

3,12-Diaza-6,9-diazonia-2,13-dioxotetra-decane bis(perchlorate)

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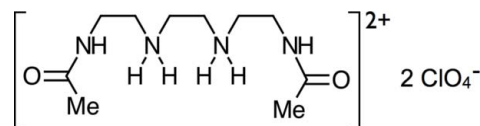
Received 19 December 2011; accepted 23 December 2011

Key indicators: single-crystal X-ray study; $T = 150$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.039; wR factor = 0.087; data-to-parameter ratio = 17.6.

The crystal structure of the title diprotonated diacetyltriethylenetetramine (DAT) perchlorate salt, $\text{C}_{10}\text{H}_{24}\text{N}_4\text{O}_2^{2+} \cdot 2\text{ClO}_4^-$, can be described as a three-dimensional assembly of alternating layers consisting of diprotonated diacetyltriethylenetetramine (H_2DAT)²⁺ strands along [100] and the anionic species ClO_4^- . The (H_2DAT)²⁺ cations in the strands are connected *via* $\text{N}-\text{H} \cdots \text{O}$ hydrogen bonding between the acetyl groups and the amine groups of neighbouring (H_2DAT)²⁺ cations. Layers of (H_2DAT)²⁺ strands and perchlorate anions are connected by a network of hydrogen bonds between the NH and NH_2 groups and the O atoms of the perchlorate anion. The asymmetric unit consists of one perchlorate anion in a general position, as well as of one cation that is located on a center of inversion.

Related literature

For background to pharmaceutical chelating agents in the treatment of diabetes, see: Cooper *et al.* (2004); Gong *et al.* (2006, 2008); Jüllig *et al.* (2007); Lu *et al.* (2010). For the detection of a new group of TETA metabolites, see: Lu *et al.* (2007). For the preparation and characterization of DAT mono- and dihydrochloride salts, see: Jonas *et al.* (2006); Wichmann *et al.* (2011). For related structures, see: Elaoud *et al.* (1999); Fu *et al.* (2005); Ilioudis *et al.* (2000, 2002); Ilioudis & Steed (2003); Wichmann *et al.* (2007).



Experimental

Crystal data

$\text{C}_{10}\text{H}_{24}\text{N}_4\text{O}_2^{2+} \cdot 2\text{ClO}_4^-$
 $M_r = 431.23$
Monoclinic, $P2_1/c$
 $a = 6.0888$ (5) Å
 $b = 10.9415$ (9) Å
 $c = 14.8160$ (11) Å
 $\beta = 110.846$ (6)°

$V = 922.44$ (13) Å³
 $Z = 2$
Mo $K\alpha$ radiation
 $\mu = 0.41$ mm⁻¹
 $T = 150$ K
 $0.45 \times 0.35 \times 0.17$ mm

Data collection

Stoe IPDS II diffractometer
Absorption correction: numerical
(*X-RED32*; Stoe & Cie, 2001)
 $T_{\min} = 0.837$, $T_{\max} = 0.936$

11528 measured reflections
2113 independent reflections
1624 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.114$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.039$
 $wR(F^2) = 0.087$
 $S = 1.03$
2113 reflections

120 parameters
H-atom parameters constrained
 $\Delta\rho_{\max} = 0.38$ e Å⁻³
 $\Delta\rho_{\min} = -0.42$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
$\text{N3}-\text{H3} \cdots \text{O4}$	0.88	2.12	2.989 (2)	167
$\text{N6}-\text{H6A} \cdots \text{O1}^i$	0.92	1.77	2.6745 (19)	168
$\text{N6}-\text{H6B} \cdots \text{O2}^{ii}$	0.92	2.13	2.9265 (17)	145
$\text{N6}-\text{H6B} \cdots \text{O5}^{ii}$	0.92	2.40	3.2141 (19)	147

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

Data collection: *X-Area* (Stoe & Cie, 2002); cell refinement: *X-Area*; data reduction: *X-Area*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *VESTA* (Momma & Izumi, 2011); software used to prepare material for publication: *publCIF* (Westrip, 2010).

We acknowledge support from the following funding sources: Endocore Research Associates; the Maurice and Phyllis Paykel Trust; Lottery Health (New Zealand); the Auckland Medical Research Foundation; the University of Auckland; the Department of Education (New Zealand) through a grant to the Maurice Wilkins Centre of Excellence for Molecular Biodiscovery; Protomix Corporation Ltd; and by program grants from the Foundation for Research Science and Technology, New Zealand and from the Health Research Council of New Zealand.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: NC2261).

