Acta Crystallographica Section C
Crystal Structure Communications
ISSN 0108-2701

Two-dimensional hydrogen-bonded supramolecular networks in the compounds of benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid) with 2,2′-biimidazole and 4,4′-dimethyl-2,2′-bipyridine

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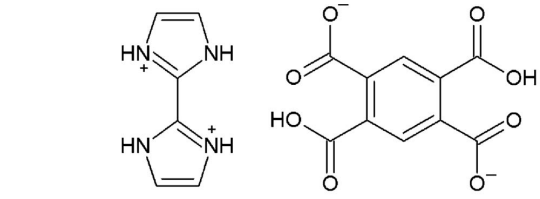
Received 24 September 2013
Accepted 9 November 2013

Two products from the proton-transfer reactions of benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid, PMA) with 2,2′-biimidazole and 4,4′-dimethyl-2,2′-bipyridine, namely 2,2′-biimidazole-3,3′-diium 2,5-dicarboxybenzene-1,4-dicarboxylate, $C_6H_8N_4^{2+}$,$C_{10}H_4O_8^{2-}$, (I), and 4-methyl-2-(4-methylpyridin-2-yl)pyridinium 2,4,5-tricarboxybenzoate monohydrate, $C_{12}H_{13}N_2^{+}\cdot C_{10}H_5O_8^{-}\cdot H_2O$, (II), have been prepared and their structures determined. Both compounds crystallize in the space group $P\overline{1}$. The asymmetric unit of (I) is composed of two independent ion pairs. Both the 2,2′-biimidazole-3,3′-diium dication and the PMA^{2-} anion are located on special positions (inversion centres). The protonated 2,2′-biimidazole-3,3′-diium ring H atoms are involved in hydrogen bonding with carboxylate O atoms to form one-dimensional hydrogen-bonded chain structures. Adjacent chains are further linked *via* carboxyl–carboxyl O—H···O hydrogen bonding, resulting in a two-dimensional supramolecular sheet with the $R_6^5(34)$ motif extending in the $(1\overline{2}1)$ plane. In (II), classical O—H···O hydrogen-bond-linked anion–anion units are extended into a one-dimensional chain running parallel to the [100] direction, giving an $R_2^2(8)R_4^4(30)$ motif. The chains are connected by water–carboxyl O—H···O hydrogen bonds to form a two-dimensional network parallel to the $(01\overline{1})$ plane. The 4-methyl-2-(4-methylpyridin-2-yl)pyridinium cations lie between the two-dimensional supramolecular layers linked *via* N—H···O hydrogen-bonding interactions.

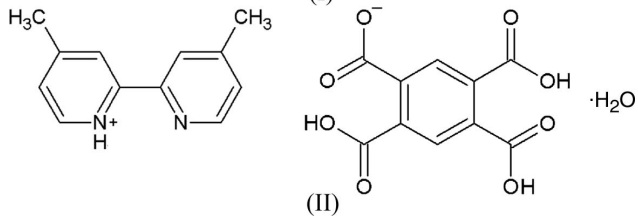
Keywords: crystal structure; hydrogen bonding; pyromellitic acid; 2,2′-biimidazole; 4,4′-dimethyl-2,2′-bipyridine.

1. Introduction

It is well established that hydrogen bonds play vital roles in molecular recognition and supramolecular chemistry (Batten & Robson, 1998; Juan *et al.*, 2002; Qiu *et al.*, 2008), owing to the fact that moderately directional intermolecular interaction can effectively control short-range packing. Polycarboxylic acids, such as benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid, PMA; Li *et al.*, 2003; Oscar *et al.*, 2008), benzene-1,3,5-tricarboxylic acid (Pasdar *et al.*, 2011) and benzene-1,2,3,4-tetracarboxylic acid (Zhang *et al.*, 2010), have been applied widely in constructing interesting supramolecular networks because they act not only as hydrogen-bond acceptors but also as hydrogen-bond donors, depending upon the number of deprotonated carboxylic acid groups. Many transition-metal complexes with benzene-1,2,4,5-tetracarboxylate have previously been synthesized and reported, such as the zinc (Rochon & Massarweh, 2000), nickel (Poleti *et al.*, 1988; Murugavel *et al.*, 2002), manganese (Hu *et al.*, 2001), cobalt



(I)



(II)

(Cheng *et al.*, 2002), copper (Cao *et al.*, 2002), silver (Jaber *et al.*, 1997) and iron complexes (Chu *et al.*, 2001). As far as we know, reports on benzene-1,2,4,5-tetracarboxylate salts with organic Lewis bases are few, *e.g.* guanidinium pyromellitate trihydrate monoperhydrate (Adams & Ramdas, 1978), 2,2′-bipyridinium hemi[benzene-1,2,4,5-tetracarboxylate(2−)] hemi(benzene-1,2,4,5-tetracarboxylic acid) (Mrvos-Sermek *et al.*, 1996), guanidinuium pyromellite (Sun *et al.*, 2002*a*), imidazolium trihydrogen benzene-1,2,4,5-tetracarboxylate (Sun *et al.*, 2002*b*), 6,21-diaza-3,9,18,24-tetraazoniatricyclo[22.2.2.$2^{11,14}$]triaconta-11,13,24,26(1),27,29-hexaene benzene-1,2,4,5-tetracarboxylate(4−) hexahydrate (Zhu *et al.*, 2002), ethylenediammonium bis(trihydrogen benzene-1,2,4,5-tetracarboxylate) dehydrate (Li *et al.*, 2006). Recently, we attempted to utilize polycarboxylate acids and N-containing bidentate ligands as mixed ligands for the design of coordination networks. The title PMA salts of 2,2′-biimidazole and 4,4′-dimethyl-2,2′-bipyridine, namely 2,2′-biimidazole-3,3′-diium 2,5-dicarboxybenzene-1,4-dicarboxylate, (I), and 4-methyl-2-(4-methylpyridin-2-yl)pyridinium 2,4,5-tricarboxybenzoate monohydrate, (II), were obtained unintentionally during an attempt to synthesize mixed-ligand transition-metal complexes with PMA and N-containing ligands *via* a solvothermal reaction. Their crystal structures have not been reported previously.

 doi:10.1107/S0108270113030801 © 2013 International Union of Crystallography

Table 1
Experimental details.

	(I)	(II)
Crystal data		
Chemical formula	$C_6H_8N_4^{2+}\cdot C_{10}H_4O_8^{2-}$	$C_{12}H_{13}N_2^{+}\cdot C_{10}H_5O_8^{-}\cdot H_2O$
M_r	388.30	456.40
Crystal system, space group	Triclinic, $P\overline{1}$	Triclinic, $P\overline{1}$
Temperature (K)	223	223
a, b, c (Å)	8.2246 (16), 8.7495 (17), 11.454 (2)	9.5166 (7), 9.9970 (8), 12.4106 (8)
α, β, γ (°)	100.67 (3), 97.26 (3), 94.68 (3)	77.979 (6), 73.421 (6), 62.655 (8)
V (Å^3)	798.8 (3)	1001.03 (13)
Z	2	2
Radiation type	Mo $K\alpha$	Mo $K\alpha$
μ (mm^{-1})	0.13	0.12
Crystal size (mm)	0.40 × 0.27 × 0.20	0.30 × 0.22 × 0.10
Data collection		
Diffractometer	Rigaku Mercury CCD diffractometer	Rigaku Mercury CCD diffractometer
Absorption correction	Multi-scan (*REQAB*; Jacobson, 1998)	Multi-scan (*REQAB*; Jacobson, 1998)
T_{min}, T_{max}	0.720, 1.000	0.997, 1.000
No. of measured, independent and observed reflections	7722, 3595, 2808 [$I > \sigma(I)$]	9371, 3516, 2681 [$I > 2\sigma(I)$]
R_{int}	0.032	0.041
(sin $\theta/\lambda)_{max}$ (Å^{-1})	0.649	0.595
Refinement		
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.046, 0.122, 1.02	0.051, 0.126, 1.01
No. of reflections	3595	3516
No. of parameters	254	304
No. of restraints	0	3
H-atom treatment	H-atom parameters constrained	H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	0.35, −0.57	0.39, −0.40

Computer programs: *CrystalClear* (Rigaku, 2007), *SHELXS97* (Sheldrick, 2008), *SHELXL97* (Sheldrick, 2008), *XP* in *SHELXTL* (Sheldrick, 2008) and *SHELXTL*.

