
$M_r = 338.37$	$b = 12.508\ (3)$ Å
Monoclinic, $C2/c$	$c = 10.593\ (2)$ Å
$\beta = 122.67\ (3)°$	$\mu = 0.10$ mm^{-1}
$V = 1713.2\ (8)$ Å^3	$T = 295$ K
$Z = 4$	$0.27 \times 0.25 \times 0.21$ mm
Mo $K\alpha$ radiation	

Data collection

Nonius KappaCCD area-detector diffractometer	2119 independent reflections
11720 measured reflections	1871 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.050$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.046$	H atoms treated by a mixture of independent and constrained refinement
$wR(F^2) = 0.122$	
$S = 1.06$	
2119 reflections	$\Delta\rho_{max} = 0.32$ e Å^{-3}
115 parameters	$\Delta\rho_{min} = -0.24$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2A···O1^i	0.89	1.91	2.7901 (16)	170
N2—H2B···O2^{ii}	0.89	1.91	2.779 (2)	165
N2—H2C···N1^{iii}	0.89	2.00	2.877 (2)	166
O3—H3···O1^{iv}	0.85 (2)	2.00 (3)	2.8426 (17)	169 (2)

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

Data collection: *COLLECT* (Nonius, 2000; cell refinement: *DENZO-SMN* (Otwinowski & Minor, 1997); data reduction: *DENZO-SMN*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *OLEX2* (Dolomanov *et al.*, 2009); software used to prepare material for publication: *publCIF* (Westrip, 2010).

References

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supplementary materials

Propane-1,3-diaminium bis(pyridine-4-carboxylate) monohydrate

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Comment

This paper forms part of our continuing study of the synthesis and structural characterization of a flexible ligand for preparation of coordination polymers (Brito *et al.*, 2010; 2011 and references therein). The title compound was isolated during attempts to synthesize a flexible ligand by a condensation reaction between 4-pyridinecarboxylic acid and 1,3-diaminopropane. A notable feature of the structure is the extensive network of the hydrogen bonds between the ammonium H and pyridine-carboxylate N, O atoms. The hydrogen-bonding network involves all of the ammonium H and pyridine-carboxylate O,*N* atoms, forming a three-dimensional network Fig.2, Table 1. The water H are linked to two carboxylate O atoms at $(-1/2 + x, 1/2 + y, z)$ and at $(3/2 - x, 1/2 + y, 3/2 - z)$ respectively, forming a two-dimensional network. Propane-1,3-diammonium dication has a fully extended all-*trans* zigzag conformation (N/C/C/C torsion angle 167.57 (13)°). The bond distances and angles for dication and anion are in normal range (Aghabozorg *et al.*, 2011; Turner & Batten 2010, as representative examples).

Experimental

To a solution of 4-pyridinecarboxylic acid (12.3 g, 0.1 mol) in pyridine (40 ml) was added 1,3-diaminopropane (3.71 g, 0,05 mol) in pyridine (20 ml). The solution was stirred gently for 15 min, forming a white precipitate. The resultant solution was then heated with stirring on the steam bath for 4 h. On cooling of the mixture, a white solid crystalline was obtained. Yield 15.8 g (92.9%). Analysis calculated for $C_{15}H_{22}N_4O_5$ (338.37 Dalton): C: 53.22, H: 6.52, N: 16.53; found: C: 52.97, H: 6.50, N: 16.90. IR (KBr, cm^{-1}): (NH_3^+) 1664 m, (C=C) 1600 m, (NH_3^+) 1500 m, (CH_2) 1378 w, (NH_3^+) 1155 m

Refinement

H3 atom was located directly from a Fourier map and refined freely. The positions of the remaining H atoms were located from difference maps and then treated as riding atoms, with C—H distances in the range 0.93–0.97 Å and N—H distances of 0.89 Å and with U_{iso}(H) values of $1.2U_{eq}$(C, N).

Figures
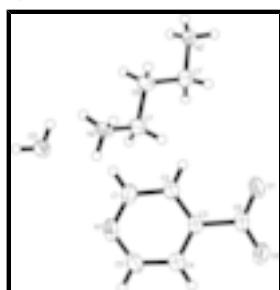
Fig. 1. A view of the molecular structure of title compound, with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. [Symmetry code i: 1 - *x*, *y*, 1/2 - *z*].

supplementary materials
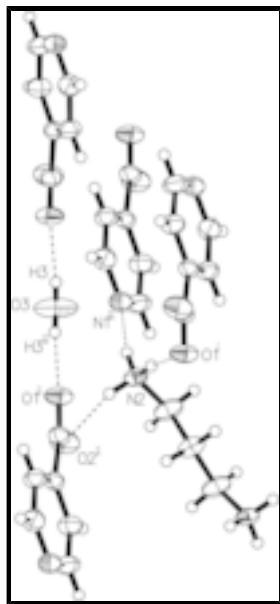
Fig. 2. A view of title compound showing the hydrogen bonds and are indicated by dashed lines. [Symmetry codes: (i) $x - 1/2$, $-y + 3/2$, $z - 1/2$; (ii) $-x + 3/2$, $y + 1/2$, $-z + 3/2$; (iii) $-x + 1$, y, $-z + 3/2$; (iv) $x - 1/2$, $y + 1/2$, z]

