

Phase transitions and twinned low-temperature structures of tetraethylammonium tetrachloridoferrate(III)

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The title compound, $[(C_2H_5)_4N][FeCl_4]$, has at room temperature a disordered structure in the high-hexagonal space group $P6_3mc$. At 230 K, the structure is merohedrally twinned in the low-hexagonal space group $P6_3$. The volume has increased by a factor of 9 with respect to the room-temperature structure. At 170 and 110 K, the structure is identical in the orthorhombic space group $Pca2_1$ and twinned by reticular pseudomerohedry. The volume has doubled with respect to the room-temperature structure. All three space groups, *viz.* $P6_3mc$, $P6_3$ and $Pca2_1$, are polar and the direction of the polar axis is not affected by the twinning. In the $P6_3$ and $Pca2_1$ structures, all cations and anions are well ordered.

Keywords: crystal structure; phase transitions; twinned structures; tetraethylammonium tetrachloridoferrate(III); low-temperature structures; group–subgroup relationship.

1. Introduction

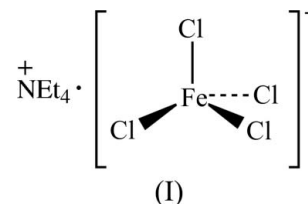
The crystal structure of tetraethylammonium tetrachloridoferrate(III), (I), is known from the literature (Evans *et al.*, 1990; Warnke *et al.*, 2010). The structure is isotypic with $[NEt_4][FeBrCl_3]$ (Evans *et al.*, 1990), $[NEt_4][InCl_4]$ (Trotter *et al.*, 1969) and $[NEt_4][TiCl_4]$ (Lenck *et al.*, 1991). After we had detected a new low-temperature phase of (I) by serendipity, we decided to investigate the temperature-dependent behaviour in more detail. The results of this study are presented here.

2. Experimental

2.1. Synthesis and crystallization

All reactions were performed at room temperature. A solution of NEt_4Cl (0.8454 g, 5 mmol) in ethanol (10 ml) was

added to a solution of $FeCl_3$ (0.8361 g, 5 mmol) in ethanol (25 ml) and the resulting suspension was stirred for 1 h. The precipitated $[Et_4N][FeCl_4]$ was isolated by filtration, dried in air overnight and redissolved in tetrahydrofuran. Slow evaporation in air afforded crystals suitable for X-ray diffraction (yield 170 mg, 10%).



2.2. Refinement

Crystal data, data collection and structure refinement details are summarized in Table 1. The crystal structure of (I) at 290 K, (Ia), was refined with a disorder model for the tetraethylammonium cation. Symmetry constraints were applied to atom N1, which is on the special position $3m1$. In order to model the disorder, the C atoms were introduced on general positions with an occupancy of $\frac{1}{6}$. The instruction ‘PART –1’ was used in the *SHELXL2013* (Sheldrick, 2008) refinement to suppress the generation of special position constraints for the C atoms. This model is overfitting the situation and also leads to a poor data-to-parameter ratio. Therefore 1,2- and 1,3-distance restraints (DFIX) for the ethyl groups were introduced together with ISOR instructions to approximate isotropic behaviour. For reflections 004 and $00\bar{4}$, the observed F^2 is significantly lower than the calculated F^2 . A correction for secondary extinction (EXTI instruction) was used to take this situation into account.

The crystal structure of (I) at 230 K, (Ib), was solved with *SHELXT* (Sheldrick, 2014) in the space group $P3$. The higher $P6_3$ symmetry was found with the ADDSYM routine of *PLATON* (Spek, 2009). The twin operation was found by coset decomposition of point group $6mm$ with respect to 6. Additional inversion twinning was included in early steps of the refinement but did not provide significant contributions [twin contributions of 0.00 (3) for both inverted components]. The inversion twinning was therefore omitted in the final refinement cycles. The twin fraction of the mirror plane refined to $BASF = 0.483$ (3).

The crystal structure of (I) at 110 K, (Id), was solved with *SHELXD* (Sheldrick, 2008) in the twin cell, with $V = 2901 \text{ \AA}^3$. The selected space group was $P2_1$, with the 12.8 \AA axis as the b axis and with $\beta = 120^\circ$. The R values remained high. Therefore, threefold twinning along b was included in *SHELXL2013*. This allowed successful refinement and completion of the structure solution. Using the ADDSYM routine of *PLATON*, the orthorhombic $Pca2_1$ subcell was located. Taking account of this information and the coset decomposition of point group $6mm$ with respect to $mm2$ (Table 2), the diffraction images were re-integrated with three orientation matrices. This integration results in a HKLF-5 type reflection file (Herbst-Irmer & Sheldrick, 1998) which contains the individual non-over-

Table 1
Experimental details.

	(Ia)	(Ib)	(Ic)	(Id)
Crystal data				
Chemical formula	(C ₈ H ₂₀ N)[FeCl ₄]	(C ₈ H ₂₀ N)[FeCl ₄]	(C ₈ H ₂₀ N)[FeCl ₄]	(C ₈ H ₂₀ N)[FeCl ₄]
<i>M_r</i>	327.90	327.90	327.90	327.90
Crystal system, space group	Hexagonal, <i>P6₃mc</i>	Hexagonal, <i>P6₃</i>	Orthorhombic, <i>Pca2₁</i>	Orthorhombic, <i>Pca2₁</i>
Temperature (K)	290	230	170	110
<i>a</i> , <i>b</i> , <i>c</i> (Å)	8.2154 (4), 8.2154 (4), 13.1972 (8)	24.5130 (6), 24.5130 (6), 13.0356 (5)	14.0182 (8), 8.1493 (5), 12.8767 (8)	13.9816 (6), 8.1243 (3), 12.8097 (6)
α , β , γ (°)	90, 90, 120	90, 90, 120	90, 90, 90	90, 90, 90
<i>V</i> (Å ³)	771.38 (10)	6783.5 (5)	1471.01 (15)	1455.06 (11)
<i>Z</i>	2	18	4	4
Radiation type	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α	Mo <i>K</i> α
μ (mm ⁻¹)	1.64	1.68	1.72	1.74
Crystal size (mm)	0.43 × 0.34 × 0.10	0.43 × 0.34 × 0.10	0.43 × 0.34 × 0.10	0.43 × 0.34 × 0.10
Data collection				
Diffractometer	Bruker Kappa APEXII diffractometer	Bruker Kappa APEXII diffractometer	Bruker Kappa APEXII diffractometer	Bruker Kappa APEXII diffractometer
Absorption correction	Multi-scan (<i>SADABS</i> ; Sheldrick, 2012)	Multi-scan (<i>SADABS</i> ; Sheldrick, 2012)	Multi-scan (<i>TWINABS</i> ; Sheldrick, 2012)	Multi-scan (<i>TWINABS</i> ; Sheldrick, 2012)
<i>T_{min}</i> , <i>T_{max}</i>	0.655, 0.746	0.660, 0.746	0.639, 0.746	0.655, 0.746
No. of measured, independent and observed [<i>I</i> > 2σ(<i>I</i>)] reflections	7971, 723, 630	75629, 10366, 8945	32765, 7746, 7535	49619, 7924, 7776
<i>R_{int}</i>	0.018	0.026	0.028	0.028
(sin θ/λ) _{max} (Å ⁻¹)	0.650	0.649	0.653	0.652
Refinement				
<i>R</i> [<i>F</i> ² > 2σ(<i>F</i> ²)], <i>wR</i> (<i>F</i> ²), <i>S</i>	0.023, 0.065, 1.09	0.032, 0.083, 1.03	0.014, 0.034, 1.03	0.012, 0.030, 1.04
No. of reflections	723	10366	7746	7924
No. of parameters	89	392	133	133
No. of restraints	67	1	1	1
H-atom treatment	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained	H-atom parameters constrained
$\Delta\rho_{\max}$, $\Delta\rho_{\min}$ (e Å ⁻³)	0.17, -0.12	0.37, -0.28	0.12, -0.27	0.12, -0.32
Absolute structure	Flack <i>x</i> determined using 279 quotients (Parsons <i>et al.</i> , 2013)	See text	See text	See text
Absolute structure parameter	0.037 (8)	–	–	–

Computer programs: *APEX2* (Bruker, 2007), *Peakref* (Schreurs, 2013), *Eval15* (Schreurs *et al.*, 2010), *SADABS* (Sheldrick, 2012), *TWINABS* (Sheldrick, 2012), *SHELXT* (Sheldrick, 2014), *SHELXD* (Sheldrick, 2008), *SHELXL2013* (Sheldrick, 2008), *PLATON* (Spek, 2009) and *DRAWxtl* (Finger *et al.*, 2007).

lapping reflections of all three twin components and the overlapping reflections with three contributors. Using all three twin components leads to an artificially high data-to-parameter ratio but allows the determination of the absolute structure for all twin components. *SHELXL2013* automatically corrects the standard uncertainties of the refined parameters for the high data-to-parameter ratio. The absolute structure was determined for the three twin components by a *SHELXL2013* refinement against subsets of the reflection file which contain only the non-overlapping reflections. The Flack

Table 2

Coset decomposition of point group $G = 6mm$ with respect to $H_1 = mm2$, $G = H_1 + g_2H_1 + g_3H_1$.

Matrices are given for a hexagonal base. They were retrieved from the Bilbao Crystallographic Server (Aroyo *et al.*, 2006). For the creation of the orientation matrices for the integration, only rotational operations can be selected to avoid left-handed coordinate systems.

<i>H</i> ₁	<i>g</i> ₂ <i>H</i> ₁	<i>g</i> ₃ <i>H</i> ₁
1 (100/010/001)	3 ⁺ _{0,0,z} (0 $\bar{1}$ 0/1 $\bar{1}$ 0/001)	<i>m</i> _{2<i>x,x,z</i>} (100/1 $\bar{1}$ 0/001)
2 _{0,0,z} ($\bar{1}$ 00/0 $\bar{1}$ 0/001)	6 ⁻ _{0,0,z} (010/1 $\bar{1}$ 0/001)	<i>m</i> _{0,y,z} ($\bar{1}$ 00/1 $\bar{1}$ 0/001)
<i>m</i> _{<i>x</i>,2<i>x,z</i>} ($\bar{1}$ 10/010/001)	<i>m</i> _{<i>x</i>,−<i>x,z</i>} (0 $\bar{1}$ 0/100/001)	3 ⁻ _{0,0,z} ($\bar{1}$ 10/100/001)
<i>m</i> _{<i>x</i>,0,z} (1 $\bar{1}$ 0/0 $\bar{1}$ 0/001)	<i>m</i> _{<i>x,x,z</i>} (010/100/001)	6 ⁺ _{0,0,z} (1 $\bar{1}$ 0/100/001)

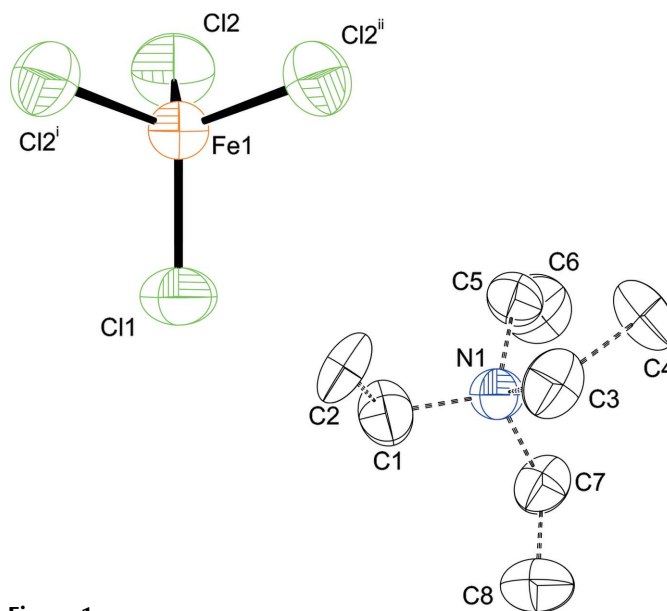
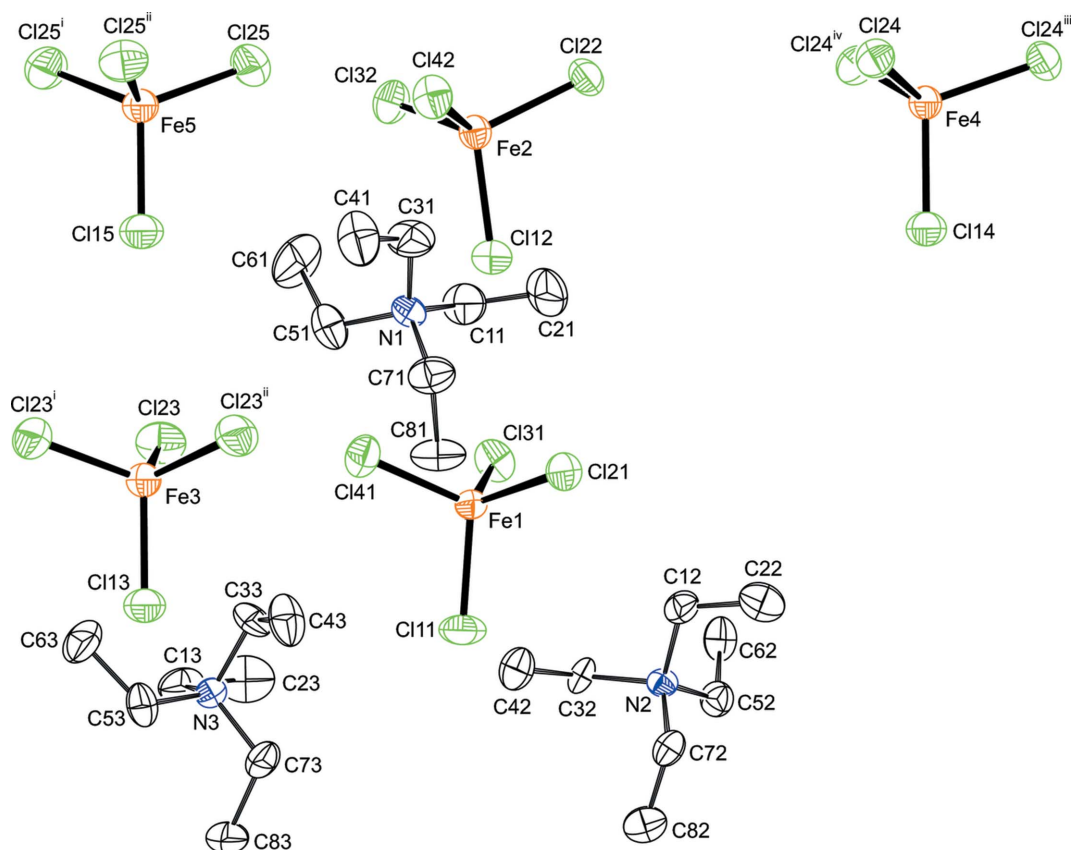


Figure 1
Displacement ellipsoid plot of (Ia) at 290 K (50% probability level). H atoms and all symmetry-generated C atoms of the disordered ethyl groups have been omitted for clarity. [Symmetry codes: (i) $-y, x - y, z$; (ii) $y - x, -x, z$.]


