Bis(2-methylquinolinium) tetrachloroferrate(III) chloride

Dariusz Wyrzykowski,[a] Artur Sikorski,[a]* Tadeusz Lis,[b] Antoni Konitz[a,c] and Zygmunt Warnke[a]

[a]University of Gdańsk, Faculty of Chemistry, J. Sobieskiego 18, 80-952 Gdańsk, Poland, [b]University of Wrocław, Faculty of Chemistry, F. Joliot-Curie 14, 50-383 Wrocław, Poland, and [c]Gdańsk University of Technology, Department of Inorganic Chemistry, G. Naruto-wicza 11/12, 80-952 Gdańsk, Poland

Correspondence e-mail: art@chem.univ.gda.pl

The asymmetric unit of the title compound, $(C_{10}H_{10}N)_2$-[FeCl$_4$]Cl, consists of two 2-methylquinolinium cations, a tetrachloroferrate(III) anion with one of the Cl atoms disordered, and a chloride anion. In the crystal structure, there are π–π stacking interactions between the cations in an *ABBA* arrangement, N—H$\cdots$Cl hydrogen bonds, and Fe—Cl$\cdots\pi$ interactions.

Comment

The position of the methyl substituent on the quinoline ring affects the stoichiometry of compounds with a tetrachloroferrate anion. The 6- and 8-methyl substituted compounds with the [FeCl$_4$]$^-$ anion synthesized by us form crystals of composition $(A$H$)_3$[FeCl$_4$]$_2$Cl (where *A*H stands for the corresponding methylquinolinium ion), whereas unsubstituted quinoline forms a binary (1:1) crystalline salt (Warnke *et al.*, 2003). Unexpectedly, during the synthesis of the analogous compound with 2-methylquinoline, we obtained the title compound, (I), which is a mixed salt of molar ratio 1:1 consisting of 2-methylquinolinium chloride and 2-methyl-quinolinium tetrachloroferrate(III). This composition is the same as that of bis(8-hydroxyquinolinium) tetrachloro-ferrate(III) chloride (Bottomley *et al.*, 1984).


(I)
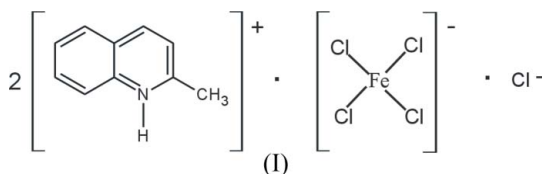
The asymmetric unit of (I) consists of two 2-methyl-quinolinium cations (denoted *A* and *B* for those containing atoms N1 and N10, respectively), a tetrachloroferrate(III) anion with one of the Cl atoms disordered, and a chloride anion (Fig. 1). The geometries of the quinolinium skeleton and [FeCl$_4$]$^-$ ion are typical of structures contained in the Cambridge Structural Database (CSD; Version 5.27; Allen, 2002) (Zora *et al.*, 1990; Barbaro *et al.*, 1992; Sieroń, 2005; Valdés-Martínez *et al.*, 2005). The mean planes delineated by all the non-H atoms of the 2-methylquinolinium cations *A* and *B* make an angle of 10.3 (1)° with respective average devia-tions from planarity of 0.006–0.007 Å.

