Acta Crystallographica Section E
Structure Reports
Online

ISSN 1600-5368

Bis(2,4′-bipyridin-1′-ium) 2,5-dicarboxybenzene-1,4-carboxylate benzene-1,2,4,5-tetracarboxylic acid

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Received 31 May 2005
Accepted 13 June 2005
Online 24 June 2005

The title organic salt, $2C_{10}H_9N_2^+\cdot C_{10}H_4O_8^{2-}\cdot C_{10}H_6O_8$ or 2(H-2,4′bpy)(H_2bta)·H_4bta (where H-2,4′bpy is the 2,4′-bipyridine cation, H_2bta is the 2,5-dicarboxybenzene-1,4-carboxylate anion and H_4bta is the benzene-1,2,4,5-tetracarboxylic acid molecule), crystallizes with both the H_2bta dianion and the H_4bta molecule lying about inversion centres in the triclinic unit cell. This organic salt is formed by an extensive and complex hydrogen-bonding network containing both homo- and heteronuclear neutral and ionic interactions.

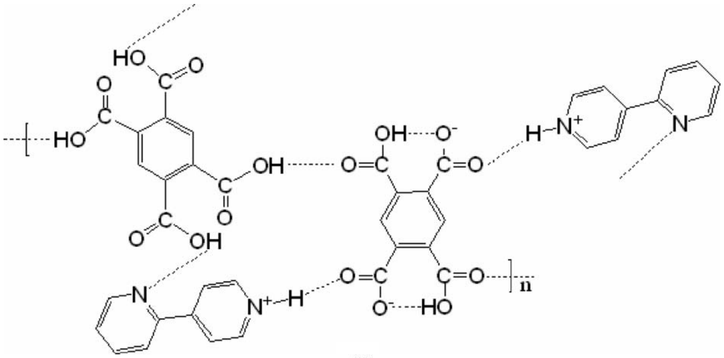
Key indicators

Single-crystal X-ray study
T = 153 K
Mean σ(C–C) = 0.003 Å
R factor = 0.050
wR factor = 0.116
Data-to-parameter ratio = 12.0

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

Comment

Lamellar materials that mimic the structure and properties of naturally occurring clays are currently of great interest in supramolecular chemistry (Holman *et al.*, 2001; Zaworotko, 2001; Beatty, Granger & Simpson, 2002; Beatty, Schneider *et al.*, 2002; Almeida, & Klinowski, 2003). The research described in this contribution focuses on the supramolecular synthesis of solid materials that will intercalate or adsorb small molecules and ions for storage, separation and catalysis. Pyromellitic acid (1,2,4,5-benzenetetracarboxylic acid, H_4bta), which has been used as a ligand in coordination polymers and coordination complexes, is a suitable building block for two-dimensional arrays. In addition, the carboxylic acid can form homo- or heterodimers with a variety of complementary bases, such as pyridine. There have been structural reports of salts of pyromellitic acid with 2,2′-bipyridine and 4,4′-bipyridine, respectively (Mrvos-Sermek *et al.*, 1996; Ruiz-Pérez *et al.*, 2004). We have prepared the title organic salt, (I), and its crystal structure is presented here.



(I)

The organic salt, (I), contains half of a pyromellitic acid dianion [$(H_2bta)^{2-}$], half of a neutral pyromellitic acid molecule (H_4bta) and one 2,4′-bipyridine cation [$(H\text{-}2,4'\text{-bpy})^+$] in the asymmetric unit (Fig. 1). Both the neutral pyromellitic acid and its dianion lie about inversion centres located at the

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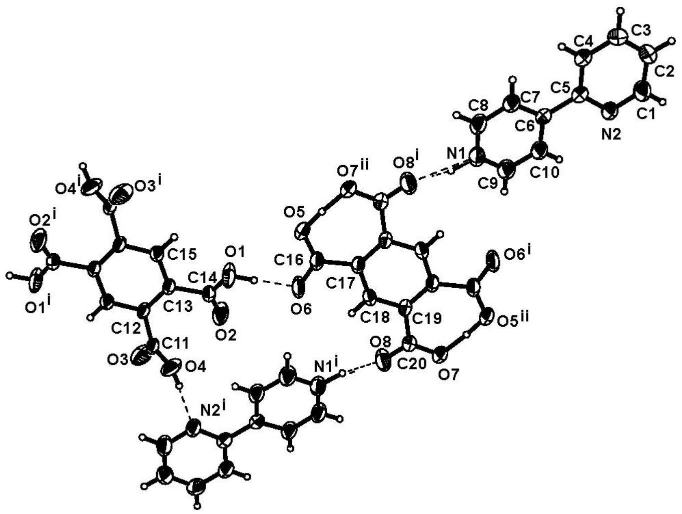

