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A new pyrimidinium tetrachloroferrate(III) salt with a low band gap:

Hirshfeld surface analysis, crystal structure and physicochemical studies

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Abstract

The chemical preparation, characterization by single crystal X-ray diffraction, elemental analysis and IR spectroscopy of the new Fe(III) complex $(C_5H_{7.50}N_3O)_2[FeCl_4]$ are reported. The Fe(III) cation is four-coordinated, in tetrahedral fashion, by four chlorine atoms. The $[FeCl_4]^-$ tetrahedra are located parallel to the **(a, b)** plane at $z = \frac{1}{4} (2n + 1)$ between layers of organic cations $(C_5H_{7.50}N_3O)_2^+$. The $FeCl_4$ moieties are inserted between these planes by establishing N-H...Cl and C-H...Cl hydrogen bonds generated by amino and methyl groups as donors and Cl^- anions as acceptors to form a three-dimensional network. The organic groups are linked together by N-H...N hydrogen bonds to form chains extending along the [110] direction. These chains are arranged in planes parallel to **(a, b)** at $z = \frac{1}{2} n$. Intermolecular contacts on the Hirshfeld surface were investigated statistically. The most favored and stabilizing contacts are the strong (N-H... Cl^- , N-H...N) hydrogen bonds as well as the weaker ones C-H... Cl^- . The vibrational absorption bands were identified by infrared spectroscopy. Electronic properties such as HOMO and LUMO energies were also derived.

Keywords: Hirshfeld surface • Contacts enrichment • Quantum mechanics • X-ray diffraction

• Coordination compound

Introduction

The design and synthesis of hybrid compounds have been of interest in recent years because of their potential applications in the fields of magnetism, photoluminescence, optoelectronics, catalysis and medicals or pharmaceuticals [1-4]. Among these compounds, iron complexes attract considerable attention. Iron is the most abundant element in the environment and plays a crucial role in the survival of terrestrial organisms. Several iron (III) complexes are known as contrast agents for magnetic resonance imaging (MRI) [5]. They are also known in catalytic, antitumor and antimicrobial domains [6-10]. As a contribution to the study of these materials, we undertook the synthesis of a Fe(III) complex containing a 4-amino-6-methoxypyrimidinium organic cation which was chosen for its practical importance. Indeed, pyrimidines and their derivatives are simple aromatic compounds consisting of two nitrogen atoms and four carbon atoms. The carbon and nitrogen atoms are connected by alternating double and single bonds. This bonding structure allows for resonance, or aromaticity, causing the ring to be very stable. They are of extreme importance since three of the four nucleic bases of DNA, namely cytosine, thymine and uracil are pyrimidine derivatives. We report in this article the Hirshfeld surface analysis of this compound. This analysis was performed to characterize the intermolecular interactions and explain the crystal architecture. In addition, the complex was studied by spectroscopy and DFT calculations were used for the interpretation of the vibration results.

Experimental

Chemical preparation

Hydrochloric acid HCl 37% (0.4 mmol, Sigma-Aldrich) dissolved in 10 mL of ethanol was added dropwise to a mixture of iron(III) chloride FeCl_3 97 % (0.4 mmol, Sigma-Aldrich) and 4-amino-6-metoxypyrimidine (0.4 mmol, Sigma-Aldrich) dissolved in 20 ml of ethanol. The whole was stirred at room temperature for 40 minutes until disappearance of precipitate and then the solution was covered with a cellophane paper. The resulting solution was kept at ambient temperature until formation of single crystals of sufficient size for the structural study. These crystals remained stable under normal conditions of temperature and humidity (yield 72%). Anal. Calc.: C, 26.73; H, 3.34 %; N, 18.17 %. Found: C, 26.40; H, 3.63; N, 18.78 %.