Figure 2

Displacement ellipsoid plot of (Ib) at 230 K (50% probability level). H atoms have been omitted for clarity. [Symmetry codes: (i) $-y + 1, x - y, z$; (ii) $-x + y + 1, -x + 1, z$; (iii) $-y, x - y, z$; (iv) $y - x, -x, z$.]

x values (Parsons *et al.*, 2013) were 0.021 (8), 0.026 (9) and 0.043 (9) for the three twin components. The refined twin fractions BASF for the pseudo-hexagonal twinning in the complete data set are 0.3244 (5) and 0.2933 (4) in (Id). Structure (Ic) was refined in the same way as (Id) using structure (Id) as the starting model. The Flack parameters based on the non-overlapping subsets of reflections result in $x = 0.034$ (9), 0.040 (10) and 0.039 (10). The pseudo-hexagonal twinning contributions refined to 0.3240 (5) and 0.2932 (5) in the full data set of (Ic).

The temperature-dependent unit-cell determinations were performed on a fresh crystal by cooling from 290 to 110 K with a cooling rate of 120 K h⁻¹. The temperature was controlled by a 700 Series cryostream manufactured by Oxford Cryo-systems.

3. Results and discussion

At 290 K [structure (Ia)], we could confirm the structure from the literature (Fig. 1). The identity of the unit-cell parameters was checked by simulated precession photos and by extensive peak searches. The space group is $P6_3mc$ and the $[\text{FeCl}_4]^-$ anion (see Table 3 for geometry) is located on a site with $3m1$ symmetry (C_{3v} , Wyckoff position a). The NET_4^+ cation is severely disordered on a second $3m1$ site (Wyckoff position b). The modelling of this disorder involves the fitting of the S_4 -

symmetric NET_4^+ cation on the C_{3v} site (see *Experimental*) and results in a featureless residual electron density. As already described by Trotter *et al.* (1969), the structure consists of alternating hexagonal layers of cations and anions, stacked in the c direction, and resembles a close-packed structure of the anti-NiAs structure type. The $[\text{FeCl}_4]^-$ anion is octahedrally surrounded by six NET_4^+ cations, with $\text{Fe}\cdots\text{N}$ distances of 5.723 (3) and 5.833 (3) Å. The NET_4^+ cation is in a trigonal prismatic environment of six $[\text{FeCl}_4]^-$ anions. Using the 'CALC SOLV' algorithm of *PLATON* (Spek, 2009), we estimate a volume of 286 Å³ for the $[\text{FeCl}_4]^-$ anion and a volume of 519 Å³ for the NET_4^+ cation.

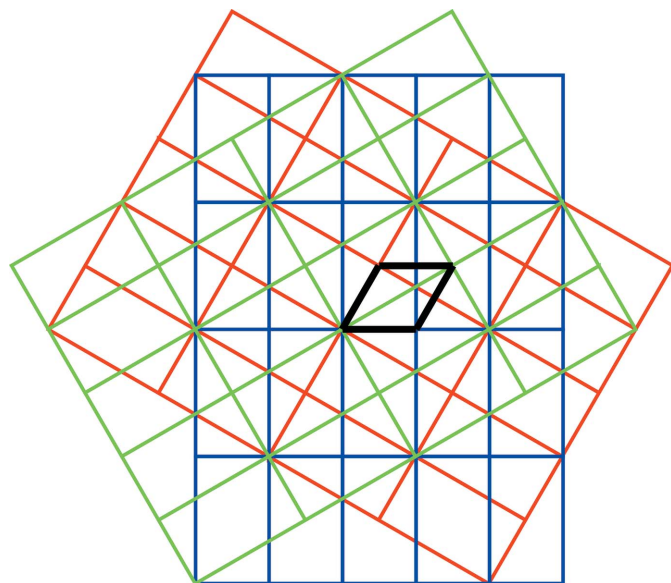
At 230 K [structure (Ib)], the lengths of the a and b axes increase by a factor of 3, respectively, and consequently the unit-cell volume increases by a factor of 9. The symmetry changes from $P6_3mc$ (point group $6mm$) to $P6_3$ (point group 6). Crystal structure (Ib) is twinned and the twin operation can be obtained by a coset decomposition (Flack, 1987) of the high-hexagonal $6mm$ with respect to the low-hexagonal point

Table 3

Selected geometric parameters (Å, °) for (Ia).

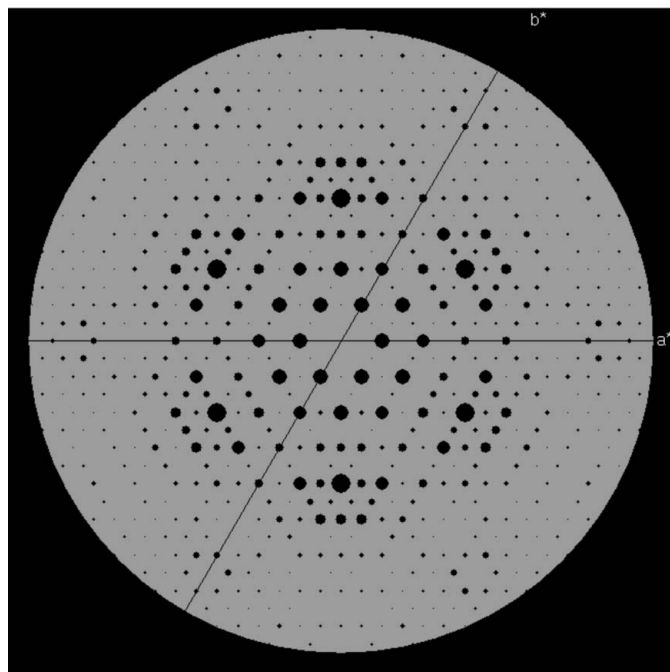
Fe1—Cl1	2.1853 (18)	Fe1—Cl2	2.1874 (12)
Cl1—Fe1—Cl2	109.06 (5)	Cl2 ⁱ —Fe1—Cl2	109.88 (5)

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


Figure 3

Threefold twin relationship between orthorhombic unit cells in (*Ic*) and (*Id*) in the reciprocal (*hk0*) plane. The selected twin operations are a 60° rotation and a 120° rotation about the *c* axis. The hexagonal twin cell is drawn with thick lines.

group 6. The subgroup index is 2 and all symmetry operations of the second coset are equally suitable. Arbitrarily, the matrix $(0\bar{1}0/\bar{1}00/001)$ was selected which corresponds to the mirror plane $m_{x,-x,z}$. Because this symmetry operation belongs to the hexagonal holoedry, the twinning is merohedral and reflections are not split. The twin operation has a determinant of -1 , but nevertheless does not invert the polarity of the *c* axis.


Figure 4

X-ray intensities in the (*hk0*) plane of structure (*Id*). Simulated precession image prepared with the *LAYER* software (Barbour, 1999). The drawn *a** and *b** axes are based on the hexagonal twin cell.

Table 4

Selected geometric parameters (Å, °) for (*Ib*).

Fe1—Cl11	2.1886 (17)	Fe2—Cl12	2.1968 (19)
Fe1—Cl41	2.196 (2)	Fe3—Cl13	2.188 (4)
Fe1—Cl31	2.198 (2)	Fe3—Cl23	2.198 (2)
Fe1—Cl21	2.2026 (18)	Fe4—Cl24	2.1999 (19)
Fe2—Cl32	2.189 (2)	Fe4—Cl14	2.202 (4)
Fe2—Cl22	2.1933 (18)	Fe5—Cl15	2.191 (4)
Fe2—Cl42	2.1940 (19)	Fe5—Cl25	2.196 (2)
Cl11—Fe1—Cl41	109.70 (9)	Cl32—Fe2—Cl12	108.32 (8)
Cl11—Fe1—Cl31	109.15 (8)	Cl22—Fe2—Cl12	108.24 (8)
Cl41—Fe1—Cl31	109.56 (8)	Cl42—Fe2—Cl12	109.76 (8)
Cl11—Fe1—Cl21	109.33 (8)	Cl13—Fe3—Cl23	109.07 (7)
Cl41—Fe1—Cl21	108.82 (8)	Cl23—Fe3—Cl23 ⁱ	109.87 (7)
Cl31—Fe1—Cl21	110.26 (7)	Cl24—Fe4—Cl24 ⁱⁱ	109.91 (6)
Cl32—Fe2—Cl22	110.84 (8)	Cl24—Fe4—Cl14	109.03 (6)
Cl32—Fe2—Cl42	109.88 (7)	Cl15—Fe5—Cl25	109.04 (8)
Cl22—Fe2—Cl42	109.76 (8)	Cl25 ⁱ —Fe5—Cl25	109.90 (7)

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

Table 5

Selected geometric parameters (Å, °) for (*Ic*).

Fe1—Cl4	2.1966 (7)	Fe1—Cl3	2.1985 (6)
Fe1—Cl1	2.1977 (7)	Fe1—Cl2	2.2030 (7)
Cl4—Fe1—Cl1	110.41 (3)	Cl4—Fe1—Cl2	110.58 (3)
Cl4—Fe1—Cl3	108.67 (3)	Cl1—Fe1—Cl2	107.85 (3)
Cl1—Fe1—Cl3	109.08 (3)	Cl3—Fe1—Cl2	110.24 (3)

Table 6

Twinned reflection data at 110 (2) K.

Analysis of systematic absences with *PLATON* (Spek, 2009). The corresponding unit cell is in the hexagonal setting (twin lattice), with $a = b = 16.1794$ (10), $c = 12.7974$ (5) Å, $\alpha = \beta = 90$, $\gamma = 120^\circ$ and $V = 2901.2$ (4) Å³.

Condition	$\langle I/\sigma \rangle$ true	$\langle I/\sigma \rangle$ false
$0kl, k = 2n$	26.27	0.21
$h0l, h = 2n$	26.30	0.23
$h00, h = 2n$	27.29	0.31
$0k0, k = 2n$	27.80	0.26
$00l, l = 2n$	31.90	0.79
$hhl, h = 2n$	26.57	0.21

This is in contrast to twofold twinning axes perpendicular to *c*, which would change the polarity. The latter are suggested by the twinning programs *TwinRotMat* in *PLATON* (Spek, 2009) and *ROTAX* (Cooper *et al.*, 2002).

The asymmetric unit of (*Ib*) contains three NEt_4^+ cations on general positions, two $[\text{FeCl}_4]^-$ anions on general positions and $3 \times \frac{1}{3} [\text{FeCl}_4]^-$ anions on threefold axes. The tetrahedra of the $[\text{FeCl}_4]^-$ anions in (*Ib*) (see Table 4 for geometry) fulfill nearly perfectly the symmetry of the $P6_3mc$ subcell in (*Ia*) and a transformation of the FeCl_4 substructure would be possible with the matrix $(\frac{1}{3}00/0\frac{1}{3}0/001)$, and by raising the symmetry to $P6_3mc$. The major difference with (*Ia*) is thus the ordering of the NEt_4^+ cations: in (*Ia*), the cation is heavily disordered, while the three independent cations in (*Ib*) are well ordered (Fig. 2). All three NEt_4^+ cations have approximate $\bar{4}$ (S_4) symmetry. The anti-NiAs structure type is maintained in (*Ib*), but as consequence of the lower symmetry there are now 18 independent $\text{Fe} \cdots \text{N}$ distances with a large variation between 5.581 (5) and 5.996 (6) Å. If the transformation matrix of the

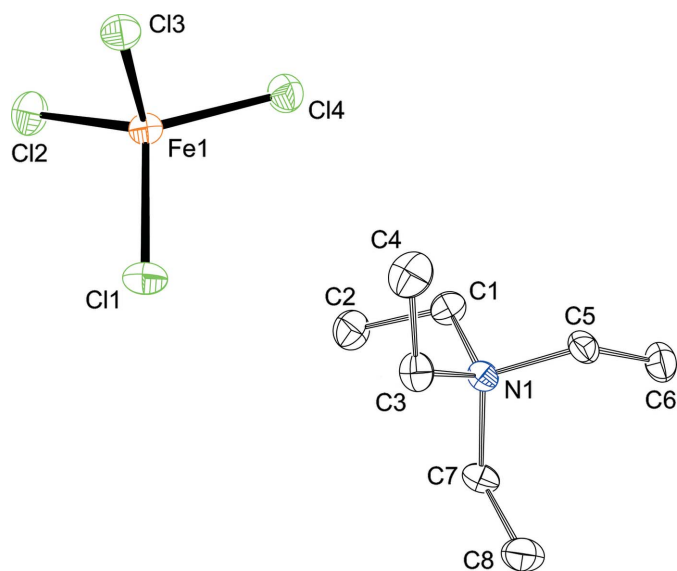


Figure 5 Displacement ellipsoid plot of (Ic) at 170 K (50% probability level). H atoms have been omitted for clarity.