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supplementary materials

Acta Cryst. (2012). E68, o333-o334 [doi:10.1107/S1600536811055516]

3,12-Diaza-6,9-diazonia-2,13-dioxotetradecane bis(perchlorate)

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Comment

As part of a larger project focusing on TETA and its metabolites as pharmaceutical chelating agents in Diabetes treatment (Cooper *et al.*, 2004, Gong *et al.* 2006, 2008, Jüllig *et al.* 2007, Lu *et al.* 2010), we previously published the detection of a new group of TETA metabolites, N^1 -Monoacetyltriethylenetetramine (MAT) and the N^1, N^{10} -Diacetyltriethylenetetramine (DAT) (Lu *et al.* 2007), as well as just recently the development of a new selective synthetic route and the characterization of the DAT mono- and dihydrochloride salts (Wichmann *et al.*, 2011).

TETA and its metabolites belong into the polyamine family, ambivalent and multidentate ligands, which are well known for their ability to form a variety of interesting open-chain, macrocyclic and three-dimensional architectures. TETA salts exist in variable protonation states with different anionic species (Ilioudis, *et al.* 2000, 2002, 2003, Elaoud *et al.* 1999, Fu *et al.* 2005, Wichmann *et al.* 2007). Therefore, we investigated the metabolite forms MAT and DAT towards their protonation and complexation behaviour (Wichmann *et al.*, 2011). The obtained crystal structure of the new DAT salt [(H₂DAT) * 2 ClO₄] is described in this paper.

The (H₂DAT)²⁺ cations are arranged as a linear symmetric chain with the terminal NH—CO—CH₃ groups in *trans*-position to each other (Fig. 1).

The crystal structure consists of a three-dimensional-network, containing alternating assembly of two-dimensional-layers of (H₂DAT)²⁺ cations (Fig. 2) and the ClO₄⁻ anions. The (H₂DAT)²⁺ cations form linear strands along [100] (Fig. 3), connected *via* hydrogen bonding between the acetyl groups and the amine groups of neighbouring (H₂DAT)²⁺ cations, with a C2=O1 ... H6A/N6 distance of 1.767 (1) Å. These linear strands of the (H₂DAT)²⁺ cations form two-dimensional-layers in the (001) plane. However, the two-dimensional-layers of (H₂DAT)²⁺ cations and the perchlorate anions were stabilized by a network of intermolecular hydrogen bonds between the NH- and NH₂-groups and the oxygen atoms of the perchlorate anion, with N6—H6B...O2—C11—O4...H3—N3 between 2.126 (1) Å and 2.125 (1) Å, (Table 1). The terminal NH-groups of a (H₂DAT)²⁺ cation binds to an O-atom of a perchlorate anion, which itself bound to an internal NH-group of another (H₂DAT)²⁺ cation and *vice versa*. Therefore each (H₂DAT)²⁺ cation is connected to four different (H₂DAT)²⁺ cations, two from the above and two from the below layer.

Experimental

The DAT * 2 HCl powder material was synthesized by CarboGen, Switzerland according to literature procedure (Jonas *et al.* 2006, Wichmann *et al.* 2011). Cu(ClO₄)₂ is commercially available and was used as received. Crystals of the title compound were grown by slow evaporation of an aqueous solution of DAT * 2 HCl and Cu(ClO₄)₂ in stoichiometric ratio in water over a period of 6 weeks.

Refinement

H atoms bonded to C and N atoms were positioned geometrically (C—H = 0.98–0.99 Å, N—H = 0.88–0.92 Å) and refined using a riding-model approximation, with $U_{\text{iso}}(\text{H}) = 1.5 U_{\text{eq}}(\text{C}, \text{N})$.

Figures

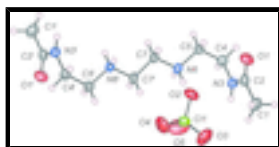


Fig. 1. Crystal structure of the title compound with labeling and displacement ellipsoids drawn at the 75% probability level. [symmetry code: (i) $-x, -y - z + 1$].

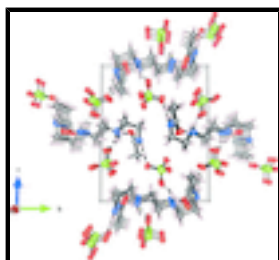


Fig. 2. Crystal structure of the title compound with view along the a axis. Hydrogen bonding interactions are shown as dashed lines.

