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Bis(hexamethylenetetraminium) chloranilate tetrahydrate

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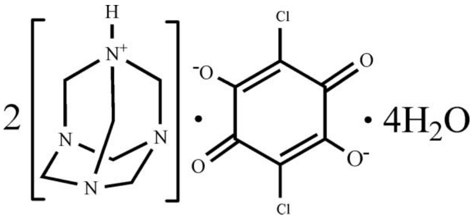
Key indicators: single-crystal X-ray study; T = 298 K; mean σ(C–C) = 0.003 Å; disorder in solvent or counterion; R factor = 0.049; wR factor = 0.133; data-to-parameter ratio = 13.0.

The anion of the title compound, $2C_6H_{13}N_4^+\cdot C_6Cl_2O_4^{2-}\cdot 4H_2O$, is centrosymmetric. The crystal structure is stabilized by a network of intermolecular hydrogen bonds. The solvent water molecules are disordered, each with approximate 2:1 occupancy of two positions.

Related literature

For related literature, see: Allen *et al.* (1987); Yang & Qu (2006).



Experimental

Crystal data

$2C_6H_{13}N_4^+\cdot C_6Cl_2O_4^{2-}\cdot 4H_2O$
M_r = 561.44
Monoclinic, $P2_1/n$
a = 6.1794 (4) Å
b = 16.8362 (12) Å
c = 12.2627 (9) Å
β = 98.7910 (10)°
V = 1260.79 (15) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.32 mm^{-1}
T = 298 (2) K
0.20 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2001)
$T_{\min}$ = 0.939, $T_{\max}$ = 0.981
10757 measured reflections
2737 independent reflections
2185 reflections with $I > 2\sigma(I)$
$R_{\rm int}$ = 0.031

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.049
$wR(F^2)$ = 0.133
S = 1.06
2737 reflections
210 parameters
37 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{\max}$ = 0.31 e Å^{-3}
$\Delta\rho_{\min}$ = −0.23 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
C9—H9A···O2$^{\rm i}$	0.97	2.44	3.320 (3)	151
C7—H7B···N4$^{\rm ii}$	0.97	2.54	3.503 (3)	170
C7—H7A···O3$^{\rm iii}$	0.97	2.56	3.378 (6)	142
C6—H6B···O3$^{\rm i}$	0.97	2.52	3.485 (16)	173
O4—H4D···Cl1$^{\rm iv}$	0.828 (10)	3.03 (8)	3.278 (5)	100 (6)
C4—H4A···O3	0.97	2.57	3.413 (10)	146
O4—H4C···O3	0.828 (11)	2.62 (4)	3.41 (2)	160 (10)
O3—H3B···O2	0.827 (11)	1.98 (2)	2.781 (6)	162 (8)
N3—H3···O2	0.86 (2)	2.20 (2)	2.854 (2)	132 (2)
N3—H3···O1	0.86 (2)	1.98 (2)	2.746 (2)	147 (2)

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

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT-Plus* (Bruker, 2001); data reduction: *SAINT-Plus*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *PLATON* (Spek, 2003); software used to prepare material for publication: *PLATON*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2362).

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supplementary materials

Acta Cryst. (2007). E**63**, o2600 [**doi:10.1107/S1600536807018569**]

Bis(hexamethylenetetraminium) chloranilate tetrahydrate

D.-J. Yang

Comment

As part of our continuing studies on co-crystals involving chloranilic acid (Yang & Qu, 2006), we report herein the crystal structure of the title compound, (I).

In (I), the H atoms have been transferred from the hydroxyl group of the chloranilic acid molecule to the amine group N atom of hexamethylenetetramine molecule, forming a 1:2 organic salt. In addition, there are two solvent water molecules in the asymmetric unit (Fig.1). The protonated amine atom N3 acts as hydrogen bond donor, *via* H3, to two adjacent O atoms, forming the inter-ion three-centre hydrogen bond. In addition, the C–N bond distances involved the protonated atom N3 are slightly longer than for the unprotonated ones N atoms. On the contrary, the deprotonated *C–O*(hydroxyl) bond distances of 1.251 (5) and 1.237 (5)Å are shorter than the *C–O*(hydroxyl) value of 1.362 (15) Å in phenol, but longer than the standard bond distance of a C=O double bond (in benzoquinones), 1.222 (13) Å. (Allen *et al.*, 1987).