FeCl₄ substructure is applied to the NEt₄⁺ cations, this will lead to severe NEt₄⁺ disorder.

The structures at 170 [structure (Ic)] and 110 K [structure (Id)] are identical (see Table 5 for geometry). They are described as a threefold twin ('Drilling') with an orthorhombic unit cell (Fig. 3). As a consequence of the twinning, a hexagonal twin cell with doubled volume is generated (Fig. 4). The hexagonal twin cell shows systematic absences which do not correspond to any of the hexagonal/trigonal space groups (Table 6). The orthorhombic space group *Pca*₂₁ belongs to point group *mm*2. A coset decomposition of point group *6mm* [structure (Ia)] with respect to *mm*2 [structures (Ic) and (Id)] has a subgroup index of 3 and the twin operations can be taken from the second and third coset (Table 6). We selected a 60°

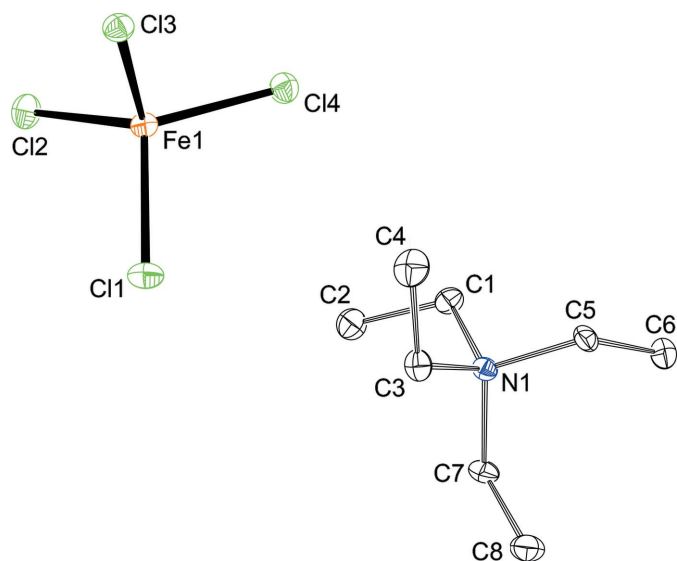


Figure 6 Displacement ellipsoid plot of (Id) at 110 K (50% probability level). H atoms have been omitted for clarity.

Table 7

Unit-cell parameters during the cooling of a single crystal of (I).

In the temperature range 220–110 K, the unit cell of the twin lattice is presented. The last column gives the number of reflections used for the cell refinement with the *Peakref* software (Schreurs, 2013). The detector position was kept fixed during the experiment. At each temperature, 3 ω scans of 6° were measured, respectively (0.5° scan angle).

<i>T</i> (K)	<i>a</i> , <i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Number of reflections
290	8.230 (6)	13.217 (14)	775.3 (14)	126
280	8.223 (6)	13.202 (15)	773.1 (16)	126
270	8.220 (6)	13.190 (12)	771.7 (15)	124
260	8.213 (6)	13.176 (14)	769.6 (16)	127
250	8.206 (5)	13.164 (14)	767.8 (16)	127
240	8.200 (6)	13.149 (11)	765.7 (15)	127
230	24.566 (12)	13.065 (6)	6829 (9)	581
220	16.328 (11)	12.972 (8)	2995 (5)	404
210	16.311 (8)	12.957 (7)	2985 (3)	416
200	16.299 (11)	12.944 (7)	2978 (5)	419
190	16.289 (8)	12.931 (7)	2971 (3)	426
180	16.278 (10)	12.916 (7)	2964 (4)	427
170	16.269 (9)	12.900 (7)	2957 (4)	440
160	16.259 (7)	12.890 (7)	2951 (3)	447
150	16.249 (10)	12.881 (7)	2945 (4)	448
140	16.241 (10)	12.863 (7)	2938 (4)	441
130	16.229 (10)	12.849 (7)	2931 (4)	449
120	16.218 (9)	12.838 (7)	2924 (4)	435
110	16.213 (8)	12.826 (7)	2920 (3)	438

rotation and a 120° rotation about the *c* axis as twin operations. According to the classification of Donnay & Donnay (1974), the twinning can be described as twinning by reticular pseudomerohedry or reticular TLQS. Nevertheless, no splitting of the overlapping reflections was observed in the diffraction images.

In the orthorhombic setting of (Ic) and (Id), the length of the *ab* diagonal is approximately 2*b*. Therefore, the orthorhombic unit cell can be transformed into the hexagonal twin cell using the matrix (1 $\bar{1}$ 0/020/001) with a determinant of +2. The resulting γ angles are 120.171 (2)° for (Ic) and 120.1596 (14)° for (Id). For the other two twin components, the corresponding matrices are (0 $\bar{2}$ 0/110/001) and ($\bar{1}\bar{1}$ 0/1 $\bar{1}$ 0/001). The geometrical situation is thus similar to the famous pseudo-hexagonal twinning of aragonite (Cahn, 1954), where

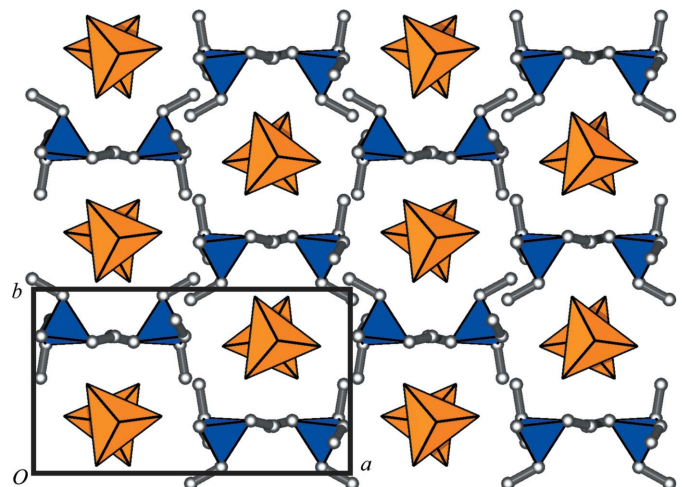


Figure 7 Pseudo-hexagonal packing in the crystal structure of (Id).

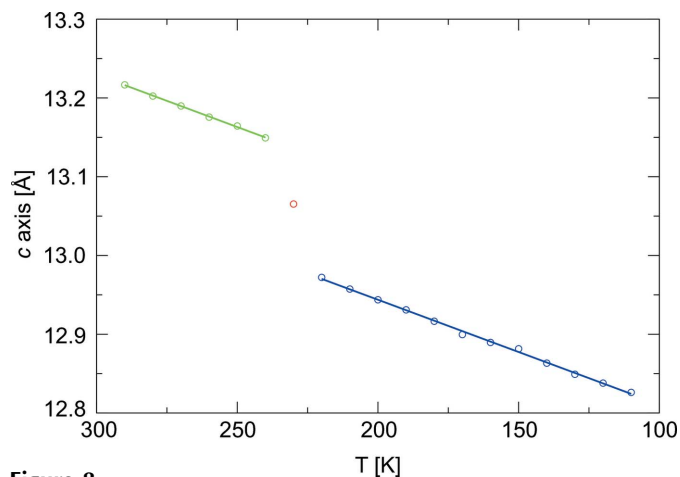


Figure 8
Length of the c axis as a function of temperature.

the ab diagonal of the orthorhombic cell has approximately the length of $2a$.

The FeCl_4 substructure in (Ic) and (Id) does not fulfill the translational symmetry of the (Ia) subcell. In (Id), the maximum difference in the distances between nearest Fe centres is 0.4787 (8) Å. For the distances between Cl centres, the maximal difference is 0.9896 (13) Å. The angle with the greatest deviation is $\text{Cl}\cdots\text{Cl}\cdots\text{Cl}$ of 113.83 (1)° (ideal value = 120°). If only the lattices of (Ia) and (Id) are considered, the degree of lattice distortion is $S = 0.0124$ (Capillas *et al.*, 2007).

In the $Pca2_1$ structures of (Ic) and (Id), all atoms are located on general positions. Plots of the asymmetric units of the two structures are shown in Figs. 5 and 6. The packing geometry of an octahedral surrounding of the $[\text{FeCl}_4]^-$ anion by six NEt_4^+ cations is retained, as well as the trigonal prismatic surrounding of NEt_4^+ by $[\text{FeCl}_4]^-$, but due to the lower symmetry there are now six independent $\text{Fe}\cdots\text{N}$ distances in the range 5.5315 (19)–5.8010 (19) Å. The pseudo-hexagonal packing of the cations and anions in orthorhombic structure (Id) is shown in Fig. 7.

In (Ia), the $[\text{FeCl}_4]^-$ anion has exact C_{3v} symmetry. A search for noncrystallographic symmetry (Pilati & Forni, 1998) results in the approximate point group T_d with an r.m.s. deviation of 0.0078 Å. This approximate T_d symmetry is retained in structures (Ib), (Ic) and (Id). In (Ib), two $[\text{FeCl}_4]^-$ ions are on general positions, and three anions have C_3 symmetry (Wyckoff positions a and b). In (Ic) and (Id), the $[\text{FeCl}_4]^-$ ion is on a general position. Over the whole temperature range, no significant changes were observed in the Fe–Cl distances. The range between 2.184 (3) and 2.2068 (6) Å is indicative of an Fe^{III} ion in high-spin state (Lauher & Ibers, 1975). One of the Fe–Cl bonds remains approximately collinear with the c axis over the whole temperature range.

The NEt_4^+ cation is disordered in the room-temperature structure (Ia) and ordered in the low-temperature phases (Ib) and (Ic)/(Id). In the low-temperature phases, the NEt_4^+ cations are on general positions but have an approximate noncrystallographic $\bar{4}$ (S_4) symmetry. The principal axis of

point group $\bar{4}$ (S_4) is not aligned to the unit-cell axes of (Ib) and (Ic)/(Id).

In a temperature-dependent unit-cell determination with fixed detector distance, the changes in the unit-cell parameters were monitored. The results are presented in Table 7 and a graphical representation of the c -axis length is shown in Fig. 8. From the symmetry considerations described above and the reversibility of the phase transitions, we conclude that the transitions are enantiomorphic. The change of the c axis is noncontinuous so that the transitions should be considered first-order. It becomes clear that structure (Ib) is stable only in a narrow temperature window. This is consistent with calorimetric studies (Navarro *et al.*, 1988), where transition temperatures of 234.7 (1) and 226.6 (1) K have been found. A third transition point at 217.5 (1) K was not detected in our unit-cell determinations. From the literature it is known that the phase transitions also affect the linewidth in electron paramagnetic resonance (EPR) spectra (Puertolas *et al.*, 1983). Unusual magnetic behaviour at the liquid helium temperature may be ascribed to the phase transitions above the liquid nitrogen temperature (Puertolas *et al.*, 1983a).

The thermal expansion tensor for the unit cells at 240 and 290 K shows the largest expansion along the c axis. The same situation is found in the low temperature phase for the unit cells at 110 and 220 K.

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Supporting information for this paper is available from the IUCr electronic archives (Reference: GZ3264).

References

- Aroyo, M. I., Perez-Mato, J. M., Capillas, C., Kroumova, E., Ivantchev, S., Madariaga, G., Kirov, A. & Wondratschek, H. (2006). *Z. Kristallogr.* **221**, 15–27.
- Barbour, L. J. (1999). *J. Appl. Cryst.* **32**, 351–352.
- Bruker (2007). *APEX2*. Bruker AXS Inc., Madison, Wisconsin, USA.
- Cahn, R. W. (1954). *Adv. Phys.* **3**, 363–445.
- Capillas, C., Perez-Mato, J. M. & Aroyo, M. I. (2007). *J. Phys. Condens. Matter*, **19**, 275203.
- Cooper, R. I., Gould, R. O., Parsons, S. & Watkin, D. J. (2002). *J. Appl. Cryst.* **35**, 168–174.
- Donnay, G. & Donnay, J. D. H. (1974). *Can. Mineral.* **12**, 422–425.
- Evans, D. J., Hills, A., Hughes, D. L. & Leigh, G. J. (1990). *Acta Cryst.* **C46**, 1818–1821.
- Finger, L. W., Kroeker, M. & Toby, B. H. (2007). *J. Appl. Cryst.* **40**, 188–192.
- Flack, H. D. (1987). *Acta Cryst.* **A43**, 564–568.
- Herbst-Irmer, R. & Sheldrick, G. M. (1998). *Acta Cryst.* **B54**, 443–449.
- Lauher, J. W. & Ibers, J. A. (1975). *Inorg. Chem.* **14**, 348–352.
- Lenck, M., Dou, S.-q. & Weiss, A. (1991). *Z. Naturforsch. Teil A Phys. Sci.* **46**, 777–784.
- Navarro, R., Puertolas, J. A., Palacio, F. & Gonzalez, D. (1988). *J. Chem. Thermodyn.* **20**, 373–384.
- Parsons, S., Flack, H. D. & Wagner, T. (2013). *Acta Cryst.* **B69**, 249–259.
- Pilati, T. & Forni, A. (1998). *J. Appl. Cryst.* **31**, 503–504.