Propane-1,3-diaminium bis(pyridine-4-carboxylate) monohydrate

Crystal data
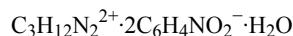
$C_3H_{12}N_2{}^{2+} \cdot 2C_6H_4NO_2{}^- \cdot H_2O$	$F(000) = 720$
$M_r = 338.37$	$D_x = 1.312$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Hall symbol: -C 2yc	Cell parameters from 9511 reflections
$a = 15.360$ (3) Å	$\theta = 3.9$–$28.5°$
$b = 12.508$ (3) Å	$\mu = 0.10$ mm^{-1}
$c = 10.593$ (2) Å	$T = 295$ K
$\beta = 122.67$ (3)°	Block, colourless
$V = 1713.2$ (8) Å^3	$0.27 \times 0.25 \times 0.21$ mm
$Z = 4$	

Data collection

Nonius KappaCCD area-detector diffractometer	1871 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{int} = 0.050$
graphite	$\theta_{max} = 28.5°$, $\theta_{min} = 4.0°$
φ and ω scans with κ offsets	$h = -20 \rightarrow 20$
11720 measured reflections	$k = -16 \rightarrow 16$
2119 independent reflections	$l = -14 \rightarrow 11$

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map

$R[F^2 > 2\sigma(F^2)] = 0.046$

$wR(F^2) = 0.122$

$S = 1.06$

2119 reflections

115 parameters

0 restraints

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 1.0503P]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} = 0.003$

$\Delta\rho_{max} = 0.32$ e Å^{-3}

$\Delta\rho_{min} = -0.24$ e Å^{-3}

Special details

Geometry. All s.u.'s (except the s.u. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell s.u.'s are taken into account individually in the estimation of s.u.'s in distances, angles and torsion angles; correlations between s.u.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell s.u.'s is used for estimating s.u.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > 2\sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}	Occ. (<1)
O1	0.87262 (8)	0.51431 (8)	0.82722 (12)	0.0447 (3)	
O2	0.81345 (8)	0.36420 (8)	0.86906 (13)	0.0480 (3)	
O3	0.5000	0.90541 (13)	0.7500	0.0712 (6)	
H3	0.4617 (17)	0.9452 (17)	0.766 (2)	0.072 (6)*	
N1	0.60893 (9)	0.65138 (10)	0.92600 (13)	0.0405 (3)	
N2	0.48117 (8)	0.79864 (8)	0.46730 (12)	0.0340 (3)	
H2A	0.4411	0.8559	0.4258	0.041*	
H2B	0.5458	0.8194	0.5334	0.041*	
H2C	0.4579	0.7600	0.5136	0.041*	
C1	0.64814 (10)	0.69083 (11)	0.84955 (15)	0.0389 (3)	
H1	0.6312	0.7605	0.8136	0.047*	
C2	0.71275 (10)	0.63306 (11)	0.82123 (14)	0.0355 (3)	
H2	0.7383	0.6636	0.7675	0.043*	
C3	0.73892 (9)	0.52889 (10)	0.87425 (13)	0.0301 (3)	
C4	0.69716 (10)	0.48635 (11)	0.95152 (16)	0.0386 (3)	
H4	0.7115	0.4163	0.9866	0.046*	
C5	0.63370 (11)	0.55061 (13)	0.97516 (17)	0.0437 (3)	
H5	0.6068	0.5220	1.0282	0.052*	
C6	0.81423 (9)	0.46330 (10)	0.85422 (14)	0.0339 (3)	
C7	0.47907 (13)	0.73319 (11)	0.34918 (17)	0.0431 (3)	
H7B	0.4119	0.6993	0.2884	0.052*	
H7A	0.5309	0.6773	0.3956	0.052*	
C8	0.5000	0.80121 (15)	0.2500	0.0401 (4)	

