

Triethylammonium hydrogen chloranilate

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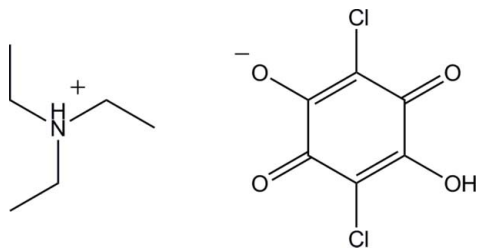
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Key indicators: single-crystal X-ray study; $T = 180$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.031; wR factor = 0.092; data-to-parameter ratio = 23.2.

In the crystal structure of the title compound (systematic name: triethylammonium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate), $\text{C}_6\text{H}_{16}\text{N}^+\cdot\text{C}_6\text{HCl}_2\text{O}_4^-$, two hydrogen chloranilate anions are connected by a pair of bifurcated $\text{O}-\text{H}\cdots\text{O}$ hydrogen bonds into a dimeric unit. The triethylammonium cations are linked on both sides of the dimer *via* bifurcated $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonds into a centrosymmetric 2:2 aggregate. The 2:2 aggregates are further linked by intermolecular $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds.

Related literature

For related structures, see, for example: Gotoh *et al.* (2008, 2009); Gotoh & Ishida (2009); Yang (2007). For details of the double π system of chloranilic acid, see: Andersen (1967); Benchekroun & Savariault (1995).



Experimental

Crystal data

$\text{C}_6\text{H}_{16}\text{N}^+\cdot\text{C}_6\text{HCl}_2\text{O}_4^-$
 $M_r = 310.18$
 Triclinic, $P\bar{1}$
 $a = 7.6404$ (5) Å
 $b = 9.5352$ (3) Å

$c = 11.2976$ (5) Å
 $\alpha = 99.9621$ (15)°
 $\beta = 108.732$ (3)°
 $\gamma = 106.536$ (3)°
 $V = 714.84$ (6) Å³

$Z = 2$
 Mo $K\alpha$ radiation
 $\mu = 0.46$ mm⁻¹

$T = 180$ K
 $0.42 \times 0.35 \times 0.25$ mm

Data collection

Rigaku R-Axis RAPID II diffractometer
 Absorption correction: numerical (NUMABS; Higashi, 1999)
 $T_{\min} = 0.829$, $T_{\max} = 0.891$

14757 measured reflections
 4176 independent reflections
 3631 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.034$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.031$
 $wR(F^2) = 0.092$
 $S = 1.07$
 4176 reflections
 180 parameters

H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.59$ e Å⁻³
 $\Delta\rho_{\min} = -0.36$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}$	0.847 (18)	2.411 (15)	2.9805 (12)	125.1 (13)
$\text{N1}-\text{H1}\cdots\text{O4}$	0.847 (18)	2.069 (18)	2.8833 (12)	161.1 (14)
$\text{O2}-\text{H2}\cdots\text{O3}$	0.765 (19)	2.147 (19)	2.6331 (11)	121.9 (17)
$\text{O2}-\text{H2}\cdots\text{O3}^{\text{i}}$	0.765 (19)	2.082 (19)	2.7089 (12)	139.4 (19)
$\text{C7}-\text{H7B}\cdots\text{O2}^{\text{ii}}$	0.99	2.47	3.2859 (15)	140
$\text{C8}-\text{H8A}\cdots\text{O4}^{\text{iii}}$	0.98	2.47	3.3977 (14)	158

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

Data collection: *PROCESS-AUTO* (Rigaku/MSK, 2004); cell refinement: *PROCESS-AUTO*; data reduction: *CrystalStructure* (Rigaku/MSK, 2004); program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *ORTEP-3* (Farrugia, 1997); software used to prepare material for publication: *CrystalStructure* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: HG2739).

