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Bis(3-carboxyanilinum) bis(perchlorate) monohydrate

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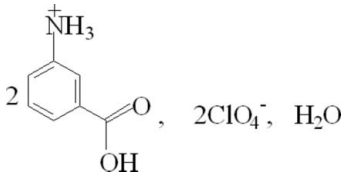
Key indicators: single-crystal X-ray study; T = 120 K; mean σ(C–C) = 0.002 Å; R factor = 0.039; wR factor = 0.102; data-to-parameter ratio = 24.2.

In the structure of the title compound, $2C_7H_8NO_2^+\cdot 2ClO_4^-\cdot H_2O$, the ions are connected *via* N—H···O, N—H···(O,O), O—H···O, O—H···(O,O) and C—H···O hydrogen bonds into a three-dimensional network.

Related literature

Hydrogen bonds play a crucial role in supramolecular organization (Jeffrey, 1997; Nangia & Desiraju, 1998). Knowledge of hydrogen-bond geometries (Taylor & Kennard, 1984; Murray-Rust & Glusker, 1984) and motif formation is vital in the modeling of protein–ligand interactions (Tintelnot & Andrews, 1989; Böhm & Klebe, 1996). For hydriogen-bond motifs, see: Bernstein *et al.* (1995). For the structures of organic salts of carboxylic acids, see: Bendjeddou *et al.* (2003); Cherouana *et al.* (2003). For a description of the Cambridge Structural Database, see: Allen (2002);



Experimental

Crystal data

$2C_7H_8NO_2^+\cdot 2ClO_4^-\cdot H_2O$
M_r = 493.20
Triclinic, $P\overline{1}$
a = 4.9170 (3) Å
b = 12.4030 (2) Å
c = 17.1030 (4) Å
α = 70.520 (2)°
β = 88.697 (3)°
γ = 86.166 (4)°
V = 981.13 (7) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.41 mm^{-1}
T = 120 K
0.3 × 0.03 × 0.02 mm

Data collection

Enraf–Nonius KappaCCD diffractometer
Absorption correction: none
45183 measured reflections
7071 independent reflections
4775 reflections with $I > 2\sigma(I)$
R_{int} = 0.049

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.039
$wR(F^2)$ = 0.102
S = 0.99
7071 reflections
292 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.45 e Å^{-3}
$\Delta\rho_{min}$ = −0.57 e Å^{-3}

Table 1
Hydrogen-bonding geometry (Å, °) and unitary motifs.

D—H···A	D—A	H···A	D···A	D—H···A	Motifs
N1—H1*A*···O1*W*^{i}	0.89	1.98	2.8664 (18)	171	*D*
N1—H1*B*···O6^{ii}	0.89	2.11	2.9421 (19)	156	*D*
N1—H1*B*···O8	0.89	2.57	3.0343 (18)	114	*D*
N1—H1*C*···O1*W*^{iii}	0.89	1.98	2.8636 (18)	174	*D*
O1*W*—H1*W*···O1^{i}	0.840 (14)	2.534 (19)	2.9435 (14)	111.2 (15)	*D*
O1*W*—H1*W*···O3^{iii}	0.840 (14)	2.258 (14)	3.0356 (16)	153.9 (16)	*D*
O1*W*—H2*W*···O1	0.863 (14)	2.019 (15)	2.8504 (17)	161.4 (18)	*D*
N2—H2*A*···O6	0.89	2.10	2.9336 (19)	155	*D*
N2—H2*A*···O7	0.89	2.57	2.9584 (18)	107	*D*
N2—H2*B*···O4^{iv}	0.89	2.06	2.9382 (18)	168	*D*
N2—H2*C*···O3^{v}	0.89	2.55	3.1176 (19)	122	*D*
N2—H2*C*···O4^{v}	0.89	1.98	2.8683 (18)	175	*D*
O12—H12···O11^{vi}	0.82	1.82	2.6425 (14)	178	$R_2^2(8)$
O22—H22···O21^{vii}	0.82	1.82	2.6428 (17)	178	$R_2^2(8)$
C13—H13···O8	0.93	2.31	3.1193 (19)	145	*D*
C15—H15···O2^{i}	0.93	2.43	3.3058 (19)	156	*D*
C23—H23···O4^{iv}	0.93	2.55	3.2529 (19)	133	*D*
C25—H25···O8^{viii}	0.93	2.49	3.384 (2)	162	*D*
C27—H27···O11^{vi}	0.93	2.60	3.136 (2)	117	*D*

Symmetry codes: (i) $-x+2, -y+1, -z+1$; (ii) $x+1, y, z$; (iii) $-x+1, -y+1, -z+1$; (iv) $-x+1, -y, -z+1$; (v) $-x, -y, -z+1$; (vi) $-x, -y+1, -z$; (vii) $-x+1, -y, -z$; (viii) $x-1, y, z$. Motifs: *R* = ring; *D* = finite patterns.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SIR92* (Altomare *et al.*, 1993); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999), *PARST97* (Nardelli, 1995), *Mercury* (Macrae *et al.*, 2006) and *POV-RAY* (Persistence of Vision Team, 2004).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: BQ2150).

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supplementary materials

Acta Cryst. (2009). E**65**, o1770-o1771 [**doi:10.1107/S1600536809025173**]

Bis(3-carboxyanilinum) bis(perchlorate) monohydrate

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Comment

Hydrogen bonds play a crucial role in supramolecular organization (Jeffrey, 1997; Nangia & Desiraju, 1998). Knowledge of hydrogen-bond geometries (Taylor & Kennard, 1984; Murray-Rust & Glusker, 1984) and motif formation is vital in the modeling of protein-ligand interactions (Tintelnot & Andrews, 1989; Böhm & Klebe, 1996). The supramolecular networks become especially interesting when the cation and anion can participate in hydrogen-bonding. In this regard previous studies have been concerned with organic salts of carboxylic acids (Bendjeddou *et al.*, 2003), Cherouana *et al.*, 2003). The asymmetric unit of (I) (Fig. 1) contains two carboxyanilinium cations (A and B), two perchlorate anion and one water molecule. A proton transfer from the perchloric acid to atom N1 and N2 of *m*-carboxyalinine resulted in the formation of salts.

