

Acta Crystallographica Section E

Structure Reports

Online

ISSN 1600-5368

2-Carbamylpyridinium tetrachlorido-ferrate(III)

Anne Nielsen, Christine J. McKenzie and Andrew D.

Bond*

University of Southern Denmark, Department of Physics and Chemistry, Campusvej 55, 5230 Odense M, Denmark

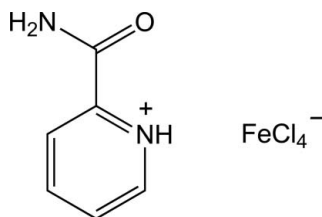
Correspondence e-mail: adb@chem.sdu.dk

Received 29 September 2009; accepted 1 October 2009

 Key indicators: single-crystal X-ray study; $T = 180$ K; mean $\sigma(\text{C}-\text{C}) = 0.002$ Å; R factor = 0.020; wR factor = 0.049; data-to-parameter ratio = 20.1.

The title compound, $(\text{C}_6\text{H}_7\text{N}_2\text{O})[\text{FeCl}_4]$, contains two carbamylpyridinium (picolinamidinium) cations, which are linked into chains by $\text{N}^+-\text{H}\cdots\text{O}$ hydrogen bonds formed between protonated pyridyl N atoms and carbonyl groups. Tetrachloridoferrate(III) anions lie between these chains, accepting $\text{N}-\text{H}\cdots\text{Cl}$ hydrogen bonds from both H atoms of the picolinamidium $-\text{NH}_2$ group.

Related literature

 For related structures containing picolinamidium cations, see: Uçar *et al.* (2004); Gotoh *et al.* (2009).


Experimental

Crystal data

 $(\text{C}_6\text{H}_7\text{N}_2\text{O})[\text{FeCl}_4]$
 $M_r = 320.79$
 Monoclinic, $P2_1/n$
 $a = 13.5252$ (8) Å
 $b = 6.1704$ (3) Å
 $c = 14.1165$ (7) Å

 $\beta = 93.853$ (2)°
 $V = 1175.44$ (11) Å³
 $Z = 4$
 Mo $K\alpha$ radiation

 $\mu = 2.16$ mm⁻¹
 $T = 180$ K
 $0.40 \times 0.30 \times 0.20$ mm

Data collection

 Bruker APEXII CCD diffractometer
 Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003)
 $T_{\min} = 0.484$, $T_{\max} = 0.672$

 15093 measured reflections
 2808 independent reflections
 2420 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.024$

Refinement

 $R[F^2 > 2\sigma(F^2)] = 0.020$
 $wR(F^2) = 0.049$
 $S = 1.05$
 2808 reflections
 140 parameters
 2 restraints

 H atoms treated by a mixture of independent and constrained refinement
 $\Delta\rho_{\max} = 0.26$ e Å⁻³
 $\Delta\rho_{\min} = -0.23$ e Å⁻³

Table 1

Hydrogen-bond geometry (Å, °).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$\text{N1}-\text{H1}\cdots\text{O1}^{\text{i}}$	0.85 (2)	2.00 (2)	2.7234 (16)	142 (2)
$\text{N2}-\text{H22}\cdots\text{Cl3}$	0.84 (1)	2.78 (2)	3.5710 (15)	160 (2)
$\text{N2}-\text{H21}\cdots\text{Cl1}^{\text{ii}}$	0.82 (1)	2.69 (2)	3.4811 (14)	163 (2)

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

Data collection: *APEX2* (Bruker, 2004); cell refinement: *SAINT* (Bruker, 2003); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

We are grateful to the Danish Natural Sciences Research Council and the Carlsberg Foundation for provision of the X-ray equipment.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: ZQ2012).