References

- Andersen, E. K. (1967). *Acta Cryst.* **22**, 196–201.
 Benchekroun, R. & Savariault, J.-M. (1995). *Acta Cryst.* **C51**, 186–188.
 Farrugia, L. J. (1997). *J. Appl. Cryst.* **30**, 565.
 Gotoh, K., Asaji, T. & Ishida, H. (2008). *Acta Cryst.* **C64**, o550–o553.
 Gotoh, K. & Ishida, H. (2009). *Acta Cryst.* **E65**, o2467.
 Gotoh, K., Nagoshi, H. & Ishida, H. (2009). *Acta Cryst.* **C65**, o273–o277.
 Higashi, T. (1999). *NUMABS*. Rigaku Corporation, Tokyo, Japan.
 Rigaku/MSK. (2004). *PROCESS-AUTO* and *CrystalStructure*. Rigaku/MSK Inc., The Woodlands, Texas, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
 Yang, D.-J. (2007). *Acta Cryst.* **E63**, o2600.

supplementary materials

Acta Cryst. (2010). E66, o3255 [doi:10.1107/S1600536810047744]

Triethylammonium hydrogen chloranilate

K. Gotoh, S. Maruyama and H. Ishida

Comment

The title compound, (I), was prepared in order to extend our study on $D-H\cdots A$ hydrogen bonding ($D = N, O, \text{ or } C$; $A = N, O \text{ or } Cl$) in amine–chloranilic acid systems (Gotoh *et al.*, 2008,2009; Gotoh & Ishida, 2009). The crystal structure of bis(hexamethylenetetraminium) chloranilate tetrahydrate has been reported for the tertiary amine–chloranilic acid 2:1 system (Yang, 2007).

In the crystal structure of the title compound, an acid-base interaction involving proton transfer is observed between chloranilic acid and triethylamine, and two hydrogen chloranilate anions and two triethylammonium cations are linked by bifurcated $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds (Table 1) to afford a centrosymmetric 2:2 aggregate (Fig. 1). The anion shows a characteristic structure of the double π system (Andersen, 1967; Benchekroun & Savariault, 1995) with two long $C1-C6$ [1.5442 (13) Å] and $C3-C4$ [1.5063 (13) Å] bonds. The $O3-C4$ and $O4-C6$ bonds [1.2529 (11) and 1.2510 (11) Å, respectively] in one π system are almost same and comparable to the $O-C$ bonds in the dianion of bis(hexamethylenetetraminium) chloranilate tetrahydrate (Yang, 2007). On the other hand, the $O1-C1$ and $O2-C3$ bonds [1.2199 (12) and 1.3324 (11) Å, respectively] in the other π system correspond to double and single bonds, respectively. The 2:2 aggregates are further linked by intermolecular $C-H\cdots O$ hydrogen bonds, forming a three-dimensional network (Fig. 2).

Experimental

Single crystals were obtained by slow evaporation from an acetonitrile solution (25 ml) of chloranilic acid (97 mg) and triethylamine (42 mg) at room temperature.

Refinement

C-bound H atoms were positioned geometrically ($C-H = 0.98 \text{ or } 0.99$ Å) and refined as riding, allowing for free rotation of the methyl group. $U_{iso}(H)$ values were set at $1.2U_{eq}(C)$ or $1.5U_{eq}(\text{methyl } C)$. The O- and N-bound H atoms were found in a difference Fourier map and refined isotropically. The refined $O-H$ and $N-H$ distances are 0.765 (19) and 0.847 (18) Å, respectively.

Figures

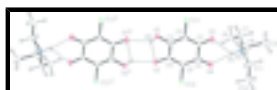


Fig. 1. The molecular structure of the title compound, with the atom-labeling. Displacement ellipsoids of non-H atoms are drawn at the 35% probability level. The dashed lines indicate $O-H\cdots O$ and $N-H\cdots O$ hydrogen bonds. [Symmetry code: (i) $-x + 1, -y + 2, -z$].

