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Tetraammonium benzene-1,2,4,5-tetracarboxylate dihydrate

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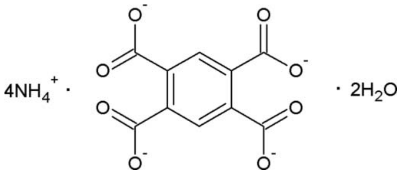
Key indicators: single-crystal X-ray study; T = 130 K; mean σ(C–C) = 0.002 Å; R factor = 0.026; wR factor = 0.076; data-to-parameter ratio = 7.4.

In the crystal structure of $4NH_4^+\cdot C_{10}H_2O_8^{4-}\cdot 2H_2O$, the tetracarboxylate anion resides on a twofold crystallographic axis. The supramolecular structure arises from eight N—H···O [N···O ranges from 2.783 (2) to 3.003 (2) Å] and two O—H···O [O···O distances of 2.7313 (18) and 2.9102 (18) Å] hydrogen bonds.

Related literature

For related literature, see: Allen (2002); Bergstrom *et al.* (2000); Borowiak, Dutkiewicz *et al.* (2005); Borowiak, Kubicki *et al.* (2005); Ejsmont & Zaleski (2006); Rafizadeh *et al.* (2006); Wang *et al.* (2005); Zheng *et al.* (2002).



Experimental

Crystal data

$4NH_4^+C_{10}H_2O_8^{4-}\cdot 2H_2O$
M_r = 358.32
Monoclinic, $C2$
a = 11.6054 (10) Å
b = 6.7122 (6) Å
c = 10.5718 (8) Å
β = 102.821 (7)°
V = 802.99 (12) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.13 mm^{-1}
T = 130 (2) K
0.5 × 0.2 × 0.1 mm

Data collection

Kuma KM-4 CCD diffractometer
Absorption correction: multi-scan (*CrysAlis RED*; Oxford Diffraction, 2007)
T_{min} = 0.972, T_{max} = 1.000 (expected range = 0.959–0.987)
3224 measured reflections
1088 independent reflections
1042 reflections with $I > 2\sigma(I)$
R_{int} = 0.011

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.026
$wR(F^2)$ = 0.076
S = 1.11
1088 reflections
147 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H11···O2^{i}	0.94 (2)	1.88 (2)	2.8114 (16)	170 (2)
N1—H12···O4	0.91 (3)	1.87 (3)	2.783 (2)	175 (2)
N1—H13···O2^{ii}	0.96 (2)	1.91 (2)	2.8585 (16)	171 (2)
N1—H14···O3^{iii}	0.97 (3)	1.85 (3)	2.819 (2)	179 (3)
N2—H21···O4^{iv}	1.04 (3)	1.78 (3)	2.786 (2)	163 (2)
N2—H22···O1	0.87 (3)	1.94 (3)	2.811 (2)	172 (3)
N2—H23···O5^{iii}	0.88 (4)	2.00 (4)	2.857 (2)	162 (3)
N2—H24···O5^{v}	0.99 (4)	2.18 (3)	3.003 (2)	139 (2)
N2—H24···O3^{ii}	0.99 (4)	2.23 (3)	2.984 (2)	132 (3)
O5—H51···O1	0.90	1.90	2.7313 (18)	153
O5—H52···O3^{vi}	0.90	2.02	2.9102 (18)	170

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

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2007); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2007); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *Stereochemical Workstation* (Siemens 1989); *Mercury* (Macrae *et al.*, 2006); 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: GG2029).

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supplementary materials

Acta Cryst. (2007). E**63**, o4101 [**doi:10.1107/S1600536807045205**]

Tetraammonium benzene-1,2,4,5-tetracarboxylate dihydrate

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Comment

The compound (I) crystallizes in the space group C2, with two water molecules of crystallization. The crystal structure of the tetrahydrate was determined previously (Bergstrom *et al.*, 2000).