A combination of N (or O)–H···O, C–H···O(or N) and C–H···Cl hydrogen bonds (Table 1) stabilizes the crystal structure (Fig. 2).

Experimental

All the reagents and solvents were used as obtained without further purification. Equivalent molar amount of Chloranilic acid and hexamethylenetetramine were dissolved in methanol (20 ml). The mixture was stirred for half an hour at ambient temperature and then filtered. The resulting red solution was kept in air for one week. Crystals of (I) suitable for single-crystal X-ray diffraction analysis were grown by slow evaporation of the solution at the bottom of the vessel.

Refinement

H atoms bonded to C atoms were included in calculated positions with C–H=0.97 Å and $U_{\mathrm{iso}}(\mathrm{H}) = 1.2U_{\mathrm{eq}}(\mathrm{C})$. Atom H3 was located in a difference map its positional parameters were refined and its U_{iso} value was set 1.2 times of the U_{eq} of N3 atom. The water H atoms were located from the difference maps and their U_{iso} values were set 1.5 times of their carrier atoms. The O(water)-H distances were refined by using the *DFIX* command in SHELXL (Sheldrick, 1997). Both water molecules containing atoms O3 and O4 atoms were disordered over two positions with a ratio of refined occupacies of 0.68 (6):0.32 (6) and 0.63 (3):0.36 (3), respectively, for the major and minor components. The disorder with respect to the solvent water molecules made it difficult to interpret all the hydrogen bond interactions in which they are involved. Table 1 lists only seclected hydrogen bond involving the water molecules.

Figures

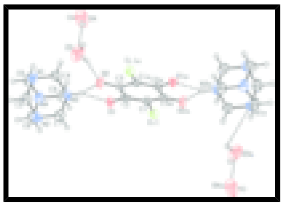

Fig. 1. Molecular structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level. hydrogen bonds are shown as dashed lines. Atoms marked with suffix 'a' are realted by the symmetry operator (1 - *x*, 1 - *y*, 1 - *z*).

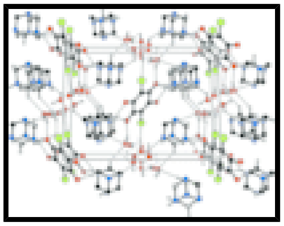

Fig. 2. Part of the crystal structure of (I), showing the formation of the three-dimensional network. Hydrogen bonding are shown as dashed lines. For the sake of clarity, H atoms not involved in the motif have been omitted.

Bis(hexamethylenetetraminium) chloranilate tetrahydrate

Crystal data

$2C_6H_{13}N_4^+\cdot C_6Cl_2O_4^{2-}\cdot 4H_2O$

$M_r = 561.44$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 6.1794$ (4) Å

$b = 16.8362$ (12) Å

$c = 12.2627$ (9) Å

$\beta = 98.7910$ (10)°

$V = 1260.79$ (15) Å^3

$Z = 2$

$F_{000} = 592$

$D_x = 1.479$ Mg m^{-3}

Mo *Kα* radiation
$\lambda = 0.71073$ Å

Cell parameters from 1255 reflections

$\theta = 2.4$–25.4°

$\mu = 0.32$ mm^{-1}

$T = 298$ (2) K

Block, red

0.20 × 0.16 × 0.15 mm

Data collection

Bruker SMART APEX CCD diffractometer

Radiation source: fine focus sealed Siemens Mo tube

Monochromator: graphite

$T = 298(2)$ K

0.3° wide ω exposures scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2001)

$T_{\min} = 0.939$, $T_{\max} = 0.981$

10757 measured reflections

2737 independent reflections

2185 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.031$

$\theta_{\max} = 27.0$°

$\theta_{\min} = 2.1$°

$h = -7\rightarrow 7$

$k = -21\rightarrow 21$

$l = -15\rightarrow 15$

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)] = 0.049$	$w = 1/[\sigma^2(F_o^2) + (0.0705P)^2 + 0.2943P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.133$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.31$ e Å^{-3}
2737 reflections	$\Delta\rho_{min} = -0.23$ e Å^{-3}
210 parameters	Extinction correction: none
37 restraints	
Primary atom site location: structure-invariant direct methods	
Secondary atom site location: difference Fourier map	

