

Butane-1,4-diammonium bis(pyridine-2-carboxylate) monohydrate

Nam-Ho Kim and Kwang Ha*

School of Applied Chemical Engineering, the Research Institute of Catalysis, Chonnam National University, Gwangju 500-757, Republic of Korea
Correspondence e-mail: hakwang@chonnam.ac.kr

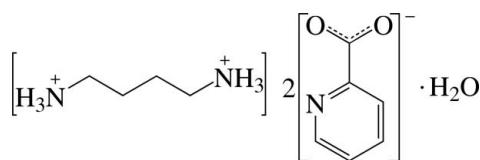
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Key indicators: single-crystal X-ray study; $T = 296$ K; mean $\sigma(\text{C}-\text{C}) = 0.004$ Å; R factor = 0.056; wR factor = 0.152; data-to-parameter ratio = 14.2.

The asymmetric unit of the title compound, $\text{C}_4\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{C}_6\text{H}_4\text{NO}_2^- \cdot \text{H}_2\text{O}$, consists of half of a doubly protonated tetramethylenediammonium dication, a pyridine-2-carboxylate anion and half of a solvent water molecule; the dication is located on a centre of inversion and a twofold rotation axis passes through the O atom of the water molecule. The carboxylate group of the anion appears to be delocalized on the basis of the C—O bond lengths. In the crystal structure, the components are linked by intermolecular N—H \cdots O, N—H \cdots N and O—H \cdots O hydrogen bonds.

Related literature

For the crystal structures of some butane-1,4-diammonium compounds, see: Natarajan & Cheetham (1997); Zheng *et al.* (1999); Sediri *et al.* (2002); Srinivasan *et al.* (2005); Lemmerer & Billing (2006); van Blerk & Kruger (2007, 2008); Jayasundera *et al.* (2008). For the structure of pyridine-2-carboxylic acid, see: Hamazaki *et al.* (1998). For a related hexane-1,6-diammonium compound, see: Kim & Ha (2009).



Experimental

Crystal data

$\text{C}_4\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{C}_6\text{H}_4\text{NO}_2^- \cdot \text{H}_2\text{O}$

$M_r = 352.39$

Monoclinic, $C2/c$

$a = 20.655$ (3) Å

$b = 7.6170$ (11) Å

$c = 12.910$ (2) Å

$\beta = 113.789$ (4)°

$V = 1858.5$ (5) Å³

$Z = 4$

Mo $K\alpha$ radiation

$\mu = 0.10$ mm⁻¹

$T = 296$ K

$0.27 \times 0.21 \times 0.16$ mm

Data collection

Bruker SMART 1000 CCD

diffractometer

Absorption correction: multi-scan

(*SADABS*; Bruker, 2000)

$T_{\min} = 0.740$, $T_{\max} = 0.985$

6674 measured reflections

2298 independent reflections

1040 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.048$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.056$

$wR(F^2) = 0.152$

$S = 0.99$

2298 reflections

162 parameters

All H-atom parameters refined

$\Delta\rho_{\text{max}} = 0.18$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.16$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

D—H \cdots A	D—H	H \cdots A	D \cdots A	D—H \cdots A
N2—H2A \cdots O2 ⁱ	0.99 (3)	1.77 (3)	2.749 (3)	170 (2)
N2—H2B \cdots O1 ⁱⁱ	0.96 (3)	1.84 (3)	2.792 (3)	176 (2)
N2—H2C \cdots O1 ⁱⁱⁱ	0.95 (3)	2.26 (3)	2.997 (3)	134 (2)
N2—H2C \cdots N1 ⁱⁱⁱ	0.95 (3)	2.06 (3)	2.917 (3)	149 (2)
O3—H3O \cdots O1 ^{iv}	0.92 (4)	2.02 (4)	2.926 (3)	172 (4)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *S SAINT* (Bruker, 2000); data reduction: *S SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997) and *PLATON* (Spek, 2009); software used to prepare material for publication: *SHELXL97*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2449).

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supplementary materials

Acta Cryst. (2009). E65, o2151 [doi:10.1107/S1600536809031493]

Butane-1,4-diammonium bis(pyridine-2-carboxylate) monohydrate

N.-H. Kim and K. Ha

Comment

The title compound, $C_4H_{14}N_2^{2+} \cdot 2C_6H_4NO_2^- \cdot H_2O$, consists of a doubly protonated tetramethylenediammonium dication, two pyridine-2-carboxylate anions and a solvent water molecule and the asymmetric unit contains one half of the formula unit (Fig. 1); a centre of inversion is located at the mid-point of the dication and the water molecule is disposed about a twofold rotation axis through O atom with the special position at $(0, y, 1/4)$ (Wyckoff letter e). The carboxylate groups of the anions appear to be delocalized on the basis of the C—O bond lengths [C—O: 1.235 (3) and 1.251 (3) Å]. The torsion angles within the dication reveal that all N and C atoms of the dication display the anti conformation. In the crystal structure, the components are linked by intermolecular N—H \cdots O, N—H \cdots N and O—H \cdots O hydrogen bonds (Table 1 and Fig. 2). There may also be intermolecular π – π interactions between adjacent pyridine rings, with a centroid-centroid distance of 3.796 (2) Å.