- Puertolas, J. A., Navarro, R., Palacio, F., Gonzalez, D., Carlin, R. L. & van Duyneveldt, A. J. (1983a). *J. Magn. Magn. Mater.* **31–34**, 1067–1068.
- Puertolas, J. A., Orera, V. M., Palacio, F. & van Duyneveldt, A. J. (1983). *Phys. Lett. A*, **98**, 374–376.
- Schreurs, A. M. M. (2013). *Peakref*. Utrecht University, The Netherlands.
- Schreurs, A. M. M., Xian, X. & Kroon-Batenburg, L. M. J. (2010). *J. Appl. Cryst.* **43**, 70–82.
- Sheldrick, G. M. (2008). *Acta Cryst.* **A64**, 112–122.
- Sheldrick, G. M. (2012). *SADABS* and *TWINABS*. University of Göttingen, Germany.
- Sheldrick, G. M. (2014). *SHELXT*. University of Göttingen, Germany.
- Spek, A. L. (2009). *Acta Cryst.* **D65**, 148–155.
- Trotter, J., Einstein, F. W. B. & Tuck, D. G. (1969). *Acta Cryst.* **B25**, 603–604.
- Warnke, Z., Styczeń, E., Wyrzykowski, D., Sikorski, A., Klak, J. & Mroziński, J. (2010). *Struct. Chem.* **21**, 285–289.

supplementary materials

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Phase transitions and twinned low-temperature structures of tetraethylammonium tetrachloridoferrate(III)

Martin Lutz, Yuxing Huang, Marc-Etienne Moret and Robertus J. M. Klein Gebbink

Computing details

For all compounds, data collection: *APEX2* (Bruker, 2007). Cell refinement: *Peakref* (Schreurs, 2013) for (Ia); *Peakref* (Schreurs, 2013) for (Ib), (Ic), (Id). Data reduction: *Eval15* (Schreurs *et al.*, 2010) and *SADABS* (Sheldrick, 2012) for (Ia); *Eval15* (Schreurs *et al.*, 2010) and *SADABS* (Sheldrick, 2012) for (Ib); *Eval15* (Schreurs *et al.*, 2010) and *TWINABS* (Sheldrick, 2012) for (Ic), (Id). Program(s) used to solve structure: coordinates from the literature (Evans *et al.*, 1990) for (Ia); *SHELXT* (Sheldrick, 2014) for (Ib); *SHELXD* (Sheldrick, 2008) for (Ic), (Id). For all compounds, program(s) used to refine structure: *SHELXL2013* (Sheldrick, 2008). Molecular graphics: *PLATON* (Spek, 2009) for (Ia), (Ib), (Ic); *PLATON* (Spek, 2009) and *DRAWxtl* (Finger *et al.*, 2007) for (Id). For all compounds, software used to prepare material for publication: manual editing of the *SHELXL* output.

(Ia) Tetraethylammonium tetrachloridoferrate(III)

Crystal data

(C₈H₂₀N)[FeCl₄]
 $M_r = 327.90$
 Hexagonal, *P6₃mc*
 $a = 8.2154$ (4) Å
 $c = 13.1972$ (8) Å
 $V = 771.38$ (10) Å³
 $Z = 2$
 $F(000) = 338$

$D_x = 1.412$ Mg m⁻³
 Mo *Kα* radiation, $\lambda = 0.71073$ Å
 Cell parameters from 6539 reflections
 $\theta = 1.5$ – 27.4°
 $\mu = 1.64$ mm⁻¹
 $T = 290$ K
 Block, yellow
 $0.43 \times 0.34 \times 0.10$ mm

Data collection

Bruker Kappa APEXII
 diffractometer
 Radiation source: sealed tube
 φ and ω scans
 Absorption correction: multi-scan
 (*SADABS*; Sheldrick, 2012)
 $T_{\min} = 0.655$, $T_{\max} = 0.746$
 7971 measured reflections

723 independent reflections
 630 reflections with $I > 2\sigma(I)$
 $R_{\text{int}} = 0.018$
 $\theta_{\text{max}} = 27.5^\circ$, $\theta_{\text{min}} = 2.9^\circ$
 $h = -9 \rightarrow 10$
 $k = -10 \rightarrow 10$
 $l = -17 \rightarrow 17$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.023$
 $wR(F^2) = 0.065$
 $S = 1.09$
 723 reflections

89 parameters
 67 restraints
 Primary atom site location: heavy-atom method
 Secondary atom site location: difference Fourier
 map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0438P)^2 + 0.020P]$$

$$\text{where } P = (F_o^2 + 2F_c^2)/3$$

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

$$\Delta\rho_{\max} = 0.17 \text{ e } \text{\AA}^{-3}$$

$$\Delta\rho_{\min} = -0.12 \text{ e } \text{\AA}^{-3}$$

Extinction correction: *SHELXL2013* (Sheldrick, 2008), $F_c^* = kF_c[1 + 0.001x F_c^2 \lambda^3 / \sin(2\theta)]^{-1/4}$

Extinction coefficient: 0.029 (5)

Absolute structure: Flack *x* determined using 279 quotients $[(I^+) - (I^-)] / [(I^+) + (I^-)]$ (Parsons *et al.*, 2013)

Absolute structure parameter: 0.037 (8)

Special details

Experimental. loop_diffn_orient_matrix_type_diffn_orient_matrix_UB_11_diffn_orient_matrix_UB_12_diffn_orient_matrix_UB_13_diffn_orient_matrix_UB_21_diffn_orient_matrix_UB_22_diffn_orient_matrix_UB_23_diffn_orient_matrix_UB_31_diffn_orient_matrix_UB_32_diffn_orient_matrix_UB_33 'Nonius RMAT' -0.1081025 -0.1109448 -0.0330182 0.0870893 -0.0431466 -0.0249854 -0.0219582 -0.0747162 0.0634565

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.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ. (<1)
N1	0.6667	0.3333	0.2509 (4)	0.0514 (9)	
C1	0.506 (2)	0.1351 (13)	0.2329 (13)	0.070 (5)	0.1667
H1A	0.3914	0.1284	0.2564	0.084*	0.1667
H1B	0.4939	0.1132	0.1603	0.084*	0.1667
C2	0.521 (4)	-0.0216 (18)	0.2812 (14)	0.062 (7)	0.1667
H2A	0.4105	-0.1391	0.2655	0.093*	0.1667
H2B	0.5311	-0.0040	0.3533	0.093*	0.1667
H2C	0.6299	-0.0223	0.2559	0.093*	0.1667
C3	0.8493 (18)	0.319 (2)	0.2650 (13)	0.071 (5)	0.1667
H3A	0.8150	0.1975	0.2935	0.085*	0.1667
H3B	0.9055	0.3281	0.1991	0.085*	0.1667
C4	0.992 (3)	0.470 (3)	0.333 (3)	0.061 (10)	0.1667
H4A	1.0998	0.4551	0.3389	0.092*	0.1667
H4B	0.9377	0.4612	0.3983	0.092*	0.1667
H4C	1.0289	0.5913	0.3039	0.092*	0.1667
C5	0.643 (2)	0.422 (2)	0.3435 (8)	0.065 (5)	0.1667
H5A	0.7614	0.4816	0.3797	0.078*	0.1667
H5B	0.5514	0.3228	0.3866	0.078*	0.1667
C6	0.582 (6)	0.565 (5)	0.330 (3)	0.086 (12)	0.1667
H6A	0.5713	0.6109	0.3955	0.128*	0.1667
H6B	0.4626	0.5087	0.2966	0.128*	0.1667
H6C	0.6736	0.6682	0.2904	0.128*	0.1667
C7	0.6973 (19)	0.4544 (16)	0.1589 (7)	0.057 (4)	0.1667
H7A	0.5858	0.4649	0.1493	0.068*	0.1667
H7B	0.8007	0.5795	0.1733	0.068*	0.1667
C8	0.739 (2)	0.390 (5)	0.0602 (7)	0.077 (7)	0.1667
H8A	0.7578	0.4783	0.0078	0.115*	0.1667
H8B	0.6350	0.2687	0.0426	0.115*	0.1667

H8C	0.8503	0.3805	0.0676	0.115*	0.1667
Fe1	0.0000	0.0000	0.50819 (8)	0.0649 (3)	
Cl1	0.0000	0.0000	0.34260 (12)	0.0928 (8)	
Cl2	-0.14530 (8)	0.14530 (8)	0.56231 (13)	0.1007 (4)	

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0534 (12)	0.0534 (12)	0.047 (2)	0.0267 (6)	0.000	0.000
C1	0.062 (8)	0.059 (8)	0.079 (10)	0.022 (6)	-0.008 (7)	-0.003 (7)
C2	0.049 (15)	0.054 (8)	0.090 (12)	0.031 (7)	0.032 (10)	0.034 (7)
C3	0.059 (8)	0.073 (8)	0.089 (11)	0.040 (7)	0.010 (8)	0.015 (9)
C4	0.084 (14)	0.03 (2)	0.089 (15)	0.045 (10)	-0.033 (11)	-0.024 (10)
C5	0.069 (11)	0.058 (10)	0.055 (6)	0.022 (9)	0.007 (5)	-0.018 (6)
C6	0.07 (2)	0.10 (3)	0.089 (18)	0.05 (2)	0.009 (14)	-0.013 (15)
C7	0.050 (9)	0.062 (6)	0.062 (6)	0.032 (5)	0.002 (5)	0.018 (5)
C8	0.100 (11)	0.089 (15)	0.053 (4)	0.055 (9)	0.003 (6)	-0.003 (9)
Fe1	0.0668 (4)	0.0668 (4)	0.0613 (5)	0.03339 (18)	0.000	0.000
Cl1	0.1090 (13)	0.1090 (13)	0.0606 (13)	0.0545 (6)	0.000	0.000
Cl2	0.1134 (7)	0.1134 (7)	0.1018 (7)	0.0767 (7)	0.0080 (3)	-0.0080 (3)

Geometric parameters (Å, °)

N1—C5	1.486 (9)	C5—C6	1.500 (14)
N1—C7	1.509 (9)	C5—H5A	0.9700
N1—C1	1.516 (10)	C5—H5B	0.9700
N1—C3	1.572 (10)	C6—H6A	0.9600
C1—C2	1.493 (13)	C6—H6B	0.9600
C1—H1A	0.9700	C6—H6C	0.9600
C1—H1B	0.9700	C7—C8	1.509 (15)
C2—H2A	0.9600	C7—H7A	0.9700
C2—H2B	0.9600	C7—H7B	0.9700
C2—H2C	0.9600	C8—H8A	0.9600
C3—C4	1.502 (13)	C8—H8B	0.9600
C3—H3A	0.9700	C8—H8C	0.9600
C3—H3B	0.9700	Fe1—Cl1	2.1853 (18)
C4—H4A	0.9600	Fe1—Cl2 ⁱ	2.1874 (12)
C4—H4B	0.9600	Fe1—Cl2 ⁱⁱ	2.1874 (12)
C4—H4C	0.9600	Fe1—Cl2	2.1874 (12)
C5—N1—C7	111.0 (6)	N1—C5—C6	117.8 (13)
C5—N1—C1	113.6 (9)	N1—C5—H5A	107.9
C7—N1—C1	110.5 (8)	C6—C5—H5A	107.9
C5—N1—C3	107.7 (8)	N1—C5—H5B	107.9
C7—N1—C3	107.0 (8)	C6—C5—H5B	107.9
C1—N1—C3	106.7 (7)	H5A—C5—H5B	107.2
C2—C1—N1	117.3 (11)	C5—C6—H6A	109.5
C2—C1—H1A	108.0	C5—C6—H6B	109.5
N1—C1—H1A	108.0	H6A—C6—H6B	109.5
C2—C1—H1B	108.0	C5—C6—H6C	109.5

N1—C1—H1B	108.0	H6A—C6—H6C	109.5
H1A—C1—H1B	107.2	H6B—C6—H6C	109.5
C1—C2—H2A	109.5	C8—C7—N1	117.0 (13)
C1—C2—H2B	109.5	C8—C7—H7A	108.0
H2A—C2—H2B	109.5	N1—C7—H7A	108.0
C1—C2—H2C	109.5	C8—C7—H7B	108.0
H2A—C2—H2C	109.5	N1—C7—H7B	108.0
H2B—C2—H2C	109.5	H7A—C7—H7B	107.3
C4—C3—N1	112.8 (11)	C7—C8—H8A	109.5
C4—C3—H3A	109.0	C7—C8—H8B	109.5
N1—C3—H3A	109.0	H8A—C8—H8B	109.5
C4—C3—H3B	109.0	C7—C8—H8C	109.5
N1—C3—H3B	109.0	H8A—C8—H8C	109.5
H3A—C3—H3B	107.8	H8B—C8—H8C	109.5
C3—C4—H4A	109.5	Cl1—Fe1—Cl2 ⁱ	109.06 (6)
C3—C4—H4B	109.5	Cl1—Fe1—Cl2 ⁱⁱ	109.06 (5)
H4A—C4—H4B	109.5	Cl2 ⁱ —Fe1—Cl2 ⁱⁱ	109.88 (5)
C3—C4—H4C	109.5	Cl1—Fe1—Cl2	109.06 (5)
H4A—C4—H4C	109.5	Cl2 ⁱ —Fe1—Cl2	109.88 (5)
H4B—C4—H4C	109.5	Cl2 ⁱⁱ —Fe1—Cl2	109.88 (5)
C5—N1—C1—C2	-88.2 (16)	C7—N1—C5—C6	22 (2)
C7—N1—C1—C2	146.3 (15)	C1—N1—C5—C6	-103 (2)
C3—N1—C1—C2	30 (2)	C3—N1—C5—C6	139 (2)
C5—N1—C3—C4	-28 (2)	C5—N1—C7—C8	175.4 (11)
C7—N1—C3—C4	91 (2)	C1—N1—C7—C8	-57.7 (14)
C1—N1—C3—C4	-150.6 (19)	C3—N1—C7—C8	58.1 (13)

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

(Ib) Tetraethylammonium tetrachloridoferrate(III)

Crystal data

(C₈H₂₀N)[FeCl₄]

