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Bis(2-methylimidazolium) chloranilate

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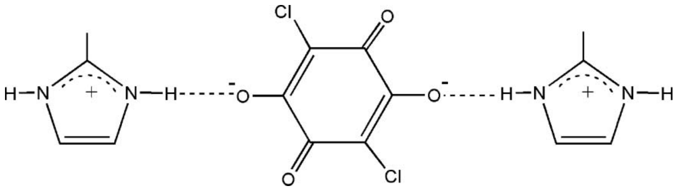
Key indicators: single-crystal X-ray study; T = 296 K; mean σ(C–C) = 0.004 Å; R factor = 0.052; wR factor = 0.132; data-to-parameter ratio = 16.2.

The asymmetric unit of the title structure, $2C_4H_7N_2^+\cdot C_6Cl_2O_4^{2-}$, consists of one 2-methylimidazolium cation and one-half of a chloranilate anion, the formula unit being generated by crystallographic inversion symmetry. N—H···O hydrogen bonds link the ions into a two-dimensional framework parallel to the (102) plane. No π–π stacking or C—H···π interactions are observed in the crystal structure.

Related literature

For related literature, see: Bernstein *et al.* (1995); Ishida & Kashino (2001); Ishida (2004*a*,*b*); Meng & Qian (2006); Min *et al.* (2006); Wang & Wei (2005).



Experimental

Crystal data

$2C_4H_7N_2^+\cdot C_6Cl_2O_4^{2-}$
M_r = 373.20
Monoclinic, $P2_1/c$
a = 8.5092 (10) Å
b = 7.6658 (9) Å
c = 12.7204 (16) Å
β = 91.204 (2)°
V = 829.57 (17) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.42 mm^{-1}
T = 296 (2) K
0.12 × 0.05 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.942, T_{max} = 0.992
9164 measured reflections
1880 independent reflections
1150 reflections with $I > 2\sigma(I)$
R_{int} = 0.067

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.052
$wR(F^2)$ = 0.132
S = 1.01
1880 reflections
116 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.28 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
N1—H1A···O1	0.99 (3)	1.73 (3)	2.713 (3)	172 (2)
N2—H2A···O2^{i}	0.82 (3)	1.96 (3)	2.719 (3)	152 (3)
N2—H2A···O1^{i}	0.82 (3)	2.40 (3)	3.014 (3)	132 (3)

Symmetry code: (i) $-x+2, y-\frac{1}{2}, -z+\frac{1}{2}$.

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: LH2514).

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supplementary materials

Acta Cryst. (2008). E**64**, o32 [**doi:10.1107/S1600536807048374**]

Bis(2-methylimidazolium) chloranilate

L.-H. Jia, Z.-E. Mu and Z.-L. Liu

Comment

Chloranilic acid (CA) is a potential bridging ligand which is often used in the synthesis of metal organic frameworks (Min *et al.*, 2006). Also some organic salts containing chloranilate have been reported recently (Ishida, 2004*a*,*b*; Ishida & Kashino, 2001; Wang & Wei, 2005, Meng & Qian, 2006). In the hydrothermal process using equimolar amounts of CA, 2-Methylimidazole (2-MeIm) and copper nitrate, we unexpectedly obtained the title compound, and report herein its crystal structure.

The asymmetric unit contains one 2-methylimidazolium cation, half of a chloranilate anion the formula unit being generated by crystallogrphic inversion symmetry (Fig. 1). A proton has been transferred from the hydroxyl group in CA to the 2-MeIm N atom, forming the 1:2 organic salt.

In the crystal structure, by a combination of three N—H···O hydrogen bonds (Table 1) the molecules are linked into a two-dimensional framework (Fig. 2) built from the $R^2_1(5)$ and $R^6_8(32)$ rings (Bernstein *et al.*, 1995) running parallel to the (102) plane. Two such networks pass through the cell and analysis using *PLATON* (Spek, 2003) shows that there are no direction-specific interactions such as π–π and C–H···π interactions observed in the packing of the structure.