Experimental

A solution of 1,4-diaminobutane (0.200 g, 2.269 mmol) and pyridine-2-carboxylic acid (1.173 g, 9.528 mmol) in H_2O (20 ml) was stirred for 3 h at 60 °C. The solvent was removed under vacuum and the residue was washed with acetone/ether, to give a white powder (0.830 g). Crystals suitable for X-ray analysis were obtained by slow evaporation from an acetone solution.

Refinement

All H atoms were located from Fourier difference maps and refined isotropically; C—H = 0.91 (2)–1.05 (3) Å, N—H = 0.95 (3)–0.99 (3) Å and O—H = 0.92 (4) Å.

Figures

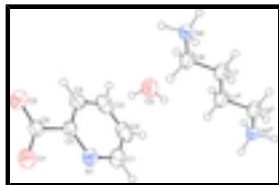


Fig. 1. The structure of the title compound, with displacement ellipsoids drawn at the 40% probability level for non-H atoms. The superscript a corresponds to symmetry code: $-x, -y + 1, -z$.

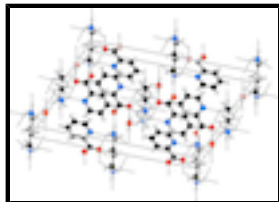
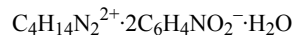


Fig. 2. View of the unit-cell contents of the title compound. Hydrogen-bond interactions are drawn with dashed lines.

Butane-1,4-diammonium bis(pyridine-2-carboxylate) monohydrate

Crystal data

 $M_r = 352.39$ Monoclinic, $C2/c$ Hall symbol: $-C\ 2yc$ $a = 20.655\ (3)\ \text{\AA}$ $b = 7.6170\ (11)\ \text{\AA}$ $c = 12.910\ (2)\ \text{\AA}$ $\beta = 113.789\ (4)^\circ$ $V = 1858.5\ (5)\ \text{\AA}^3$ $Z = 4$ $F_{000} = 752$ $D_x = 1.259\ \text{Mg m}^{-3}$ Mo $K\alpha$ radiation, $\lambda = 0.71073\ \text{\AA}$

Cell parameters from 1114 reflections

 $\theta = 2.9\text{--}22.5^\circ$ $\mu = 0.10\ \text{mm}^{-1}$ $T = 296\ \text{K}$

Block, colorless

 $0.27 \times 0.21 \times 0.16\ \text{mm}$

Data collection

Bruker SMART 1000 CCD
diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

 $T = 296\ \text{K}$ φ and ω scansAbsorption correction: multi-scan
(*SADABS*; Bruker, 2000) $T_{\min} = 0.740$, $T_{\max} = 0.985$

6674 measured reflections

2298 independent reflections

1040 reflections with $I > 2\sigma(I)$ $R_{\text{int}} = 0.048$ $\theta_{\max} = 28.3^\circ$ $\theta_{\min} = 2.2^\circ$ $h = -27 \rightarrow 27$ $k = -10 \rightarrow 9$ $l = -17 \rightarrow 15$

Refinement

Refinement on F^2

Least-squares matrix: full

 $R[F^2 > 2\sigma(F^2)] = 0.056$ $wR(F^2) = 0.152$ $S = 0.99$

2298 reflections

162 parameters

Primary atom site location: structure-invariant direct
methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring
sites

All H-atom parameters refined

$$w = 1/[\sigma^2(F_o^2) + (0.0576P)^2]$$

where $P = (F_o^2 + 2F_c^2)/3$ $(\Delta/\sigma)_{\max} < 0.001$ $\Delta\rho_{\max} = 0.18\ \text{e \AA}^{-3}$ $\Delta\rho_{\min} = -0.16\ \text{e \AA}^{-3}$

Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations

between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'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 $F^2 > \sigma(F^2)$ 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 (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.42900 (8)	0.4778 (2)	0.55250 (14)	0.0629 (6)
O2	0.36511 (9)	0.6362 (3)	0.61996 (15)	0.0793 (7)
N1	0.31266 (9)	0.3696 (3)	0.37672 (16)	0.0541 (6)
C1	0.25453 (15)	0.3005 (4)	0.2959 (2)	0.0663 (8)
H1	0.2608 (13)	0.230 (4)	0.235 (2)	0.089 (9)*
C2	0.18842 (15)	0.3185 (4)	0.2948 (3)	0.0685 (8)
H2	0.1484 (13)	0.262 (3)	0.233 (2)	0.073 (8)*
C3	0.18017 (14)	0.4148 (4)	0.3778 (3)	0.0646 (8)
H3	0.1342 (14)	0.439 (3)	0.380 (2)	0.085 (9)*
C4	0.23908 (13)	0.4901 (4)	0.4606 (2)	0.0547 (7)
H4	0.2350 (11)	0.556 (3)	0.517 (2)	0.055 (7)*
C5	0.30461 (11)	0.4623 (3)	0.45825 (18)	0.0429 (6)
C6	0.37158 (13)	0.5323 (3)	0.5513 (2)	0.0483 (6)
N2	0.05485 (12)	0.8325 (3)	0.15154 (19)	0.0463 (5)
H2A	0.0797 (12)	0.853 (3)	0.234 (2)	0.072 (8)*
H2B	0.0116 (14)	0.898 (3)	0.121 (2)	0.070 (8)*
H2C	0.0864 (14)	0.863 (4)	0.117 (2)	0.091 (10)*
C7	0.00642 (18)	0.5974 (3)	0.0102 (2)	0.0599 (8)
H7A	-0.0362 (16)	0.665 (4)	-0.025 (3)	0.106 (11)*
H7B	0.0374 (16)	0.642 (4)	-0.025 (3)	0.116 (12)*
C8	0.04043 (18)	0.6425 (4)	0.1318 (2)	0.0612 (8)
H8A	0.0144 (16)	0.604 (4)	0.173 (3)	0.113 (13)*
H8B	0.0889 (17)	0.577 (4)	0.175 (3)	0.127 (13)*
O3	0.0000	0.2467 (4)	0.2500	0.0872 (10)
H3O	0.018 (2)	0.173 (5)	0.311 (3)	0.176 (18)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0443 (9)	0.0705 (12)	0.0630 (12)	-0.0030 (9)	0.0102 (8)	-0.0125 (9)
O2	0.0782 (13)	0.0863 (15)	0.0542 (12)	0.0161 (11)	0.0066 (10)	-0.0263 (11)
N1	0.0472 (12)	0.0625 (14)	0.0459 (12)	-0.0017 (10)	0.0117 (10)	-0.0095 (10)
C1	0.0599 (18)	0.0692 (19)	0.0532 (17)	-0.0025 (15)	0.0056 (14)	-0.0149 (14)
C2	0.0483 (17)	0.0638 (19)	0.068 (2)	-0.0074 (14)	-0.0032 (14)	0.0020 (15)
C3	0.0429 (16)	0.073 (2)	0.071 (2)	0.0037 (14)	0.0156 (15)	0.0136 (16)
C4	0.0538 (16)	0.0597 (18)	0.0500 (16)	0.0119 (13)	0.0202 (13)	0.0062 (13)
C5	0.0462 (13)	0.0407 (13)	0.0368 (13)	0.0041 (11)	0.0116 (10)	0.0035 (10)

supplementary materials

C6	0.0527 (14)	0.0423 (14)	0.0412 (14)	0.0048 (12)	0.0097 (12)	0.0015 (11)
N2	0.0456 (12)	0.0466 (13)	0.0425 (13)	0.0015 (10)	0.0134 (11)	-0.0049 (10)
C7	0.082 (2)	0.0495 (16)	0.0436 (15)	-0.0082 (16)	0.0205 (15)	-0.0045 (12)
C8	0.089 (2)	0.0471 (17)	0.0409 (15)	-0.0074 (15)	0.0191 (15)	-0.0047 (12)
O3	0.108 (2)	0.072 (2)	0.063 (2)	0.000	0.0152 (18)	0.000

Geometric parameters (Å, °)