2. Experimental

2.1. Synthesis and crystallization

2,2′-Biimidazole (0.1 mmol, 0.0134 g), benzene-1,2,4,5-tetracarboxylic acid (0.1 mmol, 0.0254 g), $ZnSO_4\cdot 7H_2O$ (0.1 mmol, 0.0287 g) and water (2.0 ml) were mixed and placed in a thick Pyrex tube, which was sealed and heated to 383 K for 72 h, whereupon colourless block-shaped crystals of (I) were obtained. Colourless block-shaped crystals of (II) were obtained by a procedure similar to that described for (I), using 4,4′-dimethyl-2,2′-bipyridine instead of 2,2′-biimidazole.

2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. H atoms bound to C, N and O atoms were positioned geometrically and allowed to ride on their parent atoms, with C—H = 0.93 Å and U_{iso}(H) = 1.2U_{eq}(C), N—H = 0.96 Å and U_{iso}(H) = 1.2U_{eq}(N), and O—H = 0.82 Å and U_{iso}(H) = 1.5U_{eq}(O). The H atoms of water molecules were located in difference Fourier maps and placed in calculated positions so as to form a reasonable hydrogen-bond network, as far as possible. Their positions were refined with tight restraints on the O—H and H···H distances [0.820 (1) and 1.35 (1) Å, respectively], and with U_{iso}(H) = 1.5U_{eq}(O).

3. Results and discussion

In both title compounds, (I) and (II), proton transfer has occurred. However, the differences between the structures are significant so the discussion considers each structure individually. Compound (I) crystallizes in the space group $P\overline{1}$. Its asymmetric unit consists of two halves of the 2,2′-biimidazole-3,3′-diium dication, each protonated at two imidazole ring N atoms and two halves of the 2,5-dicarboxybenzene-1,4-dicarboxylate dianion (PMA^{2-}), each with two of the carboxylic acid groups deprotonated (Fig. 1). In (I), the two PMA^{2-} anions lie on crystallographic centres of symmetry at (0, $\frac{1}{2}$, $\frac{1}{2}$) and ($\frac{1}{2}$, $\frac{1}{2}$, 0), respectively. They are connected by an O1—H1···O7 hydrogen bond (Table 2). The two 2,2′-biimidazole-3,3′-diium dications lie on crystallographic centres of symmetry at ($\frac{1}{2}$, 0, 0) and (0, $\frac{1}{2}$, 0), respectively, and are linked by N3—H3*A*···O3, N4—H4*B*···O4^{ii}, N1—H1*B*···O7^{iv} and N2—H2*B*···O8^{iii} hydrogen bonds with adjacent PMA^{2-} dianions (Fig. 1; see Table 2 for symmetry codes and geometric details). The environments of the two independent 2,2′-biimidazole-3,3′-diium cations is similar. In contrast, both independent PMA^{2-} anions are different in that only one anion has an intramolecular O—H···O hydrogen bond (O6—H6···O8^{i}; Table 2). The bond lengths and angles of the PMA^{2-} dianion are comparable with values reported previously in guanidinuium pyromellite (Sun *et al.*, 2002*a*). The benzene rings of the two PMA^{2-} dianions are planar except for the carboxyl groups. The planes defined by the COO^{-} groups (C17/O7/O8 and C11/O3/O4) and the least-squares plane of the benzene ring subtend dihedral angles of 32.2 (1) and 60.6 (1)°, respectively, while the planes defined by the COOH groups (C13/O5/O6 and C7/O1/O2) are oriented at 15.2 (1) and 25.4 (1)°, respectively, to that of the benzene ring.

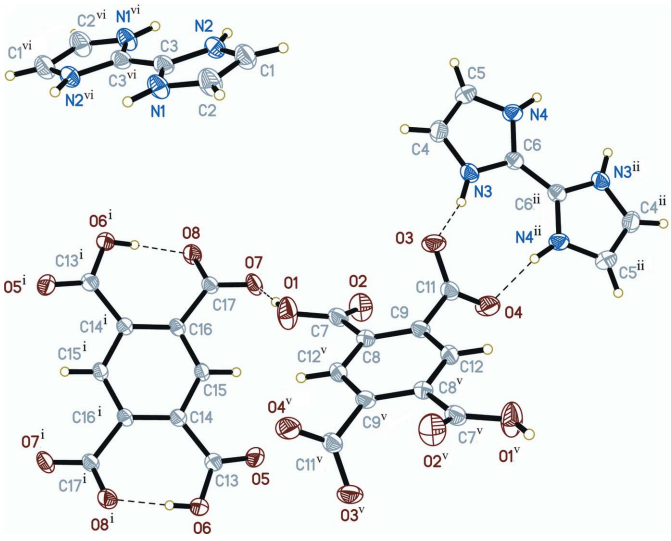


Figure 1
The unique species in the structure of (I), showing the atom-numbering scheme and with displacement ellipsoids drawn at the 35% probability level. The dashed lines represent O—H···O and N—H···O intra- and intermolecular interactions. H atoms are shown as small spheres of arbitrary radii. [Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, -y, -z$; (v) $-x+2, -y+1, -z+1$; (vi) $-x, -y+2, -z+1$.]

The two imidazole rings of the two cations are almost coplanar, the mean deviations from the least-squares planes being 0.0126 (5) and 0.0055 (4) Å, respectively. The dihedral angle between the mean planes of the two cations is 51.7 (1)°. The C—N and C—C bond lengths in the cations are consistent with those usually found (Liu & Zhu, 2010). The dication interacts with two neighbouring PMA^{2-} anions *via* pairs of asymmetric intermolecular N—H···O hydrogen bonds that form a primary cyclic $R_2^2(9)$ association (Bernstein *et al.*, 1995) (Fig. 2). These aggregate units generate a one-dimensional supramolecular chain. Adjacent chains are further linked *via* carboxyl–carboxyl O—H···O hydrogen bonds, resulting in a two-dimensional supramolecular sheet extending parallel to the $(1\bar{2}1)$ plane. Within the sheet, the $R_6^5(34)$ motif can be discerned (Fig. 2).

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

D—H···A	D—H	H···A	D···A	D—H···A
O6—H6···O8^{i}	0.82	1.67	2.4939 (18)	177
O1—H1···O7	0.82	1.91	2.7228 (18)	173
N3—H3A···O3	0.86	1.75	2.553 (2)	154
N4—H4B···O4^{ii}	0.86	1.89	2.738 (2)	170
N2—H2B···O8^{iii}	0.86	1.83	2.676 (2)	168
N1—H1B···O7^{iv}	0.86	1.90	2.733 (2)	162

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

Hydrated salt (II) crystallizes in the space group $P\bar{1}$. The asymmetric unit is comprised of a 4-methyl-2-(4-methylpyridin-2-yl)pyridinium cation, a 2,4,5-tricarboxybenzoate anion and a water molecule (Fig. 3). Only one carboxyl group of the benzene-1,2,3,4-tetracarboxylic acid molecule is deprotonated, which is different from what was observed in the nonsubstituted 2,2′-bipyridine analogue (Mrvos-Sermek *et al.*, 1996). Proton transfer from a carboxylic acid group of PMA to a ring N atom (N2) of 4,4′-dimethyl-2,2′-bipyridine is manifested in an increased internal angle [C10—N2—C6 = 123.4 (2)°] of the pyridine ring, compared with that at the