Experimental

All the reagents and solvents were used as obtained without further purification. Equivalent molar amount of CA (0.2 mmol, 41.4 mg), 2-MeIm (0.2 mmol, 16.2 mg) and $Cu(NO_3)_2·3(H_2O)$(0.2 mmol, 48 mg) in 10 ml water solvent sealed in a 25 ml Teflon-lined autoclave. The mixture was heated to 393 K and maintained for 48 h. After slowly cooling to room temperature with the rate of 5°/h, dark red crystals suitable for single-crystal X-ray diffraction analysis were obtained. The crystals were filtered and washed with distilled water and dried in air.

Refinement

H atoms bonded to carbon atoms were located at the geometrical positions [C—H = 0.96 Å (methyl) or 0.93 Å (aromatic), and $U_{iso}(H) = 1.5U_{eq}$ (methyl) or $1.2U_{eq}$ (aromatic). H atoms attached to N atoms were located in difference fourier maps and N—H distance refined freely and their U_{iso} values set 1.2 times of their carrier atoms.

Figures

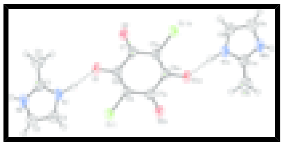

Fig. 1. Molecular structure, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. H-bonds are shown as dashed lines.

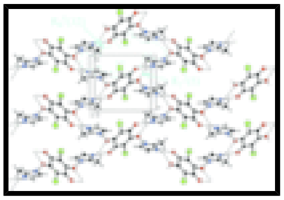

Fig. 2. Part of the crystal structure, showing the formation of the two-dimensional network by N—H···O hydrogen bonds. H-bonds are shown as dashed lines.

Bis(2-methylimidazolium) chloranilate

Crystal data

$2C_4H_7N_2^+\cdot C_6Cl_2O_4^{2-}$

$M_r = 373.20$

Monoclinic, $P2_1/c$

Hall symbol: -P 2ybc

$a = 8.5092$ (10) Å

$b = 7.6658$ (9) Å

$c = 12.7204$ (16) Å

$\beta = 91.204$ (2)°

$V = 829.57$ (17) Å^3

$Z = 2$

$F_{000} = 384$

$D_x = 1.494$ Mg m^{-3}

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 863 reflections

$\theta = 2.4$–19.5°

$\mu = 0.42$ mm^{-1}

$T = 296$ (2) K

Plate, red

0.12 × 0.05 × 0.02 mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer

Radiation source: fine focus sealed Siemens Mo tube

Monochromator: graphite

0.3° wide ω exposures scans

Absorption correction: multi-scan (SADABS; Sheldrick, 1996)

$T_{min} = 0.942$, $T_{max} = 0.992$

9164 measured reflections

1880 independent reflections

1150 reflections with $I > 2\sigma(I)$

$R_{int} = 0.067$

$\theta_{max} = 27.5$°

$\theta_{min} = 2.4$°

$h = -10 \rightarrow 10$

$k = -9 \rightarrow 9$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.052$

$wR(F^2) = 0.132$

$S = 1.01$

1880 reflections

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

$w = 1/[\sigma^2(F_o^2) + (0.0635P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{max} < 0.001$

$\Delta\rho_{max} = 0.28$ e Å^{-3}

116 parameters	$\Delta\rho_{min} = -0.23$ e Å^{-3}
Primary atom site location: structure-invariant direct methods	Extinction correction: none