H8A	0.4408	0.8468	0.1876	0.048*	0.50
H8B	0.5592	0.8468	0.3124	0.048*	0.50

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0438 (5)	0.0454 (6)	0.0626 (7)	0.0006 (4)	0.0402 (5)	−0.0077 (5)
O2	0.0492 (6)	0.0347 (5)	0.0702 (7)	0.0085 (4)	0.0389 (6)	−0.0020 (5)
O3	0.0961 (14)	0.0306 (8)	0.146 (2)	0.000	0.1046 (16)	0.000
N1	0.0363 (6)	0.0498 (7)	0.0401 (6)	0.0113 (5)	0.0237 (5)	−0.0029 (5)
N2	0.0406 (6)	0.0330 (5)	0.0414 (6)	−0.0052 (4)	0.0306 (5)	0.0008 (4)
C1	0.0392 (7)	0.0383 (7)	0.0402 (7)	0.0127 (5)	0.0220 (6)	0.0027 (5)
C2	0.0361 (6)	0.0375 (7)	0.0393 (6)	0.0060 (5)	0.0246 (5)	0.0030 (5)
C3	0.0264 (5)	0.0332 (6)	0.0320 (6)	0.0027 (4)	0.0165 (5)	−0.0045 (4)
C4	0.0402 (7)	0.0371 (7)	0.0469 (7)	0.0049 (5)	0.0289 (6)	0.0036 (5)
C5	0.0438 (7)	0.0528 (8)	0.0483 (7)	0.0067 (6)	0.0340 (6)	0.0031 (6)
C6	0.0298 (6)	0.0366 (6)	0.0371 (6)	0.0048 (5)	0.0194 (5)	−0.0049 (5)
C7	0.0649 (9)	0.0301 (6)	0.0561 (8)	−0.0059 (6)	0.0469 (8)	−0.0024 (6)
C8	0.0597 (12)	0.0308 (9)	0.0484 (10)	0.000	0.0413 (10)	0.000

Geometric parameters (Å, °)

O1—C6	1.2531 (16)	C2—H2	0.9300
O2—C6	1.2503 (17)	C3—C4	1.3896 (18)
O3—H3	0.85 (2)	C3—C6	1.5237 (15)
N1—C1	1.3373 (18)	C4—C5	1.3865 (18)
N1—C5	1.338 (2)	C4—H4	0.9300
N2—C7	1.4809 (17)	C5—H5	0.9300
N2—H2A	0.8900	C7—C8	1.5151 (16)
N2—H2B	0.8900	C7—H7B	0.9700
N2—H2C	0.8900	C7—H7A	0.9700
C1—C2	1.3851 (17)	C8—C7^i	1.5151 (16)
C1—H1	0.9300	C8—H8A	0.9700
C2—C3	1.3897 (18)	C8—H8B	0.9700
C1—N1—C5	117.18 (11)	N1—C5—C4	123.75 (13)
C7—N2—H2A	109.5	N1—C5—H5	118.1
C7—N2—H2B	109.5	C4—C5—H5	118.1
H2A—N2—H2B	109.5	O2—C6—O1	126.17 (11)
C7—N2—H2C	109.5	O2—C6—C3	117.18 (11)
H2A—N2—H2C	109.5	O1—C6—C3	116.64 (12)
H2B—N2—H2C	109.5	N2—C7—C8	111.07 (11)
N1—C1—C2	123.24 (13)	N2—C7—H7B	109.4
N1—C1—H1	118.4	C8—C7—H7B	109.4
C2—C1—H1	118.4	N2—C7—H7A	109.4
C1—C2—C3	119.10 (12)	C8—C7—H7A	109.4
C1—C2—H2	120.5	H7B—C7—H7A	108.0
C3—C2—H2	120.5	C7^i—C8—C7	111.68 (15)
C4—C3—C2	118.18 (11)	C7^i—C8—H8A	109.3

C4—C3—C6	120.16 (12)	C7—C8—H8A	109.3
C2—C3—C6	121.62 (11)	C7^i—C8—H8B	109.3
C5—C4—C3	118.52 (13)	C7—C8—H8B	109.3
C5—C4—H4	120.7	H8A—C8—H8B	107.9
C3—C4—H4	120.7		
C5—N1—C1—C2	−0.7 (2)	C3—C4—C5—N1	0.9 (2)
N1—C1—C2—C3	−0.1 (2)	C4—C3—C6—O2	20.19 (18)
C1—C2—C3—C4	1.19 (19)	C2—C3—C6—O2	−162.03 (12)
C1—C2—C3—C6	−176.62 (12)	C4—C3—C6—O1	−158.46 (13)
C2—C3—C4—C5	−1.6 (2)	C2—C3—C6—O1	19.31 (17)
C6—C3—C4—C5	176.26 (12)	N2—C7—C8—C7^i	167.76 (14)
C1—N1—C5—C4	0.2 (2)		

Symmetry codes: (i) −*x*+1, *y*, −*z*+1/2.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2A···O1^{ii}	0.89	1.91	2.7901 (16)	170
N2—H2B···O2^{iii}	0.89	1.91	2.779 (2)	165
N2—H2C···N1^{iv}	0.89	2.00	2.877 (2)	166
O3—H3···O1^v	0.85 (2)	2.00 (3)	2.8426 (17)	169 (2)

Symmetry codes: (ii) *x*−1/2, −*y*+3/2, *z*−1/2; (iii) −*x*+3/2, *y*+1/2, −*z*+3/2; (iv) −*x*+1, *y*, −*z*+3/2; (v) *x*−1/2, *y*+1/2, *z*.

Fig. 1

Fig. 2