$M_r = 327.90$

Hexagonal, $P6_3$

$a = 24.5130$ (6) Å

$c = 13.0356$ (5) Å

$V = 6783.5$ (5) Å³

$Z = 18$

$F(000) = 3042$

$D_x = 1.445$ Mg m⁻³

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

Cell parameters from 54564 reflections

$\theta = 1.6$ – 27.5°

$\mu = 1.68$ mm⁻¹

$T = 230$ K

Block, yellow

$0.43 \times 0.34 \times 0.10$ mm

Data collection

Bruker Kappa APEXII

diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan

(*SADABS*; Sheldrick, 2012)

$T_{\min} = 0.660$, $T_{\max} = 0.746$

75629 measured reflections

10366 independent reflections

8945 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.026$

$\theta_{\max} = 27.5^\circ$, $\theta_{\min} = 1.6^\circ$

$h = -27 \rightarrow 31$

$k = -30 \rightarrow 30$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2
 Least-squares matrix: full
 $R[F^2 > 2\sigma(F^2)] = 0.032$
 $wR(F^2) = 0.083$
 $S = 1.03$
 10366 reflections
 392 parameters
 1 restraint
 Primary atom site location: heavy-atom method

Secondary atom site location: difference Fourier map
 Hydrogen site location: inferred from neighbouring sites
 H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0386P)^2 + 1.8713P]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.019$
 $\Delta\rho_{\max} = 0.37 \text{ e } \text{\AA}^{-3}$
 $\Delta\rho_{\min} = -0.28 \text{ e } \text{\AA}^{-3}$

Special details

Experimental. loop_diffn_orient_matrix_type_diffn_orient_matrix_UB_11_diffn_orient_matrix_UB_12_diffn_orient_matrix_UB_13_diffn_orient_matrix_UB_21_diffn_orient_matrix_UB_22_diffn_orient_matrix_UB_23_diffn_orient_matrix_UB_31_diffn_orient_matrix_UB_32_diffn_orient_matrix_UB_33 'Nonius RMat' -0.0007468 0.0364094 -0.0331586 -0.0437700 -0.0289410 -0.0250654 -0.0173985 0.0074731 0.0644811

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. Refined as a 2-component inversion twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.4403 (2)	0.2207 (2)	0.5833 (5)	0.0306 (13)
C11	0.3821 (3)	0.1560 (3)	0.5953 (5)	0.0551 (18)
H11A	0.3784	0.1309	0.5345	0.066*
H11B	0.3883	0.1352	0.6547	0.066*
C21	0.3212 (4)	0.1560 (3)	0.6091 (6)	0.065 (3)
H21A	0.3276	0.1893	0.6564	0.097*
H21B	0.2895	0.1157	0.6365	0.097*
H21C	0.3072	0.1631	0.5434	0.097*
C31	0.4484 (4)	0.2584 (3)	0.6780 (5)	0.0600 (17)
H31A	0.4526	0.2360	0.7369	0.072*
H31B	0.4102	0.2611	0.6883	0.072*
C41	0.5046 (3)	0.3245 (4)	0.6758 (7)	0.068 (2)
H41A	0.5431	0.3225	0.6788	0.102*
H41B	0.5027	0.3480	0.7343	0.102*
H41C	0.5039	0.3453	0.6129	0.102*
C51	0.4964 (3)	0.2122 (3)	0.5650 (5)	0.0502 (15)
H51A	0.5335	0.2536	0.5521	0.060*
H51B	0.4887	0.1867	0.5030	0.060*
C61	0.5117 (4)	0.1801 (4)	0.6554 (7)	0.079 (3)
H61A	0.5105	0.1994	0.7197	0.119*
H61B	0.5533	0.1855	0.6457	0.119*
H61C	0.4807	0.1356	0.6570	0.119*
C71	0.4329 (3)	0.2544 (3)	0.4953 (4)	0.0529 (17)
H71A	0.4717	0.2952	0.4875	0.063*

H71B	0.3986	0.2627	0.5100	0.063*
C81	0.4186 (5)	0.2170 (4)	0.3908 (6)	0.068 (2)
H81A	0.4553	0.2146	0.3698	0.101*
H81B	0.4084	0.2386	0.3384	0.101*
H81C	0.3832	0.1747	0.4001	0.101*
N2	0.2260 (2)	0.10845 (19)	0.0871 (4)	0.0263 (12)
C12	0.2195 (3)	0.1384 (3)	0.1860 (4)	0.0383 (13)
H12A	0.2171	0.1119	0.2439	0.046*
H12B	0.2577	0.1795	0.1948	0.046*
C22	0.1629 (3)	0.1479 (4)	0.1904 (5)	0.058 (2)
H22A	0.1684	0.1801	0.1416	0.088*
H22B	0.1590	0.1609	0.2590	0.088*
H22C	0.1251	0.1086	0.1735	0.088*
C32	0.2836 (2)	0.1016 (2)	0.0990 (4)	0.0308 (12)
H32A	0.2851	0.0772	0.0406	0.037*
H32B	0.2782	0.0767	0.1610	0.037*
C42	0.3474 (3)	0.1622 (3)	0.1062 (5)	0.0462 (17)
H42A	0.3521	0.1895	0.0491	0.069*
H42B	0.3808	0.1519	0.1040	0.069*
H42C	0.3498	0.1835	0.1702	0.069*
C52	0.1688 (3)	0.0441 (3)	0.0678 (5)	0.0374 (13)
H52A	0.1323	0.0496	0.0572	0.045*
H52B	0.1757	0.0272	0.0041	0.045*
C62	0.1532 (3)	-0.0035 (4)	0.1507 (4)	0.0465 (15)
H62A	0.1907	-0.0052	0.1690	0.070*
H62B	0.1209	-0.0445	0.1265	0.070*
H62C	0.1378	0.0083	0.2104	0.070*
C72	0.2332 (3)	0.1518 (2)	-0.0031 (4)	0.0332 (13)
H72A	0.1942	0.1536	-0.0088	0.040*
H72B	0.2672	0.1944	0.0132	0.040*
C82	0.2465 (3)	0.1341 (3)	-0.1035 (5)	0.0443 (16)
H82A	0.2849	0.1319	-0.0994	0.066*
H82B	0.2517	0.1653	-0.1542	0.066*
H82C	0.2118	0.0933	-0.1234	0.066*
N3	0.5579 (2)	0.1076 (2)	0.0842 (4)	0.0273 (12)
C13	0.5644 (3)	0.0495 (3)	0.0986 (5)	0.0533 (18)
H13A	0.5894	0.0548	0.1603	0.064*
H13B	0.5871	0.0455	0.0398	0.064*
C23	0.5005 (4)	-0.0111 (4)	0.1086 (5)	0.066 (3)
H23A	0.4752	-0.0051	0.1597	0.098*
H23B	0.5070	-0.0454	0.1294	0.098*
H23C	0.4789	-0.0210	0.0430	0.098*
C33	0.5298 (3)	0.1180 (3)	0.1804 (5)	0.0462 (15)
H33A	0.4894	0.0799	0.1942	0.055*
H33B	0.5579	0.1240	0.2382	0.055*
C43	0.5193 (3)	0.1730 (3)	0.1758 (7)	0.058 (2)
H43A	0.5592	0.2117	0.1853	0.086*
H43B	0.4903	0.1692	0.2295	0.086*
H43C	0.5018	0.1738	0.1095	0.086*

C53	0.6236 (2)	0.1631 (3)	0.0666 (5)	0.0461 (14)
H53A	0.6403	0.1553	0.0034	0.055*
H53B	0.6201	0.2007	0.0554	0.055*
C63	0.6709 (4)	0.1771 (4)	0.1517 (6)	0.067 (3)
H63A	0.6505	0.1716	0.2176	0.101*
H63B	0.7053	0.2201	0.1453	0.101*
H63C	0.6874	0.1485	0.1466	0.101*
C73	0.5187 (3)	0.1018 (3)	-0.0061 (4)	0.0452 (14)
H73A	0.5179	0.1412	-0.0139	0.054*
H73B	0.4754	0.0682	0.0071	0.054*
C83	0.5414 (4)	0.0874 (6)	-0.1086 (6)	0.065 (2)
H83A	0.5829	0.1220	-0.1254	0.098*
H83B	0.5121	0.0821	-0.1630	0.098*
H83C	0.5433	0.0490	-0.1013	0.098*
Fe1	0.33737 (4)	0.00273 (4)	0.33582 (7)	0.0309 (3)
Cl11	0.34314 (9)	-0.00199 (9)	0.16880 (12)	0.0561 (5)
Cl21	0.28054 (8)	0.04653 (8)	0.37520 (14)	0.0416 (4)
Cl31	0.29398 (9)	-0.09301 (9)	0.39937 (15)	0.0476 (4)
Cl41	0.43228 (9)	0.06036 (9)	0.39996 (15)	0.0495 (5)
Fe2	0.33198 (4)	0.00257 (4)	0.83363 (8)	0.0343 (3)
Cl12	0.31821 (9)	-0.00591 (9)	0.66663 (12)	0.0527 (4)
Cl22	0.23922 (8)	-0.03776 (9)	0.90686 (15)	0.0445 (4)
Cl32	0.37979 (9)	-0.04888 (9)	0.87898 (15)	0.0477 (5)
Cl42	0.38968 (9)	0.10216 (8)	0.87606 (16)	0.0490 (5)
Fe3	0.6667	0.3333	0.35736 (15)	0.0378 (5)
Cl13	0.6667	0.3333	0.1895 (3)	0.0494 (11)
Cl23	0.62767 (10)	0.23610 (10)	0.41246 (14)	0.0596 (6)
Fe4	0.0000	0.0000	0.86279 (12)	0.0346 (4)
Cl14	0.0000	0.0000	0.6938 (2)	0.0467 (8)
Cl24	0.06233 (8)	0.09662 (9)	0.91781 (13)	0.0459 (4)
Fe5	0.6667	0.3333	0.85790 (15)	0.0395 (5)
Cl15	0.6667	0.3333	0.6898 (3)	0.0532 (11)
Cl25	0.56964 (10)	0.27434 (10)	0.91285 (14)	0.0594 (5)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.036 (3)	0.024 (3)	0.031 (3)	0.014 (2)	0.007 (2)	0.006 (2)
C11	0.048 (4)	0.042 (4)	0.053 (4)	0.006 (3)	0.000 (3)	0.000 (3)
C21	0.041 (5)	0.055 (5)	0.073 (6)	0.005 (3)	0.013 (4)	0.007 (4)
C31	0.076 (5)	0.067 (4)	0.045 (3)	0.042 (4)	-0.006 (4)	-0.023 (3)
C41	0.050 (4)	0.046 (4)	0.098 (6)	0.017 (4)	0.000 (4)	-0.027 (5)
C51	0.043 (4)	0.046 (4)	0.065 (4)	0.025 (3)	0.012 (3)	0.000 (3)
C61	0.092 (7)	0.089 (7)	0.090 (6)	0.070 (6)	-0.026 (5)	0.007 (5)
C71	0.064 (5)	0.042 (4)	0.043 (3)	0.020 (3)	-0.002 (3)	0.006 (3)
C81	0.095 (8)	0.075 (6)	0.032 (4)	0.042 (6)	-0.003 (4)	-0.007 (4)
N2	0.030 (3)	0.023 (2)	0.025 (2)	0.013 (2)	-0.001 (2)	-0.006 (2)
C12	0.036 (3)	0.039 (3)	0.035 (3)	0.016 (3)	-0.008 (3)	-0.008 (3)
C22	0.068 (5)	0.062 (5)	0.050 (3)	0.036 (4)	0.007 (3)	-0.006 (3)
C32	0.024 (3)	0.029 (3)	0.040 (3)	0.013 (2)	-0.012 (2)	-0.002 (2)