References

- Bruker (2003). *SAINT*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Bruker (2004). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Gotoh, K., Nagoshi, H. & Ishida, H. (2009). *Acta Cryst.* **C65**, o273–o277.
 Sheldrick, G. M. (2003). *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.
 Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
 Uçar, İ., Bulut, A., Yeşilel, O. Z. & Büyükgüngör, O. (2004). *Acta Cryst.* **C60**, o585–o588.

supplementary materials

Acta Cryst. (2009). E65, m1359 [doi:10.1107/S1600536809040148]

2-Carbamylpyridinium tetrachloridoferrate(III)

A. Nielsen, C. J. McKenzie and A. D. Bond

Comment

Picolinamidium cations are present in two other structures in the Cambridge Structural Database. One structure (refcode: EYIXAL; Uçar *et al.*, 2004) includes squarate anions, $C_4HO_4^-$, and contains planar picolinadinium:squarate layers in which all three N—H donors in picolinadinium form hydrogen bonds to squarate. The other (refcode: POVZEG; Gotoh *et al.*, 2009) contains chloranilate anions, $C_6HCl_2O_4^-$, in which all three N—H donors in picolinadinium form hydrogen bonds to chloranilate.

Experimental

Picolinamide (35 mg, 28 mmol) was dissolved in acetonitrile (2.75 ml) and anhydrous $FeCl_3$ (46 mg, 28 mmol) trimethylamine-*N*-oxide (32 mg, 28 mmol) and concentrated hydrochloric acid (0.2 ml) were added. After one week, a few milligrams of the title compound were deposited as yellow crystals.

Refinement

H atoms bound to C atoms were placed in idealized positions with C—H = 0.95 Å and refined as riding with $U_{iso}(H) = 1.2U_{eq}(C)$. H atoms bound to N were located in difference Fourier maps and refined with isotropic displacement parameters. The distances N2—H21 and N2—H22 were restrained to a common refined value, with an s.u. of 0.01 Å, and atom H1 was refined without restraint.

Figures

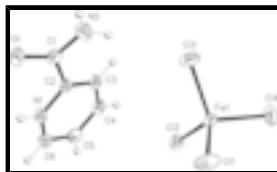


Fig. 1. Molecular structure with displacement ellipsoids shown at 50% probability for non-H atoms.

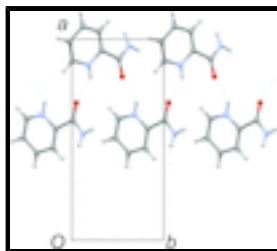


Fig. 2. Picolinamidium cations linked into chains along the *b* axis by $N^+—H\cdots O$ hydrogen bonds.

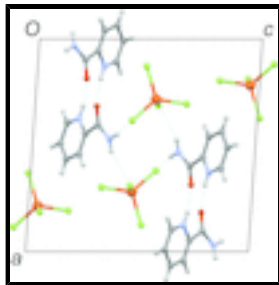


Fig. 3. Unit-cell contents projected along the *b* axis, showing FeCl_4^- anions between the hydrogen-bonded chains of picolinamidium cations.

2-Carbamylpyridinium tetrachloridoferrate(III)

Crystal data

$(\text{C}_6\text{H}_7\text{N}_2\text{O})[\text{FeCl}_4]$

$M_r = 320.79$

Monoclinic, $P2_1/n$

Hall symbol: -P 2yn

$a = 13.5252$ (8) Å

$b = 6.1704$ (3) Å

$c = 14.1165$ (7) Å

$\beta = 93.853$ (2)°

$V = 1175.44$ (11) Å³

$Z = 4$

$F_{000} = 636$

$D_x = 1.813$ Mg m⁻³

Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å

Cell parameters from 8949 reflections

$\theta = 2.2\text{--}28.1^\circ$

$\mu = 2.16$ mm⁻¹

$T = 180$ K

Block, yellow

$0.40 \times 0.30 \times 0.20$ mm

Data collection

Bruker–Nonius X8 APEXII CCD diffractometer

Radiation source: fine-focus sealed tube

Monochromator: graphite

$T = 180$ K

Thin-slice ω and φ scans

Absorption correction: multi-scan (SADABS; Sheldrick, 2003)

$T_{\min} = 0.484$, $T_{\max} = 0.672$

15093 measured reflections

2808 independent reflections

2420 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.024$

$\theta_{\max} = 28.3^\circ$

$\theta_{\min} = 3.6^\circ$

$h = -17 \rightarrow 15$

$k = -7 \rightarrow 8$

$l = -16 \rightarrow 18$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.020$