O1—C6	1.251 (3)	C5—C6	1.517 (3)
O2—C6	1.235 (3)	N2—C8	1.479 (3)
N1—C5	1.332 (3)	N2—H2A	0.99 (3)
N1—C1	1.341 (3)	N2—H2B	0.96 (3)
C1—C2	1.367 (4)	N2—H2C	0.95 (3)
C1—H1	1.01 (3)	C7—C8	1.478 (3)
C2—C3	1.364 (4)	C7—C7 ⁱ	1.512 (5)
C2—H2	0.98 (2)	C7—H7A	0.96 (3)
C3—C4	1.380 (4)	C7—H7B	0.98 (3)
C3—H3	0.98 (3)	C8—H8A	0.95 (3)
C4—C5	1.383 (3)	C8—H8B	1.05 (3)
C4—H4	0.91 (2)	O3—H3O	0.92 (4)
C5—N1—C1	117.7 (2)	C8—N2—H2A	108.6 (15)
N1—C1—C2	123.1 (3)	C8—N2—H2B	110.4 (14)
N1—C1—H1	117.5 (15)	H2A—N2—H2B	111 (2)
C2—C1—H1	119.4 (15)	C8—N2—H2C	106.6 (17)
C3—C2—C1	119.1 (3)	H2A—N2—H2C	108 (2)
C3—C2—H2	122.5 (15)	H2B—N2—H2C	112 (2)
C1—C2—H2	118.4 (15)	C8—C7—C7 ⁱ	112.8 (3)
C2—C3—C4	118.8 (3)	C8—C7—H7A	109.3 (19)
C2—C3—H3	123.6 (16)	C7 ⁱ —C7—H7A	112.5 (19)
C4—C3—H3	117.5 (16)	C8—C7—H7B	106.8 (19)
C3—C4—C5	119.0 (3)	C7 ⁱ —C7—H7B	111.1 (19)
C3—C4—H4	120.6 (14)	H7A—C7—H7B	104 (2)
C5—C4—H4	120.4 (14)	C7—C8—N2	112.7 (2)
N1—C5—C4	122.3 (2)	C7—C8—H8A	113.3 (19)
N1—C5—C6	116.6 (2)	N2—C8—H8A	108.9 (19)
C4—C5—C6	121.1 (2)	C7—C8—H8B	113.5 (17)
O2—C6—O1	125.5 (2)	N2—C8—H8B	106.6 (17)
O2—C6—C5	117.7 (2)	H8A—C8—H8B	101 (3)
O1—C6—C5	116.8 (2)		
C5—N1—C1—C2	-1.1 (4)	C3—C4—C5—C6	-176.1 (2)
N1—C1—C2—C3	1.7 (5)	N1—C5—C6—O2	171.3 (2)
C1—C2—C3—C4	-0.4 (4)	C4—C5—C6—O2	-10.4 (3)
C2—C3—C4—C5	-1.4 (4)	N1—C5—C6—O1	-9.5 (3)
C1—N1—C5—C4	-0.8 (4)	C4—C5—C6—O1	168.8 (2)
C1—N1—C5—C6	177.5 (2)	C7 ⁱ —C7—C8—N2	178.3 (3)
C3—C4—C5—N1	2.1 (4)		

Symmetry codes: (i) $-x, -y+1, -z$.

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>
N2—H2A···O2 ⁱⁱ	0.99 (3)	1.77 (3)	2.749 (3)	170 (2)
N2—H2B···O1 ⁱⁱⁱ	0.96 (3)	1.84 (3)	2.792 (3)	176 (2)
N2—H2C···O1 ^{iv}	0.95 (3)	2.26 (3)	2.997 (3)	134 (2)
N2—H2C···N1 ^{iv}	0.95 (3)	2.06 (3)	2.917 (3)	149 (2)
O3—H3O···O1 ^v	0.92 (4)	2.02 (4)	2.926 (3)	172 (4)

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

Fig. 1

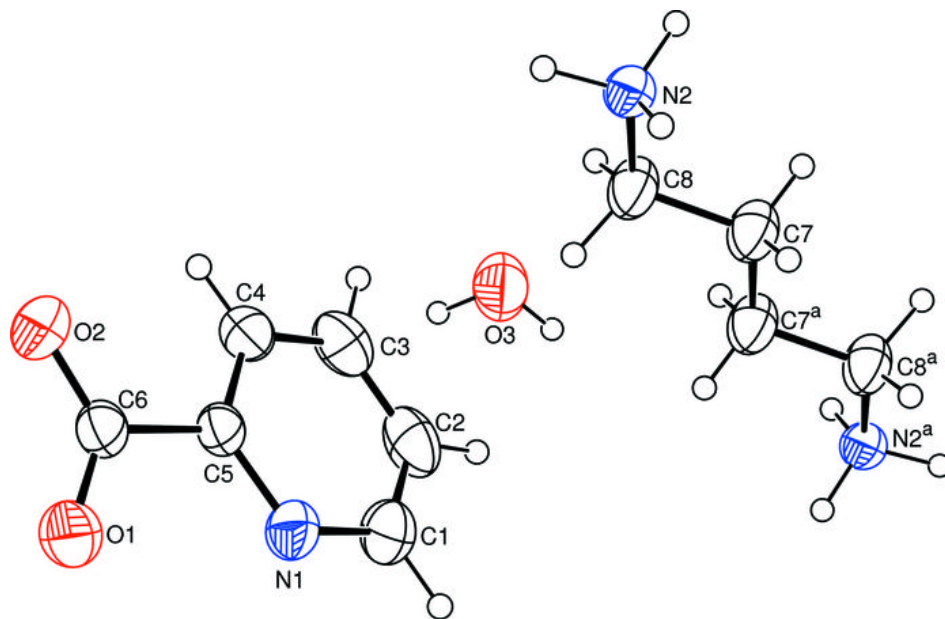


Fig. 2