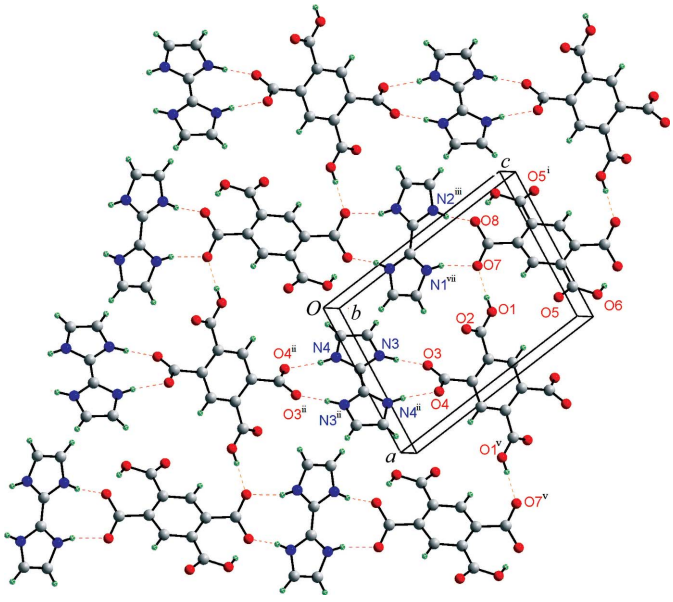


Figure 2
A view of the two-dimensional hydrogen-bonded network of (I) along the b axis, showing the formation of $R_2^2(9)$ and $R_6^5(34)$ motifs. The dashed lines represent O—H···O interactions. [Symmetry codes: (i) $-x+1, -y+1, -z+2$; (ii) $-x+1, -y, -z$; (iii) $-x, -y+1, -z+1$; (v) $-x+2, -y+1, -z+1$; (vii) $x, y-1, z$.]

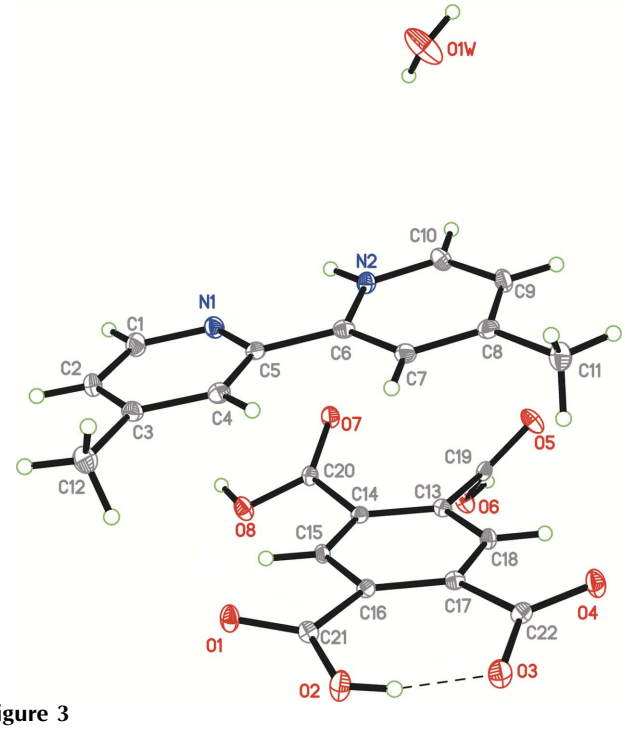


Figure 3
The asymmetric unit of (II), showing the atom-numbering scheme and with displacement ellipsoids drawn at the 30% probability level. The dashed line represents an intramolecular O—H···O interaction.

Table 3
Hydrogen-bond geometry (Å, °) for (II).

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H1WA···O5^{i}	0.82 (1)	2.12 (1)	2.916 (3)	163 (3)
O1W—H1WB···O4^{ii}	0.82 (1)	2.06 (1)	2.880 (3)	175 (3)
N2—H2B···O3^{ii}	0.86	1.99	2.792 (3)	154
O6—H6···O1^{iii}	0.82	1.79	2.609 (2)	174
O8—H8···O7^{iv}	0.82	1.84	2.644 (2)	166

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

unprotonated N1 atom of the pyridine ring [C1—N1—C5 = 116.7 (2)°]. Protonated atom N2 diminishes the steric effect of the lone pair of electrons and is responsible for the slightly increased C10—N2—C6 angle (Fig. 3). The two rings of the cation are twisted slightly away from each other, forming a dihedral angle of 7.03 (8)°. The planes of the benzene ring of the PMA^{-} anion and the two pyridine rings (C1–C5/N1 and C6–C10/N2) of the cation are oriented at 6.22 (8) and 10.99 (9)°, respectively. The dihedral angles between the least-squares plane of the benzene ring of PMA^{-} and those of the the carboxylic acid groups (COOH) are 13.35 (7) (O1/C21/O2), 31.20 (2) (O7/C20/O8) and 53.04 (9)° (O5/C19/O6). The O3/C22/O4 carboxylate group (COO^{-}) is twisted by 16.22 (1)° with respect to the plane of the benzene ring, which is similar to the value found in a previously reported PMA^{-} compound (Sun *et al.*, 2002*b*). The PMA^{-} anions form a one-dimensional chain along the [100] direction *via* O6^{vi}—H6^{vi}···O1, O8—H8···O7^{iv} and O8^{iv}—H8^{iv}···O7 hydrogen bonds, enclosing $R_2^2(8)R_4^4(30)$ rings (Fig. 4; see Table 3 for symmetry codes). Such chains are further joined together through water–carboxylate O—H···O hydrogen bonds, *viz* O1W—H1WA···O5^{i} and O1W—H1WB···O4^{ii}, to yield a two-dimensional supramolecular layer extending in the $(01\bar{1})$ plane, involving $R_4^4(20)$ and $R_6^6(26)$ motifs (Fig. 4 and Table 3). The 4-methyl-2-(4-methylpyridin-2-yl)pyridinium cations are linked to the PMA^{-} anions through N2—H2···O3^{ii} hydrogen bonds and lie between the above-mentioned two-dimensional supramolecular layers (Table 3).

This work was partially supported by the Scientific Research Foundation of Nanjing College of Chemical Technology (grant No. NHKY-2013–10).

Supplementary data for this paper are available from the IUCr electronic archives (Reference: SF3209). Services for accessing these data are described at the back of the journal.

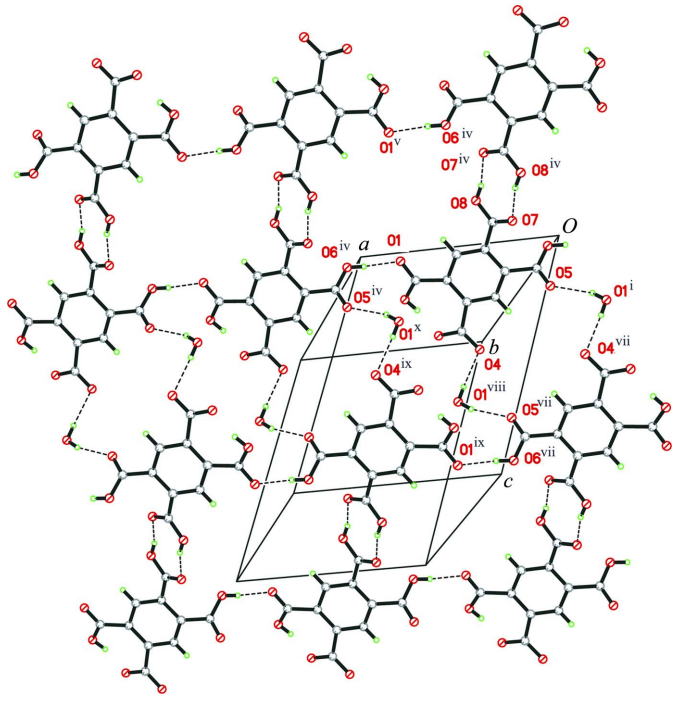


Figure 4
The two-dimensional hydrogen-bonded anionic layer in (II), extending parallel to the $(10\bar{2})$ crystallographic plane, showing the formation of $R_2^2(8)$, $R_4^4(30)$, $R_4^4(20)$ and $R_6^6(26)$ motifs. Hydrogen bonds are represented by dashed lines. [Symmetry codes: (i) $-x, -y+1, -z+1$; (iv) $-x+1, -y+1, -z$; (v) $-x+2, -y+1, -z$; (vi) $x+1, y, z$; (vii) $-x, -y+2, -z+1$; (viii) $x, y+1, z$; (ix) $-x+1, -y+2, -z+1$; (x) $-x+1, -y+1, -z+1$.]