$wR(F^2) = 0.049$

$S = 1.05$

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

$$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.2718P]$$

where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.002$

2808 reflections $\Delta\rho_{\max} = 0.26 \text{ e } \text{\AA}^{-3}$
 140 parameters $\Delta\rho_{\min} = -0.23 \text{ e } \text{\AA}^{-3}$
 2 restraints Extinction correction: none
 Primary atom site location: structure-invariant direct methods

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>	$U_{\text{iso}}^*/U_{\text{eq}}$
O1	0.68522 (7)	1.05039 (17)	0.72326 (8)	0.0328 (2)
N1	0.62577 (9)	0.68301 (19)	0.79936 (8)	0.0223 (2)
H1	0.6851 (13)	0.703 (3)	0.7851 (11)	0.029 (4)*
N2	0.53208 (10)	1.1233 (2)	0.65734 (10)	0.0332 (3)
H21	0.5522 (13)	1.219 (3)	0.6233 (12)	0.044 (5)*
H22	0.4739 (11)	1.081 (3)	0.6457 (13)	0.045 (5)*
C1	0.59653 (10)	1.0119 (2)	0.71214 (10)	0.0236 (3)
C2	0.55609 (10)	0.8255 (2)	0.76671 (9)	0.0201 (3)
C3	0.45980 (10)	0.7950 (2)	0.78930 (9)	0.0229 (3)
H3A	0.4095	0.8939	0.7674	0.027*
C4	0.43698 (10)	0.6185 (2)	0.84436 (10)	0.0251 (3)
H4A	0.3707	0.5966	0.8608	0.030*
C5	0.51019 (11)	0.4743 (2)	0.87552 (10)	0.0279 (3)
H5A	0.4948	0.3523	0.9128	0.034*
C6	0.60612 (11)	0.5101 (2)	0.85165 (10)	0.0266 (3)
H6A	0.6576	0.4128	0.8722	0.032*
Fe1	0.283137 (14)	0.53471 (3)	0.540664 (13)	0.02141 (7)
Cl1	0.38209 (3)	0.39866 (6)	0.43917 (3)	0.04193 (11)
Cl2	0.30476 (3)	0.37620 (6)	0.67908 (2)	0.02817 (9)
Cl3	0.31100 (3)	0.88308 (6)	0.55199 (3)	0.03815 (10)
Cl4	0.12782 (3)	0.49004 (7)	0.48904 (3)	0.03714 (10)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
O1	0.0187 (5)	0.0355 (6)	0.0441 (6)	-0.0075 (4)	0.0024 (5)	0.0018 (5)
N1	0.0161 (6)	0.0268 (6)	0.0242 (6)	-0.0002 (5)	0.0030 (5)	-0.0048 (5)

supplementary materials

N2	0.0235 (7)	0.0325 (7)	0.0440 (8)	-0.0003 (6)	0.0041 (6)	0.0106 (6)
C1	0.0208 (7)	0.0231 (7)	0.0276 (7)	-0.0014 (5)	0.0058 (6)	-0.0055 (6)
C2	0.0186 (6)	0.0224 (6)	0.0194 (6)	-0.0013 (5)	0.0007 (5)	-0.0066 (5)
C3	0.0181 (7)	0.0290 (7)	0.0212 (7)	-0.0001 (5)	-0.0002 (5)	-0.0062 (6)
C4	0.0195 (7)	0.0341 (8)	0.0221 (7)	-0.0061 (6)	0.0048 (6)	-0.0083 (6)
C5	0.0337 (8)	0.0273 (7)	0.0232 (7)	-0.0047 (6)	0.0050 (6)	-0.0023 (6)
C6	0.0286 (8)	0.0259 (7)	0.0250 (7)	0.0032 (6)	-0.0001 (6)	-0.0015 (6)
Fe1	0.02269 (12)	0.01900 (10)	0.02251 (11)	-0.00276 (7)	0.00133 (8)	-0.00228 (8)
Cl1	0.0585 (3)	0.03076 (19)	0.0393 (2)	0.00053 (18)	0.0235 (2)	-0.00672 (16)
Cl2	0.03014 (19)	0.03054 (18)	0.02317 (18)	-0.00099 (14)	-0.00311 (14)	-0.00080 (14)
Cl3	0.0468 (2)	0.01959 (17)	0.0481 (2)	-0.00492 (15)	0.00358 (19)	-0.00486 (16)
Cl4	0.0283 (2)	0.0439 (2)	0.0376 (2)	-0.00929 (16)	-0.00973 (16)	0.01353 (17)