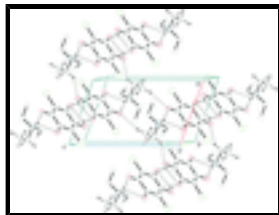


Fig. 2. A partial packing diagram of the title compound. The dashed lines indicate O—H···O, N—H···O and C—H···O hydrogen bonds. H atoms of the ethyl groups not involved in the C—H···O hydrogen bonds have been omitted.

Triethylammonium 2,5-dichloro-4-hydroxy-3,6-dioxocyclohexa-1,4-dien-1-olate

Crystal data

$C_6H_{16}N^+ \cdot C_6HCl_2O_4^-$	$Z = 2$
$M_r = 310.18$	$F(000) = 324.00$
Triclinic, $P\bar{1}$	$D_x = 1.441 \text{ Mg m}^{-3}$
Hall symbol: -P 1	Mo $K\alpha$ radiation, $\lambda = 0.71075 \text{ \AA}$
$a = 7.6404 (5) \text{ \AA}$	Cell parameters from 12766 reflections
$b = 9.5352 (3) \text{ \AA}$	$\theta = 3.0\text{--}30.1^\circ$
$c = 11.2976 (5) \text{ \AA}$	$\mu = 0.46 \text{ mm}^{-1}$
$\alpha = 99.9621 (15)^\circ$	$T = 180 \text{ K}$
$\beta = 108.732 (3)^\circ$	Block, brown
$\gamma = 106.536 (3)^\circ$	$0.42 \times 0.35 \times 0.25 \text{ mm}$
$V = 714.84 (6) \text{ \AA}^3$	

Data collection

Rigaku R-Axis RAPID II diffractometer	3631 reflections with $I > 2\sigma(I)$
Detector resolution: $10.00 \text{ pixels mm}^{-1}$	$R_{\text{int}} = 0.034$
ω scans	$\theta_{\text{max}} = 30.0^\circ$
Absorption correction: numerical (NUMABS; Higashi, 1999)	$h = -10 \rightarrow 10$
$T_{\text{min}} = 0.829$, $T_{\text{max}} = 0.891$	$k = -13 \rightarrow 13$
14757 measured reflections	$l = -15 \rightarrow 15$
4176 independent reflections	

Refinement

Refinement on F^2	Primary atom site location: structure-invariant direct methods
Least-squares matrix: full	Secondary atom site location: difference Fourier map
$R[F^2 > 2\sigma(F^2)] = 0.031$	Hydrogen site location: inferred from neighbouring sites
$wR(F^2) = 0.092$	H atoms treated by a mixture of independent and constrained refinement
$S = 1.07$	$w = 1/[\sigma^2(F_o^2) + (0.0543P)^2 + 0.1133P]$
4176 reflections	where $P = (F_o^2 + 2F_c^2)/3$
	$(\Delta/\sigma)_{\text{max}} = 0.001$