References

Adams, J. M. & Ramdas, V. (1978). *Acta Cryst.* B**34**, 2781–2785.
Batten, S. R. & Robson, R. (1998). *Angew. Chem. Int. Ed.* **37**, 1460–1494.
Bernstein, J., Davis, R. E., Shimoni, L. & Chang, N.-L. (1995). *Angew. Chem. Int. Ed. Engl.* **34**, 1555–1573.
Cao, R., Shi, Q., Sun, D., Hong, M., Bi, W. & Zhao, Y. (2002). *Inorg. Chem.* **41**, 6161–6168.
Cheng, D., Khan, M. A. & Houser, R. P. (2002). *Cryst. Growth Des.* **2**, 415–420.
Chu, D., Xu, J., Duan, L., Wang, T., Tang, A. & Ye, L. (2001). *Eur. J. Inorg. Chem.* pp. 1135–1137.
Hu, M., Cheng, D., Liu, J. & Xu, D. (2001). *J. Coord. Chem.* **53**, 7–13.
Jaber, F., Charbonnier, F. & Faure, R. (1997). *J. Chem. Crystallogr.* **27**, 397–400.
Jacobson, R. (1998). *REQAB.* Molecular Structure Corporation, The Woodlands, Texas, USA.
Juan, C. N., Myoung, S. L., Rico, E. D. S., Atta, M. A., Joel, S. M. & Peter, J. S. (2002). *J. Am. Chem. Soc.* **124**, 6613–6625.
Li, Y., Hao, N., Lu, Y. & Wang, E.-B. (2003). *Inorg. Chem.* **42**, 3119–3124.
Li, X.-F., Liu, D.-S., Luo, Q.-Y. & Huang, C.-C. (2006). *Acta Cryst.* E**62**, o460–o462.
Liu, X. & Zhu, W. (2010). *Acta Cryst.* E**66**, o1245.
Mrvos-Sermek, D., Popovic, Z. & Matkovic-Calogovic, D. (1996). *Acta Cryst.* C**52**, 2538–2541.
Murugavel, R., Krishnamurthy, D. & Sathiyendiran, M. (2002). *J. Chem. Soc. Dalton Trans.* pp. 34–39.
Oscar, F., Jorge, P., Francesc, L., Miguel, J. & Catalina, R.-P. (2008). *Inorg. Chem.* **47**, 3568–3576.
Pasdar, H., Namegh, M., Aghabozorg, H. & Notash, B. (2011). *Acta Cryst.* E**67**, m353–m354.
Poleti, D., Stojaković, D. R., Prelesnik, B. V. & Herak, R. M. (1988). *Acta Cryst.* C**44**, 242–245.
Qiu, Y., Liu, Z., Li, Y., Deng, H., Zeng, R. & Zeller, M. (2008). *Inorg. Chem.* **47**, 5122–5128.
Rigaku (2007). *CrystalClear*. Rigaku Corporation, Tokyo, Japan.
Rochon, F. D. & Massarweh, G. (2000). *Inorg. Chim. Acta*, **304**, 190–198.
Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.
Sun, Y.-Q., Zhang, J. & Yang, G.-Y. (2002*a*). *Acta Cryst.* E**58**, o904–o906.
Sun, Y.-Q., Zhang, J. & Yang, G.-Y. (2002*b*). *Acta Cryst.* E**58**, o1100–o1102.
Zhang, L.-P., Ma, J.-F., Yang, J., Pang, Y.-Y. & Ma, J.-C. (2010). *Inorg. Chem.* **49**, 1535–1550.
Zhu, L.-G., Ellern, A. M. & Kostić, N. M. (2002). *Acta Cryst.* C**58**, o129–o130.

supplementary materials

Acta Cryst. (2013). C**69**, 1537-1540 [doi:10.1107/S0108270113030801]

Two-dimensional hydrogen-bonded supramolecular networks in the compounds of benzene-1,2,4,5-tetracarboxylic acid (pyromellitic acid) with 2,2′-bi-imidazole and 4,4′-dimethyl-2,2′-bipyridine

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Computing details

For both compounds, data collection: *CrystalClear* (Rigaku, 2007); cell refinement: *CrystalClear* (Rigaku, 2007); data reduction: *CrystalClear* (Rigaku, 2007); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Sheldrick, 2008); software used to prepare material for publication: *SHELXTL* (Sheldrick, 2008).

(I) 2-(Imidazol-1-ium-2-yl)imidazol-1-ium 2,5-dicarboxybenzene-1,4-dicarboxylate

Crystal data

$C_6H_8N_4^{2+}\cdot C_{10}H_4O_8^{2-}$
$M_r = 388.30$
Triclinic, $P\overline{1}$
Hall symbol: -p 1
$a = 8.2246\ (16)$ Å
$b = 8.7495\ (17)$ Å
$c = 11.454\ (2)$ Å
$\alpha = 100.67\ (3)°$
$\beta = 97.26\ (3)°$
$\gamma = 94.68\ (3)°$
$V = 798.8\ (3)$ Å^3
$Z = 2$
$F(000) = 400$
$D_x = 1.614$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 3731 reflections
$\theta = 3.3–27.5°$
$\mu = 0.13$ mm^{-1}
$T = 223$ K
Block, colourless
0.40 × 0.27 × 0.20 mm

Data collection

Rigaku Mercury CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite Monochromator monochromator
Detector resolution: 28.5714 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (REQAB: Jacobson, 1998)
$T_{min} = 0.720$, $T_{max} = 1.000$
7722 measured reflections
3595 independent reflections
2808 reflections with $I > \sigma(I)$
$R_{int} = 0.032$
$\theta_{max} = 27.5°$, $\theta_{min} = 3.3°$
$h = -10\rightarrow10$
$k = -11\rightarrow9$
$l = -13\rightarrow14$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.046$
$wR(F^2) = 0.122$
$S = 1.02$
3595 reflections
254 parameters
0 restraints
Primary atom site location: structure-invariant direct methods

Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.072P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.35$ e Å^{-3}
$\Delta\rho_{min} = -0.57$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 2008), $Fc^*=kFc[1+0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
Extinction coefficient: 0.074 (7)

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	0.62669 (16)	0.47277 (17)	0.63757 (13)	0.0491 (4)
H1	0.5411	0.4294	0.6516	0.074*
O2	0.62998 (16)	0.24608 (15)	0.51284 (12)	0.0423 (4)
O3	0.65637 (14)	0.31690 (14)	0.27534 (11)	0.0352 (3)
O4	0.83769 (16)	0.14191 (15)	0.27634 (12)	0.0417 (3)
O5	0.82217 (15)	0.24782 (15)	0.95079 (12)	0.0384 (3)
O6	0.94434 (13)	0.42861 (15)	1.10085 (10)	0.0320 (3)
H6	0.9227	0.5087	1.1430	0.048*
O7	0.35869 (14)	0.30795 (14)	0.68918 (10)	0.0321 (3)
O8	0.13262 (13)	0.33080 (14)	0.77385 (10)	0.0312 (3)
N1	0.20074 (17)	1.10573 (16)	0.48835 (13)	0.0305 (3)
H1B	0.2289	1.1748	0.5533	0.037*
N2	0.06550 (17)	0.91666 (16)	0.35546 (12)	0.0285 (3)
H2B	−0.0088	0.8421	0.3198	0.034*
N3	0.43654 (16)	0.15350 (16)	0.11289 (12)	0.0272 (3)
H3A	0.5170	0.1808	0.1708	0.033*
N4	0.28846 (16)	0.03652 (16)	−0.05601 (12)	0.0268 (3)
H4B	0.2594	−0.0243	−0.1250	0.032*
C1	0.2026 (2)	0.9631 (2)	0.31045 (16)	0.0350 (4)
H1A	0.2319	0.9213	0.2363	0.042*
C2	0.2880 (2)	1.0814 (2)	0.39394 (16)	0.0373 (4)
H2A	0.3876	1.1361	0.3882	0.045*
C3	0.0645 (2)	1.00457 (18)	0.46313 (14)	0.0255 (4)
C4	0.2873 (2)	0.2127 (2)	0.10564 (16)	0.0308 (4)
H4A	0.2552	0.2900	0.1629	0.037*
C5	0.1944 (2)	0.1398 (2)	0.00105 (16)	0.0307 (4)
H5A	0.0874	0.1567	−0.0266	0.037*
C6	0.43411 (18)	0.04627 (18)	0.01405 (13)	0.0232 (3)
C7	0.68894 (19)	0.3774 (2)	0.55609 (14)	0.0274 (4)
C8	0.84615 (18)	0.44614 (18)	0.52423 (13)	0.0229 (3)