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

O1—C1	1.2225 (17)	C3—H3A	0.950
N1—C6	1.3341 (19)	C4—C5	1.381 (2)
N1—C2	1.3473 (18)	C4—H4A	0.950
N1—H1	0.85 (2)	C5—C6	1.380 (2)
N2—C1	1.319 (2)	C5—H5A	0.950
N2—H21	0.82 (1)	C6—H6A	0.950
N2—H22	0.84 (1)	Fe1—Cl3	2.1863 (4)
C1—C2	1.5073 (19)	Fe1—Cl2	2.1870 (4)
C2—C3	1.3744 (18)	Fe1—Cl1	2.1923 (4)
C3—C4	1.385 (2)	Fe1—Cl4	2.1941 (4)
C6—N1—C2	123.39 (13)	C5—C4—C3	120.23 (13)
C6—N1—H1	118.4 (11)	C5—C4—H4A	119.9
C2—N1—H1	118.2 (11)	C3—C4—H4A	119.9
C1—N2—H21	119.2 (13)	C6—C5—C4	119.00 (13)
C1—N2—H22	121.9 (13)	C6—C5—H5A	120.5
H21—N2—H22	117.1 (19)	C4—C5—H5A	120.5
O1—C1—N2	125.32 (14)	N1—C6—C5	119.25 (14)
O1—C1—C2	117.99 (13)	N1—C6—H6A	120.4
N2—C1—C2	116.68 (12)	C5—C6—H6A	120.4
N1—C2—C3	118.90 (13)	Cl3—Fe1—Cl2	111.243 (17)
N1—C2—C1	113.78 (12)	Cl3—Fe1—Cl1	108.329 (17)
C3—C2—C1	127.24 (12)	Cl2—Fe1—Cl1	111.207 (17)
C2—C3—C4	119.22 (13)	Cl3—Fe1—Cl4	107.713 (18)
C2—C3—H3A	120.4	Cl2—Fe1—Cl4	107.946 (16)
C4—C3—H3A	120.4	Cl1—Fe1—Cl4	110.350 (19)
C6—N1—C2—C3	1.15 (19)	N1—C2—C3—C4	-0.38 (19)
C6—N1—C2—C1	178.00 (12)	C1—C2—C3—C4	-176.75 (13)
O1—C1—C2—N1	-19.00 (18)	C2—C3—C4—C5	-0.5 (2)
N2—C1—C2—N1	162.32 (12)	C3—C4—C5—C6	0.6 (2)
O1—C1—C2—C3	157.53 (14)	C2—N1—C6—C5	-1.0 (2)
N2—C1—C2—C3	-21.1 (2)	C4—C5—C6—N1	0.1 (2)

Hydrogen-bond geometry (Å, °)

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N1—H1 \cdots O1 ⁱ	0.85 (2)	2.00 (2)	2.7234 (16)	142 (2)
N2—H22 \cdots Cl3	0.84 (1)	2.78 (2)	3.5710 (15)	160 (2)
N2—H21 \cdots Cl1 ⁱⁱ	0.82 (1)	2.69 (2)	3.4811 (14)	163 (2)

Symmetry codes: (i) $-x+3/2, y-1/2, -z+3/2$; (ii) $-x+1, -y+2, -z+1$.