1- Supramolecular organization:

The structure is formed by double anionic and cationic chains that extend along the *b* axis, giving rise to layers parallel to the plane (b, c). Chains of water molecules are sandwiched between the anionic double chains (Fig2.).

1–1- Overview.

The supramolecular architecture is generated by the nineteen independent interactions of the Table 1. Three types of intermolecular interactions are present in the structure, including O—H···O, N—H···O and C—H···O hydrogen bonds. The presence of water molecule in the structure results in the presence of additional hydrogen bonds. The construction of graphs-set of the twenty hydrogen bonds in this compound has led to a first-level graph set noted: N1 = $R^2_2(8)R^2_2(8)$ (Bernstein *et al.*, 1995) (Table 1.).

1–2- The O—H···O hydrogen-bonded network

The carboxylic acid groups at the opposite end of the carboxyanilinium cations forms a centrosymmetric hydrogen-bonded dimers with its counterpart in a cation from an adjacent ribbon and are centered at (0 1/2 0) and (1/2 0 0) respectively for cation A and cation B (Fig. 3). These interactions lead to the graph-set motif $R^2_2(8)$, which is a characteristic feature found in most salts of 3- and 4-aminobenzoic acid (Cambridge Structural Database; Allen, 2002).

The water molecule, bridges the anionic perchlorate *via the* O—H···O hydrogen bonds. The centrosymmetric hydrogen-bonded rings formed by two water molecules and two Cl(1)O4- anions can be described by the graph-set $R^4_4(12)$ and $R^2_4(8)$. The aggregation of this two ring motifs results in an overall one-dimensional hydrogen-bonded chain structure along the [100] direction (Fig. 4).

1–3- The N—H···O hydrogen-bonded network

In the first cationic (A) entity, all ammonium H atoms are involved in hydrogen bonds with the perchlorate (Cl(2) O_4^-) anion and water molecule. Two of these interactions link the anions and cations in an alternating fashion into extended chains

along the [100] direction, which can be described by the graph-set $C^2_2(4)$. The two other interactions are in a crosslink from an adjacent chain $C^2_2(4)$. The combination of these two chain motifs generates noncentrosymmetric fused rings which can be described by the graph-set motif $R^3_4(10)$.

In the second cationic (B) entitie, all ammonium H atoms are involved in hydrogen bonds, with the two different perchlorate ion, so forming an alternating noncentrosymmetric rings a long [100] direction which can be described by the graph-set $R^3_4(10)$. Only one H atom (H2C) is involved in bifurcated hydrogen bonds with O(3) and O(4) perchlorate atoms, to form a four-membered hydrogen bonded ring $R^2_1(4)$. The junction betwen this two different cations (A and B) entities are assured by the perchlorate ($Cl(2)\ O_4^-$) anion *via* N1—H1B···O6, N1—H1B···O8, N2—H2A···O6, N2—H2A···O7 hydrogen bonds, so generete $R^3_2(6)$ rings along [100] direction (Fig. 5)

1–4- The C—H···O hydrogen-bonded network:

The junction between the cationic entity is consolidated by five weak independent C—H···O hydrogen bonds *via* the perchlorate anions, forming an alternating of $R^4_6(22)$ and $R^5_6(30)$centrosymmetric Rings a long *b* axis (Fig. 6).

Experimental

m-carboxyanilinium acid and perchloric acid were mixed in a 2:2 stoichiometric ratio and dissolved in water. Crystal were obtained by slow evaporation.

Refinement

H atoms were positioned geometrically and refined in the riding-model approximation, with C—H = 0.97 Å, N—H = 0.89 Å, O—H = 0.82 Å, and with U_{iso}(H) = 1.2Ueq(C, N) or 1.5Ueq(O). The H atoms of the water molecule were located in a difference Fourier map and reined as riding, with O—H = 0.85 Å and U_{iso}(H) = 1.5Ueq(O).

Figures

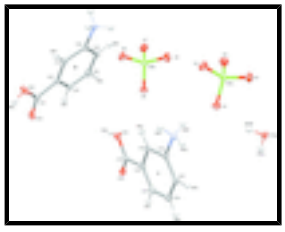


Fig. 1. The asymmetric unit of (I), showing the crystallographic numbering scheme. Displacement ellipsoids are drawn at the 50% probability level and H atoms are shown as spheres of arbitrary radii.

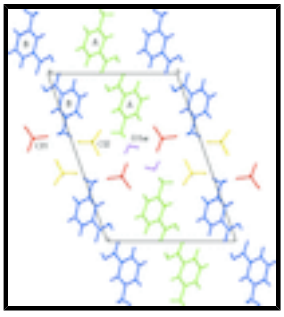


Fig. 2. A packing diagram for the title compound, viewed along the *a* axis, showing the mixture layers.

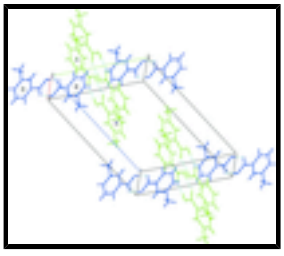


Fig. 3. Part of the crystal structure, showing the formation of dimers A and B *via* O—H···O hydrogen bonds.

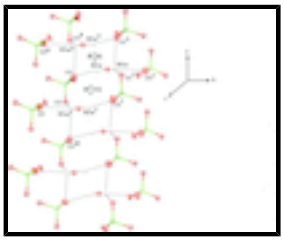


Fig. 4. A view of the two-dimensional O—H···O hydrogen-bonded network paralel to the (100) plane of (I), showing the aggregation of $R^4_4(12)$ and $R^2_4(8)$ hydrogen-bonding motifs. Atoms marked with an ampersand (&), an at sign (@), a hash symbol (#) or a dollar sign ($) are at the symmetry positions (1 + *x*, *y*, *z*), (-1 + *x*, *y*, *z*), (1 - *x*, 1 - *y*, 1 - *z*), (2 - *x*, 1 - *y*, 1 - *z*), respectively.

