organic compounds

Piperazinediium bis(2-carboxypyridine-3-carboxylate)

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The asymmetric unit of the title salt, $C_4H_{12}N_2^{2+}\cdot 2C_7H_4NO_4^-$ or pipzH$_2^{2+}\cdot$2(py-2,3-dcH$^-$), prepared by a reaction between pyridine-2,3-dicarboxylic acid (py-2,3-dcH$_2$) and piperazine (pipz), contains a monoanion and half of a centrosymmetric dication. The anionic fragment individually has two intramolecular hydrogen bonds, an almost linear O—H···O bond between two carboxylate groups and a C—H···O bond between the aromatic ring and carboxylate group. Other O—H···O, N—H···O and C—H···O hydrogen bonds are responsible for three-dimensional expansion of the structure.

Related literature

For related literature, see: Aghabozorg et al. (2006); Aghabozorg, Daneshvar et al. (2007); Aghabozorg, Sadr-khanlou et al. (2007); Khalil & Attia (1999); Manteghi et al. (2007).
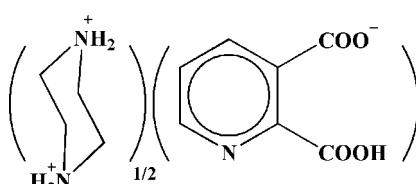
Experimental

Crystal data

$C_4H_{12}N_2^{2+}\cdot 2C_7H_4NO_4^-$	$V = 888.42$ (11) Å^3
$M_r = 420.38$	$Z = 2$
Monoclinic, $P2_1/c$	Mo $K\alpha$ radiation
$a = 8.0116$ (6) Å	$\mu = 0.13$ mm^{-1}
$b = 11.0588$ (9) Å	$T = 100$ (2) K
$c = 10.4621$ (7) Å	$0.20 \times 0.15 \times 0.15$ mm
$\beta = 106.574$ (2)°	

Data collection

Bruker SMART APEXII diffractometer	2341 independent reflections
	2104 reflections with $I > 2\sigma(I)$
Absorption correction: none	$R_{int} = 0.015$
6962 measured reflections	

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.034$	136 parameters
$wR(F^2) = 0.084$	H-atom parameters constrained
$S = 1.03$	$\Delta\rho_{max} = 0.43$ e Å^{-3}
2341 reflections	$\Delta\rho_{min} = -0.22$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O1	0.85	1.57	2.4219 (11)	175
N2—H2A···O2^i	0.90	1.94	2.7778 (12)	154
N2—H2B···O1	0.90	1.97	2.7571 (11)	146
C3—H3A···O4	0.95	2.31	2.6773 (13)	102
C8—H8A···O2^{ii}	0.99	2.58	3.2982 (13)	130
C9—H9A···O4^{iii}	0.99	2.39	3.3491 (14)	163

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

Data collection: APEX2 (Bruker, 2005); cell refinement: APEX2; data reduction: APEX2; program(s) used to solve structure: SHELXTL (Sheldrick, 1998); program(s) used to refine structure: SHELXTL; molecular graphics: SHELXTL and Mercury (Version 1.4.2; Macrae et al., 2006); software used to prepare material for publication: SHELXTL.

References

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supporting information

Piperazinediium bis(2-carboxypyridine-3-carboxylate)

### Hossein Aghabozorg, Faranak Manteghi and Mohammad Ghadermazi

S1. Comment

Pyridinedicarboxylic acids are of great interest in medicinal chemistry because of the wide variety of their physiological properties displayed by natural as well as synthetic acids. These acids are present in many natural products, such as alkaloids, vitamins and coenzymes. Pyridinedicarboxylic acid metal complexes are therefore, especially interesting model systems (Khalil & Attia, 1999). Pyridine-2,3-dicarboxylic acid (py-2,3-dcH$_2$) and piperazine (pipz) with other acids and bases are found in many ion pairs, such as (pipzH$_2$)$_2$(pydc) (Aghabozorg *et al.*, 2006) and (pnH$_2$)(py-2,3-dc).H$_2$O (Manteghi *et al.*, 2007). Moreover, a polymeric complex {(pipzH$_2$)[Zn(py-2,3-dc)$_2$].4H$_2$O}$_n$ including fragments of the title zwitterion has been synthesized (Aghabozorg, Daneshvar *et al.*, 2007). In all mentioned compounds, piperazine is biprotonated and pyridine-2,3-dicarboxylic acid is doubly deprotonated. But in the title ion pair and a complex formulated as [Zn(py-2,3-dcH)$_2$(H$_2$O)$_2$] (Aghabozorg, Sadr-khanlou *et al.*, 2007), pyridine-2,3-dicarboxylic acid is singly deprotonated. Fig. 1 shows the monoanion and the dication and the strong intramolecular hydrogen bond (see table of hydrogen-bond geometry). Fig. 2 illustrates the hydrogen bonded layers parallel to *bc* plane. The title ion pair has three C—H···O hydrogen bonds amongst them the C3—H3A···O4 has a short distance (H···O, 2.31 Å) compared with common C—H···O bonds, although its angle is far from linearity. Additionally, as shown in Fig. 3, the ion pair has a π-π stacking at the distance of 3.6623 (7) Å between the π-rings (symmetry code: 1 - *x*, -*y*, 1 - *z*).