Figure 1
The structure of (I), with the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as small spheres of arbitrary radii. Hydrogen bonds are drawn as dashed lines. Symmetry codes are as in Table 2.

centroids of the aromatic rings. The two 2,4′-bipyridine cations are formed by the donation of two H atoms from mutually *para* carboxylate residues to atoms N1 and N1[i], respectively, and this produces the $(H_2bta)^{2-}$ dianion [symmetry code: (i) $-x - 1, -y + 1, -z + 2$]. For the $(H\text{-}2,4'\text{-bpy})^+$ cation, the average N—C bond length is 1.327 (3) Å, and the C9—N1—C8 and C1—N2—C5 angles are 121.2 (3) and 117.7 (2)°, respectively. Predictably, the bond lengths and angles in $(H_2bta)^{2-}$ are slightly different from those in the neutral H_4bta. The O—C bond lengths for $(H_2bta)^{2-}$ are in the range 1.215 (3)–1.260 (3) Å, while both independent O—C—O angles are 121.1 (2)°. For H_4bta, the corresponding bond lengths are in the range 1.193 (3)–1.312 (3) Å, with angles of 124.0 (2) and 124.7 (2)° (Table 1).

A strong intramolecular O5—HO5···O7⁻ hydrogen bond links adjacent carboxylic acid and carboxylate anion substituents, resulting in a planar $(H_2bta)^{2-}$ dianion. The dihedral angles O5—C16—C17—C18, O6—C16—C17—C18, C18—C19—C20—O7 and C18—C19—C20—O8 are −172.7 (2), 7.0 (3), 178.6 (2) and 0.7 (3)°, respectively, which confirms this planarity. In addition, an O1—HO1···O6 hydrogen bond links the neutral H_4bta molecule to an adjacent $(H_2bta)^{2-}$ dianion. Thus, the pyromellitic acid residues self-assemble into one-dimensional supramolecular chains, formed by alternation of planar $(H_2bta)^{2-}$ and neutral H_4bta molecules, in which the carboxylic acid substituents lie out of the plane of the benzene ring. N1—HN1···O8 and O4—HO4···N2 hydrogen bonds link the $(H\text{-}2,4'\text{-bpy})^+$ cations to the neighbouring anionic and neutral pyromellitic acid residues (Table 2, Figs. 1 and 2), to form zigzag supramolecular chains. Neighbouring zigzag chains interdigitate approximately along the *c* axis, to give two-dimensional undulating layers (Figs. 2 and 3), which pack along the *a* axis in an overall motif similar to that of an *AB* clay (Fig. 3).

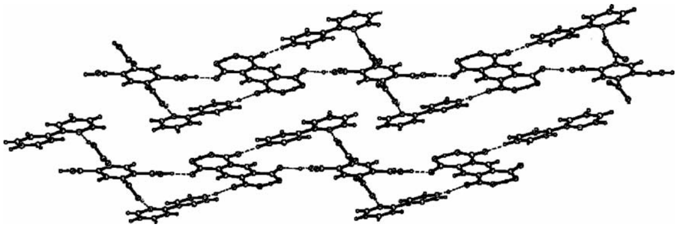

Figure 2
A perspective view of the undulating layers of one-dimensional zigzag chains. Hydrogen bonds are drawn as dashed lines.

Experimental

Pyromellitic acid (171 mg, 0.67 mmol) and 2,4′-bipyridine (49 mg, 0.31 mmol) were dissolved in distilled water (10 ml) with vigorous magnetic stirring. The mixture was placed in a Teflon-lined autoclave and heated to 413 K for 4 d, and then cooled at 10 K h^{-1} to room temperature, yielding brown crystals of (I).

Crystal data

$2C_{10}H_9N_2^+\cdot C_{10}H_4O_8^{2-}\cdot C_{10}H_6O_8$
$M_r = 820.66$
Triclinic, $P\bar{1}$
$a = 8.090$ (2) Å
$b = 9.576$ (2) Å
$c = 11.456$ (3) Å
$\alpha = 85.739$ (4)°
$\beta = 81.378$ (4)°
$\gamma = 79.820$ (5)°
$V = 862.6$ (4) Å^3

$Z = 1$
$D_x = 1.580$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5020 reflections
$\theta = 1.8$–26.4°
$\mu = 0.13$ mm^{-1}
$T = 153$ (2) K
Thick plate, brown
0.21 × 0.17 × 0.09 mm

Data collection

Siemens SMART CCD area-detector diffractometer
ω scans
Absorption correction: none
5020 measured reflections
3434 independent reflections