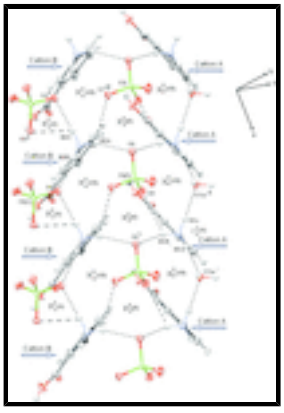


Fig. 5. Part of the crystal structure, showing the aggregation of $C^2_2(4)$ $R^3_4(10)$ and $R^3_2(6)$ motifs *via* N—H···O hydrogen bonds. Atoms marked with an ampersand (&), an at sign (@), a hash symbol (#), dollar sign ($), percent sign (%), or a star sign (*) are at the symmetry positions (1 - *x*, 1 - *y*, 1 - *z*), (-1 + *x*, *y*, *z*), (1 - *x*, *y*, 1 - *z*), (-*x*, -*y*, 1 - *z*), (1 + *x*, *y*, *z*), (2 - *x*, 1 - *y*, 1 - *z*), respectively.

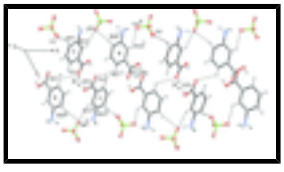


Fig. 6. A view of part of the crystal structure of (I), showing the formation of $R^4_6(22)$ and $R^5_6(30)$ rings. Atoms marked with an ampersand (&), a hash symbol (#), dollar sign ($), percent sign (%), or a star sign (*) are at the symmetry positions (2 - *x*, -*y*, 1 - *z*), (-*x*, 1 - *y*, -*z*), (1 - *x*, 1 - *y*, -*z*), (1 + *x*, *y*, *z*), (2 - *x*, 1 - *y*, 1 - *z*), respectively.

Bis(3-carboxyanilinum) bis(perchlorate) monohydrate

Crystal data

$2C_7H_8NO_2^+·2ClO_4^-·H_2O$	$Z = 2$
$M_r = 493.20$	$F_{000} = 508$
Triclinic, $P\overline{1}$	$D_x = 1.669$ Mg m^{-3}

Hall symbol: -P 1	Mo $K\alpha$ radiation, λ = 0.71073 Å
a = 4.9170 (3) Å	Cell parameters from 7071 reflections
b = 12.4030 (2) Å	θ = 3.3–32.6º
c = 17.1030 (4) Å	μ = 0.41 mm^{-1}
α = 70.520 (2)º	T = 120 K
β = 88.697 (3)º	Needle, brown
γ = 86.166 (4)º	0.3 × 0.03 × 0.02 mm
V = 981.13 (7) Å^3	

Data collection

Enraf–Nonius KappaCCD diffractometer	4775 reflections with $I > 2\sigma(I)$
Radiation source: fine-focus sealed tube	R_{int} = 0.049
Monochromator: graphite	θ_{max} = 32.6º
T = 120 K	θ_{min} = 3.3º
ω scans	h = 0→7
Absorption correction: none	k = −18→18
45183 measured reflections	l = −25→25
7071 independent reflections	

Refinement

Refinement on F^2	H atoms treated by a mixture of independent and constrained refinement
Least-squares matrix: full	$w = 1/[\sigma^2(F_o^2) + (0.0526P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$R[F^2 > 2\sigma(F^2)]$ = 0.039	$(\Delta/\sigma)_{max}$ = 0.021
$wR(F^2)$ = 0.102	$\Delta\rho_{max}$ = 0.45 e Å^{-3}
S = 0.99	$\Delta\rho_{min}$ = −0.57 e Å^{-3}
7071 reflections	Extinction correction: none
292 parameters	

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	y	z	U_{iso}*/U_{eq}
O11	0.2368 (2)	0.58575 (9)	0.00162 (6)	0.0167 (3)
O12	0.1451 (2)	0.42214 (9)	0.10223 (6)	0.0176 (3)
N1	0.6845 (3)	0.40582 (11)	0.35093 (7)	0.0142 (4)
C11	0.2756 (3)	0.51695 (13)	0.07149 (9)	0.0136 (4)
C12	0.4736 (3)	0.53492 (13)	0.12947 (9)	0.0131 (4)
C13	0.4963 (3)	0.45953 (13)	0.21027 (9)	0.0132 (4)
C14	0.6728 (3)	0.48155 (13)	0.26416 (9)	0.0127 (4)
C15	0.8297 (3)	0.57585 (13)	0.23929 (9)	0.0154 (4)
C16	0.8057 (3)	0.65062 (13)	0.15814 (9)	0.0172 (5)
C17	0.6279 (3)	0.63090 (13)	0.10338 (9)	0.0154 (4)
O21	0.2424 (2)	0.08889 (10)	−0.00149 (6)	0.0195 (3)
O22	0.3663 (3)	−0.06863 (10)	0.10513 (7)	0.0231 (4)