The asymmetric unit of (I) (Fig. 1) contains two cations, one half-anion, and a water molecule; the anion lies on a twofold axis of symmetry. All carboxylic H atoms are transferred to the N atoms, thus forming ammonium cations. The conformation of pyromellitate anion is similar to that in the crystal structures determined previously (Bergstrom *et al.*, 2000; Zheng *et al.*, 2002; Wang *et al.*, 2005; Ejsmont & Zaleski, 2006; Rafizadeh *et al.*, 2006) where one pair of carboxylate groups is almost coplanar with the aromatic ring (8.1°) while the other one is almost perpendicular (82.6°).

The molecules form two different types of hydrogen-bonded layers. In one of them each ammonium cation is connected to four pyromellitate anions *via* four distinct $N1^+—H\cdots O^-$ hydrogen bonds (Table 1) that make a kind of a patchwork (Fig. 2, Fig. 3). The second type is formed *via* three different hydrogen bonds: $N—H\cdots O^-_{\text{carboxylate}}$, $N—H\cdots O_{\text{water}}$, $O_{\text{water}}—H\cdots O^-_{\text{carboxylate}}$ (Fig. 4). These layers are parallel to the *ab* crystallographic plane.

The two kinds of layers are placed alternately, thus forming the supramolecular structure (Fig. 5).

Experimental

The 0.047 g (~ 0.1 m*M*) of the macrocyclic amine (Borowiak, Dutkiewicz *et al.*, 2005*a*; Borowiak, Kubicki *et al.*, 2005*b*), was dissolved in 2 ml of ethanol. Then 0.025 g (~0.1 m*M*) of pyromellitic acid dissolved in 1 ml of water was added. The white precipitate was not dissolved after refluxing the reaction mixture. The 1 ml of formamide was added to the mixture and was warmed until dissolution of the product. The solution was cooled down slowly and after two days colorless crystals were deposited. We expected the adduct of macrocyclic amine and pyromellitic acid, instead crystals comprised both pyromellitic anion and ammonium cation. It can be explained in this way that formamide was hydrolyzed in slightly basic conditions to form ammonia that substituted for the macrocyclic amine cation.

Refinement

Initial trials to refine the structural model of (I) in the centrosymmetric space group C2/m (No. 12) provided a solution that did not provide a satisfactory refinement convergence. A satisfactory convergence was achieved in the non-centrosymmetric space group C2 (No. 5).

Hydrogen atoms were located in difference Fourier maps and refined except for the hydrogen atoms of the water molecule, which were constrained to ride on their parent O atom.

Figures

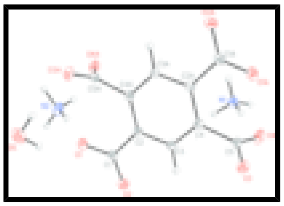


Fig. 1. The asymmetric unit of (I) with 50% probability displacement ellipsoids (Siemens, 1989).

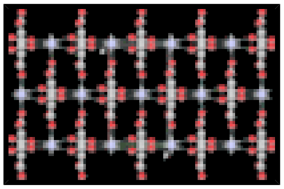


Fig. 2. The molecular layer in (I) generated by four $N1^+$—H(11,12,13,14)···O^- hydrogen bonds with a view along the *c* axis (Macrae *et al.*, 2006).

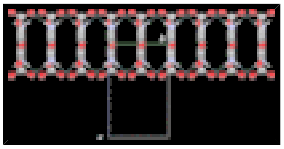


Fig. 3. The molecular layer in (I) generated by four $N1^+$—H(11,12,13,14)···O^- hydrogen bonds with a view along the *a* axis (Macrae *et al.*, 2006).

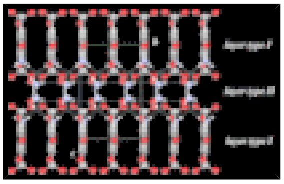


Fig. 4. A second type of the molecular layer in (I) generated by $N—H\cdots O^-_{\text{carboxylate}}$, N—H···$O_{\text{water}}$, O_{water}—$H\cdots O^-_{\text{carboxylate}}$ hydrogen bonds with a view along the *a* axis (Macrae *et al.*, 2006).