180 parameters

$$\Delta\rho_{\max} = 0.59 \text{ e } \text{\AA}^{-3}$$

0 restraints

$$\Delta\rho_{\min} = -0.35 \text{ e } \text{\AA}^{-3}$$

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 (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
C11	0.05941 (4)	0.44199 (3)	-0.17017 (2)	0.03282 (8)
C12	0.79265 (4)	0.85112 (3)	0.35611 (2)	0.03113 (8)
O1	0.23295 (13)	0.35023 (9)	0.06660 (8)	0.03546 (18)
O2	0.29888 (11)	0.77018 (9)	-0.10218 (8)	0.02849 (16)
O3	0.60830 (11)	0.93820 (8)	0.11497 (7)	0.02933 (16)
O4	0.53520 (12)	0.51893 (9)	0.29193 (8)	0.03090 (17)
N1	0.31226 (12)	0.21786 (9)	0.28996 (8)	0.02410 (16)
C1	0.31746 (14)	0.48352 (11)	0.07566 (9)	0.02382 (18)
C2	0.25857 (14)	0.55307 (11)	-0.02828 (9)	0.02340 (18)
C3	0.35511 (14)	0.70234 (11)	-0.01071 (9)	0.02249 (18)
C4	0.53096 (14)	0.80246 (10)	0.11283 (9)	0.02232 (17)
C5	0.59095 (14)	0.73644 (11)	0.21385 (9)	0.02326 (18)
C6	0.49384 (14)	0.58366 (11)	0.20508 (9)	0.02325 (18)
C7	0.12245 (15)	0.22545 (12)	0.29816 (11)	0.0307 (2)
H7A	0.0632	0.1399	0.3289	0.037*
H7B	0.0275	0.2125	0.2098	0.037*
C8	0.15318 (17)	0.37395 (13)	0.38885 (11)	0.0323 (2)
H8A	0.2209	0.3765	0.4795	0.048*
H8B	0.0242	0.3827	0.3768	0.048*
H8C	0.2344	0.4594	0.3693	0.048*
C9	0.27183 (18)	0.08580 (12)	0.17789 (11)	0.0320 (2)
H9A	0.3979	0.0937	0.1676	0.038*
H9B	0.1802	0.0938	0.0967	0.038*
C10	0.1828 (2)	-0.06935 (13)	0.19402 (15)	0.0435 (3)
H10A	0.2787	-0.0831	0.2686	0.065*
H10B	0.1502	-0.1493	0.1145	0.065*
H10C	0.0619	-0.0762	0.2094	0.065*
C11	0.45590 (16)	0.22080 (13)	0.41806 (11)	0.0313 (2)
H11A	0.3995	0.1271	0.4406	0.038*
H11B	0.4747	0.3098	0.4872	0.038*

supplementary materials

C12	0.65531 (19)	0.23066 (17)	0.41462 (15)	0.0461 (3)
H12A	0.6413	0.1348	0.3574	0.069*
H12B	0.7501	0.2480	0.5031	0.069*
H12C	0.7037	0.3156	0.3811	0.069*
H1	0.365 (2)	0.2974 (19)	0.2713 (14)	0.037 (4)*
H2	0.364 (3)	0.855 (2)	-0.0717 (17)	0.055 (5)*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C11	0.03108 (13)	0.02407 (13)	0.03098 (14)	0.00336 (10)	0.00192 (10)	0.00952 (9)
C12	0.03405 (14)	0.02543 (13)	0.02406 (13)	0.00126 (10)	0.00727 (10)	0.00770 (9)
O1	0.0406 (4)	0.0198 (4)	0.0355 (4)	0.0021 (3)	0.0070 (3)	0.0134 (3)
O2	0.0304 (4)	0.0204 (4)	0.0303 (4)	0.0052 (3)	0.0067 (3)	0.0140 (3)
O3	0.0342 (4)	0.0184 (3)	0.0333 (4)	0.0056 (3)	0.0114 (3)	0.0128 (3)
O4	0.0353 (4)	0.0252 (4)	0.0283 (4)	0.0050 (3)	0.0091 (3)	0.0153 (3)
N1	0.0257 (4)	0.0190 (4)	0.0277 (4)	0.0046 (3)	0.0123 (3)	0.0098 (3)
C1	0.0266 (4)	0.0192 (4)	0.0267 (4)	0.0069 (3)	0.0112 (3)	0.0101 (3)
C2	0.0235 (4)	0.0195 (4)	0.0255 (4)	0.0059 (3)	0.0079 (3)	0.0088 (3)
C3	0.0244 (4)	0.0203 (4)	0.0257 (4)	0.0082 (3)	0.0113 (3)	0.0109 (3)
C4	0.0252 (4)	0.0183 (4)	0.0262 (4)	0.0076 (3)	0.0124 (3)	0.0092 (3)
C5	0.0260 (4)	0.0193 (4)	0.0230 (4)	0.0051 (3)	0.0094 (3)	0.0083 (3)
C6	0.0261 (4)	0.0206 (4)	0.0249 (4)	0.0069 (3)	0.0117 (3)	0.0103 (3)
C7	0.0232 (4)	0.0292 (5)	0.0376 (5)	0.0063 (4)	0.0120 (4)	0.0104 (4)
C8	0.0319 (5)	0.0344 (6)	0.0357 (5)	0.0164 (4)	0.0144 (4)	0.0131 (4)
C9	0.0415 (6)	0.0214 (5)	0.0327 (5)	0.0066 (4)	0.0187 (4)	0.0070 (4)
C10	0.0536 (7)	0.0218 (5)	0.0571 (8)	0.0075 (5)	0.0306 (6)	0.0101 (5)
C11	0.0301 (5)	0.0330 (5)	0.0312 (5)	0.0120 (4)	0.0103 (4)	0.0127 (4)
C12	0.0337 (6)	0.0490 (8)	0.0561 (8)	0.0214 (5)	0.0146 (5)	0.0117 (6)