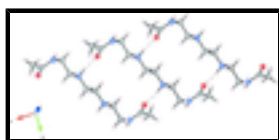


Fig. 3. The strands of $(\text{H}_2\text{DAT})^{2+}$ cations viewed along the a axis. The dashed bonds indicate the hydrogen bonds.

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Crystal data



$M_r = 431.23$

Monoclinic, $P2_1/c$

Hall symbol: $-P 2_1/c$

$a = 6.0888$ (5) Å

$b = 10.9415$ (9) Å

$c = 14.8160$ (11) Å

$\beta = 110.846$ (6)°

$V = 922.44$ (13) Å³

$Z = 2$

$F(000) = 452$

$D_x = 1.553$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 12054 reflections

$\theta = 4.7\text{--}59.0^\circ$

$\mu = 0.41$ mm⁻¹

$T = 150$ K

Not regular, colourless

$0.45 \times 0.35 \times 0.17$ mm

Data collection

Stoe IPDS II
diffractometer

Radiation source: fine-focus sealed tube
graphite

2113 independent reflections

1624 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.114$

Image plate detector scans $\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 2.4^\circ$
 Absorption correction: numerical $h = -7 \rightarrow 6$
 (*X-RED32*; Stoe & Cie, 2001)
 $T_{\min} = 0.837$, $T_{\max} = 0.936$ $k = -14 \rightarrow 14$
 11528 measured reflections $l = -19 \rightarrow 19$

Refinement

Refinement on F^2 Secondary atom site location: difference Fourier map
 Least-squares matrix: full Hydrogen site location: inferred from neighbouring sites
 $R[F^2 > 2\sigma(F^2)] = 0.039$ H-atom parameters constrained
 $wR(F^2) = 0.087$ $w = 1/[\sigma^2(F_o^2) + (0.0435P)^2 + 0.0412P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $S = 1.03$ $(\Delta/\sigma)_{\max} = 0.001$
 2113 reflections $\Delta\rho_{\max} = 0.38 \text{ e } \text{\AA}^{-3}$
 120 parameters $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$
 0 restraints Extinction correction: *SHELXL97* (Sheldrick, 2008),
 $F_c^* = kFc[1 + 0.001xFc^2\lambda^3/\sin(2\theta)]^{-1/4}$
 Primary atom site location: structure-invariant direct Extinction coefficient: 0.0082 (19)
 methods

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.7492 (2)	-0.27758 (14)	0.49858 (8)	0.0292 (3)
N3	0.4849 (2)	-0.35281 (14)	0.55667 (8)	0.0203 (3)
H3	0.4552	-0.3783	0.6075	0.030*
N6	0.1286 (2)	-0.15588 (13)	0.49690 (8)	0.0180 (3)
H6A	0.0102	-0.2008	0.5058	0.027*
H6B	0.2493	-0.1497	0.5556	0.027*
C1	0.8854 (3)	-0.3315 (2)	0.66635 (12)	0.0306 (4)
H1A	0.9869	-0.4013	0.6669	0.046*
H1B	0.8082	-0.3455	0.7133	0.046*
H1C	0.9805	-0.2570	0.6835	0.046*
C2	0.7025 (3)	-0.31761 (17)	0.56731 (10)	0.0212 (3)