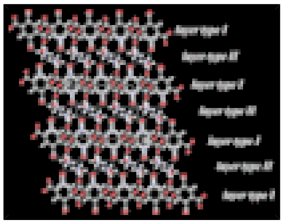


Fig. 5. Three types of hydrogen bonds: $N—H\cdots O^-_{\text{carboxylate}}$, N—H···$O_{\text{water}}$, O_{water}—$H\cdots O^-_{\text{carboxylate}}$ connect layers (see Fig. 2a, 2 b, 2c) into the supramolecular structure (Macrae *et al.*, 2006).

Tetraammonium benzene-1,2,4,5-tetracarboxylate dihydrate

Crystal data

$4NH_4^+\cdot C_{10}H_2O_8^{4-}\cdot 2H_2O$

$M_r = 358.32$

Monoclinic, *C*2

$a = 11.6054\ (10)$ Å

$b = 6.7122\ (6)$ Å

$c = 10.5718\ (8)$ Å

$\beta = 102.821\ (7)$°

$V = 802.99\ (12)$ Å^3

$Z = 2$

$F_{000} = 380$

$D_x = 1.482$ Mg m^{-3}

Mo *K*α radiation
$\lambda = 0.71073$ Å

Cell parameters from 2581 reflections

$\theta = 2.4$–29.1°

$\mu = 0.13$ mm^{-1}

$T = 130\ (2)$ K

Block, colourless

0.5 × 0.2 × 0.1 mm

Data collection

Kuma KM-4 CCD diffractometer	1088 independent reflections
Radiation source: fine-focus sealed tube	1042 reflections with $I > 2\sigma(I)$
Monochromator: graphite	$R_{\text{int}} = 0.011$
Detector resolution: 8.1929 pixels mm^{-1}	$\theta_{\text{max}} = 29.1°$
$T = 130(2)$ K	$\theta_{\text{min}} = 3.5°$
ω–scan	$h = -15 \rightarrow 15$
Absorption correction: multi-scan [empirical (using intensity measurements) absorption correction (CrysAlis RED; Oxford Diffraction, 2007)]	$k = -9 \rightarrow 6$
$T_{\text{min}} = 0.972$, $T_{\text{max}} = 1.000$	$l = -14 \rightarrow 13$
3224 measured reflections	

Refinement

Refinement on F^2	Hydrogen site location: difference Fourier map
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.026$	$w = 1/[\sigma^2(F_o^2) + (0.0551P)^2 + 0.094P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.076$	$(\Delta/\sigma)_{\text{max}} < 0.001$
$S = 1.11$	$\Delta\rho_{\text{max}} = 0.28$ e Å^{-3}
1088 reflections	$\Delta\rho_{\text{min}} = -0.20$ e Å^{-3}
147 parameters	Extinction correction: none
1 restraint	Absolute structure: [Flack, H. D. (1983). Acta Cryst. A39, 876–881]
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.1 (12)
Secondary atom site location: difference Fourier map	

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 $F^2 > 2\text{sigma}(F^2)$ 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*	$U_{\text{iso}}*/U_{\text{eq}}$