N2	−0.2091 (3)	−0.04135 (11)	0.34838 (7)	0.0132 (3)
C21	0.2141 (3)	0.02587 (13)	0.07045 (9)	0.0162 (4)
C22	0.0034 (3)	0.05317 (13)	0.12572 (9)	0.0146 (4)
C23	−0.0102 (3)	−0.01242 (13)	0.20967 (9)	0.0137 (4)
C24	−0.1986 (3)	0.02235 (13)	0.25877 (9)	0.0130 (4)
C25	−0.3762 (3)	0.11787 (14)	0.22733 (9)	0.0171 (4)
C26	−0.3649 (3)	0.18137 (14)	0.14357 (10)	0.0193 (5)
C27	−0.1724 (3)	0.14958 (14)	0.09290 (9)	0.0173 (4)
Cl1	0.58901 (7)	0.29103 (3)	0.61432 (2)	0.0133 (1)
O1	0.7010 (2)	0.36508 (9)	0.53790 (6)	0.0191 (3)
O2	0.6783 (2)	0.32216 (11)	0.68248 (7)	0.0237 (4)
O3	0.2956 (2)	0.30140 (10)	0.60921 (7)	0.0208 (3)
O4	0.6805 (2)	0.17339 (9)	0.62552 (7)	0.0201 (3)
Cl2	0.14254 (7)	0.15743 (3)	0.40892 (2)	0.0128 (1)
O5	0.2017 (3)	0.17301 (10)	0.48568 (7)	0.0244 (4)
O6	−0.1515 (2)	0.15994 (10)	0.39893 (7)	0.0220 (3)
O7	0.2591 (2)	0.04883 (9)	0.40697 (7)	0.0207 (3)
O8	0.2470 (2)	0.24934 (9)	0.34137 (7)	0.0205 (3)
O1W	0.8260 (2)	0.56613 (10)	0.57195 (7)	0.0156 (3)
H1A	0.82677	0.42111	0.37583	0.0212*
H1B	0.70185	0.33315	0.35272	0.0212*
H1C	0.53190	0.41728	0.37684	0.0212*
H12	0.02648	0.42104	0.06961	0.0263*
H13	0.39432	0.39521	0.22790	0.0159*
H15	0.94884	0.58893	0.27615	0.0185*
H16	0.90976	0.71430	0.14051	0.0206*
H17	0.61145	0.68159	0.04935	0.0185*
H2A	−0.22591	0.00789	0.37622	0.0198*
H2B	−0.05642	−0.08563	0.36380	0.0198*
H2C	−0.35139	−0.08481	0.35926	0.0198*
H22	0.48980	−0.07414	0.07338	0.0345*
H23	0.10478	−0.07783	0.23186	0.0165*
H25	−0.50154	0.13923	0.26186	0.0205*
H26	−0.48533	0.24494	0.12131	0.0232*
H27	−0.16175	0.19302	0.03700	0.0208*
H1W	0.826 (4)	0.6178 (12)	0.5253 (8)	0.037 (6)*
H2W	0.827 (4)	0.5046 (10)	0.5589 (11)	0.039 (6)*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O11	0.0196 (6)	0.0163 (6)	0.0123 (5)	−0.0034 (4)	−0.0031 (4)	−0.0017 (4)
O12	0.0198 (6)	0.0159 (6)	0.0155 (5)	−0.0059 (5)	−0.0060 (4)	−0.0020 (4)
N1	0.0141 (6)	0.0172 (7)	0.0120 (6)	−0.0003 (5)	−0.0017 (5)	−0.0059 (5)
C11	0.0135 (7)	0.0131 (7)	0.0144 (7)	−0.0001 (6)	0.0004 (6)	−0.0049 (6)
C12	0.0130 (7)	0.0140 (7)	0.0124 (7)	−0.0006 (6)	−0.0006 (5)	−0.0044 (6)
C13	0.0129 (7)	0.0123 (7)	0.0148 (7)	−0.0008 (6)	0.0000 (5)	−0.0049 (6)
C14	0.0131 (7)	0.0134 (7)	0.0114 (7)	0.0002 (6)	0.0009 (5)	−0.0040 (5)

C15	0.0144 (7)	0.0173 (8)	0.0165 (7)	−0.0013 (6)	−0.0018 (6)	−0.0080 (6)
C16	0.0173 (8)	0.0144 (8)	0.0200 (8)	−0.0043 (6)	0.0009 (6)	−0.0054 (6)
C17	0.0161 (8)	0.0147 (7)	0.0134 (7)	−0.0008 (6)	−0.0003 (6)	−0.0020 (6)
O21	0.0220 (6)	0.0200 (6)	0.0128 (5)	0.0032 (5)	0.0050 (4)	−0.0019 (4)
O22	0.0253 (7)	0.0218 (6)	0.0164 (6)	0.0091 (5)	0.0070 (5)	−0.0013 (5)
N2	0.0145 (6)	0.0139 (6)	0.0115 (6)	−0.0022 (5)	0.0010 (5)	−0.0044 (5)
C21	0.0172 (8)	0.0159 (8)	0.0155 (7)	0.0011 (6)	0.0004 (6)	−0.0058 (6)
C22	0.0168 (7)	0.0145 (7)	0.0122 (7)	−0.0008 (6)	0.0022 (6)	−0.0043 (6)
C23	0.0138 (7)	0.0128 (7)	0.0130 (7)	0.0003 (6)	−0.0009 (5)	−0.0024 (6)
C24	0.0147 (7)	0.0125 (7)	0.0112 (7)	−0.0032 (6)	0.0006 (5)	−0.0029 (5)
C25	0.0174 (8)	0.0177 (8)	0.0163 (7)	0.0004 (6)	0.0044 (6)	−0.0063 (6)
C26	0.0216 (8)	0.0160 (8)	0.0167 (8)	0.0064 (6)	0.0009 (6)	−0.0020 (6)
C27	0.0214 (8)	0.0157 (8)	0.0119 (7)	0.0015 (6)	0.0021 (6)	−0.0012 (6)
Cl1	0.0122 (2)	0.0142 (2)	0.0143 (2)	−0.0018 (1)	−0.0003 (1)	−0.0057 (1)
O1	0.0220 (6)	0.0172 (6)	0.0156 (5)	−0.0045 (5)	0.0030 (4)	−0.0018 (4)
O2	0.0246 (6)	0.0332 (7)	0.0196 (6)	−0.0101 (5)	−0.0005 (5)	−0.0156 (5)
O3	0.0109 (5)	0.0266 (7)	0.0263 (6)	0.0002 (5)	0.0003 (4)	−0.0109 (5)
O4	0.0175 (6)	0.0120 (5)	0.0289 (6)	0.0014 (4)	−0.0016 (5)	−0.0048 (5)
Cl2	0.0145 (2)	0.0117 (2)	0.0122 (2)	−0.0018 (1)	0.0007 (1)	−0.0039 (1)
O5	0.0355 (7)	0.0256 (7)	0.0138 (5)	−0.0047 (5)	−0.0032 (5)	−0.0081 (5)
O6	0.0127 (5)	0.0219 (6)	0.0340 (7)	−0.0021 (5)	0.0002 (5)	−0.0127 (5)
O7	0.0203 (6)	0.0123 (5)	0.0302 (6)	0.0016 (4)	0.0008 (5)	−0.0087 (5)
O8	0.0284 (7)	0.0152 (6)	0.0155 (5)	−0.0072 (5)	0.0062 (5)	−0.0013 (4)
O1W	0.0175 (6)	0.0136 (5)	0.0145 (5)	−0.0022 (4)	−0.0012 (4)	−0.0028 (4)

Geometric parameters (Å, °)