S2. Experimental

The title compound was synthesized *via* reaction of 1.67 g (10 mmol) of pyridine-2,3-dicarboxylic acid with 0.86 g (20 mmol) piperazine in a teterahydrofuran (THF) solution (50 ml). After a while, the obtained white precipitate was filtered out and dissolved in water to recrystallize. Colorless crystals of the title compound were obtained after 1 week.

S3. Refinement

The H(N) and H(O) atoms were found from difference Fourier map. The H(C) atom positions were calculated. All the hydrogen atoms were refined in isotropic approximatiom within riding model with the U_{iso}(H) parameters equal to 1.2Ueq(Ci), 1.2Ueq(Nj) and 1.5Ueq(O) where U(Ci), U(Cj) and U(O) are the equivalent thermal parameters of the carbon, nitrogen and oxygen atoms correspondingly to which corresponding H atoms are bonded.
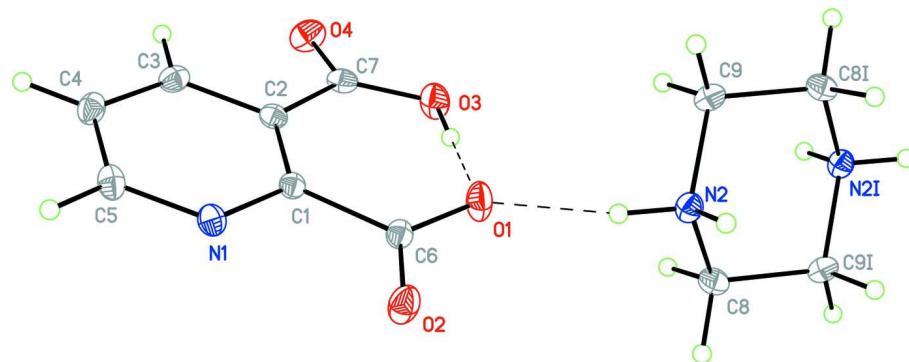
Figure 1

A view of the ion pair drawn at 50% probability level. Symmetry related atoms are labeled "i" and are generated by 2 - *x*, 1 - *y*, 1 - *z*. Some of the hydrogen bonds are shown and are depicted by dashed lines.
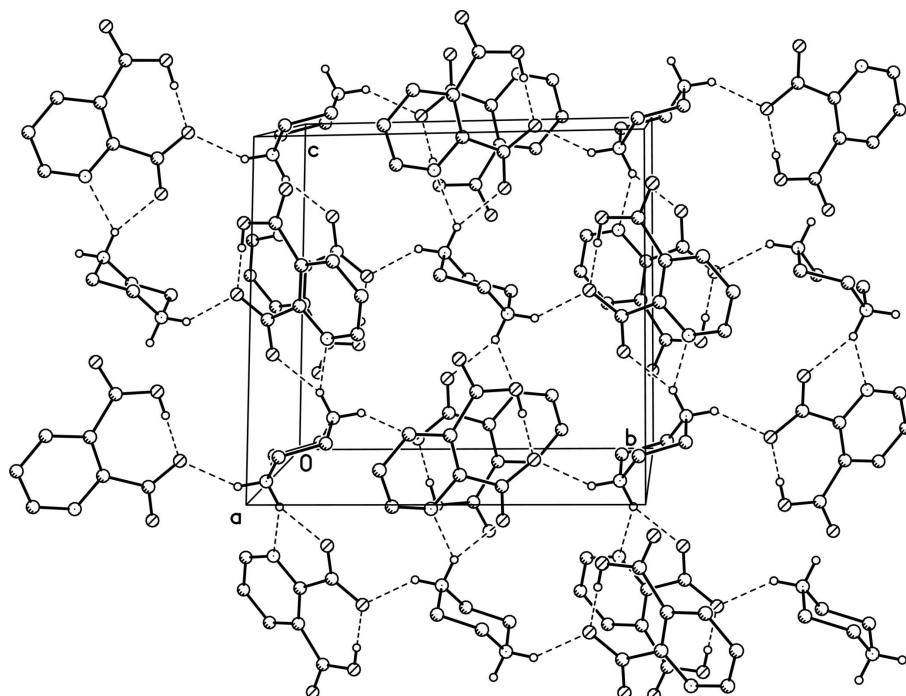
Figure 2