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_{iso}*/U_{eq}
C1	0.9935 (3)	0.3795 (3)	0.1722 (2)	0.0386 (7)
C2	0.8754 (4)	0.2917 (4)	0.0266 (2)	0.0472 (7)
H2	0.8591	0.2450	−0.0403	0.057*
C3	0.7656 (3)	0.3549 (4)	0.0898 (2)	0.0457 (7)
H3	0.6582	0.3609	0.0751	0.055*
C4	1.1147 (4)	0.4178 (5)	0.2537 (2)	0.0614 (9)
H4A	1.1663	0.3116	0.2745	0.092*
H4B	1.0661	0.4695	0.3136	0.092*
H4C	1.1905	0.4974	0.2260	0.092*
C5	0.5122 (3)	0.3827 (3)	0.41260 (19)	0.0346 (6)
C6	0.6258 (3)	0.5121 (3)	0.42497 (17)	0.0310 (6)
C7	0.6127 (3)	0.6382 (3)	0.51780 (19)	0.0336 (6)
Cl1	0.52835 (9)	0.23376 (10)	0.31053 (5)	0.0543 (3)
N1	0.8402 (3)	0.4086 (3)	0.17996 (17)	0.0404 (6)
H1A	0.794 (3)	0.452 (3)	0.246 (2)	0.049*
N2	1.0162 (3)	0.3091 (3)	0.07907 (18)	0.0419 (6)
H2A	1.105 (4)	0.275 (4)	0.066 (2)	0.050*
O1	0.7415 (2)	0.5352 (2)	0.36643 (13)	0.0413 (5)
O2	0.7146 (2)	0.7533 (3)	0.52727 (15)	0.0512 (6)

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.0307 (16)	0.0390 (16)	0.0466 (16)	−0.0006 (13)	0.0121 (12)	−0.0012 (12)
C2	0.0474 (19)	0.0524 (18)	0.0419 (15)	−0.0007 (15)	0.0054 (14)	−0.0076 (14)
C3	0.0331 (16)	0.0542 (18)	0.0500 (17)	0.0010 (14)	0.0045 (14)	−0.0066 (14)
C4	0.0455 (19)	0.074 (2)	0.065 (2)	0.0006 (17)	−0.0009 (16)	−0.0138 (17)
C5	0.0292 (14)	0.0381 (15)	0.0370 (13)	−0.0020 (12)	0.0105 (11)	−0.0084 (11)
C6	0.0245 (14)	0.0386 (15)	0.0299 (12)	0.0022 (11)	0.0042 (11)	0.0018 (11)

C7	0.0285 (14)	0.0361 (15)	0.0363 (13)	−0.0010 (12)	0.0059 (11)	0.0007 (11)
Cl1	0.0482 (5)	0.0624 (5)	0.0532 (5)	−0.0135 (4)	0.0227 (4)	−0.0260 (4)
N1	0.0347 (14)	0.0444 (14)	0.0428 (13)	0.0027 (11)	0.0158 (11)	−0.0063 (11)
N2	0.0347 (14)	0.0450 (15)	0.0468 (13)	0.0075 (11)	0.0177 (12)	−0.0038 (11)
O1	0.0315 (11)	0.0521 (12)	0.0409 (10)	−0.0071 (9)	0.0177 (8)	−0.0033 (9)
O2	0.0441 (12)	0.0547 (13)	0.0557 (12)	−0.0212 (10)	0.0237 (10)	−0.0174 (10)

Geometric parameters (Å, °)

C1—N2	1.319 (3)	C4—H4C	0.9600
C1—N1	1.329 (3)	C5—C6	1.392 (3)
C1—C4	1.477 (4)	C5—C7$^{\text{i}}$	1.406 (3)
C2—C3	1.337 (4)	C5—Cl1	1.737 (2)
C2—N2	1.366 (4)	C6—O1	1.259 (3)
C2—H2	0.9300	C6—C7	1.532 (3)
C3—N1	1.363 (3)	C7—O2	1.242 (3)
C3—Cl1	3.613 (3)	C7—C5$^{\text{i}}$	1.406 (3)
C3—H3	0.9300	N1—H1A	0.99 (3)
C4—H4A	0.9600	N2—H2A	0.82 (3)
C4—H4B	0.9600		