Cl1—O2	1.4307 (11)	N1—H1C	0.89
Cl1—O3	1.4418 (11)	C22—C27	1.389 (2)
Cl1—O1	1.4454 (11)	C22—C23	1.397 (2)
Cl1—O4	1.4484 (11)	C22—C21	1.484 (2)
Cl2—O5	1.4282 (11)	C24—C23	1.379 (2)
Cl2—O7	1.4386 (11)	C24—C25	1.383 (2)
Cl2—O8	1.4390 (11)	C14—C13	1.3833 (19)
Cl2—O6	1.4568 (11)	C14—C15	1.385 (2)
O12—C11	1.3208 (17)	C12—C13	1.388 (2)
O12—H12	0.82	C12—C17	1.394 (2)
O1W—H2W	0.863 (9)	C12—C11	1.484 (2)
O1W—H1W	0.840 (9)	C27—C26	1.394 (2)
O11—C11	1.2252 (17)	C27—H27	0.93
O22—C21	1.3135 (19)	C16—C17	1.386 (2)
O22—H22	0.82	C16—C15	1.391 (2)
O21—C21	1.2286 (18)	C16—H16	0.93
N2—C24	1.4732 (18)	C23—H23	0.93
N2—H2A	0.89	C15—H15	0.93
N2—H2B	0.89	C25—C26	1.388 (2)
N2—H2C	0.89	C25—H25	0.93
N1—C14	1.4679 (18)	C17—H17	0.93
N1—H1A	0.89	C13—H13	0.93

N1—H1B	0.89	C26—H26	0.93
O2—Cl1—O3	110.41 (7)	C15—C14—N1	119.21 (13)
O2—Cl1—O1	109.66 (7)	C13—C12—C17	120.21 (13)
O3—Cl1—O1	109.24 (7)	C13—C12—C11	120.24 (13)
O2—Cl1—O4	109.82 (7)	C17—C12—C11	119.48 (13)
O3—Cl1—O4	108.57 (7)	O11—C11—O12	123.69 (13)
O1—Cl1—O4	109.11 (7)	O11—C11—C12	122.07 (13)
O5—Cl2—O7	110.85 (7)	O12—C11—C12	114.24 (13)
O5—Cl2—O8	109.49 (7)	O21—C21—O22	123.78 (14)
O7—Cl2—O8	110.20 (7)	O21—C21—C22	121.54 (14)
O5—Cl2—O6	109.62 (7)	O22—C21—C22	114.67 (13)
O7—Cl2—O6	108.29 (7)	C22—C27—C26	120.12 (14)
O8—Cl2—O6	108.34 (7)	C22—C27—H27	119.9
C11—O12—H12	109.5	C26—C27—H27	119.9
H2W—O1W—H1W	102.4 (15)	C17—C16—C15	120.47 (14)
C21—O22—H22	109.5	C17—C16—H16	119.8
C24—N2—H2A	109.5	C15—C16—H16	119.8
C24—N2—H2B	109.5	C24—C23—C22	118.26 (14)
H2A—N2—H2B	109.5	C24—C23—H23	120.9
C24—N2—H2C	109.5	C22—C23—H23	120.9
H2A—N2—H2C	109.5	C14—C15—C16	118.76 (14)
H2B—N2—H2C	109.5	C14—C15—H15	120.6
C14—N1—H1A	109.5	C16—C15—H15	120.6
C14—N1—H1B	109.5	C24—C25—C26	119.11 (14)
H1A—N1—H1B	109.5	C24—C25—H25	120.4
C14—N1—H1C	109.5	C26—C25—H25	120.4
H1A—N1—H1C	109.5	C16—C17—C12	119.84 (14)
H1B—N1—H1C	109.5	C16—C17—H17	120.1
C27—C22—C23	120.41 (14)	C12—C17—H17	120.1
C27—C22—C21	118.25 (13)	C14—C13—C12	118.99 (13)
C23—C22—C21	121.26 (14)	C14—C13—H13	120.5
C23—C24—C25	122.28 (14)	C12—C13—H13	120.5
C23—C24—N2	119.74 (13)	C25—C26—C27	119.79 (15)
C25—C24—N2	117.96 (13)	C25—C26—H26	120.1
C13—C14—C15	121.73 (14)	C27—C26—H26	120.1
C13—C14—N1	119.00 (12)		

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1A···O1W^{i}	0.8900	1.9800	2.8664 (18)	171.00
N1—H1B···O6^{ii}	0.8900	2.1100	2.9421 (19)	156.00
N1—H1B···O8	0.8900	2.5700	3.0343 (18)	114.00
N1—H1C···O1W^{iii}	0.8900	1.9800	2.8636 (18)	174.00
O1W—H1W···O1^{i}	0.840 (14)	2.534 (19)	2.9435 (14)	111.2 (15)
O1W—H1W···O3^{iii}	0.840 (14)	2.258 (14)	3.0356 (16)	153.9 (16)
N2—H2A···O6	0.8900	2.1000	2.9336 (19)	155.00
N2—H2A···O7	0.8900	2.5700	2.9584 (18)	107.00

N2—H2B···O4^{iv}	0.8900	2.0600	2.9382 (18)	168.00
N2—H2C···O3^{v}	0.8900	2.5500	3.1176 (19)	122.00
N2—H2C···O4^{v}	0.8900	1.9800	2.8683 (18)	175.00
O1W—H2W···O1	0.863 (14)	2.019 (15)	2.8504 (17)	161.4 (18)
O12—H12···O11^{vi}	0.8200	1.8200	2.6425 (14)	178.00
O22—H22···O21^{vii}	0.8200	1.8200	2.6428 (17)	178.00
C13—H13···O8	0.9300	2.3100	3.1193 (19)	145.00
C15—H15···O2^{i}	0.9300	2.4300	3.3058 (19)	156.00
C23—H23···O4^{iv}	0.9300	2.5500	3.2529 (19)	133.00
C25—H25···O8^{viii}	0.9300	2.4900	3.384 (2)	162.00
C27—H27···O11^{vi}	0.9300	2.602	3.136 (2)	117.05