Special details

Geometry. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds 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 > 2sigma(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}	Occ. (<1)
Cl1	0.89623 (9)	0.50143 (3)	0.69782 (5)	0.0446 (2)	
C1	0.6796 (3)	0.50143 (10)	0.58940 (16)	0.0314 (4)	
C2	0.6864 (3)	0.44703 (10)	0.50282 (15)	0.0302 (4)	
C3	0.4961 (3)	0.44760 (10)	0.40595 (15)	0.0307 (4)	
C4	0.8090 (4)	0.29530 (14)	0.2118 (2)	0.0515 (6)	
H4A	0.6521	0.3007	0.1900	0.062*	
H4B	0.8790	0.3421	0.1871	0.062*	
C5	0.7769 (5)	0.15608 (15)	0.1997 (2)	0.0588 (7)	
H5A	0.8241	0.1088	0.1646	0.071*	
H5B	0.6198	0.1611	0.1781	0.071*	
C6	1.1214 (4)	0.21767 (15)	0.1967 (2)	0.0564 (7)	
H6A	1.1737	0.1711	0.1622	0.068*	
H6B	1.1950	0.2637	0.1721	0.068*	
C7	0.7510 (4)	0.21626 (14)	0.3717 (2)	0.0513 (6)	
H7A	0.7842	0.2110	0.4513	0.062*	

H7B	0.5936	0.2213	0.3516	0.062*	
C8	1.0649 (4)	0.14114 (14)	0.3518 (3)	0.0595 (7)	
H8A	1.0990	0.1361	0.4314	0.071*	
H8B	1.1173	0.0937	0.3193	0.071*	
C9	1.1054 (4)	0.28014 (14)	0.3675 (2)	0.0476 (6)	
H9A	1.1787	0.3266	0.3440	0.057*	
H9B	1.1418	0.2758	0.4470	0.057*	
N1	0.8852 (3)	0.22567 (12)	0.16102 (16)	0.0503 (5)	
N2	0.8262 (3)	0.14696 (11)	0.31982 (18)	0.0524 (5)	
N3	0.8615 (3)	0.28880 (10)	0.33541 (15)	0.0409 (4)	
H3	0.816 (4)	0.3304 (14)	0.366 (2)	0.049*	
N4	1.1781 (3)	0.21049 (12)	0.31625 (18)	0.0502 (5)	
O1	0.8326 (2)	0.39727 (8)	0.49978 (12)	0.0423 (4)	
O2	0.5122 (2)	0.40054 (9)	0.32866 (12)	0.0454 (4)	
O3	0.339 (3)	0.3923 (6)	0.1059 (5)	0.105 (3)	0.68 (3)
H3A	0.251 (12)	0.425 (3)	0.075 (6)	0.157*	0.68 (3)
H3B	0.392 (13)	0.405 (4)	0.169 (3)	0.157*	0.68 (3)
O4	0.7867 (13)	0.4992 (3)	0.0620 (5)	0.137 (3)	0.642 (11)
H4C	0.676 (9)	0.471 (5)	0.055 (9)	0.206*	0.642 (11)