C42	0.036 (4)	0.036 (3)	0.058 (4)	0.012 (3)	-0.008 (3)	-0.003 (3)
C52	0.033 (3)	0.035 (3)	0.040 (3)	0.014 (3)	-0.001 (3)	0.000 (3)
C62	0.033 (4)	0.040 (3)	0.063 (4)	0.016 (3)	-0.001 (3)	0.001 (4)
C72	0.030 (3)	0.023 (3)	0.041 (3)	0.009 (2)	-0.010 (3)	-0.006 (2)
C82	0.058 (4)	0.034 (3)	0.041 (3)	0.023 (3)	-0.003 (3)	0.007 (3)
N3	0.031 (3)	0.024 (3)	0.028 (3)	0.015 (2)	-0.002 (2)	0.001 (2)
C13	0.079 (5)	0.069 (5)	0.038 (3)	0.058 (4)	-0.010 (3)	-0.007 (3)
C23	0.100 (7)	0.028 (4)	0.069 (6)	0.031 (4)	0.003 (4)	0.011 (4)
C33	0.051 (4)	0.061 (4)	0.037 (3)	0.035 (3)	0.013 (3)	-0.006 (3)
C43	0.043 (4)	0.044 (4)	0.089 (5)	0.025 (3)	0.005 (4)	-0.018 (4)
C53	0.028 (3)	0.041 (3)	0.061 (4)	0.011 (3)	0.009 (3)	0.007 (3)
C63	0.040 (4)	0.081 (6)	0.057 (4)	0.013 (4)	-0.018 (4)	-0.002 (4)
C73	0.044 (4)	0.059 (4)	0.042 (3)	0.033 (3)	-0.011 (3)	0.000 (3)
C83	0.067 (5)	0.109 (7)	0.032 (4)	0.053 (5)	-0.004 (3)	-0.013 (5)
Fe1	0.0328 (5)	0.0332 (5)	0.0268 (4)	0.0165 (4)	-0.0002 (4)	0.0014 (4)
Cl11	0.0794 (12)	0.0780 (13)	0.0277 (8)	0.0518 (12)	0.0004 (7)	-0.0016 (8)
Cl21	0.0432 (10)	0.0404 (9)	0.0459 (9)	0.0243 (8)	0.0004 (7)	-0.0003 (7)
Cl31	0.0504 (9)	0.0358 (9)	0.0573 (11)	0.0221 (8)	0.0105 (8)	0.0082 (7)
Cl41	0.0374 (9)	0.0486 (10)	0.0571 (10)	0.0176 (8)	-0.0069 (8)	0.0024 (9)
Fe2	0.0337 (6)	0.0336 (5)	0.0368 (5)	0.0177 (4)	0.0006 (3)	-0.0005 (4)
Cl12	0.0534 (9)	0.0697 (12)	0.0363 (8)	0.0318 (8)	0.0007 (7)	0.0003 (8)
Cl22	0.0379 (9)	0.0491 (10)	0.0438 (8)	0.0198 (8)	0.0093 (8)	0.0003 (8)
Cl32	0.0459 (10)	0.0447 (9)	0.0596 (11)	0.0279 (8)	-0.0059 (8)	0.0020 (8)
Cl42	0.0452 (10)	0.0340 (9)	0.0617 (11)	0.0151 (8)	-0.0001 (8)	-0.0057 (8)
Fe3	0.0386 (8)	0.0386 (8)	0.0361 (13)	0.0193 (4)	0.000	0.000
Cl13	0.0560 (16)	0.0560 (16)	0.036 (2)	0.0280 (8)	0.000	0.000
Cl23	0.0746 (13)	0.0447 (10)	0.0542 (11)	0.0260 (10)	0.0034 (10)	0.0066 (9)
Fe4	0.0342 (5)	0.0342 (5)	0.0354 (10)	0.0171 (3)	0.000	0.000
Cl14	0.0519 (11)	0.0519 (11)	0.0364 (16)	0.0260 (6)	0.000	0.000
Cl24	0.0437 (10)	0.0397 (9)	0.0483 (9)	0.0164 (8)	-0.0039 (9)	-0.0083 (8)
Fe5	0.0412 (8)	0.0412 (8)	0.0360 (12)	0.0206 (4)	0.000	0.000
Cl15	0.0615 (16)	0.0615 (16)	0.037 (2)	0.0308 (8)	0.000	0.000
Cl25	0.0461 (9)	0.0654 (13)	0.0559 (11)	0.0197 (9)	0.0096 (9)	0.0039 (10)

Geometric parameters (Å, °)

N1—C71	1.476 (8)	C72—H72B	0.9800
N1—C31	1.494 (8)	C82—H82A	0.9700
N1—C51	1.511 (7)	C82—H82B	0.9700
N1—C11	1.521 (7)	C82—H82C	0.9700
C11—C21	1.505 (10)	N3—C73	1.481 (7)
C11—H11A	0.9800	N3—C33	1.512 (7)
C11—H11B	0.9800	N3—C53	1.518 (7)
C21—H21A	0.9700	N3—C13	1.523 (7)
C21—H21B	0.9700	C13—C23	1.532 (10)
C21—H21C	0.9700	C13—H13A	0.9800
C31—C41	1.514 (10)	C13—H13B	0.9800
C31—H31A	0.9800	C23—H23A	0.9700
C31—H31B	0.9800	C23—H23B	0.9700
C41—H41A	0.9700	C23—H23C	0.9700

C41—H41B	0.9700	C33—C43	1.495 (9)
C41—H41C	0.9700	C33—H33A	0.9800
C51—C61	1.562 (10)	C33—H33B	0.9800
C51—H51A	0.9800	C43—H43A	0.9700
C51—H51B	0.9800	C43—H43B	0.9700
C61—H61A	0.9700	C43—H43C	0.9700
C61—H61B	0.9700	C53—C63	1.515 (9)
C61—H61C	0.9700	C53—H53A	0.9800
C71—C81	1.581 (9)	C53—H53B	0.9800
C71—H71A	0.9800	C63—H63A	0.9700
C71—H71B	0.9800	C63—H63B	0.9700
C81—H81A	0.9700	C63—H63C	0.9700
C81—H81B	0.9700	C73—C83	1.555 (9)
C81—H81C	0.9700	C73—H73A	0.9800
N2—C32	1.511 (6)	C73—H73B	0.9800
N2—C52	1.518 (6)	C83—H83A	0.9700
N2—C12	1.531 (7)	C83—H83B	0.9700
N2—C72	1.536 (7)	C83—H83C	0.9700
C12—C22	1.519 (9)	Fe1—Cl11	2.1886 (17)
C12—H12A	0.9800	Fe1—Cl141	2.196 (2)
C12—H12B	0.9800	Fe1—Cl131	2.198 (2)
C22—H22A	0.9700	Fe1—Cl21	2.2026 (18)
C22—H22B	0.9700	Fe2—Cl32	2.189 (2)
C22—H22C	0.9700	Fe2—Cl22	2.1933 (18)
C32—C42	1.528 (8)	Fe2—Cl42	2.1940 (19)
C32—H32A	0.9800	Fe2—Cl12	2.1968 (19)
C32—H32B	0.9800	Fe3—Cl13	2.188 (4)
C42—H42A	0.9700	Fe3—Cl23	2.198 (2)
C42—H42B	0.9700	Fe3—Cl23 ⁱ	2.198 (2)
C42—H42C	0.9700	Fe3—Cl23 ⁱⁱ	2.198 (2)
C52—C62	1.493 (8)	Fe4—Cl24	2.1999 (19)
C52—H52A	0.9800	Fe4—Cl24 ⁱⁱⁱ	2.1999 (19)
C52—H52B	0.9800	Fe4—Cl24 ^{iv}	2.1999 (19)
C62—H62A	0.9700	Fe4—Cl14	2.202 (4)
C62—H62B	0.9700	Fe5—Cl15	2.191 (4)
C62—H62C	0.9700	Fe5—Cl25 ⁱ	2.196 (2)
C72—C82	1.467 (8)	Fe5—Cl25 ⁱⁱ	2.196 (2)
C72—H72A	0.9800	Fe5—Cl25	2.196 (2)
C71—N1—C31	108.2 (4)	C82—C72—N2	116.3 (4)
C71—N1—C51	109.3 (5)	C82—C72—H72A	108.2
C31—N1—C51	111.6 (5)	N2—C72—H72A	108.2
C71—N1—C11	110.5 (5)	C82—C72—H72B	108.2
C31—N1—C11	108.9 (5)	N2—C72—H72B	108.2
C51—N1—C11	108.4 (4)	H72A—C72—H72B	107.4
C21—C11—N1	115.2 (5)	C72—C82—H82A	109.5
C21—C11—H11A	108.5	C72—C82—H82B	109.5
N1—C11—H11A	108.5	H82A—C82—H82B	109.5
C21—C11—H11B	108.5	C72—C82—H82C	109.5

N1—C11—H11B	108.5	H82A—C82—H82C	109.5
H11A—C11—H11B	107.5	H82B—C82—H82C	109.5
C11—C21—H21A	109.5	C73—N3—C33	110.3 (4)
C11—C21—H21B	109.5	C73—N3—C53	108.2 (5)
H21A—C21—H21B	109.5	C33—N3—C53	110.1 (5)
C11—C21—H21C	109.5	C73—N3—C13	112.0 (5)
H21A—C21—H21C	109.5	C33—N3—C13	109.0 (5)
H21B—C21—H21C	109.5	C53—N3—C13	107.2 (4)
N1—C31—C41	114.5 (6)	N3—C13—C23	112.5 (5)
N1—C31—H31A	108.6	N3—C13—H13A	109.1
C41—C31—H31A	108.6	C23—C13—H13A	109.1
N1—C31—H31B	108.6	N3—C13—H13B	109.1
C41—C31—H31B	108.6	C23—C13—H13B	109.1
H31A—C31—H31B	107.6	H13A—C13—H13B	107.8
C31—C41—H41A	109.5	C13—C23—H23A	109.5
C31—C41—H41B	109.5	C13—C23—H23B	109.5
H41A—C41—H41B	109.5	H23A—C23—H23B	109.5
C31—C41—H41C	109.5	C13—C23—H23C	109.5
H41A—C41—H41C	109.5	H23A—C23—H23C	109.5
H41B—C41—H41C	109.5	H23B—C23—H23C	109.5
N1—C51—C61	114.5 (6)	C43—C33—N3	114.6 (6)
N1—C51—H51A	108.6	C43—C33—H33A	108.6
C61—C51—H51A	108.6	N3—C33—H33A	108.6
N1—C51—H51B	108.6	C43—C33—H33B	108.6
C61—C51—H51B	108.6	N3—C33—H33B	108.6
H51A—C51—H51B	107.6	H33A—C33—H33B	107.6
C51—C61—H61A	109.5	C33—C43—H43A	109.5
C51—C61—H61B	109.5	C33—C43—H43B	109.5
H61A—C61—H61B	109.5	H43A—C43—H43B	109.5
C51—C61—H61C	109.5	C33—C43—H43C	109.5
H61A—C61—H61C	109.5	H43A—C43—H43C	109.5
H61B—C61—H61C	109.5	H43B—C43—H43C	109.5
N1—C71—C81	113.5 (5)	C63—C53—N3	116.2 (5)
N1—C71—H71A	108.9	C63—C53—H53A	108.2
C81—C71—H71A	108.9	N3—C53—H53A	108.2
N1—C71—H71B	108.9	C63—C53—H53B	108.2
C81—C71—H71B	108.9	N3—C53—H53B	108.2
H71A—C71—H71B	107.7	H53A—C53—H53B	107.4
C71—C81—H81A	109.5	C53—C63—H63A	109.5
C71—C81—H81B	109.5	C53—C63—H63B	109.5
H81A—C81—H81B	109.5	H63A—C63—H63B	109.5
C71—C81—H81C	109.5	C53—C63—H63C	109.5
H81A—C81—H81C	109.5	H63A—C63—H63C	109.5
H81B—C81—H81C	109.5	H63B—C63—H63C	109.5
C32—N2—C52	109.3 (4)	N3—C73—C83	114.6 (5)
C32—N2—C12	107.1 (5)	N3—C73—H73A	108.6
C52—N2—C12	112.0 (5)	C83—C73—H73A	108.6
C32—N2—C72	111.5 (4)	N3—C73—H73B	108.6
C52—N2—C72	108.6 (4)	C83—C73—H73B	108.6

C12—N2—C72	108.4 (4)	H73A—C73—H73B	107.6
C22—C12—N2	115.3 (5)	C73—C83—H83A	109.5
C22—C12—H12A	108.4	C73—C83—H83B	109.5
N2—C12—H12A	108.4	H83A—C83—H83B	109.5
C22—C12—H12B	108.4	C73—C83—H83C	109.5
N2—C12—H12B	108.4	H83A—C83—H83C	109.5
H12A—C12—H12B	107.5	H83B—C83—H83C	109.5
C12—C22—H22A	109.5	Cl11—Fe1—Cl41	109.70 (9)
C12—C22—H22B	109.5	Cl11—Fe1—Cl31	109.15 (8)
H22A—C22—H22B	109.5	Cl41—Fe1—Cl31	109.56 (8)
C12—C22—H22C	109.5	Cl11—Fe1—Cl21	109.33 (8)
H22A—C22—H22C	109.5	Cl41—Fe1—Cl21	108.82 (8)
H22B—C22—H22C	109.5	Cl31—Fe1—Cl21	110.26 (7)
N2—C32—C42	117.3 (5)	Cl32—Fe2—Cl22	110.84 (8)
N2—C32—H32A	108.0	Cl32—Fe2—Cl42	109.88 (7)
C42—C32—H32A	108.0	Cl22—Fe2—Cl42	109.76 (8)
N2—C32—H32B	108.0	Cl32—Fe2—Cl12	108.32 (8)
C42—C32—H32B	108.0	Cl22—Fe2—Cl12	108.24 (8)
H32A—C32—H32B	107.2	Cl42—Fe2—Cl12	109.76 (8)
C32—C42—H42A	109.5	Cl13—Fe3—Cl23	109.07 (7)
C32—C42—H42B	109.5	Cl13—Fe3—Cl23 ⁱ	109.07 (7)
H42A—C42—H42B	109.5	Cl23—Fe3—Cl23 ⁱ	109.87 (7)
C32—C42—H42C	109.5	Cl13—Fe3—Cl23 ⁱⁱ	109.07 (7)
H42A—C42—H42C	109.5	Cl23—Fe3—Cl23 ⁱⁱ	109.87 (7)
H42B—C42—H42C	109.5	Cl23 ⁱ —Fe3—Cl23 ⁱⁱ	109.87 (7)
C62—C52—N2	115.8 (5)	Cl24—Fe4—Cl24 ⁱⁱⁱ	109.91 (6)
C62—C52—H52A	108.3	Cl24—Fe4—Cl24 ^{iv}	109.91 (6)
N2—C52—H52A	108.3	Cl24 ⁱⁱⁱ —Fe4—Cl24 ^{iv}	109.91 (6)
C62—C52—H52B	108.3	Cl24—Fe4—Cl14	109.03 (6)
N2—C52—H52B	108.3	Cl24 ⁱⁱⁱ —Fe4—Cl14	109.03 (6)
H52A—C52—H52B	107.4	Cl24 ^{iv} —Fe4—Cl14	109.03 (6)
C52—C62—H62A	109.5	Cl15—Fe5—Cl25 ⁱ	109.04 (8)
C52—C62—H62B	109.5	Cl15—Fe5—Cl25 ⁱⁱ	109.04 (8)
H62A—C62—H62B	109.5	Cl25 ⁱ —Fe5—Cl25 ⁱⁱ	109.90 (7)
C52—C62—H62C	109.5	Cl15—Fe5—Cl25	109.04 (8)
H62A—C62—H62C	109.5	Cl25 ⁱ —Fe5—Cl25	109.90 (7)
H62B—C62—H62C	109.5	Cl25 ⁱⁱ —Fe5—Cl25	109.90 (7)
C71—N1—C11—C21	-57.5 (8)	C32—N2—C52—C62	60.7 (7)
C31—N1—C11—C21	61.2 (8)	C12—N2—C52—C62	-57.9 (7)
C51—N1—C11—C21	-177.2 (6)	C72—N2—C52—C62	-177.5 (5)
C71—N1—C31—C41	-59.3 (8)	C32—N2—C72—C82	56.3 (6)
C51—N1—C31—C41	60.9 (7)	C52—N2—C72—C82	-64.2 (6)
C11—N1—C31—C41	-179.4 (6)	C12—N2—C72—C82	174.0 (5)
C71—N1—C51—C61	176.9 (6)	C73—N3—C13—C23	-56.9 (7)
C31—N1—C51—C61	57.4 (7)	C33—N3—C13—C23	65.5 (6)
C11—N1—C51—C61	-62.6 (8)	C53—N3—C13—C23	-175.4 (5)
C31—N1—C71—C81	-175.4 (7)	C73—N3—C33—C43	-55.2 (7)
C51—N1—C71—C81	62.9 (8)	C53—N3—C33—C43	64.1 (6)

