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A hydrogen-bonded supramolecular complex between the chloranilic acid dianion (CA) and the 4-methylimidazole cation

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Key indicators

Single-crystal X-ray study
T = 292 K
Mean σ(C–C) = 0.003 Å
R factor = 0.043
wR factor = 0.113
Data-to-parameter ratio = 14.6

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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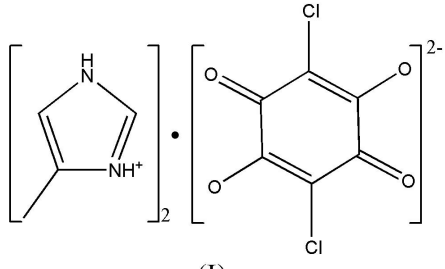
The title salt, bis(4-methylimidazolium) chloranilate, $2C_4H_7N_2^+\cdot C_6Cl_2O_4^{2-}$, is composed of a centrosymmetric chloranilate (CA) dianion and two 4-methylimidazolium cations, which are held together by intermolecular hydrogen-bond interactions and ultimately construct a two-dimensional supramolecular complex.

Comment

Hydrogen bonding, due to its strong directing capability of organizing molecules into supramolecular aggregates, is considered as one of the most important strategies for controlling molecular self-assembly during crystallization (Rodríguez-Martín *et al.*, 2002). In recent decades, hydrogen bonds have been used to generate supramolecular assemblies and some novel related complexes have been reported (Aakeröy *et al.*, 1998; Qin *et al.*, 2001). Here, we report the supramolecular complex (4-methylimidazole)$_2$(CA), (I).



(I)

The complex unit of (I) consists of a doubly deprotonated CA^{2-} anion and two singly protonated 2-methylimidazole cations, as a result of transfer of two protons (Fig. 1). The ions are held together by a complicated hydrogen-bond network forming a supramolecular complex, in which four O atoms of

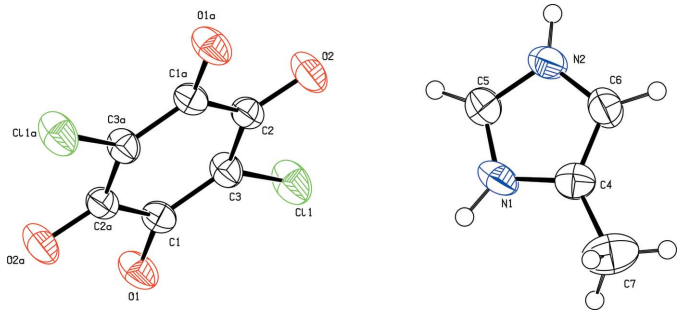


Figure 1
The cation and anion of the title compound. Displacement ellipsoids are drawn at the 50% probability level. [Symmetry code: (a) $2-x, 1-y, -z$.]

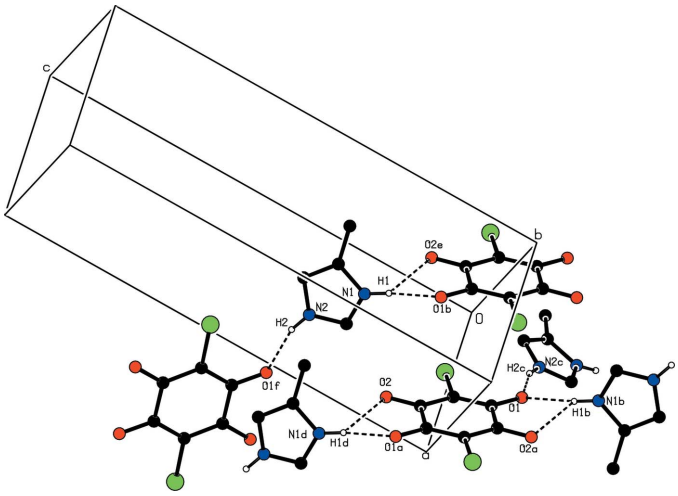


Figure 2
A perspective view of the crystal packing in the unit cell, showing the hydrogen bonding (dashed lines). H atoms not involved in the hydrogen bonds have been omitted for clarity. [Symmetry codes: (a) $2-x, 1-y, -z$; (b) $1-x, 1-y, -z$; (c) $-\frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; (d) $1+x, y, z$; (e) $-1+x, y, z$; (f) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.]

CA^{2-} act as acceptors and imidazolium NH act as donors in N—H···O hydrogen bonds (Fig. 2 and Table 1). Each O atom forms double hydrogen bonds with two adjacent cations. As shown in Fig. 2, one anion interacts with six cations *via* hydrogen bonds. In contrast, each cation interacts with three neighbouring anions, to build the two-dimensional supramolecular framework.

Experimental

All reagents and solvents were used as obtained without further purification. Chloranilic acid (1 mmol, 0.21 g) and 4-methylimidazole (1 mmol, 0.081 g) were dissolved in an ammonia solution (10 ml, 30%), and the mixture was stirred for about 20 min at room temperature. The resulting clear red solution was kept in air and, after slow evaporation of the solvent over a period of a week, red **needle** crystals of (I) formed at the bottom of the vessel.

Crystal data

$2C_4H_7N_2^+\cdot C_6Cl_2O_4^{2-}$
$M_r = 373.20$
Monoclinic, $P2_1/n$
$a = 5.2739\ (10)$ Å
$b = 9.5018\ (17)$ Å
$c = 16.560\ (3)$ Å
$\beta = 99.157\ (3)^\circ$
$V = 819.3\ (3)$ Å^3
$Z = 2$
$D_x = 1.513$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 1642 reflections
$\theta = 2.5$–24.6°
$\mu = 0.42$ mm^{-1}
$T = 292\ (2)$ K
Needle, red
$0.40 \times 0.20 \times 0.10$ mm

Data collection

Bruker SMART APEX CCD area-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
$T_{min} = 0.849$, $T_{max} = 0.959$
4373 measured reflections
1620 independent reflections
1373 reflections with $I > 2\sigma(I)$
$R_{int} = 0.029$
$\theta_{max} = 26.0^\circ$
$h = -6 \rightarrow 4$
$k = -11 \rightarrow 11$
$l = -18 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.113$
$S = 1.07$
1620 reflections
111 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0599P)^2 + 0.1001P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.28$ e Å^{-3}
$\Delta\rho_{min} = -0.28$ e Å^{-3}
Extinction correction: *SHELXL97* (Sheldrick, 1997)
Extinction coefficient: 0.012 (2)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···O1^{i}	0.86	1.98	2.825 (2)	167
N1—H1···O2^{i}	0.86	2.36	2.867 (2)	118
N2—H2···O1^{ii}	0.86	1.87	2.703 (2)	162

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

All H atoms were placed in idealized positions, with C—H(methyl) = 0.96 Å, other C—H = 0.93 Å and N—H = 0.86 Å, and included in the refinement in the riding-model approximation, with $U_{iso}(H) = 1.5U_{eq}$(methyl C) or $1.2U_{eq}$(other carrier atoms).

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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