Hydrogen bonded layers parallel to *bc* plane. Hydrogen atoms are omitted for clarity except those involved in hydrogen bonding.
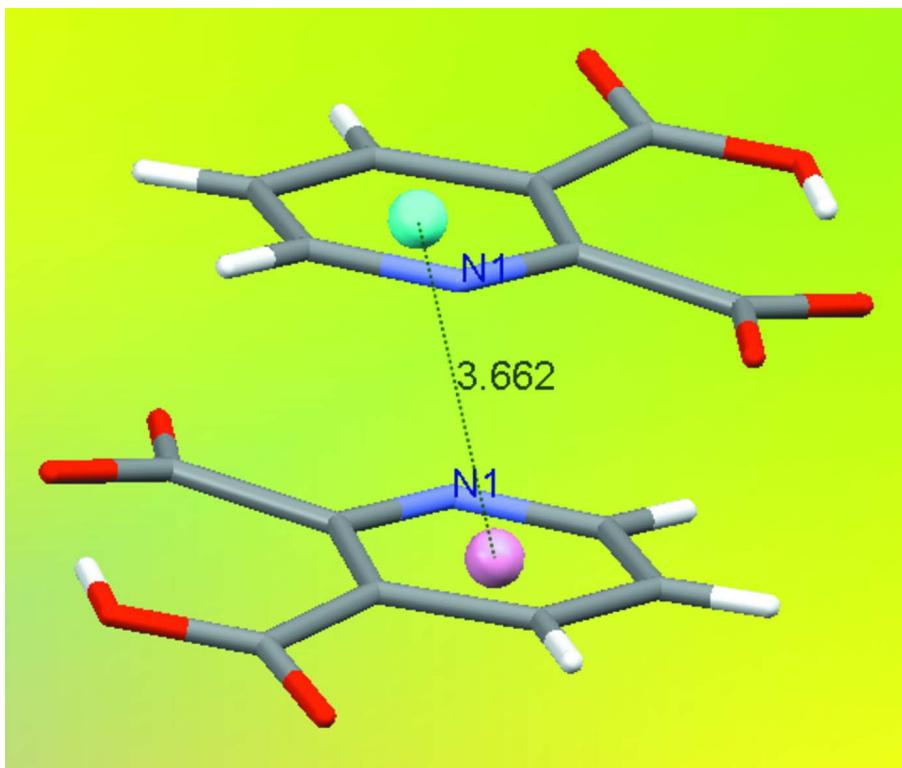
Figure 3

The π-π stacking at the distance of 3.6623 (7) Å (symmetry code: 1 - *x*, -*y*, 1 - *z*).

Piperazinediium bis(2-carboxypyridine-3-carboxylate)

Crystal data
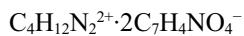
$C_4H_{12}N_2{}^{2+}$·$2C_7H_4NO_4{}^-$
$M_r = 420.38$
Monoclinic, $P2_1/c$
Hall symbol: -P 2ybc
$a = 8.0116$ (6) Å
$b = 11.0588$ (9) Å
$c = 10.4621$ (7) Å
$\beta = 106.574$ (2)°
$V = 888.42$ (11) Å^3
$Z = 2$

$F(000) = 440$
$D_x = 1.571$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 2095 reflections
$\theta = 2.7–28.6°$
$\mu = 0.13$ mm^{-1}
$T = 100$ K
Prism, colourless
$0.20 \times 0.15 \times 0.15$ mm

Data collection

Bruker SMART APEXII
  diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
6962 measured reflections
2341 independent reflections

2104 reflections with $I > 2\sigma(I)$
$R_{int} = 0.015$
$\theta_{max} = 29.0°$, $\theta_{min} = 2.7°$
$h = -10\rightarrow10$
$k = -15\rightarrow15$
$l = -14\rightarrow12$