C11—N1—C71—C81	-56.3 (8)	C13—N3—C33—C43	-178.5 (6)
C32—N2—C12—C22	-178.5 (5)	C73—N3—C53—C63	179.5 (6)
C52—N2—C12—C22	-58.7 (7)	C33—N3—C53—C63	58.9 (7)
C72—N2—C12—C22	61.1 (6)	C13—N3—C53—C63	-59.5 (7)
C52—N2—C32—C42	172.9 (5)	C33—N3—C73—C83	-176.9 (7)
C12—N2—C32—C42	-65.6 (6)	C53—N3—C73—C83	62.7 (8)
C72—N2—C32—C42	52.8 (7)	C13—N3—C73—C83	-55.3 (8)

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

(Ic) Tetraethylammonium tetrachloridoferrate(III)

Crystal data

(C₈H₂₀N)[FeCl₄]

$M_r = 327.90$

Orthorhombic, *Pca*2₁

$a = 14.0182$ (8) Å

$b = 8.1493$ (5) Å

$c = 12.8767$ (8) Å

$V = 1471.01$ (15) Å³

$Z = 4$

$F(000) = 676$

$D_x = 1.481$ Mg m⁻³

Mo *K*α radiation, $\lambda = 0.71073$ Å

Cell parameters from 6968 reflections

$\theta = 2.2$ – 27.5°

$\mu = 1.72$ mm⁻¹

$T = 170$ K

Block, yellow

$0.43 \times 0.34 \times 0.10$ mm

Data collection

Bruker Kappa APEXII

diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan

(TWINABS; Sheldrick, 2012)

$T_{\min} = 0.639$, $T_{\max} = 0.746$

32765 measured reflections

7746 independent reflections

7535 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.028$

$\theta_{\max} = 27.6^\circ$, $\theta_{\min} = 2.5^\circ$

$h = -18 \rightarrow 18$

$k = -10 \rightarrow 10$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.014$

$wR(F^2) = 0.034$

$S = 1.03$

7746 reflections

133 parameters

1 restraint

Primary atom site location: structure-invariant

direct methods

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0132P)^2 + 0.0367P]$

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

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

$\Delta\rho_{\max} = 0.12$ e Å⁻³

$\Delta\rho_{\min} = -0.27$ e Å⁻³

Special details

Experimental. loop_diffn_orient_matrix_type_diffn_orient_matrix_UB_11_diffn_orient_matrix_UB_12_diffn_orient_matrix_UB_13_diffn_orient_matrix_UB_21_diffn_orient_matrix_UB_22_diffn_orient_matrix_UB_23_diffn_orient_matrix_UB_31_diffn_orient_matrix_UB_32_diffn_orient_matrix_UB_33 'Nonius RMAT' -0.0552117 0.0570192 0.0335576 0.0438346 0.0881353 0.0255620 -0.0112121 0.0637923 -0.0653109 'Nonius RMAT' 0.0010845 0.1107900 0.0335563 0.0662764 -0.0212420 0.0255569 0.0264909 0.0486090 -0.0653135 'Nonius RMAT' 0.0562913 0.0537792 0.0335726 0.0224478 -0.1093919 0.0255528 0.0377212 -0.0151557 -0.0653067

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. Refined as a 3-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.41494 (16)	0.7816 (2)	0.48126 (18)	0.0184 (4)
C1	0.46102 (16)	0.6995 (3)	0.38735 (17)	0.0225 (4)
H1A	0.4200	0.7196	0.3261	0.027*
H1B	0.5231	0.7536	0.3741	0.027*
C2	0.47780 (17)	0.5180 (3)	0.39615 (19)	0.0293 (5)
H2A	0.5203	0.4961	0.4550	0.044*
H2B	0.5073	0.4776	0.3321	0.044*
H2C	0.4168	0.4620	0.4071	0.044*
C3	0.31528 (16)	0.7135 (3)	0.5002 (2)	0.0245 (5)
H3A	0.3205	0.5939	0.5123	0.029*
H3B	0.2897	0.7635	0.5645	0.029*
C4	0.2441 (3)	0.7420 (3)	0.4132 (4)	0.0372 (10)
H4A	0.2327	0.8600	0.4055	0.056*
H4B	0.1840	0.6866	0.4299	0.056*
H4C	0.2698	0.6978	0.3482	0.056*
C5	0.40883 (13)	0.9645 (2)	0.46156 (18)	0.0224 (4)
H5A	0.3753	0.9823	0.3948	0.027*
H5B	0.3694	1.0145	0.5170	0.027*
C6	0.50356 (15)	1.0537 (3)	0.45750 (19)	0.0290 (5)
H6A	0.5377	1.0374	0.5231	0.044*
H6B	0.4924	1.1712	0.4466	0.044*
H6C	0.5419	1.0102	0.4001	0.044*
C7	0.4758 (2)	0.7440 (2)	0.5762 (2)	0.0236 (6)
H7A	0.4742	0.6241	0.5886	0.028*
H7B	0.5427	0.7742	0.5604	0.028*
C8	0.44635 (17)	0.8304 (3)	0.67549 (18)	0.0325 (5)
H8A	0.4501	0.9494	0.6654	0.049*
H8B	0.4892	0.7978	0.7320	0.049*
H8C	0.3807	0.7998	0.6932	0.049*
Fe1	0.24092 (2)	0.27786 (4)	0.22244 (3)	0.02156 (8)
Cl1	0.23050 (5)	0.27656 (9)	0.39273 (5)	0.03161 (15)
Cl2	0.30246 (4)	0.04137 (8)	0.17363 (5)	0.03122 (13)
Cl3	0.09746 (4)	0.30823 (8)	0.15619 (5)	0.02864 (12)
Cl4	0.33085 (4)	0.48244 (7)	0.16997 (5)	0.02879 (12)

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0172 (9)	0.0192 (7)	0.0187 (10)	0.0009 (9)	0.0009 (8)	0.0020 (9)
C1	0.0224 (11)	0.0245 (12)	0.0206 (11)	0.0022 (10)	0.0032 (9)	-0.0034 (11)
C2	0.0339 (12)	0.0241 (13)	0.0299 (12)	0.0044 (10)	0.0034 (10)	-0.0040 (9)

C3	0.0178 (11)	0.0259 (10)	0.0299 (13)	-0.0024 (10)	0.0054 (10)	0.0006 (11)
C4	0.0213 (16)	0.044 (2)	0.046 (3)	-0.0027 (10)	-0.0035 (12)	-0.0027 (11)
C5	0.0278 (10)	0.0173 (9)	0.0222 (10)	0.0027 (8)	-0.0001 (9)	0.0040 (9)
C6	0.0339 (12)	0.0219 (11)	0.0314 (12)	-0.0048 (9)	0.0023 (11)	0.0026 (11)
C7	0.0242 (17)	0.0263 (18)	0.0202 (14)	0.0035 (8)	-0.0030 (11)	0.0056 (7)
C8	0.0401 (12)	0.0347 (14)	0.0227 (12)	0.0053 (10)	-0.0017 (10)	0.0020 (11)
Fe1	0.02122 (17)	0.02333 (14)	0.02012 (15)	0.00090 (12)	-0.00028 (16)	-0.0004 (2)
Cl1	0.0327 (4)	0.0415 (4)	0.0206 (3)	0.0014 (2)	-0.0002 (3)	0.0020 (3)
Cl2	0.0304 (3)	0.0252 (3)	0.0380 (3)	0.0024 (2)	0.0019 (3)	-0.0045 (3)
Cl3	0.0249 (3)	0.0325 (3)	0.0285 (3)	0.0019 (2)	-0.0044 (2)	0.0007 (3)
Cl4	0.0292 (2)	0.0274 (3)	0.0297 (3)	-0.0028 (2)	0.0012 (3)	0.0010 (3)

Geometric parameters (Å, °)

N1—C5	1.515 (3)	C5—C6	1.515 (3)
N1—C7	1.522 (4)	C5—H5A	0.9900
N1—C3	1.523 (3)	C5—H5B	0.9900
N1—C1	1.525 (3)	C6—H6A	0.9800
C1—C2	1.502 (4)	C6—H6B	0.9800
C1—H1A	0.9900	C6—H6C	0.9800
C1—H1B	0.9900	C7—C8	1.517 (4)
C2—H2A	0.9800	C7—H7A	0.9900
C2—H2B	0.9800	C7—H7B	0.9900
C2—H2C	0.9800	C8—H8A	0.9800
C3—C4	1.517 (5)	C8—H8B	0.9800
C3—H3A	0.9900	C8—H8C	0.9800
C3—H3B	0.9900	Fe1—Cl4	2.1966 (7)
C4—H4A	0.9800	Fe1—Cl1	2.1977 (7)
C4—H4B	0.9800	Fe1—Cl3	2.1985 (6)
C4—H4C	0.9800	Fe1—Cl2	2.2030 (7)
C5—N1—C7	111.36 (17)	C6—C5—N1	115.37 (17)
C5—N1—C3	109.48 (17)	C6—C5—H5A	108.4
C7—N1—C3	108.2 (2)	N1—C5—H5A	108.4
C5—N1—C1	108.83 (18)	C6—C5—H5B	108.4
C7—N1—C1	108.13 (19)	N1—C5—H5B	108.4
C3—N1—C1	110.82 (18)	H5A—C5—H5B	107.5
C2—C1—N1	116.00 (19)	C5—C6—H6A	109.5
C2—C1—H1A	108.3	C5—C6—H6B	109.5
N1—C1—H1A	108.3	H6A—C6—H6B	109.5
C2—C1—H1B	108.3	C5—C6—H6C	109.5
N1—C1—H1B	108.3	H6A—C6—H6C	109.5
H1A—C1—H1B	107.4	H6B—C6—H6C	109.5
C1—C2—H2A	109.5	C8—C7—N1	115.5 (2)
C1—C2—H2B	109.5	C8—C7—H7A	108.4
H2A—C2—H2B	109.5	N1—C7—H7A	108.4
C1—C2—H2C	109.5	C8—C7—H7B	108.4
H2A—C2—H2C	109.5	N1—C7—H7B	108.4
H2B—C2—H2C	109.5	H7A—C7—H7B	107.5
C4—C3—N1	115.4 (2)	C7—C8—H8A	109.5

C4—C3—H3A	108.4	C7—C8—H8B	109.5
N1—C3—H3A	108.4	H8A—C8—H8B	109.5
C4—C3—H3B	108.4	C7—C8—H8C	109.5
N1—C3—H3B	108.4	H8A—C8—H8C	109.5
H3A—C3—H3B	107.5	H8B—C8—H8C	109.5
C3—C4—H4A	109.5	Cl4—Fe1—Cl1	110.41 (3)
C3—C4—H4B	109.5	Cl4—Fe1—Cl3	108.67 (3)
H4A—C4—H4B	109.5	Cl1—Fe1—Cl3	109.08 (3)
C3—C4—H4C	109.5	Cl4—Fe1—Cl2	110.58 (3)
H4A—C4—H4C	109.5	Cl1—Fe1—Cl2	107.85 (3)
H4B—C4—H4C	109.5	Cl3—Fe1—Cl2	110.24 (3)
C5—N1—C1—C2	176.68 (18)	C7—N1—C5—C6	51.5 (3)
C7—N1—C1—C2	55.6 (2)	C3—N1—C5—C6	171.2 (2)
C3—N1—C1—C2	-62.9 (3)	C1—N1—C5—C6	-67.6 (2)
C5—N1—C3—C4	57.7 (3)	C5—N1—C7—C8	54.5 (3)
C7—N1—C3—C4	179.3 (2)	C3—N1—C7—C8	-65.9 (2)
C1—N1—C3—C4	-62.3 (3)	C1—N1—C7—C8	174.0 (2)

(Id) Tetraethylammonium tetrachloridoferrate(III)

Crystal data

(C₈H₂₀N)[FeCl₄]

M_r = 327.90

Orthorhombic, *Pca*2₁

a = 13.9816 (6) Å

b = 8.1243 (3) Å

c = 12.8097 (6) Å

V = 1455.06 (11) Å³

Z = 4

F(000) = 676

D_x = 1.497 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 10389 reflections

θ = 2.2–27.5°

μ = 1.74 mm⁻¹

T = 110 K

Block, yellow

0.43 × 0.34 × 0.10 mm

Data collection

Bruker Kappa APEXII
diffractometer

Radiation source: sealed tube

φ and ω scans

Absorption correction: multi-scan
(TWINABS; Sheldrick, 2012)

T_{min} = 0.655, *T_{max}* = 0.746

49619 measured reflections

7924 independent reflections

7776 reflections with *I* > 2σ(*I*)

