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## Structure Reports

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# 1,4-Diazoniabicyclo[2.2.2]octane bis(3-carboxypyridine-2-carboxylate) 2.17-hydrate

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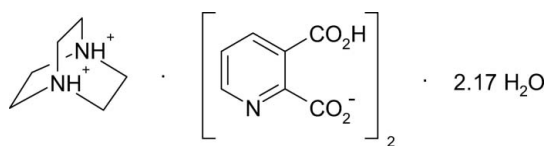
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Key indicators: single-crystal X-ray study;  $T = 293$  K; mean  $\sigma(\text{C}-\text{C}) = 0.002$  Å; some non-H atoms missing; disorder in main residue;  $R$  factor = 0.051;  $wR$  factor = 0.155; data-to-parameter ratio = 17.5.

The title compound,  $\text{C}_6\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_4\text{NO}_4^- \cdot 2.17\text{H}_2\text{O}$ , is a hydrated molecular salt. The cation has crystallographic twofold rotation symmetry, and the component species interact by way of bifurcated  $\text{N}-\text{H} \cdots (\text{O}, \text{N})$  hydrogen bonds to result in associations of two anions and one cation. The anion is stabilized by an intramolecular  $\text{O}-\text{H} \cdots \text{O}$  bond. The water molecules are disordered and occupy [001] *pseudo* channels in the structure.

## Related literature

For background, see: Harrison *et al.* (2007).



## Experimental

### Crystal data

$\text{C}_6\text{H}_{14}\text{N}_2^{2+} \cdot 2\text{C}_7\text{H}_4\text{NO}_4^- \cdot 2.17\text{H}_2\text{O}$   $V = 2127.94$  (12) Å<sup>3</sup>  
 $M_r = 488.62$   $Z = 4$   
 Orthorhombic,  $Pbcn$  Mo  $K\alpha$  radiation  
 $a = 19.4117$  (6) Å  $\mu = 0.12$  mm<sup>-1</sup>  
 $b = 8.1486$  (3) Å  $T = 293$  (2) K  
 $c = 13.4528$  (4) Å  $0.20 \times 0.15 \times 0.15$  mm

### Data collection

Bruker SMART1000 CCD 2958 independent reflections  
 diffractometer 2239 reflections with  $I > 2\sigma(I)$   
 Absorption correction: none  $R_{\text{int}} = 0.034$   
 46987 measured reflections

### Refinement

$R[F^2 > 2\sigma(F^2)] = 0.051$  169 parameters  
 $wR(F^2) = 0.155$  H-atom parameters constrained  
 $S = 1.03$   $\Delta\rho_{\text{max}} = 0.40$  e Å<sup>-3</sup>  
 2958 reflections  $\Delta\rho_{\text{min}} = -0.27$  e Å<sup>-3</sup>

**Table 1**

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{O1}-\text{H2} \cdots \text{O3}$	0.98	1.41	2.3796 (18)	176
$\text{N1}-\text{H1} \cdots \text{N2}$	0.91	2.04	2.8963 (17)	156
$\text{N1}-\text{H1} \cdots \text{O4}$	0.91	2.19	2.8143 (17)	125

Data collection: *SMART* (Bruker, 1999); cell refinement: *SAINTE* (Bruker, 1999); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *SHELXL97*.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BT2562).

## References

- Bruker (1999). *SMART* and *SAINTE*. Bruker AXS Inc., Madison, Wisconsin, USA.  
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.  
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**supplementary materials**

*Acta Cryst.* (2007). E63, o4837 [ doi:10.1107/S1600536807059818 ]

## 1,4-Diazoniabicyclo[2.2.2]octane bis(3-carboxypyridine-2-carboxylate) 2.17-hydrate

P. G. Seethalakshmi, P. Ramadevi, S. Kumaresan and W. T. A. Harrison

### Comment

As part of our investigations of supramolecular networks (Harrison *et al.*, 2007), the title compound, (I), a hydrated molecular salt, has been prepared and structurally characterized. The complete  $C_6H_{14}N_2^{2+}$  cation is generated by crystallographic 2-fold symmetry, with the rotation axis bisecting the  $C3-C3^i$  ( $i = 1 - x, y, 3/2 - z$ ) bond. The C—O bond distances of the  $C_7H_4NO_4^-$  anion suggest charge localization (*i.e.* well defined single and double bonds) in the deprotonated carboxylate group. The dihedral angles between the mean plane of the pyridine ring (N2/C4—C8) and the planes of the C9/O1/O2 and C10/O3/O4 groups are  $3.7(3)^\circ$  and  $5.0(2)^\circ$ , respectively. The anion is stabilized by an intramolecular O—H $\cdots$ O hydrogen bond (Table 2).