1913 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.041$
$\theta_{\rm max} = 26.4°$
$h = -9 \rightarrow 10$
$k = -11 \rightarrow 8$
$l = -14 \rightarrow 14$

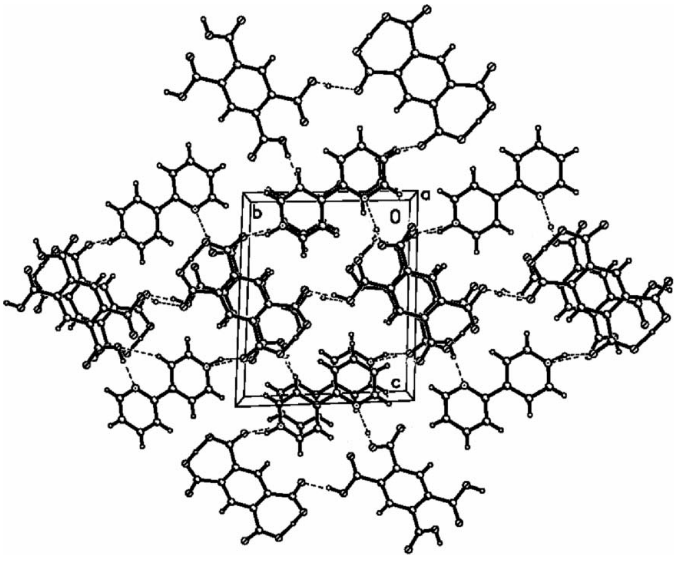

Figure 3
The crystal packing for (I), projected along the *a* axis. Hydrogen bonds are drawn as dashed lines.

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Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.050$
$wR(F^2) = 0.116$
$S = 0.88$
3434 reflections
287 parameters
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0436P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.21$ e Å^{-3}
$\Delta\rho_{min} = -0.18$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

N1—C9	1.325 (3)	O4—C11	1.312 (3)
N1—C8	1.328 (3)	O5—C16	1.260 (3)
O1—C14	1.296 (3)	O6—C16	1.222 (3)
O2—C14	1.199 (3)	O7—C20	1.260 (2)
O3—C11	1.193 (3)	O8—C20	1.215 (3)
C9—N1—C8	121.2 (2)	O2—C14—O1	124.7 (2)
C1—N2—C5	117.7 (2)	O6—C16—C17	118.3 (2)
O3—C11—O4	124.0 (2)	O8—C20—O7	121.1 (2)
O6—C16—C17—C18	7.0 (3)	C18—C19—C20—O8	0.7 (3)
O5—C16—C17—C18	−172.7 (2)	C18—C19—C20—O7	178.6 (2)

Table 2
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
N1—HN1⋯O8^{i}	1.06 (3)	1.66 (3)	2.665 (3)	158 (2)
O4—HO4⋯N2^{i}	0.89 (3)	1.84 (3)	2.717 (3)	170 (3)
O5—HO5⋯O7^{ii}	1.06 (3)	1.33 (3)	2.391 (3)	175 (3)
O1—HO1⋯O6	0.96 (4)	1.66 (4)	2.607 (2)	171 (3)

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

H atoms bound to C atoms were placed in calculated positions, with C—H = 0.93 Å, and refined using a riding model, with $U_{iso}(H) = 1.2U_{eq}(C)$. The other H atoms were found in electron-density difference Fourier maps and were refined freely.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Bruker 1998); software used to prepare material for publication: *SHELXL97*.

This work was supported by the Natural Science Foundation of China (grant No. 20274006).

References

Almeida Paz, F. A. & Klinowski, J. (2003). *CrystEngComm*, **5**, 238–244.
Beatty, A. M., Granger, K. E. & Simpson, A. E. (2002). *Chem. Eur. J.* **8**, 3254–3258.
Beatty, A. M., Schneider, C. M., Simpson, A. E. & Zaher, J. L. (2002). *CrystEngComm*, **4**, 282–287.
Bruker (1998). *XP* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Bruker (2001). *SAINT*. Version 6.28a. Bruker AXS Inc., Madison, Wisconsin, USA.
Holman, K. T., Pivovar, A. M., Swift, J. A. & Ward, M. D. (2001). *Acc. Chem. Res.* **34**, 107–118.
Mrvos-Sermek, D., Popović, Z. & Matković-Čalogović, D. (1996). *Acta Cryst.* C**52**, 2538–2541.
Ruiz-Pérez, C., Lorenzo-Luis, P. A., Hernández-Molina, M., Laz, M. M., Gili, P. & Julve, M. (2004). *Cryst. Growth Des.* **4**, 57–61.
Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
Siemens (1995). *SMART*. Version 5.05. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
Zaworotko, M. J. (2001). *Chem. Commun.* pp. 1–9.

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