N2—C1—N1	107.3 (2)	H4B—C4—H4C	109.5
N2—C1—C4	126.8 (3)	C6—C5—C7$^{\text{i}}$	122.8 (2)
N1—C1—C4	125.9 (3)	C6—C5—Cl1	119.15 (18)
C3—C2—N2	106.7 (3)	C7$^{\text{i}}$—C5—Cl1	117.96 (19)
C3—C2—H2	126.7	O1—C6—C5	125.7 (2)
N2—C2—H2	126.7	O1—C6—C7	115.9 (2)
C2—C3—N1	107.3 (3)	C5—C6—C7	118.4 (2)
C2—C3—Cl1	141.6 (2)	O2—C7—C5$^{\text{i}}$	123.7 (2)
N1—C3—Cl1	71.46 (15)	O2—C7—C6	117.5 (2)
C2—C3—H3	126.4	C5$^{\text{i}}$—C7—C6	118.8 (2)
N1—C3—H3	126.4	C5—Cl1—C3	117.80 (10)
Cl1—C3—H3	66.9	C1—N1—C3	109.1 (2)
C1—C4—H4A	109.5	C1—N1—H1A	121.6 (15)
C1—C4—H4B	109.5	C3—N1—H1A	129.0 (15)
H4A—C4—H4B	109.5	C1—N2—C2	109.6 (2)
C1—C4—H4C	109.5	C1—N2—H2A	118 (2)
H4A—C4—H4C	109.5	C2—N2—H2A	132 (2)

N2—C2—C3—N1	−0.4 (3)	C7$^{\text{i}}$—C5—Cl1—C3	161.62 (18)
N2—C2—C3—Cl1	−82.1 (4)	C2—C3—Cl1—C5	135.2 (3)
C7$^{\text{i}}$—C5—C6—O1	178.7 (2)	N1—C3—Cl1—C5	40.6 (2)
Cl1—C5—C6—O1	1.6 (4)	N2—C1—N1—C3	0.2 (3)
C7$^{\text{i}}$—C5—C6—C7	−0.7 (4)	C4—C1—N1—C3	−179.3 (3)
Cl1—C5—C6—C7	−177.85 (17)	C2—C3—N1—C1	0.2 (3)
O1—C6—C7—O2	0.9 (3)	Cl1—C3—N1—C1	139.7 (2)
C5—C6—C7—O2	−179.6 (2)	N1—C1—N2—C2	−0.4 (3)
O1—C6—C7—C5$^{\text{i}}$	−178.8 (2)	C4—C1—N2—C2	179.1 (3)

C5—C6—C7—C5^{i}	0.7 (4)	C3—C2—N2—C1	0.5 (3)
C6—C5—Cl1—C3	−21.1 (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*
N1—H1A···O1	0.99 (3)	1.73 (3)	2.713 (3)	172 (2)
N2—H2A···O2^{ii}	0.82 (3)	1.96 (3)	2.719 (3)	152 (3)
N2—H2A···O1^{ii}	0.82 (3)	2.40 (3)	3.014 (3)	132 (3)

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

Fig. 1

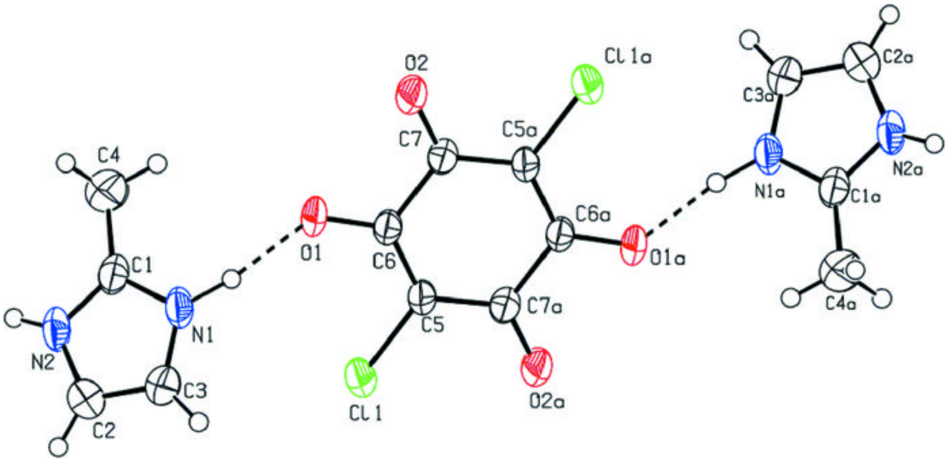
O2
Cl 1a
C2a
C3a
C4
C7
C5a
N2a
C6a
N1a
C1a
O1
C6
O1a
C1
C5
C7a
C4a
N1
N2
C3
Cl 1
O2a
C2

Fig. 2