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

Table 1

Hydrogen-bonding geometry (Å, °) and unitary motifs

D—H···A	D—A	H···A	D···A	D—H···A	Motifs
N1—H1A···O1W^{i}	0.89	1.98	2.8664 (18)	171	*D*
N1—H1B···O6^{ii}	0.89	2.11	2.9421 (19)	156	*D*
N1—H1B···O8	0.89	2.57	3.0343 (18)	114	*D*
N1—H1C···O1W^{iii}	0.89	1.98	2.8636 (18)	174	*D*
O1W—H1W···O1^{i}	0.840 (14)	2.534 (19)	2.9435 (14)	111.2 (15)	*D*
O1W—H1W···O3^{iii}	0.840 (14)	2.258 (14)	3.0356 (16)	153.9 (16)	*D*
N2—H2A···O6	0.89	2.10	2.9336 (19)	155	*D*
N2—H2A···O7	0.89	2.57	2.9584 (18)	107	*D*
N2—H2B···O4^{iv}	0.89	2.06	2.9382 (18)	168	*D*
N2—H2C···O3^{v}	0.89	2.55	3.1176 (19)	122	*D*
N2—H2C···O4^{v}	0.89	1.98	2.8683 (18)	175	*D*
O1W—H2W···O1	0.863 (14)	2.019 (15)	2.8504 (17)	161.4 (18)	*D*
O12—H12···O11^{vi}	0.82	1.82	2.6425 (14)	178	$R^2_2(8)$
O22—H22···O21^{vii}	0.82	1.82	2.6428 (17)	178	$R^2_2(8)$
C13—H13···O8	0.93	2.31	3.1193 (19)	145	*D*
C15—H15···O2^{i}	0.93	2.43	3.3058 (19)	156	*D*
C23—H23···O4^{iv}	0.93	2.55	3.2529 (19)	133	*D*
C25—H25···O8^{viii}	0.93	2.49	3.384 (2)	162	*D*
C27—H27···O11^{vi}	0.93	2.60	3.136 (2)	117	*D*

Symmetry codes: (i) -x+2, -y+1, -z+1; (ii) x+1, y, z; (iii) -x+1, -y+1, -z+1; (iv) -x+1, -y, -z+1; (v) -x, -y, -z+1; (vi) -x, -y+1, -z; (vii) -x+1, -y, -z; (viii) x-1, y, z.

Fig. 1

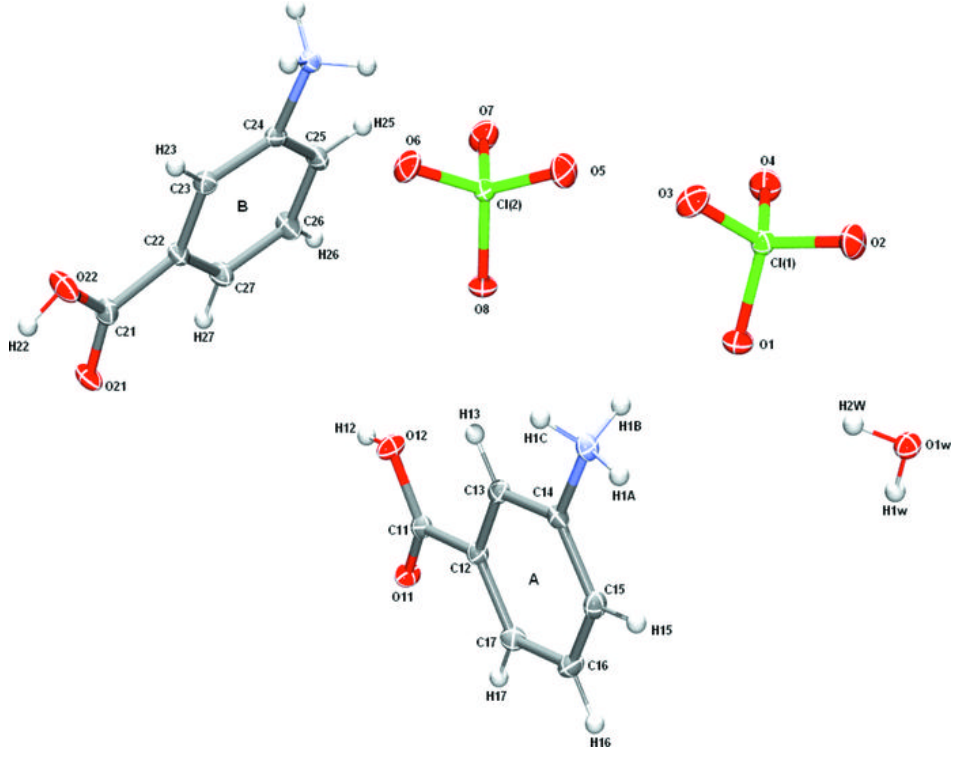

C24
C25
H25
H23
C23
B
C26
C22
H26
C27
O22
C21
H22
H27
O21
O7
O6
O5
Cl(2)
O8
O4
O3
O2
Cl(1)
O1
H2W
O1w
H1w
H13
H12
O12
H1C
H1B
C13
C14
H1A
C11
C12
A
C15
O11
H15
C17
C16
H17
H16