In the crystal of (I), associations of two anions and one cation occur, linked by bifurcated N—H $\cdots$ (N,O) hydrogen bonds arising from the symmetry equivalent N—H groupings of the cation. These trimolecular associations form a pseudo framework delimiting [001] channels containing the disordered water molecules (Fig. 2). There are no significant  $\pi$ - $\pi$  stacking interactions, the shortest centroid-centroid separation involving the pyridine rings being longer than 4.13 Å.

### Experimental

Pyridine-2,3-dicarboxylic acid (0.0835 g, 0.5 mmol) was dissolved in hot water. To the resulting clear solution was added an aqueous solution of diazabicyclo[2.2.2]octane (0.056 g, 0.5 mmol). The mixture was allowed to crystallize at room temperature. Colourless blocks of (I) were obtained after six weeks. The crystals were washed with doubly distilled water and finally with ether and then air dried.

### Refinement

The carboxylic acid hydrogen atom was located in a difference map and refined as riding in its as-found relative position. The C- and N-bound H atoms were geometrically placed (C—H = 0.93–0.97 Å, N—H = 0.91 Å) and refined as riding. The constraint  $U_{iso}(H) = 1.2U_{eq}(\text{carrier})$  was applied in all cases. The H atoms of the disordered water molecules could not be located in difference maps, nor could they be geometrically placed in an unambiguous manner.

### Figures

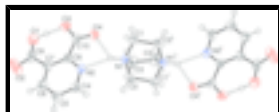


Fig. 1. A view of the trimeric association of two anions and one cation in (I), showing displacement ellipsoids at the 50% probability level (arbitrary spheres for the H atoms). Symmetry code: (i)  $1 - x, y, 3/2 - z$ . The disordered water molecule O atoms are not shown.

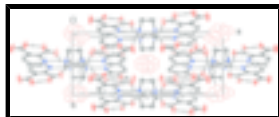


Fig. 2. Unit cell packing of (I), viewed along [001]. The C-bound H atoms are omitted for clarity and hydrogen bonds are shown as dashed lines. The disordered water-molecule O atoms are shown as open ellipses.

## 1,4-Diazoniabicyclo[2.2.2]octane bis(3-carboxypyridine-2-carboxylate) 2.17-hydrate

### Crystal data

$C_6H_{14}N_2^{2+} \cdot 2C_7H_4NO_4^- \cdot 2.17H_2O$	$F_{000} = 1030$
$M_r = 488.62$	$D_x = 1.525 \text{ Mg m}^{-3}$
Orthorhombic, <i>Pbcn</i>	Mo $K\alpha$ radiation
Hall symbol: -P 2n 2ab	$\lambda = 0.71073 \text{ \AA}$
$a = 19.4117 (6) \text{ \AA}$	Cell parameters from 35550 reflections
$b = 8.1486 (3) \text{ \AA}$	$\theta = 1.0\text{--}29.5^\circ$
$c = 13.4528 (4) \text{ \AA}$	$\mu = 0.12 \text{ mm}^{-1}$
$V = 2127.94 (12) \text{ \AA}^3$	$T = 293 (2) \text{ K}$
$Z = 4$	Block, colourless
	$0.20 \times 0.15 \times 0.15 \text{ mm}$

### Data collection

Bruker SMART1000 CCD diffractometer	2239 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	$R_{\text{int}} = 0.034$
Monochromator: graphite	$\theta_{\text{max}} = 29.5^\circ$
$T = 293(2) \text{ K}$	$\theta_{\text{min}} = 3.0^\circ$
$\omega$ scans	$h = -26 \rightarrow 26$
Absorption correction: none	$k = -11 \rightarrow 11$
46987 measured reflections	$l = -18 \rightarrow 18$
2958 independent reflections	