In the crystal structure, cations *A* and *B* are linked through the Cl$^-$ anion (Cl5) *via* N—H$\cdots$Cl hydrogen bonds (Fig. 2 and Table 1). Additionally, the cation *B* interacts with the [FeCl$_4$]$^-$ anion *via* a C—H$\cdots$Cl hydrogen bond. There are π–π stacking interactions (Table 2) between the cations in an *ABBA* arrangement, and also Fe—Cl$\cdots\pi$ interactions (Table 3).
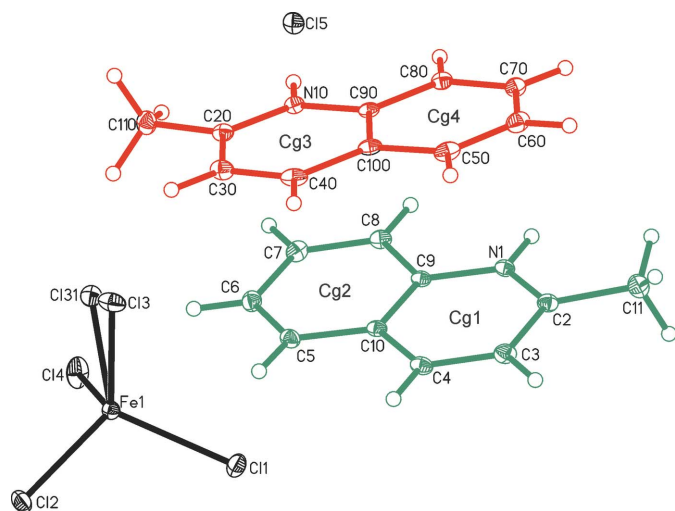
Figure 1
The asymmetric unit of (I), showing the atom-labelling scheme and 50% probability displacement ellipsoids. 2-Methylquinolinium cation *A* (which contains N1) is shown in green, and cation *B* (which contains N10) in red. Both disorder components are shown.
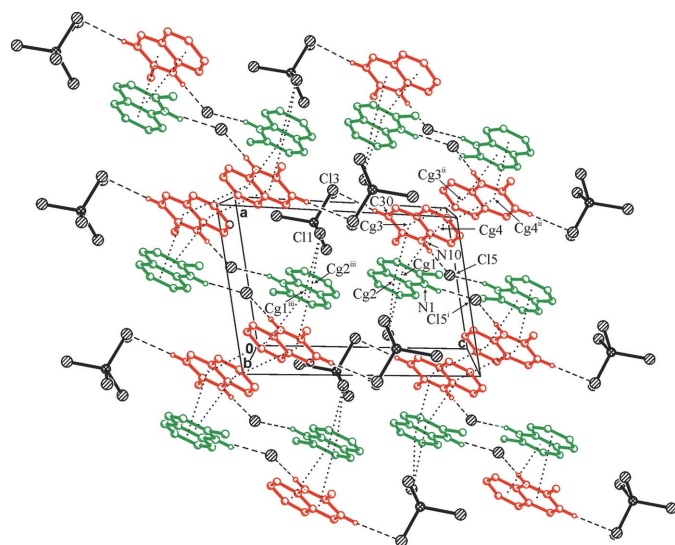
Figure 2
The crystal structure of (I), viewed approximately along the *b* axis. The N—H···Cl and C—H···Cl interactions are represented by dashed lines, and the π–π and Fe—Cl···π interactions by dotted lines. H atoms not involved in these interactions have been omitted. Only one disorder component is shown. *Cg*1–*Cg*4 are ring centroids, as indicated in Fig. 1. [Symmetry codes: (i) $1 - x, 1 - y, 2 - z$; (ii) $2 - x, 1 - y, 2 - z$; (iii) $1 - x, 1 - y, 1 - z$.]

Experimental

The synthesis of bis(2-methylquinolinium) chloride tetrachloroferrate(III) was carried out using a procedure similar to that reported for the preparation of other tetrachloroferrates(III) (Warnke *et al.*, 2001). Thus, an ethanol solution of anhydrous ferric chloride was prepared by dissolving FeCl₃ (1.623 g, 0.01 mol) in 96% ethanol (5 ml). To this solution, a stoichiometric quantity of a 12 *M* HCl solution was added, followed by 2-methylquinoline (1.43 g, 0.01 mol). The compound crystallized directly from this mixture as yellow crystals after two weeks in a refrigerator (yield *ca* 60%).

Crystal data

$(C_{10}H_{10}N)_2[FeCl_4]Cl$	$V = 1139.0 (6) \text{ Å}^3$
$M_r = 521.48$	$Z = 2$
Triclinic, $P\bar{1}$	$D_x = 1.521 \text{ Mg m}^{-3}$
$a = 8.645 (2) \text{ Å}$	Mo $K\alpha$ radiation
$b = 10.888 (3) \text{ Å}$	$\mu = 1.26 \text{ mm}^{-1}$
$c = 13.503 (3) \text{ Å}$	$T = 100 (2) \text{ K}$
$\alpha = 112.98 (3)°$	Prism, yellow
$\beta = 100.46 (3)°$	$0.5 \times 0.4 \times 0.4 \text{ mm}$
$\gamma = 93.32 (3)°$	