H4D	0.776 (9)	0.539 (4)	0.100 (7)	0.206*	0.642 (11)
O3'	0.453 (5)	0.4187 (15)	0.1031 (11)	0.104 (6)	0.32 (3)
H3C	0.334 (14)	0.439 (8)	0.079 (16)	0.156*	0.32 (3)
H3D	0.556 (17)	0.450 (7)	0.116 (15)	0.156*	0.32 (3)
O4'	0.943 (5)	0.5497 (18)	0.021 (2)	0.260 (10)	0.358 (11)
H4E	1.06 (3)	0.54 (2)	0.01 (4)	0.390*	0.358 (11)
H4F	0.90 (6)	0.595 (9)	0.00 (3)	0.390*	0.358 (11)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cl1	0.0437 (3)	0.0419 (3)	0.0436 (3)	0.0050 (2)	−0.0080 (2)	−0.0038 (2)
C1	0.0325 (10)	0.0295 (9)	0.0309 (10)	0.0002 (7)	0.0007 (8)	0.0003 (7)
C2	0.0326 (10)	0.0266 (9)	0.0326 (10)	0.0005 (7)	0.0094 (8)	0.0034 (7)
C3	0.0348 (10)	0.0260 (9)	0.0320 (10)	−0.0008 (7)	0.0071 (8)	0.0000 (7)
C4	0.0582 (15)	0.0463 (13)	0.0477 (14)	0.0078 (11)	0.0008 (11)	−0.0004 (10)
C5	0.0600 (16)	0.0520 (14)	0.0635 (17)	−0.0149 (12)	0.0066 (12)	−0.0202 (12)
C6	0.0503 (14)	0.0611 (15)	0.0633 (17)	−0.0018 (11)	0.0259 (12)	−0.0168 (12)
C7	0.0402 (12)	0.0630 (15)	0.0539 (15)	−0.0022 (11)	0.0173 (11)	−0.0025 (11)
C8	0.0620 (17)	0.0454 (14)	0.0707 (18)	0.0168 (12)	0.0088 (13)	0.0034 (12)
C9	0.0384 (12)	0.0527 (13)	0.0505 (13)	−0.0056 (10)	0.0031 (10)	−0.0151 (10)
N1	0.0590 (13)	0.0508 (11)	0.0414 (11)	−0.0029 (9)	0.0082 (9)	−0.0117 (8)
N2	0.0557 (13)	0.0402 (10)	0.0628 (13)	−0.0086 (9)	0.0134 (10)	−0.0015 (9)
N3	0.0414 (10)	0.0374 (9)	0.0447 (11)	0.0088 (8)	0.0092 (8)	−0.0118 (8)
N4	0.0331 (10)	0.0567 (12)	0.0615 (13)	0.0057 (8)	0.0097 (9)	−0.0114 (10)
O1	0.0414 (8)	0.0420 (8)	0.0428 (9)	0.0139 (6)	0.0040 (6)	−0.0058 (6)
O2	0.0495 (9)	0.0470 (9)	0.0384 (8)	0.0105 (7)	0.0031 (7)	−0.0140 (7)
O3	0.139 (7)	0.121 (4)	0.049 (2)	0.008 (4)	−0.004 (3)	−0.024 (2)
O4	0.195 (7)	0.098 (4)	0.100 (4)	0.042 (3)	−0.041 (4)	−0.028 (3)