### Refinement

Refinement on $F^2$	Secondary atom site location: difference Fourier map
Least-squares matrix: full	Hydrogen site location: difmap and geom
$R[F^2 > 2\sigma(F^2)] = 0.051$	H-atom parameters constrained
$wR(F^2) = 0.155$	$w = 1/[\sigma^2(F_o^2) + (0.0738P)^2 + 0.9232P]$
$S = 1.03$	where $P = (F_o^2 + 2F_c^2)/3$
2958 reflections	$(\Delta/\sigma)_{\text{max}} = 0.001$
169 parameters	$\Delta\rho_{\text{max}} = 0.40 \text{ e \AA}^{-3}$
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{\text{min}} = -0.26 \text{ e \AA}^{-3}$
	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  $F^2 > 2\sigma(F^2)$  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 ( $\text{\AA}^2$ )*

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.44586 (6)	0.05154 (17)	0.79953 (9)	0.0365 (3)	
H1	0.4062	0.0516	0.8357	0.044*	
C1	0.50208 (8)	-0.0217 (2)	0.85972 (12)	0.0452 (4)	
H1A	0.4877	-0.1272	0.8858	0.054*	
H1B	0.5132	0.0496	0.9152	0.054*	
C2	0.43507 (8)	-0.0429 (3)	0.70684 (12)	0.0478 (4)	
H2A	0.3942	-0.0036	0.6729	0.057*	
H2B	0.4286	-0.1581	0.7223	0.057*	
C3	0.46380 (10)	0.2233 (2)	0.77198 (16)	0.0548 (5)	
H3A	0.4622	0.2932	0.8303	0.066*	
H3B	0.4311	0.2650	0.7236	0.066*	
C4	0.26026 (9)	-0.0092 (2)	0.78806 (12)	0.0441 (4)	
H4	0.2796	-0.0662	0.7351	0.053*	
C5	0.18977 (9)	0.0058 (2)	0.79217 (13)	0.0485 (4)	
H5	0.1619	-0.0386	0.7427	0.058*	
C6	0.16167 (8)	0.0881 (2)	0.87141 (13)	0.0452 (4)	
H6	0.1141	0.0991	0.8760	0.054*	
C7	0.20344 (7)	0.15523 (19)	0.94498 (11)	0.0362 (3)	
C8	0.27499 (7)	0.13568 (18)	0.93433 (10)	0.0322 (3)	
C9	0.16358 (9)	0.2440 (2)	1.02636 (15)	0.0509 (4)	
C10	0.33207 (8)	0.1987 (2)	1.00263 (11)	0.0385 (3)	
N2	0.30195 (6)	0.05417 (17)	0.85635 (9)	0.0382 (3)	
O1	0.19488 (7)	0.3047 (2)	1.10082 (11)	0.0672 (4)	
H2	0.2447	0.2903	1.0970	0.081*	
O2	0.10145 (8)	0.2546 (3)	1.01790 (17)	0.1080 (9)	
O3	0.31596 (7)	0.26887 (19)	1.08370 (9)	0.0575 (4)	
O4	0.39173 (6)	0.1798 (2)	0.97738 (10)	0.0616 (4)	
O11	0.0514 (5)	0.0498 (6)	0.6190 (5)	0.111 (2)	0.555 (12)
O12	0.0227 (3)	0.0523 (6)	0.5563 (8)	0.090 (3)	0.445 (12)
O13	0.0231 (5)	0.0986 (13)	0.7440 (9)	0.083 (5)*	0.171 (6)

## supplementary materials

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### Atomic displacement parameters ( $\text{\AA}^2$ )