C9	0.89777 (18)	0.38360 (18)	0.41569 (13)	0.0226 (3)
C11	0.78931 (19)	0.26791 (19)	0.31646 (13)	0.0247 (4)
C12	1.05207 (18)	0.43707 (18)	0.39288 (14)	0.0242 (3)
H12A	1.0881	0.3944	0.3213	0.029*
C13	0.81518 (19)	0.36793 (19)	1.02148 (14)	0.0250 (4)
C14	0.65816 (18)	0.44640 (18)	1.01819 (13)	0.0208 (3)
C15	0.54537 (18)	0.38997 (18)	0.91379 (13)	0.0216 (3)
H15A	0.5764	0.3147	0.8546	0.026*
C16	0.39022 (18)	0.43945 (17)	0.89325 (13)	0.0202 (3)
C17	0.28687 (18)	0.35632 (18)	0.77638 (13)	0.0225 (3)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0338 (7)	0.0558 (9)	0.0483 (8)	−0.0146 (6)	0.0210 (6)	−0.0158 (7)
O2	0.0370 (7)	0.0389 (8)	0.0459 (8)	−0.0106 (6)	0.0112 (6)	−0.0017 (6)
O3	0.0285 (6)	0.0337 (7)	0.0356 (7)	0.0065 (5)	−0.0115 (5)	−0.0039 (5)
O4	0.0375 (7)	0.0345 (7)	0.0419 (7)	0.0114 (6)	−0.0127 (6)	−0.0119 (6)
O5	0.0313 (7)	0.0376 (7)	0.0391 (7)	0.0124 (6)	−0.0024 (5)	−0.0098 (6)
O6	0.0236 (6)	0.0388 (7)	0.0281 (6)	0.0067 (5)	−0.0024 (5)	−0.0047 (5)
O7	0.0273 (6)	0.0420 (7)	0.0203 (6)	−0.0038 (5)	0.0038 (5)	−0.0078 (5)
O8	0.0209 (6)	0.0371 (7)	0.0287 (6)	−0.0036 (5)	0.0007 (5)	−0.0063 (5)
N1	0.0320 (8)	0.0297 (8)	0.0237 (7)	−0.0047 (6)	−0.0012 (6)	−0.0032 (6)
N2	0.0273 (7)	0.0273 (7)	0.0247 (7)	−0.0008 (6)	−0.0036 (6)	−0.0045 (6)
N3	0.0251 (7)	0.0318 (7)	0.0210 (6)	−0.0005 (6)	0.0003 (5)	−0.0005 (6)
N4	0.0218 (7)	0.0282 (7)	0.0264 (7)	0.0013 (6)	−0.0037 (5)	0.0005 (6)
C1	0.0330 (9)	0.0418 (10)	0.0257 (8)	0.0001 (8)	0.0026 (7)	−0.0019 (8)
C2	0.0349 (10)	0.0407 (10)	0.0313 (9)	−0.0055 (8)	0.0042 (8)	−0.0013 (8)
C3	0.0275 (8)	0.0230 (8)	0.0227 (7)	0.0004 (6)	−0.0034 (6)	0.0015 (6)
C4	0.0287 (9)	0.0331 (9)	0.0303 (9)	0.0051 (7)	0.0079 (7)	0.0019 (7)
C5	0.0230 (8)	0.0332 (9)	0.0361 (9)	0.0052 (7)	0.0024 (7)	0.0074 (7)
C6	0.0220 (8)	0.0227 (8)	0.0227 (7)	−0.0015 (6)	0.0003 (6)	0.0025 (6)
C7	0.0222 (8)	0.0361 (9)	0.0211 (7)	−0.0015 (7)	0.0000 (6)	0.0029 (7)
C8	0.0197 (7)	0.0270 (8)	0.0208 (7)	0.0025 (6)	0.0006 (6)	0.0029 (6)
C9	0.0210 (8)	0.0237 (8)	0.0209 (7)	0.0014 (6)	−0.0012 (6)	0.0024 (6)
C11	0.0233 (8)	0.0268 (9)	0.0211 (7)	−0.0007 (7)	0.0009 (6)	0.0007 (6)
C12	0.0232 (8)	0.0282 (8)	0.0192 (7)	0.0022 (7)	0.0023 (6)	0.0002 (6)
C13	0.0241 (8)	0.0289 (9)	0.0216 (7)	0.0031 (7)	0.0030 (6)	0.0035 (7)
C14	0.0199 (7)	0.0225 (7)	0.0194 (7)	−0.0002 (6)	0.0035 (6)	0.0034 (6)
C15	0.0223 (8)	0.0225 (8)	0.0182 (7)	0.0005 (6)	0.0041 (6)	−0.0002 (6)
C16	0.0213 (7)	0.0203 (7)	0.0174 (7)	−0.0022 (6)	0.0028 (6)	0.0012 (6)
C17	0.0220 (8)	0.0241 (8)	0.0194 (7)	−0.0002 (6)	0.0014 (6)	0.0011 (6)

Geometric parameters (Å, º)

O1—C7	1.316 (2)	C1—C2	1.351 (2)
O1—H1	0.8200	C1—H1A	0.9300
O2—C7	1.199 (2)	C2—H2A	0.9300
O3—C11	1.274 (2)	C3—C3^{i}	1.443 (3)
O4—C11	1.231 (2)	C4—C5	1.354 (2)

O5—C13	1.212 (2)	C4—H4A	0.9300
O6—C13	1.312 (2)	C5—H5A	0.9300
O6—H6	0.8200	C6—C6^{ii}	1.438 (3)
O7—C17	1.2485 (18)	C7—C8	1.497 (2)
O8—C17	1.2658 (18)	C8—C9	1.394 (2)
N1—C3	1.336 (2)	C8—C12^{iii}	1.395 (2)
N1—C2	1.366 (2)	C9—C12	1.389 (2)
N1—H1B	0.8600	C9—C11	1.511 (2)
N2—C3	1.329 (2)	C12—C8^{iii}	1.395 (2)
N2—C1	1.361 (2)	C12—H12A	0.9300
N2—H2B	0.8600	C13—C14	1.511 (2)
N3—C6	1.327 (2)	C14—C15	1.400 (2)
N3—C4	1.370 (2)	C14—C16^{iv}	1.406 (2)
N3—H3A	0.8600	C15—C16	1.387 (2)
N4—C6	1.342 (2)	C15—H15A	0.9300
N4—C5	1.366 (2)	C16—C14^{iv}	1.406 (2)
N4—H4B	0.8600	C16—C17	1.515 (2)