Fig. 2

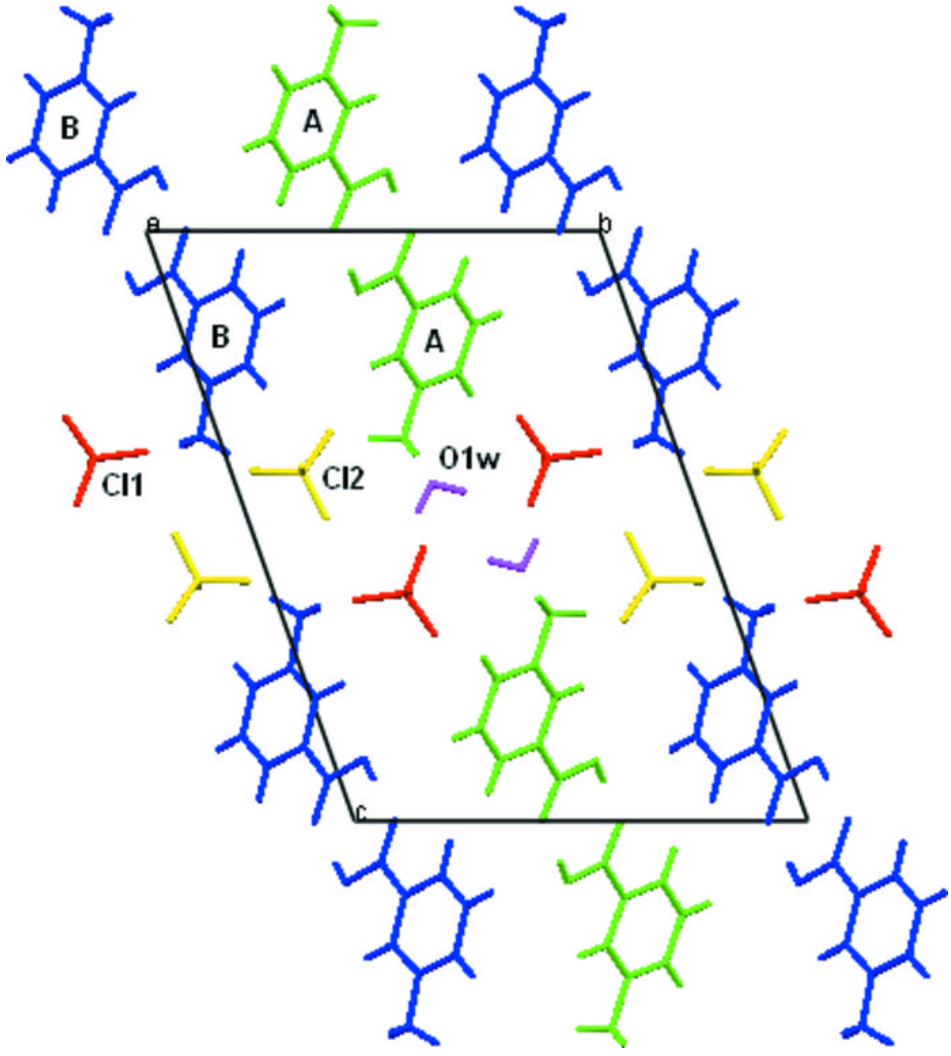


Fig. 3

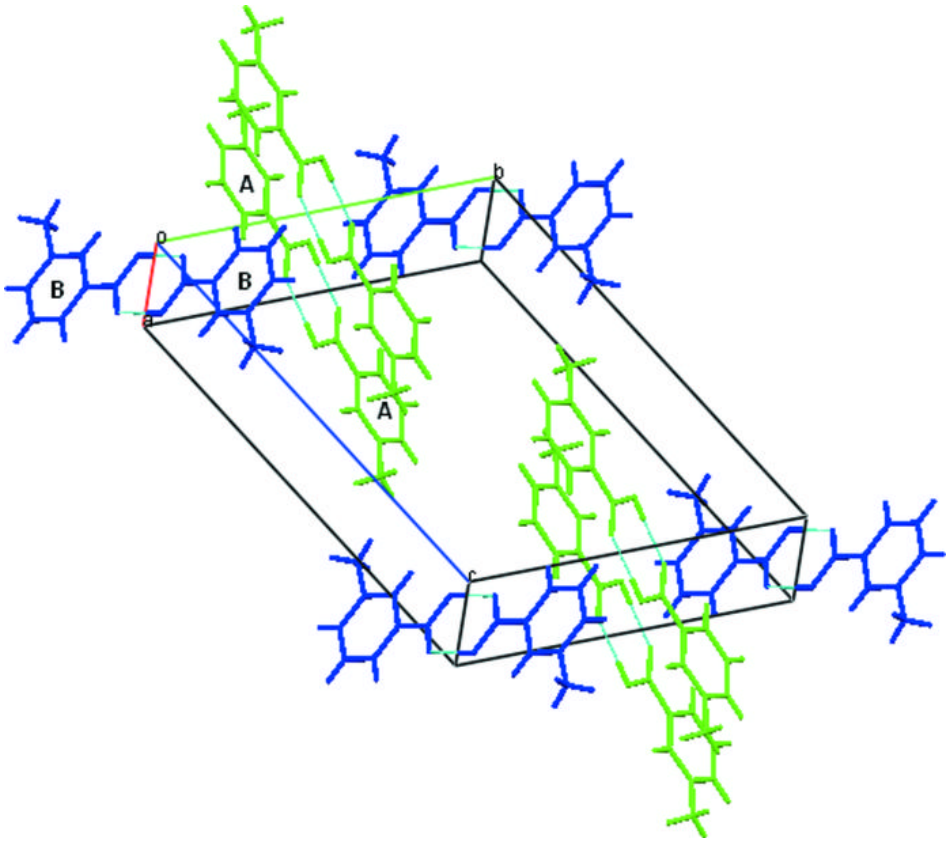


Fig. 4

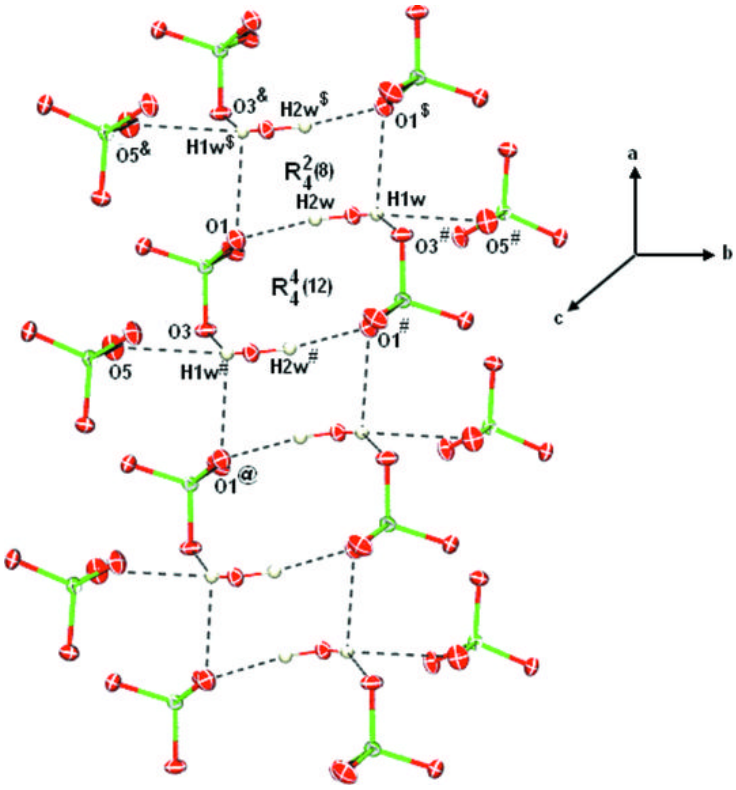

O3&
H2w$
O1$
O5&
H1w$
R2 1(8)
H2w
H1w
O1
O3#
O5#
a
b
c
R4 4(12)
O3
O1#
O5
H1w#
H2w#
O1@