C1	0.71490 (12)	0.5340 (3)	0.39876 (13)	0.0140 (3)
O1	0.70464 (10)	0.50819 (19)	0.27848 (11)	0.0194 (3)
O2	0.81107 (9)	0.5530 (2)	0.47862 (10)	0.0221 (3)
C2	0.60214 (11)	0.5412 (3)	0.44879 (12)	0.0124 (3)
C3	0.61053 (11)	0.5420 (3)	0.58230 (12)	0.0130 (3)
H3	0.6911 (17)	0.541 (4)	0.6365 (18)	0.014 (4)*
C4	0.51014 (12)	0.5424 (2)	0.63515 (13)	0.0122 (3)
C5	0.53202 (12)	0.5467 (3)	0.78232 (12)	0.0137 (3)
O3	0.55778 (11)	0.38518 (19)	0.84174 (11)	0.0187 (3)
O4	0.53126 (12)	0.71429 (19)	0.83520 (11)	0.0208 (3)
N1	0.51699 (11)	1.0495 (3)	0.67757 (12)	0.0167 (3)
H11	0.444 (2)	1.058 (4)	0.619 (2)	0.027 (5)*
H12	0.519 (2)	0.936 (4)	0.726 (2)	0.021 (6)*
H13	0.580 (2)	1.041 (5)	0.632 (2)	0.035 (6)*
H14	0.531 (2)	1.166 (5)	0.733 (3)	0.034 (7)*
N2	0.68683 (14)	0.7804 (3)	0.07294 (14)	0.0221 (3)
H21	0.618 (2)	0.744 (5)	−0.005 (3)	0.038 (7)*
H22	0.687 (2)	0.701 (5)	0.138 (3)	0.037 (7)*
H23	0.664 (3)	0.901 (6)	0.091 (3)	0.041 (8)*
H24	0.766 (3)	0.775 (6)	0.052 (3)	0.066 (10)*
O5	0.65381 (12)	0.1966 (2)	0.10908 (16)	0.0304 (3)
H51	0.6910	0.2740	0.1752	0.088 (13)*
H52	0.5839	0.2424	0.1195	0.101 (15)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0131 (6)	0.0137 (6)	0.0161 (6)	0.0009 (6)	0.0050 (5)	0.0016 (7)
O1	0.0190 (5)	0.0253 (7)	0.0154 (5)	0.0009 (5)	0.0071 (4)	−0.0001 (5)
O2	0.0127 (5)	0.0342 (7)	0.0191 (5)	−0.0008 (6)	0.0032 (4)	−0.0011 (6)
C2	0.0126 (6)	0.0125 (6)	0.0124 (6)	0.0000 (6)	0.0035 (4)	0.0002 (6)
C3	0.0121 (6)	0.0145 (6)	0.0120 (6)	−0.0003 (6)	0.0016 (4)	0.0007 (6)
C4	0.0142 (6)	0.0113 (6)	0.0111 (5)	0.0001 (6)	0.0029 (4)	−0.0001 (6)
C5	0.0119 (6)	0.0178 (7)	0.0111 (6)	−0.0006 (6)	0.0019 (4)	−0.0003 (6)
O3	0.0235 (6)	0.0183 (6)	0.0146 (6)	0.0035 (5)	0.0047 (4)	0.0033 (4)
O4	0.0325 (7)	0.0166 (6)	0.0129 (5)	−0.0024 (5)	0.0039 (4)	−0.0018 (5)
N1	0.0145 (6)	0.0179 (6)	0.0178 (6)	0.0003 (6)	0.0036 (4)	0.0021 (6)
N2	0.0292 (8)	0.0211 (7)	0.0164 (6)	−0.0028 (6)	0.0059 (6)	0.0008 (6)
O5	0.0254 (7)	0.0240 (7)	0.0425 (8)	0.0017 (6)	0.0089 (5)	−0.0101 (6)

Geometric parameters (Å, °)

C1—O1	1.2625 (18)	N1—H11	0.94 (2)
C1—O2	1.2476 (18)	N1—H12	0.91 (3)
C1—C2	1.5172 (17)	N1—H13	0.96 (2)
C2—C3	1.3931 (17)	N1—H14	0.97 (3)
C2—C4$^{\mathrm{i}}$	1.4043 (18)	N2—H21	1.04 (3)
C3—C4	1.3994 (18)	N2—H22	0.87 (3)