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

C11—C2	1.7133 (10)	C7—H7A	0.9900
C12—C5	1.7307 (10)	C7—H7B	0.9900
O1—C1	1.2199 (12)	C8—H8A	0.9800
O2—C3	1.3324 (11)	C8—H8B	0.9800
O2—H2	0.766 (18)	C8—H8C	0.9800
O3—C4	1.2529 (11)	C9—C10	1.5115 (16)
O4—C6	1.2510 (11)	C9—H9A	0.9900
N1—C11	1.4993 (13)	C9—H9B	0.9900
N1—C9	1.5033 (13)	C10—H10A	0.9800
N1—C7	1.5036 (13)	C10—H10B	0.9800
N1—H1	0.847 (16)	C10—H10C	0.9800
C1—C2	1.4564 (13)	C11—C12	1.5130 (16)
C1—C6	1.5442 (13)	C11—H11A	0.9900
C2—C3	1.3490 (13)	C11—H11B	0.9900
C3—C4	1.5063 (13)	C12—H12A	0.9800
C4—C5	1.4092 (13)	C12—H12B	0.9800
C5—C6	1.4036 (13)	C12—H12C	0.9800

C7—C8	1.5047 (16)		
C3—O2—H2	106.0 (13)	C7—C8—H8A	109.5
C11—N1—C9	113.52 (8)	C7—C8—H8B	109.5
C11—N1—C7	111.98 (8)	H8A—C8—H8B	109.5
C9—N1—C7	111.23 (8)	C7—C8—H8C	109.5
C11—N1—H1	107.6 (10)	H8A—C8—H8C	109.5
C9—N1—H1	105.4 (10)	H8B—C8—H8C	109.5
C7—N1—H1	106.5 (10)	N1—C9—C10	114.04 (9)
O1—C1—C2	123.39 (9)	N1—C9—H9A	108.7
O1—C1—C6	118.01 (8)	C10—C9—H9A	108.7
C2—C1—C6	118.60 (8)	N1—C9—H9B	108.7
C3—C2—C1	120.43 (9)	C10—C9—H9B	108.7
C3—C2—C11	121.32 (7)	H9A—C9—H9B	107.6
C1—C2—C11	118.21 (7)	C9—C10—H10A	109.5
O2—C3—C2	121.58 (9)	C9—C10—H10B	109.5
O2—C3—C4	115.99 (8)	H10A—C10—H10B	109.5
C2—C3—C4	122.42 (8)	C9—C10—H10C	109.5
O3—C4—C5	126.59 (9)	H10A—C10—H10C	109.5
O3—C4—C3	115.62 (8)	H10B—C10—H10C	109.5
C5—C4—C3	117.79 (8)	N1—C11—C12	112.26 (10)
C6—C5—C4	123.24 (9)	N1—C11—H11A	109.2
C6—C5—C12	118.80 (7)	C12—C11—H11A	109.2
C4—C5—C12	117.95 (7)	N1—C11—H11B	109.2
O4—C6—C5	126.67 (9)	C12—C11—H11B	109.2