Fig. 5

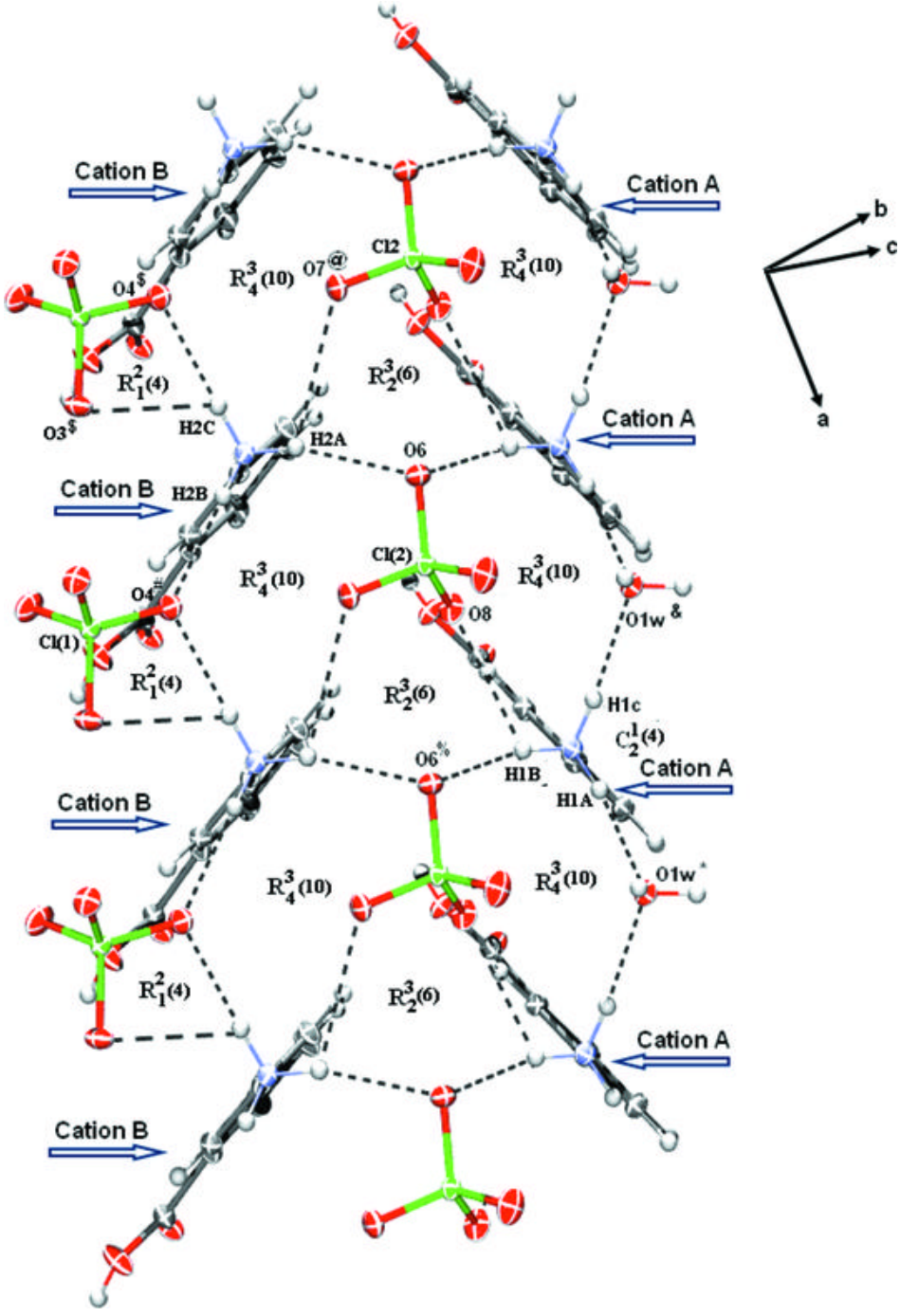
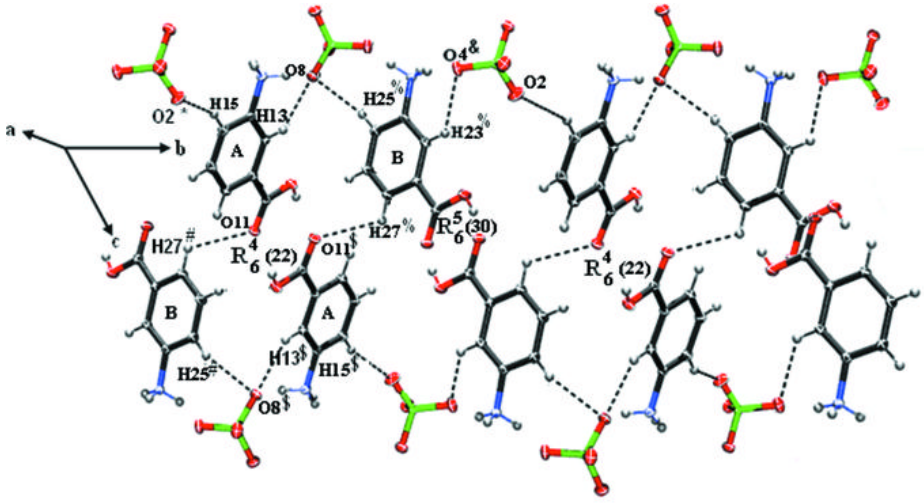

Cation B
Cation A
Cl2
O7@
O4$
O3$
H2C
H2A
O6
H2B
Cl(2)
O8
O4#
Cl(1)
O1w &
H1c
H1B
H1A
O6%
O1w *
b
c
a

Fig. 6


a
b
c
O2
H15
H13
O8
H25
O4
O2
H23
A
B
O11
H27
R 4 6 (22)
R 5 6 (30)
R 4 6 (22)
B
A
H25
H13
H15
O8
O11
H27