supplementary materials

C4	0.2944 (3)	-0.35009 (17)	0.46258 (10)	0.0218 (4)
H4A	0.1589	-0.3965	0.4668	0.033*
H4B	0.3476	-0.3914	0.4145	0.033*
C5	0.2149 (3)	-0.22157 (17)	0.42777 (10)	0.0211 (3)
H5A	0.3478	-0.1757	0.4205	0.032*
H5B	0.0875	-0.2255	0.3637	0.032*
C7	0.0392 (3)	-0.03159 (17)	0.46280 (11)	0.0230 (4)
H7A	-0.0947	-0.0376	0.4008	0.035*
H7B	0.1647	0.0169	0.4518	0.035*
C11	0.43802 (6)	-0.55724 (4)	0.77065 (2)	0.02264 (14)
O2	0.4296 (2)	-0.55967 (14)	0.86654 (8)	0.0337 (3)
O3	0.2285 (3)	-0.60503 (17)	0.70295 (10)	0.0478 (4)
O4	0.4650 (3)	-0.43253 (15)	0.74660 (10)	0.0461 (4)
O5	0.6382 (3)	-0.62675 (18)	0.77258 (10)	0.0507 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0253 (6)	0.0377 (9)	0.0282 (5)	-0.0049 (6)	0.0139 (5)	-0.0020 (5)
N3	0.0192 (6)	0.0211 (8)	0.0200 (6)	0.0012 (6)	0.0062 (5)	0.0024 (5)
N6	0.0164 (6)	0.0183 (7)	0.0180 (5)	0.0012 (6)	0.0044 (4)	0.0009 (5)
C1	0.0222 (8)	0.0346 (12)	0.0290 (8)	0.0027 (8)	0.0020 (6)	0.0014 (8)
C2	0.0204 (7)	0.0180 (9)	0.0251 (7)	0.0018 (7)	0.0081 (6)	-0.0024 (6)
C4	0.0192 (7)	0.0211 (9)	0.0226 (7)	-0.0001 (7)	0.0041 (5)	-0.0031 (6)
C5	0.0214 (7)	0.0231 (9)	0.0185 (6)	0.0032 (7)	0.0069 (5)	0.0001 (6)
C7	0.0251 (8)	0.0201 (9)	0.0265 (7)	0.0083 (7)	0.0124 (6)	0.0060 (6)
C11	0.0200 (2)	0.0276 (2)	0.01913 (18)	0.00163 (17)	0.00557 (13)	0.00246 (15)
O2	0.0382 (7)	0.0424 (9)	0.0237 (6)	0.0036 (7)	0.0150 (5)	0.0075 (5)
O3	0.0355 (8)	0.0518 (11)	0.0400 (7)	-0.0072 (8)	-0.0063 (6)	-0.0065 (7)
O4	0.0564 (9)	0.0378 (10)	0.0441 (7)	-0.0072 (8)	0.0180 (7)	0.0166 (7)
O5	0.0381 (8)	0.0661 (13)	0.0463 (8)	0.0256 (8)	0.0130 (6)	-0.0092 (8)

Geometric parameters (\AA , $^\circ$)

O1—C2	1.231 (2)	C4—C5	1.517 (2)
N3—C2	1.334 (2)	C4—H4A	0.9900
N3—C4	1.4622 (17)	C4—H4B	0.9900
N3—H3	0.8800	C5—H5A	0.9900
N6—C7	1.485 (2)	C5—H5B	0.9900
N6—C5	1.492 (2)	C7—C7 ⁱ	1.515 (3)
N6—H6A	0.9200	C7—H7A	0.9900
N6—H6B	0.9200	C7—H7B	0.9900
C1—C2	1.501 (2)	C11—O3	1.4129 (13)
C1—H1A	0.9800	C11—O5	1.4284 (15)
C1—H1B	0.9800	C11—O4	1.4344 (16)
C1—H1C	0.9800	C11—O2	1.4401 (12)
C2—N3—C4	121.60 (13)	N3—C4—H4B	109.0
C2—N3—H3	119.2	C5—C4—H4B	109.0

C4—N3—H3	119.2	H4A—C4—H4B	107.8
C7—N6—C5	112.56 (12)	N6—C5—C4	111.17 (13)
C7—N6—H6A	109.1	N6—C5—H5A	109.4
C5—N6—H6A	109.1	C4—C5—H5A	109.4
C7—N6—H6B	109.1	N6—C5—H5B	109.4
C5—N6—H6B	109.1	C4—C5—H5B	109.4
H6A—N6—H6B	107.8	H5A—C5—H5B	108.0
C2—C1—H1A	109.5	N6—C7—C7 ⁱ	110.03 (16)
C2—C1—H1B	109.5	N6—C7—H7A	109.7
H1A—C1—H1B	109.5	C7 ⁱ —C7—H7A	109.7
C2—C1—H1C	109.5	N6—C7—H7B	109.7
H1A—C1—H1C	109.5	C7 ⁱ —C7—H7B	109.7
H1B—C1—H1C	109.5	H7A—C7—H7B	108.2
O1—C2—N3	121.11 (13)	O3—C11—O5	111.45 (11)
O1—C2—C1	122.39 (15)	O3—C11—O4	109.27 (10)
N3—C2—C1	116.49 (14)	O5—C11—O4	109.82 (11)
N3—C4—C5	113.08 (13)	O3—C11—O2	110.69 (9)
N3—C4—H4A	109.0	O5—C11—O2	107.47 (8)
C5—C4—H4A	109.0	O4—C11—O2	108.06 (10)

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

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<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>
N3—H3 \cdots O4	0.88	2.12	2.989 (2)	167.
N6—H6A \cdots O1 ⁱⁱ	0.92	1.77	2.6745 (19)	168.
N6—H6B \cdots O2 ⁱⁱⁱ	0.92	2.13	2.9265 (17)	145.
N6—H6B \cdots O5 ⁱⁱⁱ	0.92	2.40	3.2141 (19)	147.