C3—H3	0.98 (2)	N2—H23	0.88 (4)
C4—C5	1.5202 (17)	N2—H24	0.99 (4)
C5—O3	1.256 (2)	O5—H51	0.90
C5—O4	1.257 (2)	O5—H52	0.90
O1—C1—O2	124.46 (13)	O4—C5—C4	117.15 (15)
O2—C1—C2	118.18 (12)	H11—N1—H12	109 (2)
O1—C1—C2	117.36 (12)	H11—N1—H13	110.2 (18)
C3—C2—C4^{i}	119.12 (12)	H12—N1—H13	108 (2)
C1—C2—C3	118.79 (12)	H11—N1—H14	111 (2)
C4^{i}—C2—C1	122.08 (11)	H12—N1—H14	110.7 (18)
C2—C3—C4	121.82 (12)	H13—N1—H14	108 (2)
C2—C3—H3	115.8 (11)	H21—N2—H22	110 (2)
C4—C3—H3	122.4 (11)	H21—N2—H23	100 (3)
C3—C4—C2^{i}	119.06 (12)	H22—N2—H23	109 (3)
C3—C4—C5	116.35 (11)	H21—N2—H24	114 (2)
C2^{i}—C4—C5	124.58 (12)	H22—N2—H24	108 (3)
O3—C5—O4	125.08 (12)	H23—N2—H24	115 (3)
O3—C5—C4	117.55 (15)	H51—O5—H52	90
O2—C1—C2—C3	−8.4 (2)	C2—C3—C4—C2^{i}	0.2 (2)
O1—C1—C2—C3	171.32 (16)	C2—C3—C4—C5	−179.04 (16)
O2—C1—C2—C4^{i}	173.12 (16)	C3—C4—C5—O3	−80.29 (19)
O1—C1—C2—C4^{i}	−7.2 (2)	C2^{i}—C4—C5—O3	100.51 (18)
C4^{i}—C2—C3—C4	0.5 (2)	C3—C4—C5—O4	94.68 (18)
C1—C2—C3—C4	−178.02 (16)	C2^{i}—C4—C5—O4	−84.5 (2)

Symmetry codes: (i) −*x*+1, *y*, −*z*+1.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H11···O2^{ii}	0.94 (2)	1.88 (2)	2.8114 (16)	170 (2)
N1—H12···O4	0.91 (3)	1.87 (3)	2.783 (2)	175 (2)
N1—H13···O2^{iii}	0.96 (2)	1.91 (2)	2.8585 (16)	171 (2)
N1—H14···O3^{iv}	0.97 (3)	1.85 (3)	2.819 (2)	179 (3)
N2—H21···O4^{v}	1.04 (3)	1.78 (3)	2.786 (2)	163 (2)
N2—H22···O1	0.87 (3)	1.94 (3)	2.811 (2)	172 (3)
N2—H23···O5^{iv}	0.88 (4)	2.00 (4)	2.857 (2)	162 (3)
N2—H24···O5^{vi}	0.99 (4)	2.18 (3)	3.003 (2)	139 (2)
N2—H24···O3^{iii}	0.99 (4)	2.23 (3)	2.984 (2)	132 (3)
O5—H51···O1	0.90	1.90	2.7313 (18)	153
O5—H52···O3^{i}	0.90	2.02	2.9102 (18)	170

Symmetry codes: (ii) *x*−1/2, *y*+1/2, *z*; (iii) −*x*+3/2, *y*+1/2, −*z*+1; (iv) *x*, *y*+1, *z*; (v) *x*, *y*, *z*−1; (vi) −*x*+3/2, *y*+1/2, −*z*; (i) −*x*+1, *y*, −*z*+1.