C7—O1—H1	109.5	N4—C6—C6^{ii}	124.99 (17)
C13—O6—H6	109.5	O2—C7—O1	124.22 (15)
C3—N1—C2	108.77 (14)	O2—C7—C8	122.18 (16)
C3—N1—H1B	125.6	O1—C7—C8	113.57 (14)
C2—N1—H1B	125.6	C9—C8—C12^{iii}	119.91 (13)
C3—N2—C1	109.35 (14)	C9—C8—C7	119.72 (14)
C3—N2—H2B	125.3	C12^{iii}—C8—C7	120.13 (14)
C1—N2—H2B	125.3	C12—C9—C8	119.12 (14)
C6—N3—C4	107.37 (14)	C12—C9—C11	117.45 (13)
C6—N3—H3A	126.3	C8—C9—C11	123.28 (13)
C4—N3—H3A	126.3	O4—C11—O3	125.17 (15)
C6—N4—C5	108.23 (14)	O4—C11—C9	119.76 (14)
C6—N4—H4B	125.9	O3—C11—C9	114.88 (14)
C5—N4—H4B	125.9	C9—C12—C8^{iii}	120.96 (14)
C2—C1—N2	107.01 (16)	C9—C12—H12A	119.5
C2—C1—H1A	126.5	C8^{iii}—C12—H12A	119.5
N2—C1—H1A	126.5	O5—C13—O6	119.60 (15)
C1—C2—N1	107.15 (15)	O5—C13—C14	119.99 (14)
C1—C2—H2A	126.4	O6—C13—C14	120.41 (14)
N1—C2—H2A	126.4	C15—C14—C16^{iv}	117.36 (14)
N2—C3—N1	107.72 (14)	C15—C14—C13	113.78 (13)
N2—C3—C3^{i}	125.75 (18)	C16^{iv}—C14—C13	128.79 (14)
N1—C3—C3^{i}	126.50 (18)	C16—C15—C14	124.03 (14)
C5—C4—N3	108.43 (15)	C16—C15—H15A	118.0
C5—C4—H4A	125.8	C14—C15—H15A	118.0
N3—C4—H4A	125.8	C15—C16—C14^{iv}	118.61 (14)
C4—C5—N4	106.62 (15)	C15—C16—C17	114.57 (13)
C4—C5—H5A	126.7	C14^{iv}—C16—C17	126.77 (14)
N4—C5—H5A	126.7	O7—C17—O8	122.99 (14)
N3—C6—N4	109.35 (14)	O7—C17—C16	118.47 (13)
N3—C6—C6^{ii}	125.66 (18)	O8—C17—C16	118.39 (13)

C3—N2—C1—C2	0.7 (2)	C12^{iii}—C8—C9—C11	−174.20 (15)
N2—C1—C2—N1	−0.4 (2)	C7—C8—C9—C11	11.4 (2)
C3—N1—C2—C1	−0.1 (2)	C12—C9—C11—O4	59.3 (2)
C1—N2—C3—N1	−0.79 (19)	C8—C9—C11—O4	−125.24 (18)
C1—N2—C3—C3^{i}	177.1 (2)	C12—C9—C11—O3	−115.92 (17)
C2—N1—C3—N2	0.6 (2)	C8—C9—C11—O3	59.6 (2)
C2—N1—C3—C3^{i}	−177.3 (2)	C8—C9—C12—C8^{iii}	−1.2 (3)
C6—N3—C4—C5	0.05 (18)	C11—C9—C12—C8^{iii}	174.46 (15)
N3—C4—C5—N4	−0.51 (18)	O5—C13—C14—C15	−14.0 (2)
C6—N4—C5—C4	0.79 (18)	O6—C13—C14—C15	166.32 (13)
C4—N3—C6—N4	0.45 (17)	O5—C13—C14—C16^{iv}	162.91 (15)
C4—N3—C6—C6^{ii}	−179.20 (19)	O6—C13—C14—C16^{iv}	−16.8 (2)
C5—N4—C6—N3	−0.78 (17)	C16^{iv}—C14—C15—C16	−0.2 (2)
C5—N4—C6—C6^{ii}	178.87 (19)	C13—C14—C15—C16	177.05 (14)
O2—C7—C8—C9	22.7 (3)	C14—C15—C16—C14^{iv}	0.2 (2)
O1—C7—C8—C9	−159.27 (16)	C14—C15—C16—C17	−177.27 (13)
O2—C7—C8—C12^{iii}	−151.64 (17)	C15—C16—C17—O7	−30.5 (2)
O1—C7—C8—C12^{iii}	26.4 (2)	C14^{iv}—C16—C17—O7	152.22 (15)
C12^{iii}—C8—C9—C12	1.2 (3)	C15—C16—C17—O8	145.24 (15)
C7—C8—C9—C12	−173.14 (15)	C14^{iv}—C16—C17—O8	−32.0 (2)

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

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O6—H6···O8^{iv}	0.82	1.67	2.4939 (18)	177
O1—H1···O7	0.82	1.91	2.7228 (18)	173
N3—H3*A*···O3	0.86	1.75	2.553 (2)	154
N4—H4*B*···O4^{ii}	0.86	1.89	2.738 (2)	170
N2—H2*B*···O8^{v}	0.86	1.83	2.676 (2)	168
N1—H1*B*···O7^{vi}	0.86	1.90	2.733 (2)	162

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

(II) 4-Methyl-2-(4-methylpyridin-2-yl)pyridinium 2,4,5-tricarboxybenzoate monohydrate

Crystal data

$C_{12}H_{13}N_2^+·C_{10}H_5O_8^-·H_2O$
M_r = 456.40
Triclinic, $P\overline{1}$
Hall symbol: -P 1
a = 9.5166 (7) Å
b = 9.9970 (8) Å
c = 12.4106 (8) Å
α = 77.979 (6)°
β = 73.421 (6)°
γ = 62.655 (8)°
V = 1001.03 (13) Å^3
Z = 2
F(000) = 476
D_x = 1.514 Mg m^{-3}
Mo *Kα* radiation, *λ* = 0.71073 Å
Cell parameters from 2637 reflections
θ = 3.5–29.2°
μ = 0.12 mm^{-1}
T = 223 K
Block, colourless
0.30 × 0.22 × 0.10 mm

Data collection

Rigaku Mercury CCD diffractometer
Radiation source: fine-focus sealed tube
Graphite Monochromator monochromator
Detector resolution: 28.5714 pixels mm^{-1}
ω scans
Absorption correction: multi-scan (REQAB: Jacobson, 1998)
T_{min} = 0.997, T_{max} = 1.000
9371 measured reflections
3516 independent reflections
2681 reflections with $I > 2\sigma(I)$
R_{int} = 0.041
θ_{max} = 25.0°, θ_{min} = 3.0°
h = −11→11
k = −11→11
l = −14→14

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)]$ = 0.051
$wR(F^2)$ = 0.126
S = 1.01
3516 reflections
304 parameters
3 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H atoms treated by a mixture of independent and constrained refinement
$w = 1/[\sigma^2(F_o^2) + (0.0474P)^2 + 0.9963P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.39 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 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 (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O1	0.8114 (2)	0.8651 (2)	0.10369 (15)	0.0220 (4)
O1W	0.2492 (3)	0.2056 (3)	0.59885 (18)	0.0538 (7)
H1WA	0.181 (3)	0.182 (4)	0.6447 (18)	0.065*
H1WB	0.239 (4)	0.211 (5)	0.5345 (9)	0.065*
O2	0.6903 (2)	1.0820 (2)	0.17697 (16)	0.0279 (5)
H2	0.5980	1.1416	0.2037	0.042*
O3	0.4308 (2)	1.2318 (2)	0.28801 (16)	0.0265 (5)
O4	0.2056 (2)	1.2092 (2)	0.37778 (15)	0.0257 (5)
O5	0.0197 (2)	0.8706 (2)	0.28052 (15)	0.0262 (5)
O6	0.0740 (2)	0.8953 (2)	0.09100 (14)	0.0203 (4)
H6	−0.0092	0.8848	0.0999	0.030*
O7	0.3591 (2)	0.60899 (19)	0.10235 (15)	0.0206 (4)
O8	0.5562 (2)	0.6521 (2)	−0.02698 (15)	0.0246 (5)
H8	0.5667	0.5778	−0.0525	0.037*
N1	0.6780 (3)	0.3858 (2)	0.20738 (17)	0.0204 (5)
N2	0.3984 (2)	0.4962 (2)	0.35502 (17)	0.0183 (5)