O3'	0.119 (10)	0.116 (9)	0.075 (6)	0.028 (7)	0.008 (6)	−0.002 (6)
O4'	0.256 (13)	0.278 (13)	0.245 (13)	0.004 (10)	0.036 (9)	−0.023 (10)

Geometric parameters (Å, °)

C1—C2	1.408 (3)	C5—H5A	0.9700
C1—C3$^{\text{i}}$	1.392 (3)	C5—H5B	0.9700
C2—O1	1.237 (2)	C6—H6A	0.9700
C2—C3	1.539 (3)	C6—H6B	0.9700
C3—O2	1.251 (2)	C7—H7A	0.9700
C4—N1	1.440 (3)	C7—H7B	0.9700
C5—N1	1.464 (3)	C8—H8A	0.9700
C6—N1	1.465 (3)	C8—H8B	0.9700
C5—N2	1.466 (3)	C9—H9A	0.9700
C7—N2	1.440 (3)	C9—H9B	0.9700
C8—N2	1.471 (3)	N3—H3	0.86 (2)
C4—N3	1.505 (3)	O3—H3A	0.825 (11)
C7—N3	1.499 (3)	O3—H3B	0.827 (11)
C9—N3	1.506 (3)	O3—H3C	0.85 (14)
C6—N4	1.459 (3)	O4—H4C	0.828 (11)
C8—N4	1.461 (3)	O4—H4D	0.828 (10)
C9—N4	1.434 (3)	O3'—H3B	0.98 (7)
Cl1—C1	1.737 (2)	O3'—H3C	0.824 (11)
C3—C1$^{\text{i}}$	1.392 (3)	O3'—H3D	0.824 (11)
C4—H4A	0.9700	O4'—H4E	0.825 (11)
C4—H4B	0.9700	O4'—H4F	0.826 (11)
C3$^{\text{i}}$—C1—C2	123.07 (18)	N4—C8—N2	111.90 (19)
C3$^{\text{i}}$—C1—Cl1	118.91 (15)	N4—C8—H8A	109.2
C2—C1—Cl1	117.97 (14)	N2—C8—H8A	109.2
O1—C2—C1	124.72 (19)	N4—C8—H8B	109.2
O1—C2—C3	117.17 (16)	N2—C8—H8B	109.2
C1—C2—C3	118.08 (16)	H8A—C8—H8B	107.9
O2—C3—C1$^{\text{i}}$	125.08 (19)	N4—C9—N3	109.44 (17)
O2—C3—C2	116.15 (16)	N4—C9—H9A	109.8
C1$^{\text{i}}$—C3—C2	118.76 (16)	N3—C9—H9A	109.8
N1—C4—N3	110.01 (18)	N4—C9—H9B	109.8
N1—C4—H4A	109.7	N3—C9—H9B	109.8
N3—C4—H4A	109.7	H9A—C9—H9B	108.2
N1—C4—H4B	109.7	C4—N1—C5	108.42 (19)
N3—C4—H4B	109.7	C4—N1—C6	108.79 (19)
H4A—C4—H4B	108.2	C5—N1—C6	108.3 (2)
N1—C5—N2	111.97 (19)	C7—N2—C5	109.1 (2)
N1—C5—H5A	109.2	C7—N2—C8	108.31 (19)
N2—C5—H5A	109.2	C5—N2—C8	108.8 (2)
N1—C5—H5B	109.2	C7—N3—C4	108.70 (18)
N2—C5—H5B	109.2	C7—N3—C9	109.06 (18)
H5A—C5—H5B	107.9	C4—N3—C9	108.83 (18)
N4—C6—N1	112.53 (18)	C7—N3—H3	109.8 (16)

N4—C6—H6A	109.1	C4—N3—H3	110.0 (16)
N1—C6—H6A	109.1	C9—N3—H3	110.4 (16)
N4—C6—H6B	109.1	C9—N4—C6	109.21 (19)
N1—C6—H6B	109.1	C9—N4—C8	109.05 (18)
H6A—C6—H6B	107.8	C6—N4—C8	108.3 (2)
N2—C7—N3	109.67 (17)	H3A—O3—H3B	113 (2)
N2—C7—H7A	109.7	H4C—O4—H4D	113 (2)
N3—C7—H7A	109.7	H3A—O3'—H3D	135 (10)
N2—C7—H7B	109.7	H3B—O3'—H3D	112 (10)
N3—C7—H7B	109.7	H3C—O3'—H3D	115 (2)
H7A—C7—H7B	108.2	H4E—O4'—H4F	115 (2)

C3^{i}—C1—C2—O1	−174.85 (18)	N1—C5—N2—C7	60.3 (3)
Cl1—C1—C2—O1	2.4 (3)	N1—C5—N2—C8	−57.6 (3)
C3^{i}—C1—C2—C3	3.5 (3)	N4—C8—N2—C7	−60.7 (3)
Cl1—C1—C2—C3	−179.25 (12)	N4—C8—N2—C5	57.8 (3)
O1—C2—C3—O2	−4.2 (2)	N2—C7—N3—C4	59.0 (2)
C1—C2—C3—O2	177.33 (17)	N2—C7—N3—C9	−59.6 (2)
O1—C2—C3—C1^{i}	175.12 (17)	N1—C4—N3—C7	−59.6 (2)
C1—C2—C3—C1^{i}	−3.4 (3)	N1—C4—N3—C9	59.1 (2)
N3—C4—N1—C5	59.4 (3)	N4—C9—N3—C7	59.1 (2)
N3—C4—N1—C6	−58.2 (2)	N4—C9—N3—C4	−59.3 (2)
N2—C5—N1—C4	−60.3 (3)	N3—C9—N4—C6	59.1 (2)
N2—C5—N1—C6	57.6 (2)	N3—C9—N4—C8	−59.0 (3)
N4—C6—N1—C4	59.3 (3)	N1—C6—N4—C9	−60.1 (2)
N4—C6—N1—C5	−58.3 (2)	N1—C6—N4—C8	58.5 (2)
N3—C7—N2—C5	−58.9 (3)	N2—C8—N4—C9	60.8 (3)
N3—C7—N2—C8	59.4 (3)	N2—C8—N4—C6	−57.9 (3)