Fig. 1

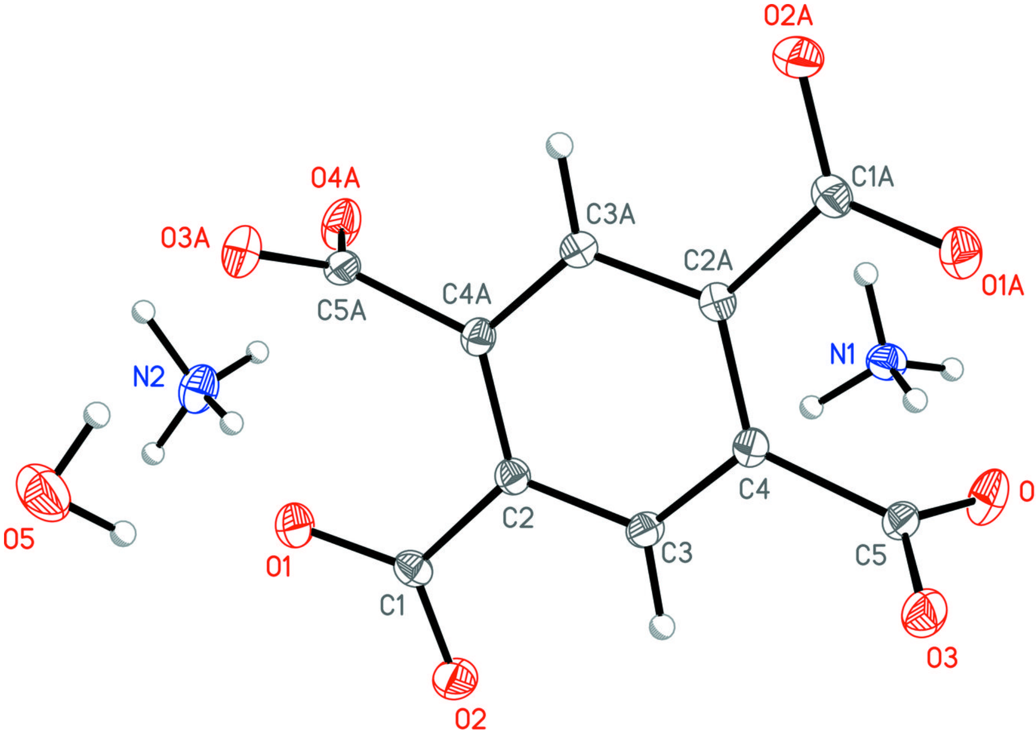

O2A
O4A
C3A
C1A
O3A
C2A
O1A
C5A
C4A
N1
N2
C4
O4
O5
C2
C3
C5
O1
C1
O3
O2

Fig. 2