Refinement

Refinement on F^2	Secondary atom site location: difference Fourier map
Least-squares matrix: full	
$R[F^2 > 2\sigma(F^2)] = 0.034$	Hydrogen site location: mixed
$wR(F^2) = 0.084$	H-atom parameters constrained
$S = 1.03$	$w = 1/[\sigma^2(F_o^2) + (0.035P)^2 + 0.450P]$
2341 reflections	where $P = (F_o^2 + 2F_c^2)/3$
136 parameters	$(\Delta/\sigma)_{max} < 0.001$
0 restraints	$\Delta\rho_{max} = 0.43$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	$\Delta\rho_{min} = -0.22$ e Å^{-3}

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 (Å²)

	x	y	z	$U_{iso}*/U_{eq}$
O1	0.88615 (11)	0.17340 (7)	0.51531 (8)	0.02036 (18)
O2	0.98274 (10)	0.08122 (7)	0.70930 (8)	0.02041 (18)
O3	0.72179 (11)	0.13267 (7)	0.28657 (8)	0.02033 (18)
H3O	0.7842	0.1467	0.3657	0.030*
O4	0.54664 (10)	−0.00934 (8)	0.17740 (8)	0.02126 (18)
N1	0.77161 (11)	−0.10247 (8)	0.63974 (9)	0.01409 (18)
N2	0.98062 (11)	0.40793 (8)	0.59237 (8)	0.01352 (17)
H2A	1.0047	0.4441	0.6726	0.016*
H2B	0.9555	0.3300	0.6036	0.016*
C1	0.76624 (12)	−0.02324 (8)	0.54104 (10)	0.01174 (18)
C2	0.65530 (12)	−0.04141 (9)	0.41030 (10)	0.01209 (19)
C3	0.54476 (13)	−0.14260 (9)	0.39063 (10)	0.0147 (2)
H3A	0.4655	−0.1565	0.3052	0.018*
C4	0.54919 (13)	−0.22223 (9)	0.49329 (11)	0.0161 (2)
H4A	0.4736	−0.2902	0.4802	0.019*
C5	0.66802 (14)	−0.19939 (9)	0.61616 (10)	0.0160 (2)
H5A	0.6760	−0.2552	0.6867	0.019*
C6	0.88903 (13)	0.08412 (9)	0.59330 (10)	0.01317 (19)
C7	0.63871 (13)	0.03075 (9)	0.28268 (10)	0.01448 (19)
C8	1.13286 (13)	0.40868 (9)	0.53727 (10)	0.0146 (2)
H8A	1.1067	0.3580	0.4560	0.018*
H8B	1.2353	0.3736	0.6036	0.018*
C9	0.82508 (13)	0.46401 (9)	0.49653 (10)	0.0147 (2)
H9A	0.7270	0.4659	0.5365	0.018*
H9B	0.7892	0.4149	0.4141	0.018*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0283 (4)	0.0139 (3)	0.0167 (4)	−0.0056 (3)	0.0029 (3)	0.0024 (3)
O2	0.0234 (4)	0.0200 (4)	0.0146 (4)	−0.0074 (3)	0.0003 (3)	0.0013 (3)
O3	0.0268 (4)	0.0184 (4)	0.0135 (3)	−0.0025 (3)	0.0021 (3)	0.0034 (3)
O4	0.0197 (4)	0.0294 (4)	0.0129 (4)	−0.0027 (3)	0.0019 (3)	0.0005 (3)
N1	0.0165 (4)	0.0130 (4)	0.0133 (4)	0.0001 (3)	0.0051 (3)	0.0006 (3)
N2	0.0147 (4)	0.0136 (4)	0.0120 (4)	−0.0018 (3)	0.0033 (3)	0.0006 (3)
C1	0.0120 (4)	0.0110 (4)	0.0129 (4)	0.0007 (3)	0.0047 (3)	−0.0008 (3)
C2	0.0119 (4)	0.0128 (4)	0.0123 (4)	0.0023 (3)	0.0047 (3)	−0.0005 (3)
C3	0.0124 (4)	0.0162 (4)	0.0158 (5)	0.0002 (3)	0.0044 (4)	−0.0040 (4)
C4	0.0160 (4)	0.0131 (4)	0.0209 (5)	−0.0022 (3)	0.0082 (4)	−0.0034 (4)
C5	0.0202 (5)	0.0125 (4)	0.0171 (5)	−0.0004 (4)	0.0084 (4)	0.0011 (4)
C6	0.0136 (4)	0.0123 (4)	0.0145 (4)	−0.0005 (3)	0.0054 (3)	−0.0009 (3)
C7	0.0130 (4)	0.0181 (5)	0.0128 (4)	0.0035 (3)	0.0044 (3)	0.0017 (4)
C8	0.0143 (4)	0.0156 (4)	0.0143 (4)	0.0032 (3)	0.0046 (4)	0.0000 (3)
C9	0.0113 (4)	0.0181 (5)	0.0138 (4)	−0.0013 (3)	0.0023 (3)	0.0003 (4)