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

Fig. 1

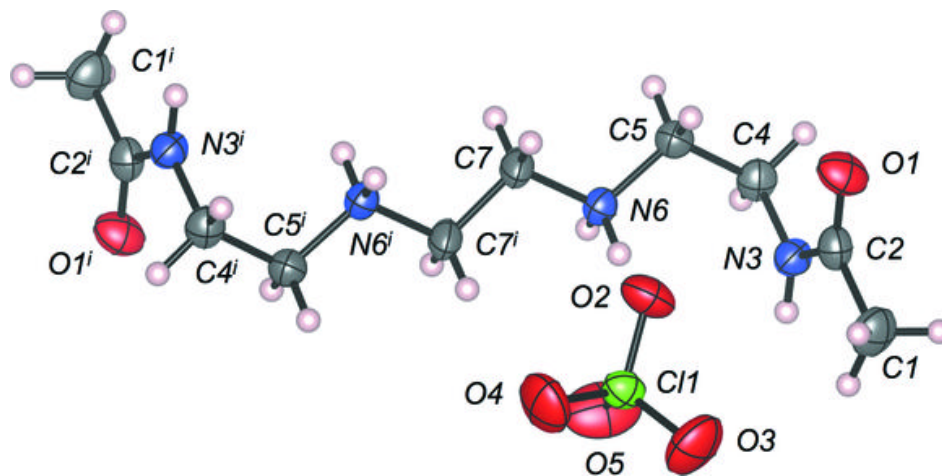


Fig. 2

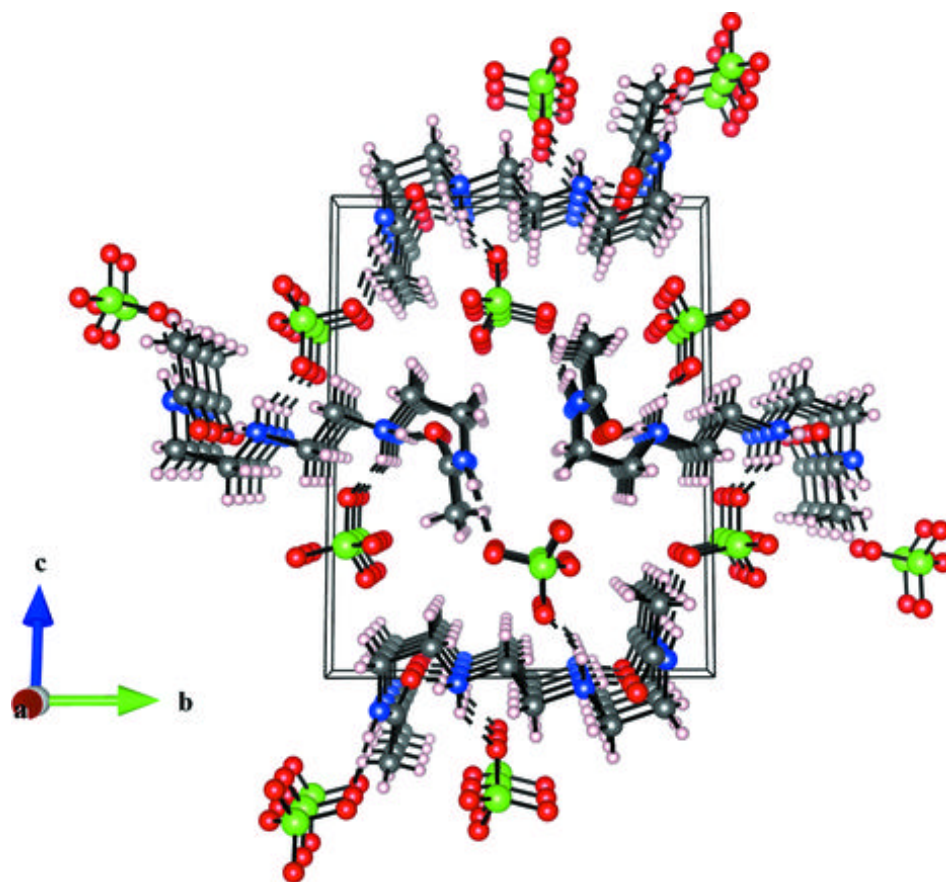


Fig. 3