H2B	0.4307	0.4206	0.3172	0.022*
C1	0.8219 (3)	0.3208 (3)	0.1372 (2)	0.0243 (6)
H1A	0.8372	0.2467	0.0950	0.029*
C2	0.9488 (3)	0.3587 (3)	0.1244 (2)	0.0232 (6)
H2A	1.0465	0.3104	0.0744	0.028*
C3	0.9308 (3)	0.4685 (3)	0.1860 (2)	0.0207 (6)
C4	0.7813 (3)	0.5371 (3)	0.2584 (2)	0.0188 (6)
H4A	0.7627	0.6122	0.3011	0.023*
C5	0.6601 (3)	0.4928 (3)	0.2665 (2)	0.0170 (6)
C6	0.5001 (3)	0.5601 (3)	0.3440 (2)	0.0171 (5)
C7	0.4475 (3)	0.6811 (3)	0.4059 (2)	0.0191 (6)
H7A	0.5156	0.7266	0.4003	0.023*
C8	0.2937 (3)	0.7353 (3)	0.4764 (2)	0.0213 (6)
C9	0.1945 (3)	0.6648 (3)	0.4831 (2)	0.0232 (6)
H9A	0.0910	0.6993	0.5291	0.028*
C10	0.2502 (3)	0.5444 (3)	0.4216 (2)	0.0225 (6)
H10A	0.1848	0.4963	0.4263	0.027*
C11	0.2372 (4)	0.8670 (3)	0.5426 (2)	0.0325 (7)
H11A	0.1293	0.8893	0.5864	0.049*
H11B	0.2375	0.9536	0.4917	0.049*
H11C	0.3087	0.8425	0.5921	0.049*
C12	1.0654 (3)	0.5124 (3)	0.1764 (2)	0.0278 (7)
H12A	1.1590	0.4539	0.1230	0.042*
H12B	1.0921	0.4933	0.2488	0.042*
H12C	1.0311	0.6180	0.1515	0.042*
C13	0.2554 (3)	0.9052 (3)	0.1798 (2)	0.0150 (5)
C14	0.4064 (3)	0.8186 (3)	0.1140 (2)	0.0144 (5)
C15	0.5373 (3)	0.8476 (3)	0.10869 (19)	0.0143 (5)
H15A	0.6373	0.7901	0.0648	0.017*
C16	0.5258 (3)	0.9592 (3)	0.1662 (2)	0.0142 (5)
C17	0.3742 (3)	1.0455 (3)	0.2337 (2)	0.0158 (5)
C18	0.2436 (3)	1.0146 (3)	0.2380 (2)	0.0160 (5)
H18A	0.1435	1.0708	0.2824	0.019*
C19	0.1040 (3)	0.8861 (3)	0.1895 (2)	0.0160 (5)
C20	0.4367 (3)	0.6847 (3)	0.0611 (2)	0.0152 (5)
C21	0.6861 (3)	0.9682 (3)	0.1483 (2)	0.0167 (6)
C22	0.3332 (3)	1.1702 (3)	0.3060 (2)	0.0177 (6)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0129 (9)	0.0237 (10)	0.0311 (11)	−0.0078 (8)	−0.0013 (8)	−0.0110 (8)
O1W	0.0750 (18)	0.090 (2)	0.0300 (12)	−0.0689 (17)	0.0080 (13)	−0.0186 (14)
O2	0.0159 (9)	0.0246 (11)	0.0477 (12)	−0.0107 (9)	0.0012 (9)	−0.0188 (9)
O3	0.0236 (10)	0.0261 (10)	0.0360 (11)	−0.0155 (9)	0.0012 (9)	−0.0148 (9)
O4	0.0236 (10)	0.0294 (11)	0.0246 (10)	−0.0130 (9)	0.0052 (8)	−0.0143 (8)
O5	0.0220 (10)	0.0417 (12)	0.0200 (10)	−0.0207 (10)	0.0011 (8)	−0.0040 (9)
O6	0.0133 (9)	0.0315 (11)	0.0221 (10)	−0.0136 (8)	−0.0034 (7)	−0.0052 (8)
O7	0.0180 (9)	0.0198 (10)	0.0267 (10)	−0.0110 (8)	0.0007 (8)	−0.0083 (8)
O8	0.0249 (10)	0.0276 (11)	0.0256 (10)	−0.0169 (9)	0.0064 (8)	−0.0142 (8)

N1	0.0201 (12)	0.0203 (12)	0.0211 (12)	−0.0098 (10)	−0.0004 (10)	−0.0053 (9)
N2	0.0186 (11)	0.0181 (11)	0.0191 (11)	−0.0074 (10)	−0.0033 (9)	−0.0055 (9)
C1	0.0246 (15)	0.0211 (14)	0.0247 (15)	−0.0086 (13)	0.0004 (12)	−0.0080 (12)
C2	0.0195 (14)	0.0217 (15)	0.0212 (14)	−0.0054 (12)	0.0015 (11)	−0.0042 (11)
C3	0.0182 (13)	0.0216 (14)	0.0202 (14)	−0.0087 (12)	−0.0047 (11)	0.0033 (11)
C4	0.0202 (13)	0.0180 (14)	0.0194 (13)	−0.0080 (12)	−0.0069 (11)	−0.0006 (11)
C5	0.0189 (13)	0.0145 (13)	0.0162 (13)	−0.0069 (11)	−0.0032 (10)	0.0001 (10)
C6	0.0209 (13)	0.0170 (13)	0.0154 (12)	−0.0092 (12)	−0.0064 (11)	0.0003 (10)
C7	0.0210 (13)	0.0176 (13)	0.0196 (13)	−0.0100 (12)	−0.0036 (11)	−0.0004 (11)
C8	0.0265 (14)	0.0163 (14)	0.0169 (13)	−0.0062 (12)	−0.0046 (11)	−0.0001 (11)
C9	0.0159 (13)	0.0262 (15)	0.0193 (14)	−0.0046 (12)	0.0006 (11)	−0.0020 (12)
C10	0.0184 (14)	0.0281 (15)	0.0221 (14)	−0.0124 (13)	−0.0011 (11)	−0.0026 (12)
C11	0.0351 (17)	0.0279 (16)	0.0278 (16)	−0.0099 (14)	0.0026 (13)	−0.0108 (13)
C12	0.0211 (14)	0.0308 (16)	0.0317 (16)	−0.0123 (13)	−0.0043 (12)	−0.0027 (13)
C13	0.0143 (12)	0.0171 (13)	0.0154 (12)	−0.0076 (11)	−0.0051 (10)	−0.0001 (10)
C14	0.0146 (12)	0.0142 (13)	0.0145 (12)	−0.0064 (11)	−0.0036 (10)	−0.0004 (10)
C15	0.0114 (12)	0.0153 (13)	0.0140 (12)	−0.0041 (11)	−0.0015 (10)	−0.0020 (10)
C16	0.0134 (12)	0.0141 (13)	0.0164 (13)	−0.0063 (11)	−0.0043 (10)	−0.0011 (10)
C17	0.0177 (13)	0.0159 (13)	0.0151 (12)	−0.0078 (11)	−0.0056 (10)	0.0000 (10)
C18	0.0120 (12)	0.0171 (13)	0.0179 (13)	−0.0051 (11)	−0.0020 (10)	−0.0041 (10)
C19	0.0145 (12)	0.0132 (13)	0.0201 (14)	−0.0044 (11)	−0.0031 (11)	−0.0056 (10)
C20	0.0112 (12)	0.0173 (13)	0.0177 (13)	−0.0048 (11)	−0.0049 (10)	−0.0036 (10)
C21	0.0162 (13)	0.0196 (14)	0.0162 (13)	−0.0086 (12)	−0.0041 (11)	−0.0025 (11)
C22	0.0184 (13)	0.0163 (13)	0.0200 (13)	−0.0073 (12)	−0.0066 (11)	−0.0019 (11)

Geometric parameters (Å, º)