	$U^{11}$	$U^{22}$	$U^{33}$	$U^{12}$	$U^{13}$	$U^{23}$
N1	0.0252 (5)	0.0537 (8)	0.0305 (6)	0.0001 (5)	0.0049 (4)	-0.0032 (5)
C1	0.0332 (7)	0.0738 (12)	0.0287 (7)	0.0002 (7)	0.0002 (5)	0.0085 (7)
C2	0.0293 (7)	0.0765 (13)	0.0378 (8)	-0.0089 (7)	-0.0013 (6)	-0.0109 (8)
C3	0.0560 (11)	0.0510 (10)	0.0575 (11)	0.0076 (8)	0.0185 (9)	0.0002 (8)
C4	0.0429 (9)	0.0551 (10)	0.0344 (7)	-0.0073 (7)	0.0047 (6)	-0.0058 (7)
C5	0.0417 (8)	0.0624 (11)	0.0412 (8)	-0.0146 (8)	-0.0032 (7)	-0.0016 (8)
C6	0.0308 (7)	0.0547 (10)	0.0500 (9)	-0.0038 (7)	0.0006 (6)	0.0052 (8)
C7	0.0329 (7)	0.0386 (7)	0.0371 (7)	0.0025 (6)	0.0060 (5)	0.0056 (6)
C8	0.0317 (6)	0.0369 (7)	0.0281 (6)	0.0017 (5)	0.0034 (5)	0.0050 (5)
C9	0.0385 (8)	0.0566 (11)	0.0577 (10)	0.0048 (7)	0.0142 (7)	-0.0071 (8)
C10	0.0356 (7)	0.0502 (9)	0.0296 (7)	0.0030 (6)	0.0012 (5)	0.0006 (6)
N2	0.0336 (6)	0.0495 (8)	0.0314 (6)	0.0000 (5)	0.0046 (5)	-0.0012 (5)
O1	0.0485 (7)	0.1003 (12)	0.0527 (8)	0.0172 (7)	0.0088 (6)	-0.0245 (8)
O2	0.0375 (8)	0.155 (2)	0.1312 (17)	0.0157 (10)	0.0101 (9)	-0.0741 (15)
O3	0.0473 (7)	0.0861 (10)	0.0391 (6)	0.0092 (7)	-0.0016 (5)	-0.0194 (6)
O4	0.0326 (6)	0.1067 (12)	0.0457 (7)	-0.0007 (7)	0.0017 (5)	-0.0208 (7)
O11	0.151 (5)	0.095 (3)	0.085 (3)	-0.052 (3)	0.005 (4)	0.012 (2)
O12	0.052 (2)	0.081 (3)	0.137 (7)	0.0051 (18)	0.017 (3)	0.020 (3)

### Geometric parameters ( $\text{\AA}$ , $^\circ$ )

N1—C2	1.480 (2)	C4—H4	0.9300
N1—C1	1.484 (2)	C5—C6	1.372 (3)
N1—C3	1.489 (2)	C5—H5	0.9300
N1—H1	0.9100	C6—C7	1.392 (2)
C1—C2 <sup>i</sup>	1.523 (2)	C6—H6	0.9300
C1—H1A	0.9700	C7—C8	1.4052 (19)
C1—H1B	0.9700	C7—C9	1.523 (2)
C2—C1 <sup>i</sup>	1.523 (2)	C8—N2	1.3475 (18)
C2—H2A	0.9700	C8—C10	1.528 (2)
C2—H2B	0.9700	C9—O2	1.214 (2)
C3—C3 <sup>i</sup>	1.525 (4)	C9—O1	1.272 (2)
C3—H3A	0.9700	C10—O4	1.2168 (19)
C3—H3B	0.9700	C10—O3	1.2704 (18)
C4—N2	1.329 (2)	O1—H2	0.9750
C4—C5	1.375 (2)		
C2—N1—C1	110.77 (13)	N2—C4—C5	122.96 (16)
C2—N1—C3	108.18 (14)	N2—C4—H4	118.5
C1—N1—C3	109.98 (14)	C5—C4—H4	118.5
C2—N1—H1	109.3	C6—C5—C4	118.04 (16)
C1—N1—H1	109.3	C6—C5—H5	121.0
C3—N1—H1	109.3	C4—C5—H5	121.0
N1—C1—C2 <sup>i</sup>	108.29 (12)	C5—C6—C7	120.86 (15)
N1—C1—H1A	110.0	C5—C6—H6	119.6