X-ray single crystal structural analysis

A single crystal suitable to X-ray diffraction analysis was carefully selected under polarizing microscope. Diffraction data were collected on a Nonius Kappa diffractometer equipped with a CCD detector with graphite-monochromatized $\text{MoK}\alpha$ radiation ($\lambda = 0.71069$ Å). Intensities were corrected for Lorentz, polarization and absorption effects [11]. The structure was solved by direct methods with the SIR97 suite of programs [12] and refinements were performed on F^2 by full-matrix least-squares methods with all non-hydrogen atoms anisotropic. C-H hydrogens were included on calculated positions, riding on their carrier atoms; all other hydrogen atoms were located in the Difference Fourier map and refined isotropically. All calculations were performed using SHELXL-97 [13] implemented in the WINGX system of programs [14]. The crystal data are reported in Table 1. The drawings were made with Diamond [15] and Mercury [16].

Infrared spectroscopy

The IR spectra were recorded in the range 4000–400 cm^{-1} with a “Perkin–Elmer FTIR” spectrophotometer1000 using samples dispersed in spectroscopically pure KBr pressed into a pellet.

Table 1 Experimental details of $(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O})_2[\text{FeCl}_4]$

Crystal data	
Chemical formula	$2(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O}) \cdot \text{Cl}_4\text{Fe}$
M_r	448.93
Crystal system, space group	Triclinic, $P1$
Temperature (K)	295
a, b, c (Å)	6.6406 (2), 7.4042 (3), 19.6212 (7)
α, β, γ (°)	88.350 (3), 87.005 (3), 77.210 (2)
V (Å ³)	939.37 (6)
Z	2
Radiation type	Mo $K\alpha$
μ (mm ⁻¹)	1.39
Crystal size (mm)	$0.29 \times 0.12 \times 0.12$
Data collection	
Diffractometer	Nonius Kappa CCD
Absorption correction	Multi-scan
$T_{\min}, T_{\max}$	0.805, 0.864
No. of measured, independent and	12546, 4036, 2999
R_{int}	0.041
$(\sin \theta/\lambda)_{\max}$ (Å ⁻¹)	0.639
Refinement	
$R[F^2 > 2\sigma(F^2)], wR(F^2), S$	0.039, 0.106, 1.04
No. of reflections	4036
No. of parameters	232
$\Delta\rho_{\max}, \Delta\rho_{\min}$ (e Å ⁻³)	0.63, -0.47

DFT calculations

The calculations were made with the Gaussian 09 revision A-02 software [17]. The starting geometry was that obtained from the X-ray structure. The positions of the protons were optimized, all other atoms being in the positions given by the X-ray diffraction study. The result of this optimization is an elongation of the CH and NH bonds and a displacement of the hydrogens of the NH₂ groups out of the plan of the aromatic cycle. These calculations were

made with the pseudo-potential LanL2DZ for iron and the base 6-31+G* for all other atoms (C, H, N, O and Cl).

Results and discussion

X-ray diffraction study

X-ray diffraction analysis of the complex $(C_5H_7.50N_3O)_2[FeCl_4]$ reveals that this compound crystallizes in the triclinic space group $P\bar{1}$. Its asymmetric unit, shown in Fig. 1, contains a tetrachloroferrate (III) $[FeCl_4]^-$ anion and two organic molecules of 4-amino-6-methoxypyrimidine. Each molecule is forming a homodimer via an inversion center. From electroneutrality appears that one of the ligands is in cationic form (pyrimidinium), while another is in neutral form. Here the crystal symmetry does not permit distinguishing between protonated and neutral forms of pyrimidine ligands. In fact, it is disorder originating from the close position of hydrogen atoms H6N and H5N to the inversion center. It means, that only half of pyrimidine molecules is protonated when considering the whole crystal. The hydrogen atoms bound to N1 and N4 atoms were given an occupancy factor of $\frac{1}{2}$.