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

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C9—H9A···O2^{ii}	0.97	2.44	3.320 (3)	151
C7—H7B···N4^{iii}	0.97	2.54	3.503 (3)	170
C7—H7A···O3^{iv}	0.97	2.56	3.378 (6)	142
C6—H6B···O3^{ii}	0.97	2.52	3.485 (16)	173
O4—H4D···Cl1^{v}	0.828 (10)	3.03 (8)	3.278 (5)	100 (6)
C4—H4A···O3	0.97	2.57	3.413 (10)	146
O4—H4C···O3	0.828 (11)	2.62 (4)	3.41 (2)	160 (10)
O3—H3B···O2	0.827 (11)	1.98 (2)	2.781 (6)	162 (8)
N3—H3···O2	0.86 (2)	2.20 (2)	2.854 (2)	132 (2)
N3—H3···O1	0.86 (2)	1.98 (2)	2.746 (2)	147 (2)

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

Fig. 1

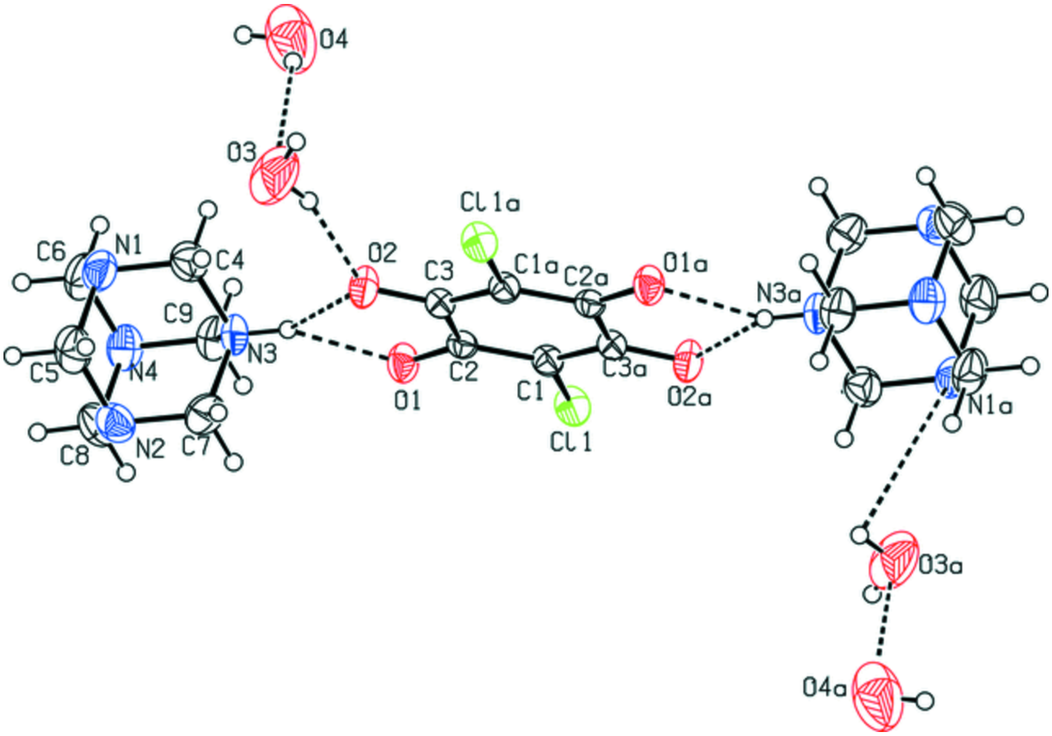
O4
O3
Cl1a
C6
N1
C4
O2
C3
C1a
C2a
O1a
N3a
C9
N3
C5
N4
O1
C2
C1
C3a
O2a
C8
N2
C7
Cl1
N1a
O3a
O4a

Fig. 2