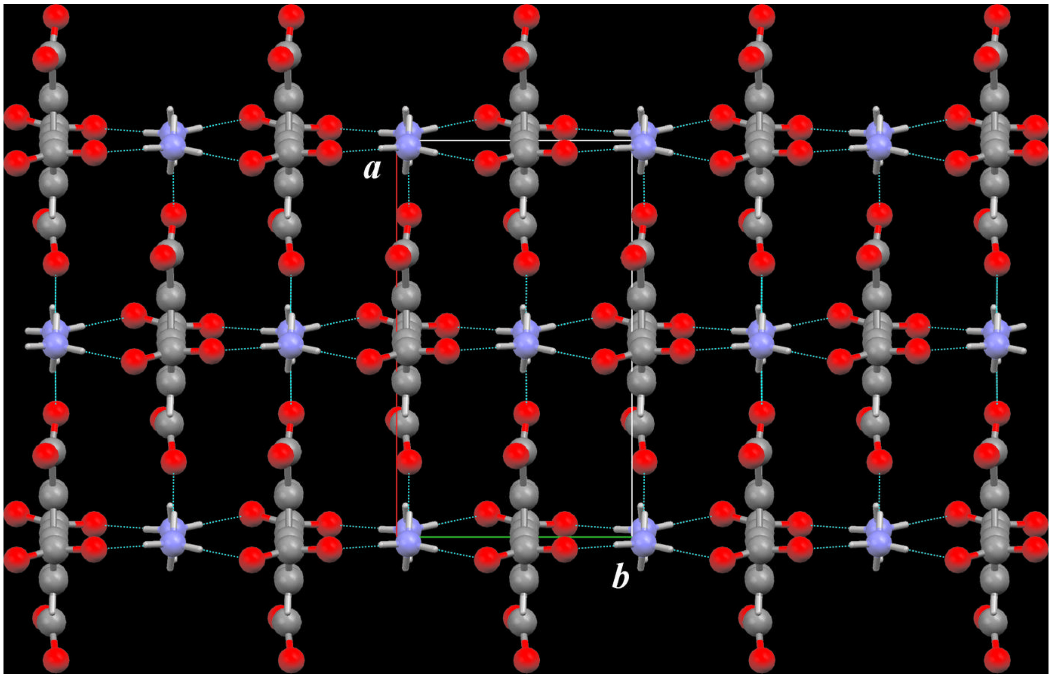


Fig. 3

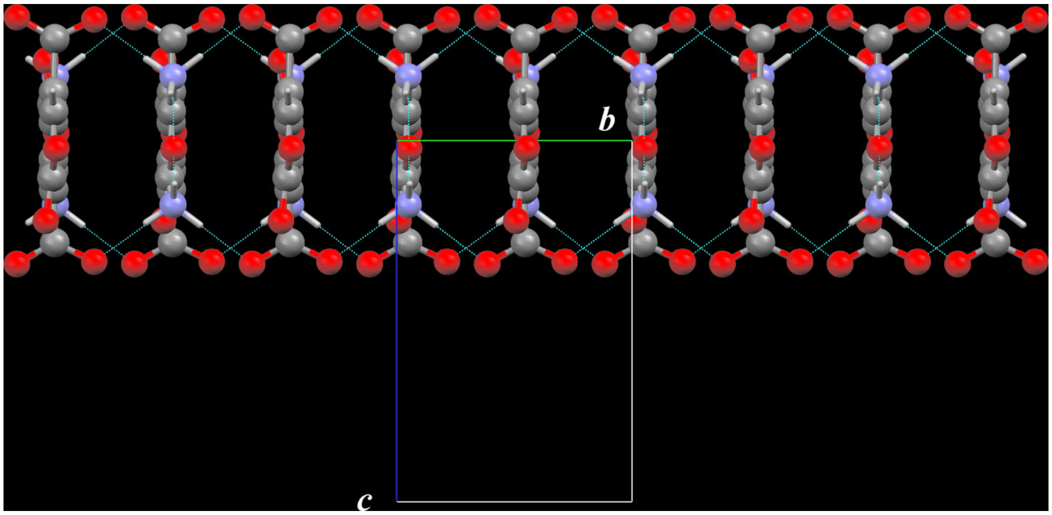


Fig. 4

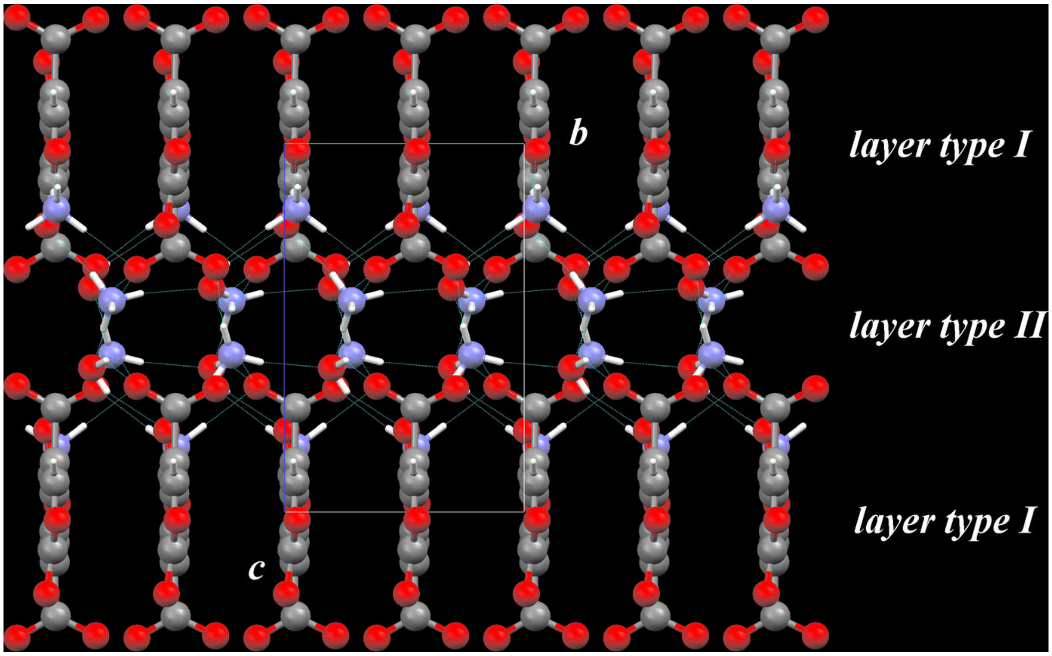