Fig. 1 Molecular structure of the title compound showing the atom-numbering scheme and displacement ellipsoids drawn at the 50% probability level

In the atomic arrangement of the title compound, the iron (III) atom is surrounded by four chlorine anions. The bond distances around the iron atom, reported in Table 2, are consistent with the literature [18]. The values of the Cl-Fe-Cl bond angles, which vary between 108.54 (4)° and 111.02(5)°, indicate that the coordination sphere geometry around the Fe(III) metal cation can be considered as slightly distorted tetrahedral, in agreement with the geometry of (CSH₆N)[FeCl₄] [19] and (NEt₄)[FeCl₄] [20].

Table 2 Selected bond distances and angles (Å,°) in (C₅H_{7.50}N₃O)₂[FeCl₄]

Fe-Cl1	2.1908(9)	Cl4-Fe1-Cl2	108.54 (4)
Fe- Cl2	2.1815(9)	Cl4-Fe1-Cl5	111.02 (5)
Fe-Cl3	2.1840 (10)	Cl2-Fe1-Cl3	109.03 (5)
Fe-Cl4	2.1789 (8)	Cl4-Fe1-Cl1	108.50 (4)
O1—C4	1.333 (3)	Cl2-Fe1-Cl1	110.64 (4)
O1—C5	1.441 (3)	Cl3-Fe1-Cl1	109.12 (4)
O2—C9	1.325 (4)	C9—O2—C10	117.2 (3)
O2—C10	1.440 (4)	C1—N1—C4	117.6 (2)
N1—C1	1.326 (3)	C1—N2—C2	115.8 (2)
N1—C4	1.354 (3)	C6—N4—C9	117.9 (3)
N2—C1	1.315 (3)	C6—N5—C7	115.5 (3)
N2—C2	1.365 (3)	N2—C1—N1	126.6 (2)
N3—C2	1.323 (3)	N3—C2—N2	116.6 (2)
N4—C6	1.328 (5)	C4—C3—C2	117.6 (2)
C2—C3	1.397 (3)	N5—C6—N4	126.8 (3)
C3—C4	1.362 (3)	N6—C7—N5	116.5 (4)
C7—C8	1.392 (5)	C9—C8—C7	117.8 (3)
C8—C9	1.367 (4)	O2—C9—N4	112.4 (3)

The distances and bond angles describing the organic groups are given in Table 2. An examination of the C-NH₂ bonds shows that in both molecules the C-N distance is short for a single bond, but not as well contracted as one could expect for a fully established double bond. This indicates that the N3 and N6 nitrogen atoms of the amino group are probably in sp² hybridization. Moreover, the bond lengths of C5-O1 [1.441 (3) Å] and C10-O2 [1.440 (4) Å] clearly indicate two simple bonds, while the distances C4-O1 [1.332 (2) Å] and C9-O2 [1.325 (4) Å] are shorter, which is probably due to the donor mesomeric effect of the methoxy group.

In the crystal lattice, the isolated [FeCl₄]⁻ tetrahedra form layers parallel to the (*a*, *b*) plane at $z = \frac{1}{4}(2n + 1)$. The organic cations are inserted between the inorganic layers and

interact with them through hydrogen bonds with the chloride anions, generated by the amine and the methyl groups as donors (Fig. 2, Table 3). The organic groups, in turn, are linked together by strong N-H...N hydrogen bonds to form chains which consist of an alternation of pyrimidine and pyrimidinium molecules and they develop along the [110] direction (Fig.3). These chains are arranged in planes parallel to (a, b) at $z = \frac{1}{2} n$.

Fig. 2 Crystallographic autostereogram showing the packing arrangement of $(C_5H_{7.50}N_3O)_2[FeCl_4]$ viewed along b -axis. Green dotted lines indicate N-H...N hydrogen bonds

Table 3 Hydrogen-bond geometry ($\text{\AA},^\circ$) in $(C_5H_{7.50}N_3O)_2[FeCl_4]$

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
$C1-H1\cdots Cl4^i$	0.93	2.84	3.623 (3)	143
$C3-H4\cdots Cl1^{ii}$	0.93	2.95	3.780 (2)	149
$C5-H6B\cdots Cl4^{iii}$	0.96	2.91	3.707 (3)	141
$C8-H10\cdots Cl2^{iv}$	0.93	2.80	3.694 (3)	163
$C10-H12B\cdots Cl3^v$	0.96	2.93	3.822 (4)	155
$N3-H1N\cdots Cl1^{ii}$	0.86 (2)	2.88 (2)	3.688 (3)	159 (3)