Fig. 1

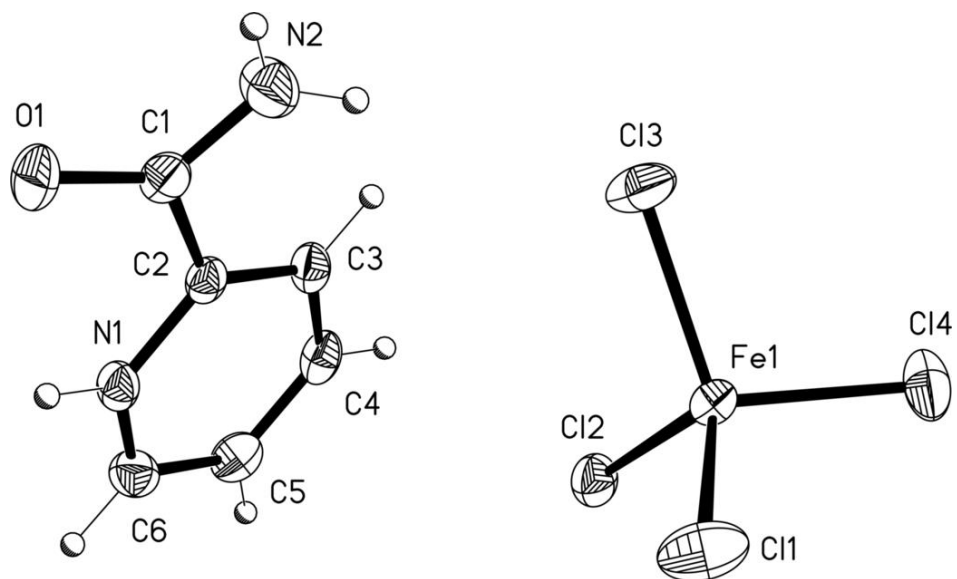


Fig. 2

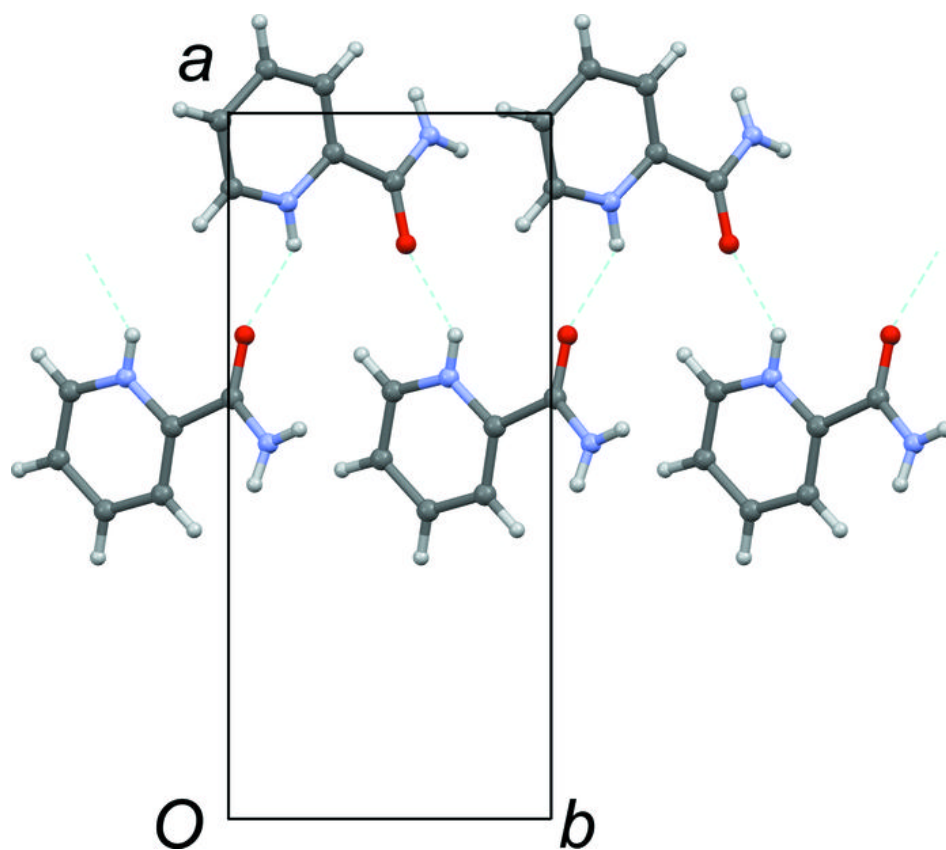


Fig. 3