O1—C21	1.234 (3)	C6—C7	1.383 (4)
O1W—H1WA	0.8201 (10)	C7—C8	1.393 (4)
O1W—H1WB	0.8201 (10)	C7—H7A	0.9300
O2—C21	1.281 (3)	C8—C9	1.391 (4)
O2—H2	0.8200	C8—C11	1.499 (4)
O3—C22	1.281 (3)	C9—C10	1.371 (4)
O4—C22	1.230 (3)	C9—H9A	0.9300
O5—C19	1.212 (3)	C10—H10A	0.9300
O6—C19	1.308 (3)	C11—H11A	0.9600
O6—H6	0.8200	C11—H11B	0.9600
O7—C20	1.231 (3)	C11—H11C	0.9600
O8—C20	1.301 (3)	C12—H12A	0.9600
O8—H8	0.8200	C12—H12B	0.9600
N1—C1	1.339 (3)	C12—H12C	0.9600
N1—C5	1.342 (3)	C13—C18	1.379 (3)
N2—C10	1.334 (3)	C13—C14	1.401 (3)
N2—C6	1.348 (3)	C13—C19	1.507 (3)
N2—H2B	0.8600	C14—C15	1.385 (3)
C1—C2	1.383 (4)	C14—C20	1.487 (3)
C1—H1A	0.9300	C15—C16	1.393 (3)
C2—C3	1.386 (4)	C15—H15A	0.9300
C2—H2A	0.9300	C16—C17	1.413 (3)
C3—C4	1.390 (4)	C16—C21	1.519 (3)

C3—C12	1.502 (4)	C17—C18	1.397 (3)
C4—C5	1.386 (3)	C17—C22	1.527 (3)
C4—H4A	0.9300	C18—H18A	0.9300
C5—C6	1.479 (3)		

H1WA—O1W—H1WB	110.2 (12)	H11A—C11—H11B	109.5
C21—O2—H2	109.5	C8—C11—H11C	109.5
C19—O6—H6	109.5	H11A—C11—H11C	109.5
C20—O8—H8	109.5	H11B—C11—H11C	109.5
C1—N1—C5	116.7 (2)	C3—C12—H12A	109.5
C10—N2—C6	123.4 (2)	C3—C12—H12B	109.5
C10—N2—H2B	118.3	H12A—C12—H12B	109.5
C6—N2—H2B	118.3	C3—C12—H12C	109.5
N1—C1—C2	123.2 (2)	H12A—C12—H12C	109.5
N1—C1—H1A	118.4	H12B—C12—H12C	109.5
C2—C1—H1A	118.4	C18—C13—C14	118.6 (2)
C1—C2—C3	120.1 (2)	C18—C13—C19	118.0 (2)
C1—C2—H2A	120.0	C14—C13—C19	123.3 (2)
C3—C2—H2A	120.0	C15—C14—C13	118.8 (2)
C2—C3—C4	116.9 (2)	C15—C14—C20	118.2 (2)
C2—C3—C12	122.2 (2)	C13—C14—C20	122.6 (2)
C4—C3—C12	120.8 (2)	C14—C15—C16	122.9 (2)
C5—C4—C3	119.5 (2)	C14—C15—H15A	118.6
C5—C4—H4A	120.3	C16—C15—H15A	118.6
C3—C4—H4A	120.3	C15—C16—C17	118.5 (2)
N1—C5—C4	123.5 (2)	C15—C16—C21	113.1 (2)
N1—C5—C6	114.9 (2)	C17—C16—C21	128.4 (2)
C4—C5—C6	121.6 (2)	C18—C17—C16	117.8 (2)
N2—C6—C7	117.9 (2)	C18—C17—C22	114.3 (2)
N2—C6—C5	116.5 (2)	C16—C17—C22	127.9 (2)
C7—C6—C5	125.6 (2)	C13—C18—C17	123.4 (2)
C6—C7—C8	120.7 (2)	C13—C18—H18A	118.3
C6—C7—H7A	119.7	C17—C18—H18A	118.3
C8—C7—H7A	119.7	O5—C19—O6	126.0 (2)
C9—C8—C7	118.4 (2)	O5—C19—C13	121.4 (2)
C9—C8—C11	121.2 (2)	O6—C19—C13	112.5 (2)
C7—C8—C11	120.4 (2)	O7—C20—O8	124.4 (2)
C10—C9—C8	119.7 (2)	O7—C20—C14	121.6 (2)
C10—C9—H9A	120.2	O8—C20—C14	114.0 (2)
C8—C9—H9A	120.2	O1—C21—O2	120.8 (2)
N2—C10—C9	119.9 (2)	O1—C21—C16	118.6 (2)
N2—C10—H10A	120.0	O2—C21—C16	120.5 (2)
C9—C10—H10A	120.0	O4—C22—O3	122.9 (2)
C8—C11—H11A	109.5	O4—C22—C17	118.2 (2)
C8—C11—H11B	109.5	O3—C22—C17	118.9 (2)

C5—N1—C1—C2	0.3 (4)	C13—C14—C15—C16	0.2 (4)
N1—C1—C2—C3	0.1 (4)	C20—C14—C15—C16	−172.5 (2)
C1—C2—C3—C4	−0.6 (4)	C14—C15—C16—C17	0.6 (4)

C1—C2—C3—C12	179.2 (2)	C14—C15—C16—C21	179.3 (2)
C2—C3—C4—C5	0.6 (4)	C15—C16—C17—C18	−0.6 (4)
C12—C3—C4—C5	−179.2 (2)	C21—C16—C17—C18	−179.1 (2)
C1—N1—C5—C4	−0.3 (4)	C15—C16—C17—C22	178.5 (2)
C1—N1—C5—C6	−179.3 (2)	C21—C16—C17—C22	0.0 (4)
C3—C4—C5—N1	−0.2 (4)	C14—C13—C18—C17	0.9 (4)
C3—C4—C5—C6	178.7 (2)	C19—C13—C18—C17	−178.5 (2)
C10—N2—C6—C7	0.5 (4)	C16—C17—C18—C13	−0.1 (4)
C10—N2—C6—C5	−180.0 (2)	C22—C17—C18—C13	−179.3 (2)
N1—C5—C6—N2	6.7 (3)	C18—C13—C19—O5	−51.5 (3)
C4—C5—C6—N2	−172.3 (2)	C14—C13—C19—O5	129.2 (3)
N1—C5—C6—C7	−173.8 (2)	C18—C13—C19—O6	125.7 (2)
C4—C5—C6—C7	7.2 (4)	C14—C13—C19—O6	−53.7 (3)
N2—C6—C7—C8	−0.5 (4)	C15—C14—C20—O7	144.7 (2)
C5—C6—C7—C8	180.0 (2)	C13—C14—C20—O7	−27.6 (4)
C6—C7—C8—C9	0.1 (4)	C15—C14—C20—O8	−31.7 (3)
C6—C7—C8—C11	−179.6 (2)	C13—C14—C20—O8	156.0 (2)
C7—C8—C9—C10	0.5 (4)	C15—C16—C21—O1	−12.1 (3)
C11—C8—C9—C10	−179.8 (3)	C17—C16—C21—O1	166.4 (2)
C6—N2—C10—C9	0.1 (4)	C15—C16—C21—O2	166.5 (2)
C8—C9—C10—N2	−0.6 (4)	C17—C16—C21—O2	−14.9 (4)
C18—C13—C14—C15	−0.9 (4)	C18—C17—C22—O4	15.0 (3)
C19—C13—C14—C15	178.4 (2)	C16—C17—C22—O4	−164.1 (3)
C18—C13—C14—C20	171.4 (2)	C18—C17—C22—O3	−163.5 (2)
C19—C13—C14—C20	−9.3 (4)	C16—C17—C22—O3	17.4 (4)

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O1*W*—H1*WA*···O5^{i}	0.82 (1)	2.12 (1)	2.916 (3)	163 (3)
O1*W*—H1*WB*···O4^{ii}	0.82 (1)	2.06 (1)	2.880 (3)	175 (3)
N2—H2*B*···O3^{ii}	0.86	1.99	2.792 (3)	154
O6—H6···O1^{iii}	0.82	1.79	2.609 (2)	174
O8—H8···O7^{iv}	0.82	1.84	2.644 (2)	166

Symmetry codes: (i) −*x*, −*y*+1, −*z*+1; (ii) *x*, *y*−1, *z*; (iii) *x*−1, *y*, *z*; (iv) −*x*+1, −*y*+1, −*z*.

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