N3—H2N $\cdots$ N2 ^{vi}	0.87 (2)	2.20 (2)	3.069 (3)	175 (3)
N6—H3N $\cdots$ Cl3 ^{vii}	0.87 (2)	2.77 (3)	3.368 (4)	127 (3)
N6—H4N $\cdots$ N5 ^{viii}	0.88 (2)	2.14 (2)	3.018 (5)	174 (4)
N1—H5N $\cdots$ N1 ^{ix}	0.81 (4)	1.89 (4)	2.695 (4)	176 (5)

Symmetry codes: (i) -x, -y, -z+1 ; (ii) x-1, y, z ; (iii) x, y+1, z ; (iv) x+1, y-1, z ; (v) x+1, y, z ; (vi) -x-1, -y, -z+1, (vii) x, y-1, z ; (viii) -x, -y-1, -z+2 ; (ix) -x, -y+1, -z+1.

Fig. 3 View of 1D zigzag chain $[(C_5H_{7.50}N_3O)_2]_n$ along the $[110]$ direction

Hirshfeld surface analysis

Analysis of intermolecular interactions on the Hirshfeld surface gives major insights into the crystal packing. The Hirshfeld surface was computed with the MoProViewer software [21]. The enrichment ratios [22, 23] of contacts between the different chemical species were computed in order to highlight which interactions are statistically favored in the crystal packing.

The chemical nature of contacts and their enrichment in the crystal structure are shown in Table 4.

For the Hirshfeld surface analysis, a dimer of the asymmetric unit was generated as the two half occupied hydrogen atoms were deleted in half of the organic cations. To obtain an integral Hirshfeld surface around each moiety, entities not in contact with each other were generated in the crystal packing. The FeCl_4^- anion was considered as an integral moiety. The same dimer was used to compute the fingerprint plots with program CrystalExplorer [24] (Fig. 4).

Table 4 Nature of intermolecular contacts on the Hirshfeld surface by chemical types. The second row shows the chemical content on the Hirshfeld surface. The % of contact types between chemical species is then given followed by their enrichment ratio. The major contacts as well as the most enriched ones are highlighted in bold. The hydrophobic Hc atoms bound to carbon were distinguished from the more polar Ho water hydrogen atoms.

atom	Fe	Cl	O	Hn	N	Hc	C
% surf	4.2	28.1	3.9	12.9	10.5	24.7	15.8
Fe	0.0	1.1	0.0	1.0	0.2	4.1	2.2
Cl		4.8	1.9	8.5	1.6	25.7	10.1
O			0.0	1.3	0.9	3.1	0.3
Hn				1.1	9.6	1.6	1.6
N	%	contacts			0.8	3.7	3.1
Hc						2.7	4.2
C							4.9
Fe	0.00	0.44	0.01	0.93	0.24	2.0	1.6
Cl		0.56	0.86	1.13	0.26	1.8	1.10
O			0.00	1.3	1.2	1.7	0.25
Hn				0.65	3.6	0.26	0.40
N		enrichment			0.71	0.76	0.96
Hc						0.48	0.56
C							2.0

The Hirshfeld surface analysis of the molecule shows that H...Cl and N...H interactions exhibit the most significant contributions (Figs. 4a and 4b, respectively). There are indeed seven H...Cl

hydrogen bonds and three N...H interactions in the crystal structure (Table 3). Globally the H...Cl and N...H interactions constitute as much as 47.5% of the contact surface; the enriched N...H-N strong H-bonds and Cl...H-C weak H-bonds are the driving force in the crystal packing stabilization.