Geometric parameters (Å, º)

O1—C6	1.2769 (12)	C2—C3	1.4053 (14)
O2—C6	1.2319 (12)	C2—C7	1.5284 (14)
O3—C7	1.3036 (13)	C3—C4	1.3815 (15)
O3—H3O	0.8501	C3—H3A	0.9500
O4—C7	1.2209 (13)	C4—C5	1.3872 (15)
N1—C5	1.3348 (13)	C4—H4A	0.9500
N1—C1	1.3456 (12)	C5—H5A	0.9500
N2—C8	1.4903 (13)	C8—C9ⁱ	1.5129 (14)
N2—C9	1.4933 (13)	C8—H8A	0.9900
N2—H2A	0.9000	C8—H8B	0.9900
N2—H2B	0.9000	C9—C8ⁱ	1.5129 (14)
C1—C2	1.4169 (13)	C9—H9A	0.9900
C1—C6	1.5394 (13)	C9—H9B	0.9900
C7—O3—H3O	110.0	N1—C5—H5A	118.5
C5—N1—C1	119.93 (9)	C4—C5—H5A	118.5
C8—N2—C9	110.87 (7)	O2—C6—O1	122.99 (9)
C8—N2—H2A	112.1	O2—C6—C1	118.55 (9)
C9—N2—H2A	110.9	O1—C6—C1	118.44 (9)
C8—N2—H2B	107.1	O4—C7—O3	120.92 (9)
C9—N2—H2B	108.1	O4—C7—C2	118.56 (9)
H2A—N2—H2B	107.5	O3—C7—C2	120.51 (9)
N1—C1—C2	121.50 (9)	N2—C8—C9ⁱ	110.92 (8)
N1—C1—C6	110.63 (8)	N2—C8—H8A	109.5
C2—C1—C6	127.85 (9)	C9ⁱ—C8—H8A	109.5
C3—C2—C1	116.74 (9)	N2—C8—H8B	109.5
C3—C2—C7	113.19 (8)	C9ⁱ—C8—H8B	109.5

C1—C2—C7	130.06 (9)	H8A—C8—H8B	108.0
C4—C3—C2	121.22 (9)	N2—C9—C8^i	110.15 (8)
C4—C3—H3A	119.4	N2—C9—H9A	109.6
C2—C3—H3A	119.4	C8^i—C9—H9A	109.6
C3—C4—C5	117.58 (9)	N2—C9—H9B	109.6
C3—C4—H4A	121.2	C8^i—C9—H9B	109.6
C5—C4—H4A	121.2	H9A—C9—H9B	108.1
N1—C5—C4	122.94 (9)		
C5—N1—C1—C2	−1.52 (14)	N1—C1—C6—O2	5.34 (13)
C5—N1—C1—C6	176.91 (9)	C2—C1—C6—O2	−176.36 (10)
N1—C1—C2—C3	3.28 (14)	N1—C1—C6—O1	−173.07 (9)
C6—C1—C2—C3	−174.85 (9)	C2—C1—C6—O1	5.23 (15)
N1—C1—C2—C7	−174.82 (9)	C3—C2—C7—O4	−6.01 (13)
C6—C1—C2—C7	7.04 (16)	C1—C2—C7—O4	172.15 (10)
C1—C2—C3—C4	−2.13 (14)	C3—C2—C7—O3	174.22 (9)
C7—C2—C3—C4	176.30 (9)	C1—C2—C7—O3	−7.62 (16)
C2—C3—C4—C5	−0.66 (15)	C9—N2—C8—C9^i	57.28 (11)
C1—N1—C5—C4	−1.56 (15)	C8—N2—C9—C8^i	−56.84 (11)
C3—C4—C5—N1	2.64 (15)		

Symmetry code: (i) −x+2, −y+1, −z+1.

Hydrogen-bond geometry (Å, º)

D—H···A	D—H	H···A	D···A	D—H···A
O3—H3O···O1	0.85	1.57	2.4219 (11)	175
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Symmetry codes: (ii) −x+2, y+1/2, −z+3/2; (iii) x, −y+1/2, z−1/2; (iv) x, −y+1/2, z+1/2.