O4—C6—C1	115.87 (8)	H11A—C11—H11B	107.9
C5—C6—C1	117.46 (8)	C11—C12—H12A	109.5
N1—C7—C8	112.65 (8)	C11—C12—H12B	109.5
N1—C7—H7A	109.1	H12A—C12—H12B	109.5
C8—C7—H7A	109.1	C11—C12—H12C	109.5
N1—C7—H7B	109.1	H12A—C12—H12C	109.5
C8—C7—H7B	109.1	H12B—C12—H12C	109.5
H7A—C7—H7B	107.8		
O1—C1—C2—C3	178.24 (10)	C3—C4—C5—C12	-179.88 (7)
C6—C1—C2—C3	-0.79 (14)	C4—C5—C6—O4	-177.80 (10)
O1—C1—C2—C11	0.38 (14)	C12—C5—C6—O4	1.38 (15)
C6—C1—C2—C11	-178.65 (7)	C4—C5—C6—C1	2.18 (14)
C1—C2—C3—O2	-177.16 (9)	C12—C5—C6—C1	-178.64 (6)
C11—C2—C3—O2	0.63 (14)	O1—C1—C6—O4	-0.58 (14)
C1—C2—C3—C4	2.41 (15)	C2—C1—C6—O4	178.50 (9)
C11—C2—C3—C4	-179.80 (7)	O1—C1—C6—C5	179.44 (9)
O2—C3—C4—O3	-1.57 (12)	C2—C1—C6—C5	-1.48 (13)
C2—C3—C4—O3	178.84 (9)	C11—N1—C7—C8	64.50 (11)
O2—C3—C4—C5	177.84 (8)	C9—N1—C7—C8	-167.30 (9)
C2—C3—C4—C5	-1.75 (14)	C11—N1—C9—C10	60.54 (13)
O3—C4—C5—C6	178.64 (9)	C7—N1—C9—C10	-66.83 (13)
C3—C4—C5—C6	-0.70 (14)	C9—N1—C11—C12	59.27 (12)
O3—C4—C5—C12	-0.55 (14)	C7—N1—C11—C12	-173.75 (9)

supplementary materials

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

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1	0.847 (18)	2.411 (15)	2.9805 (12)	125.1 (13)
N1—H1 \cdots O4	0.847 (18)	2.069 (18)	2.8833 (12)	161.1 (14)
O2—H2 \cdots O3	0.765 (19)	2.147 (19)	2.6331 (11)	121.9 (17)
O2—H2 \cdots O3 ⁱ	0.765 (19)	2.082 (19)	2.7089 (12)	139.4 (19)
C7—H7B \cdots O2 ⁱⁱ	0.99	2.47	3.2859 (15)	140
C8—H8A \cdots O4 ⁱⁱⁱ	0.98	2.47	3.3977 (14)	158

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

Fig. 1

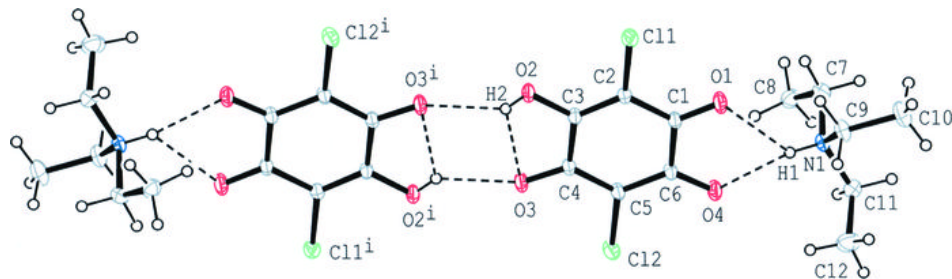


Fig. 2