C2 <sup>i</sup> —C1—H1A	110.0	C7—C6—H6	119.6
N1—C1—H1B	110.0	C6—C7—C8	117.31 (14)
C2 <sup>i</sup> —C1—H1B	110.0	C6—C7—C9	113.70 (14)
H1A—C1—H1B	108.4	C8—C7—C9	128.98 (15)
N1—C2—C1 <sup>i</sup>	108.83 (12)	N2—C8—C7	121.28 (13)
N1—C2—H2A	109.9	N2—C8—C10	110.61 (12)
C1 <sup>i</sup> —C2—H2A	109.9	C7—C8—C10	128.11 (13)
N1—C2—H2B	109.9	O2—C9—O1	121.37 (18)
C1 <sup>i</sup> —C2—H2B	109.9	O2—C9—C7	118.09 (19)
H2A—C2—H2B	108.3	O1—C9—C7	120.54 (16)
N1—C3—C3 <sup>i</sup>	108.18 (9)	O4—C10—O3	122.07 (15)
N1—C3—H3A	110.1	O4—C10—C8	118.66 (13)
C3 <sup>i</sup> —C3—H3A	110.1	O3—C10—C8	119.27 (13)
N1—C3—H3B	110.1	C4—N2—C8	119.54 (13)
C3 <sup>i</sup> —C3—H3B	110.1	C9—O1—H2	112.7
H3A—C3—H3B	108.4		
C2—N1—C1—C2 <sup>i</sup>	51.54 (17)	C9—C7—C8—C10	0.2 (3)
C3—N1—C1—C2 <sup>i</sup>	-68.01 (18)	C6—C7—C9—O2	-3.3 (3)
C1—N1—C2—C1 <sup>i</sup>	-67.61 (16)	C8—C7—C9—O2	175.6 (2)
C3—N1—C2—C1 <sup>i</sup>	53.01 (18)	C6—C7—C9—O1	176.68 (18)
C2—N1—C3—C3 <sup>i</sup>	-71.0 (2)	C8—C7—C9—O1	-4.5 (3)
C1—N1—C3—C3 <sup>i</sup>	50.1 (2)	N2—C8—C10—O4	4.8 (2)
N2—C4—C5—C6	-0.9 (3)	C7—C8—C10—O4	-174.75 (17)
C4—C5—C6—C7	0.4 (3)	N2—C8—C10—O3	-175.20 (15)
C5—C6—C7—C8	0.2 (2)	C7—C8—C10—O3	5.3 (2)
C5—C6—C7—C9	179.21 (16)	C5—C4—N2—C8	0.7 (3)
C6—C7—C8—N2	-0.4 (2)	C7—C8—N2—C4	0.0 (2)
C9—C7—C8—N2	-179.25 (15)	C10—C8—N2—C4	-179.56 (14)
C6—C7—C8—C10	179.01 (15)		

Symmetry codes: (i)  $-x+1, y, -z+3/2$ .

*Hydrogen-bond geometry* (Å, °)

<i>D</i> —H $\cdots$ <i>A</i>	<i>D</i> —H	H $\cdots$ <i>A</i>	<i>D</i> $\cdots$ <i>A</i>	<i>D</i> —H $\cdots$ <i>A</i>
O1—H2 $\cdots$ O3	0.98	1.41	2.3796 (18)	176
N1—H1 $\cdots$ N2	0.91	2.04	2.8963 (17)	156
N1—H1 $\cdots$ O4	0.91	2.19	2.8143 (17)	125

Fig. 1

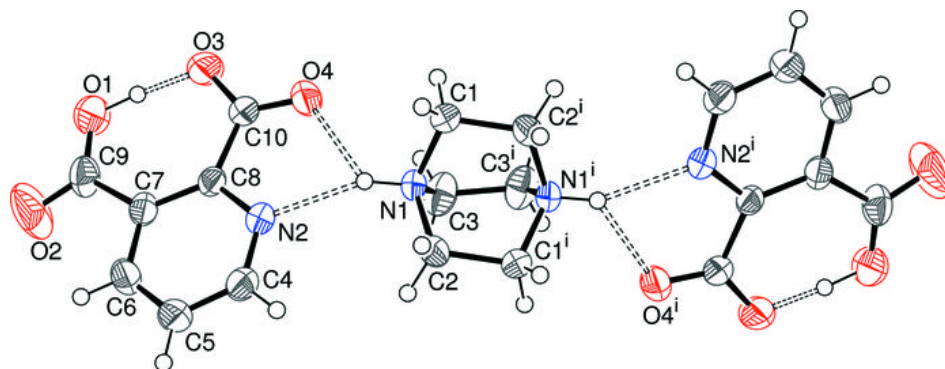




Fig. 2