Data collection

Kuma KM-4-CCD κ-geometry diffractometer	15108 measured reflections
ω scans	5318 independent reflections
Absorption correction: analytical (*CrysAlis RED*; Oxford Diffraction, 2003)	4884 reflections with $I > 2\sigma(I)$
	$R_{int} = 0.023$
$T_{min} = 0.516, T_{max} = 0.659$	$\theta_{max} = 27.8°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0324P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.026$	$+ 0.6399P]$
$wR(F^2) = 0.067$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.07$	$(\Delta/\sigma)_{max} = 0.002$
5318 reflections	$\Delta\rho_{max} = 0.37 \text{ e Å}^{-3}$
261 parameters	$\Delta\rho_{min} = -0.42 \text{ e Å}^{-3}$
H-atom parameters constrained	Extinction correction: *SHELXL97*
	Extinction coefficient: 0.0070 (7)

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1A···Cl5^i	0.88	2.20	3.059 (2)	165
N10—H10A···Cl5	0.88	2.16	3.042 (2)	178
C30—H30A···Cl3	0.95	2.78	3.566 (2)	140

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

Table 2
π–π interactions (Å, °) in (I).

CgI	CgJ	Cg···Cg	Dihedral angle	Interplanar distance	Offset
1	4	3.567 (2)	11.2	3.558 (3)	0.747 (2)
2	3	3.616 (2)	10.1	3.538 (3)	1.354 (2)
3	4^{ii}	3.782 (2)	1.1	3.369 (3)	1.719 (2)
4	4^{ii}	3.869 (2)	0.0	3.355 (3)	1.927 (2)

Symmetry code: (ii) $2 - x, 1 - y, 2 - z$. Notes: *Cg*1–*Cg*4 are the centroids of the rings as indicated in Fig. 1. The interplanar distance is the perpendicular distance of *CgI* from ring *J*. Offset is the shift of projection of *CgI* on ring *J* from *CgJ*.

Table 3
Fe—Cl···π interactions (Å, °) in (I).

Y	X	CgJ	X···Cg	Y–X···Cg
Fe1	Cl1	*Cg*1^{iii}	3.520 (1)	110.9 (1)
Fe1	Cl1	*Cg*2^{iii}	3.857 (1)	148.0 (1)

Symmetry code: (iii) $1 - x, 1 - y, 1 - z$.

All H atoms were positioned geometrically and refined using a riding model, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$ [C—H = 0.98 Å and $U_{iso}(H) = 1.5U_{eq}(C)$ for methyl groups], and N—H = 0.88 Å and $U_{iso}(H) = 1.2U_{eq}(N)$. One of the Cl atoms of $[FeCl_4]^-$ shows positional disorder. This disorder was modelled using two atomic sites (Cl3 and Cl31), with refined occupancies of 0.931 (12) and 0.069 (12), respectively.

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *MERCURY* (Bruno *et al.*, 2002); software used to prepare material for publication: *SHELXL97* and *PLATON* (Spek, 2003).

References

Allen, F. H. (2002). *Acta Cryst.* B**58**, 380–388.

Barbaro, P., Bianchini, C., Fochi, M., Masi, D. & Mealli, C. (1992). *Acta Cryst.* C**48**, 625–627.

Bottomley, G. A., Carter, A. M., Engelhardt, L. M., Lincoln, F. J., Patrick, J. M. & White, A. H. (1984). *Aust. J. Chem.* **37**, 871–877.

Bruno, I. J., Cole, J. C., Edgington, P. R., Kessler, M., Macrae, C. F., McCabe, P., Pearson, J. & Taylor, R. (2002). *Acta Cryst.* B**58**, 389–397.

Oxford Diffraction (2003). *CrysAlis CCD* and *CrysAlis RED*. Versions 1.171. Oxford Diffraction Poland, Wroclaw, Poland.

Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.

Sieroń, L. (2005). *Acta Cryst.* E**61**, o2091–o2092.

Spek, A. L. (2003). *J. Appl. Cryst.* **36**, 7–13.

Valdés-Martínez, J., Muñoz, O. & Toscano, R. A. (2005). *Acta Cryst.* E**61**, m1590–m1592.

Warnke, Z., Wawrzyniak, G., Wyrzykowski, D. & Kosmalski, J. (2001). *Pol. J. Chem.* **75**, 759–763.

Warnke, Z., Wyrzykowski, D. & Wawrzyniak, G. (2003). *Pol. J. Chem.* **77**, 1121–1129.

Zora, J. A., Seddon, K. R., Hitchock, P. B., Lowe, C. B., Shum, D. P. & Carlin, R. L. (1990). *Inorg. Chem.* **29**, 3302–3308.