R_{int} = 0.028

θ_{max} = 27.6°, θ_{min} = 2.5°

h = -18→18

k = -10→10

l = -16→16

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.012

wR(*F*²) = 0.030

S = 1.04

7924 reflections

133 parameters

1 restraint

Primary atom site location: structure-invariant
direct methods

Secondary atom site location: difference Fourier
map

Hydrogen site location: difference Fourier map

H-atom parameters constrained

w = 1/[σ²(*F_o*²) + (0.0121*P*)² + 0.0465*P*]

where *P* = (*F_o*² + 2*F_c*²)/3

(Δ/σ)_{max} < 0.001

Δρ_{max} = 0.12 e Å⁻³

Δρ_{min} = -0.32 e Å⁻³

Special details

Experimental. loop_diffn_orient_matrix_type_diffn_orient_matrix_UB_11_diffn_orient_matrix_UB_12_diffn_orient_matrix_UB_13_diffn_orient_matrix_UB_21_diffn_orient_matrix_UB_22_diffn_orient_matrix_UB_23_diffn_orient_matrix_UB_31_diffn_orient_matrix_UB_32_diffn_orient_matrix_UB_33 'Nonius RMAT' -0.0550213 0.0579395 0.0339429 0.0444204 0.0879475 0.0254721 -0.0112145 0.0640910 -0.0656385 'Nonius RMAT' 0.0016187 0.1110194 0.0339428 0.0664469 -0.0222439 0.0254671 0.0266171 0.0487782 -0.0656404 'Nonius RMAT' 0.0566363 0.0530991 0.0339597 0.0220348 -0.1102092 0.0254684 0.0378561 -0.0152918 -0.0656312

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. Refined as a 3-component twin.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	<i>x</i>	<i>y</i>	<i>z</i>	$U_{\text{iso}}^*/U_{\text{eq}}$
N1	0.41526 (14)	0.7829 (2)	0.48117 (16)	0.0114 (3)
C1	0.46138 (14)	0.7009 (3)	0.38642 (15)	0.0145 (4)
H1A	0.4201	0.7209	0.3249	0.017*
H1B	0.5236	0.7552	0.3730	0.017*
C2	0.47826 (15)	0.5183 (3)	0.39556 (16)	0.0188 (4)
H2A	0.5217	0.4966	0.4540	0.028*
H2B	0.5069	0.4772	0.3308	0.028*
H2C	0.4172	0.4622	0.4079	0.028*
C3	0.31523 (15)	0.7143 (3)	0.50026 (17)	0.0157 (4)
H3A	0.3205	0.5943	0.5122	0.019*
H3B	0.2897	0.7642	0.5650	0.019*
C4	0.2438 (2)	0.7432 (2)	0.4133 (3)	0.0237 (7)
H4A	0.2336	0.8617	0.4044	0.036*
H4B	0.1830	0.6899	0.4310	0.036*
H4C	0.2686	0.6965	0.3481	0.036*
C5	0.40905 (12)	0.9664 (2)	0.46133 (16)	0.0143 (4)
H5A	0.3692	1.0165	0.5168	0.017*
H5B	0.3758	0.9841	0.3941	0.017*
C6	0.50418 (13)	1.0561 (2)	0.45783 (16)	0.0184 (4)
H6A	0.5378	1.0405	0.5242	0.028*
H6B	0.4930	1.1738	0.4463	0.028*
H6C	0.5431	1.0119	0.4008	0.028*
C7	0.4765 (2)	0.7451 (2)	0.5765 (2)	0.0152 (5)
H7A	0.4749	0.6249	0.5890	0.018*
H7B	0.5435	0.7754	0.5605	0.018*
C8	0.44684 (15)	0.8322 (3)	0.67645 (15)	0.0205 (4)
H8A	0.4495	0.9515	0.6659	0.031*
H8B	0.4904	0.8011	0.7330	0.031*
H8C	0.3814	0.8000	0.6949	0.031*
Fe1	0.24106 (2)	0.27936 (4)	0.22245 (3)	0.01356 (7)
Cl1	0.23031 (4)	0.27868 (8)	0.39388 (4)	0.02016 (12)
Cl2	0.30236 (3)	0.04105 (7)	0.17389 (4)	0.01970 (10)
Cl3	0.09726 (3)	0.31002 (6)	0.15535 (4)	0.01782 (10)

C14 0.33172 (3) 0.48432 (6) 0.16960 (4) 0.01817 (10)

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
N1	0.0105 (8)	0.0126 (7)	0.0112 (8)	0.0005 (8)	0.0000 (7)	0.0015 (8)
C1	0.0150 (9)	0.0162 (11)	0.0122 (9)	0.0009 (8)	0.0022 (7)	-0.0026 (9)
C2	0.0220 (10)	0.0165 (11)	0.0179 (9)	0.0023 (8)	0.0021 (8)	-0.0022 (8)
C3	0.0118 (9)	0.0162 (8)	0.0190 (10)	-0.0016 (9)	0.0037 (8)	0.0004 (9)
C4	0.0140 (13)	0.0274 (15)	0.030 (2)	-0.0021 (8)	-0.0015 (10)	-0.0005 (8)
C5	0.0188 (9)	0.0103 (8)	0.0138 (9)	0.0017 (7)	0.0004 (7)	0.0026 (8)
C6	0.0218 (10)	0.0146 (9)	0.0187 (10)	-0.0032 (8)	0.0005 (8)	0.0010 (9)
C7	0.0150 (14)	0.0182 (16)	0.0123 (11)	0.0017 (7)	-0.0025 (9)	0.0039 (6)
C8	0.0252 (10)	0.0222 (11)	0.0141 (9)	0.0027 (8)	-0.0011 (8)	0.0013 (9)
Fe1	0.01334 (15)	0.01485 (12)	0.01249 (12)	0.00061 (11)	-0.00019 (13)	-0.00033 (18)
Cl1	0.0209 (3)	0.0266 (3)	0.0129 (2)	0.0008 (2)	-0.0001 (2)	0.0009 (2)
Cl2	0.0195 (2)	0.0161 (2)	0.0235 (2)	0.00146 (19)	0.0012 (2)	-0.0027 (2)
Cl3	0.0161 (2)	0.0197 (3)	0.0177 (2)	0.00132 (19)	-0.00278 (18)	0.0002 (2)
Cl4	0.0182 (2)	0.0177 (2)	0.0186 (2)	-0.0018 (2)	0.0007 (2)	0.0004 (2)

Geometric parameters (Å, °)

N1—C5	1.515 (2)	C5—C6	1.517 (2)
N1—C7	1.523 (3)	C5—H5A	0.9900
N1—C3	1.525 (3)	C5—H5B	0.9900
N1—C1	1.527 (3)	C6—H6A	0.9800
C1—C2	1.507 (3)	C6—H6B	0.9800
C1—H1A	0.9900	C6—H6C	0.9800
C1—H1B	0.9900	C7—C8	1.520 (3)
C2—H2A	0.9800	C7—H7A	0.9900
C2—H2B	0.9800	C7—H7B	0.9900
C2—H2C	0.9800	C8—H8A	0.9800
C3—C4	1.514 (4)	C8—H8B	0.9800
C3—H3A	0.9900	C8—H8C	0.9800
C3—H3B	0.9900	Fe1—Cl4	2.1995 (6)
C4—H4A	0.9800	Fe1—Cl3	2.2007 (5)
C4—H4B	0.9800	Fe1—Cl1	2.2011 (6)
C4—H4C	0.9800	Fe1—Cl2	2.2068 (6)
C5—N1—C7	111.42 (15)	N1—C5—C6	115.30 (15)
C5—N1—C3	109.48 (15)	N1—C5—H5A	108.4
C7—N1—C3	108.28 (18)	C6—C5—H5A	108.4
C5—N1—C1	108.66 (16)	N1—C5—H5B	108.4
C7—N1—C1	108.18 (17)	C6—C5—H5B	108.4
C3—N1—C1	110.83 (16)	H5A—C5—H5B	107.5
C2—C1—N1	115.70 (17)	C5—C6—H6A	109.5
C2—C1—H1A	108.4	C5—C6—H6B	109.5
N1—C1—H1A	108.4	H6A—C6—H6B	109.5
C2—C1—H1B	108.4	C5—C6—H6C	109.5
N1—C1—H1B	108.4	H6A—C6—H6C	109.5

H1A—C1—H1B	107.4	H6B—C6—H6C	109.5
C1—C2—H2A	109.5	C8—C7—N1	115.35 (18)
C1—C2—H2B	109.5	C8—C7—H7A	108.4
H2A—C2—H2B	109.5	N1—C7—H7A	108.4
C1—C2—H2C	109.5	C8—C7—H7B	108.4
H2A—C2—H2C	109.5	N1—C7—H7B	108.4
H2B—C2—H2C	109.5	H7A—C7—H7B	107.5
C4—C3—N1	115.5 (2)	C7—C8—H8A	109.5
C4—C3—H3A	108.4	C7—C8—H8B	109.5
N1—C3—H3A	108.4	H8A—C8—H8B	109.5
C4—C3—H3B	108.4	C7—C8—H8C	109.5
N1—C3—H3B	108.4	H8A—C8—H8C	109.5
H3A—C3—H3B	107.5	H8B—C8—H8C	109.5
C3—C4—H4A	109.5	Cl4—Fe1—Cl3	108.70 (2)
C3—C4—H4B	109.5	Cl4—Fe1—Cl1	110.38 (3)
H4A—C4—H4B	109.5	Cl3—Fe1—Cl1	109.12 (3)
C3—C4—H4C	109.5	Cl4—Fe1—Cl2	110.71 (3)
H4A—C4—H4C	109.5	Cl3—Fe1—Cl2	110.12 (2)
H4B—C4—H4C	109.5	Cl1—Fe1—Cl2	107.79 (3)
C5—N1—C1—C2	176.67 (16)	C7—N1—C5—C6	51.1 (2)
C7—N1—C1—C2	55.6 (2)	C3—N1—C5—C6	170.84 (17)
C3—N1—C1—C2	-63.0 (2)	C1—N1—C5—C6	-68.0 (2)
C5—N1—C3—C4	57.5 (2)	C5—N1—C7—C8	54.5 (2)
C7—N1—C3—C4	179.18 (18)	C3—N1—C7—C8	-66.0 (2)
C1—N1—C3—C4	-62.3 (2)	C1—N1—C7—C8	173.87 (17)

Twinned reflection data at 110 (2) K. Analysis of systematic absences with PLATON (Spek, 2009). The corresponding unit cell is in the hexagonal setting (twin lattice) with $a = b = 16.1794$ (10), $c = 12.7974$ (5) Å, $\alpha = \beta = 90$, $\gamma = 120^\circ$, $V = 2901.2$ (4) Å³.

Condition	$\langle I/\sigma \rangle$ true	$\langle I/\sigma \rangle$ false
$0kl, k=2n$	26.27	0.21
$h0l, h=2n$	26.30	0.23
$h00, h=2n$	27.29	0.31
$0k0, k=2n$	27.80	0.26
$00l, l=2n$	31.90	0.79
$h-hl, h=2n$	26.57	0.21

Coset decomposition of point group $G = 6mm$ with respect to $H_1 = mm2$, $G = H_1 + g_2H_1 + g_3H_1$. Matrices are given for a hexagonal base. They were retrieved from the Bilbao Crystallographic Server (Aroyo et al., 2006). For the creation of the orientation matrices for the integration, only rotational operations can be selected to avoid left-handed coordinate systems.

H_1	g_2H_1	g_3H_1
1 (100/010/001)	$3^{+}_{0,0,z}$ (0-10/1-10/001)	$m_{2x,x,z}$ (100/1-10/001)
$2_{0,0,z}$ (-100/0-10/001)	$6^{-}_{0,0,z}$ (010/-110/001)	$m_{0,y,z}$ (-100/-110/001)
$m_{x,2x,z}$ (-110/010/001)	$m_{x,-x,z}$ (0-10/-100/001)	$3^{-}_{0,0,z}$ (-110/-100/001)
$m_{x,0,z}$ (1-10/0-10/001)	$m_{x,x,z}$ (010/100/001)	$6^{+}_{0,0,z}$ (1-10/100/001)

Unit-cell parameters during the cooling of a single crystal of (I). In the temperature range 220–110 K, the unit cell of the twin lattice is presented. The last column gives the number of reflections used for the cell refinement with the Peakref software (Schreurs, 2013). The detector position was kept fixed during the experiment. At each temperature, 3 ω scans of 6° were measured, respectively (0.5° scan angle).

<i>T</i> (K)	<i>a</i> , <i>b</i> (Å)	<i>c</i> (Å)	<i>V</i> (Å ³)	Number of reflections
290	8.230 (6)	13.217 (14)	775.3 (14)	126
280	8.223 (6)	13.202 (15)	773.1 (16)	126
270	8.220 (6)	13.190 (12)	771.7 (15)	124
260	8.213 (6)	13.176 (14)	769.6 (16)	127
250	8.206 (5)	13.164 (14)	767.8 (16)	127
240	8.200 (6)	13.149 (11)	765.7 (15)	127
230	24.566 (12)	13.065 (6)	6829 (9)	581
220	16.328 (11)	12.972 (8)	2995 (5)	404
210	16.311 (8)	12.957 (7)	2985 (3)	416
200	16.299 (11)	12.944 (7)	2978 (5)	419
190	16.289 (8)	12.931 (7)	2971 (3)	426
180	16.278 (10)	12.916 (7)	2964 (4)	427
170	16.269 (9)	12.900 (7)	2957 (4)	440
160	16.259 (7)	12.890 (7)	2951 (3)	447
150	16.249 (10)	12.881 (7)	2945 (4)	448
140	16.241 (10)	12.863 (7)	2938 (4)	441
130	16.229 (10)	12.849 (7)	2931 (4)	449
120	16.218 (9)	12.838 (7)	2924 (4)	435
110	16.213 (8)	12.826 (7)	2920 (3)	438