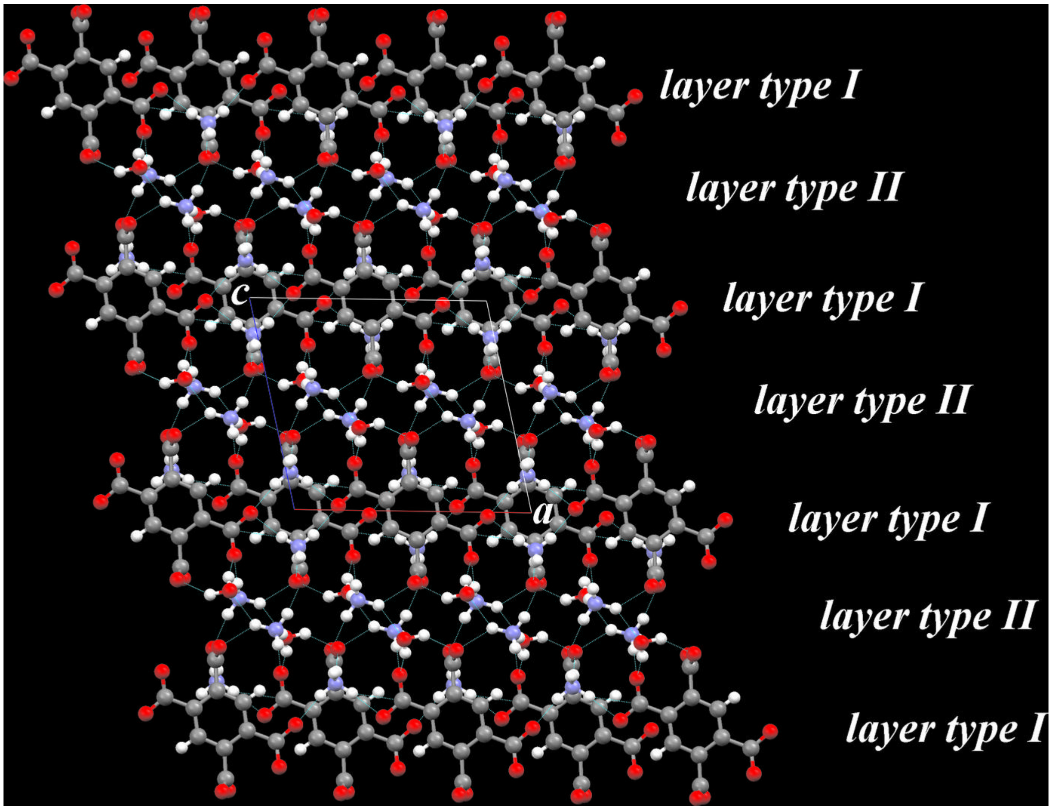


Fig. 5


layer type I
layer type II
layer type I
layer type II
layer type I
layer type II
layer type I
c
a