Fig. 4 Fingerprint plots of contacts in $(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O})_2[\text{FeCl}_4]$

Among polar atoms, the chloride anions contribute at 28% to the largest surface followed by hydrogen Hn and nitrogen atoms (Table 4). The weak hydrogen bonds $\text{C}-\text{H}^{\delta+} \dots \text{Cl}^-$ are the major contact type, representing as much as one quarter of the surface, as these two chemical species are the most abundant and the contact is enriched at $E=1.8$.

The strong hydrogen bonds $\text{Cl}^- \dots \text{Hn}$ and $\text{N} \dots \text{Hn}$ are significantly abundant, just below 10%, the latter being the most enriched contact of the crystal packing ($E=3.6$).

Each of the two independent organic cations forms a stacking interaction with itself via an inversion centre. This results in significant over-represented C...C contacts. All self contacts are generally avoided, excepted for C...C.

Globally, forty percent of the Hirshfeld surface can be considered as hydrophobic (atoms C and Hc) and sixty percent as hydrophilic (polar). The contacts between hydrophobic atoms represent only 12% of the surface and are under-represented with a global enrichment ratio $E=0.72$. Contacts between charged atoms are also under-represented at $E = 0.90$. On the other hand, the cross contacts between polar and hydrophobic atoms represent more than 55% of the surface and are enriched at $E=1.15$. This behavior in hydrid organic/inorganic crystalline materials is unusual but if the interactions within the FeCl_4 complex had been counted, polar...polar interactions would have been better represented. The over-represented cross-contacts are due, in part, to the favored weak hydrogen bonds $\text{Cl}^- \dots \text{Hc}$ and $\text{N} \dots \text{Hc}$. For the methoxy oxygen atom, the interactions with Hc are also more favored than with Hn atoms. The FeCl_4 anions form layers parallel to the (a, b) plane and the slightly electropositive methyl groups (of both independent cations) are inserted between adjacent anions.

The Hirshfeld surface was also computed around the four chloride anions. The four Cl^- atoms show similar contact types with a correlation in the range 0.87 – 0.984.

Globally, the two independent organic cations display very similar interactions, the correlation between the proportions C_{xy} of contact types reaches $r=97\%$, while for the enrichment ratios, the correlation is $r= 88\%$. The different contacts types are however not occurring on the same locations of the two independent cations, as can be seen in Fig. 5.

Fig. 5 View of the Hirshfeld surface of the two organic cations, on the side interacting with the FeCl_4 anion. (a) and (b) are colored according to the exterior interacting atom (c). View of the semitransparent surface, with inner atom coloring showing the molecule orientation. The O1 or O2 oxygen atom is marked to identify the molecule. Hc: light grey, C: black, N: blue, O: red, Hn: light blue. Fe: dark red, Cl: green

Quantum mechanical study

Quantum computation was performed from the crystal data with the DFT method. The HOMO and LUMO of the title compound are shown in Fig. 6. It is clear that the HOMO is localized on one of two organic cations, while the LUMO is located on the $[\text{FeCl}_4]^-$ anion. The gap energy value between the HOMO and LUMO orbitals in the title compound is relatively low, $E_g = (E_{\text{LUMO}} - E_{\text{HOMO}}) = 1.15 \text{ eV}$, proving that some electrons can pass from the valence band to the conduction band by application of an external electric field. Thus, the synthesized material has a semiconductor behavior. The energy distributions of the different orbitals are given in Fig. 7.

Fig. 6 Frontier orbitals of $(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O})_2[\text{FeCl}_4]$

Fig. 7 Energy distribution of the different orbitals of $(C_5H_{7.50}N_3O)_2[FeCl_4]$

Mulliken charges and Mulliken spin densities

The DFT calculations give also access to Mulliken charges and Mulliken spin densities (Tables 5 and 6). The numbering of atoms is as follows:

Table 5 Mulliken charges for the title compound

Fe	-0.568576			
Cl	-0.351097	-0.339774	-0.342693	-0.066731
Sum of FeCl ₄ charges : -1.67				
C1	-0.397632	-0.368702		
H(C1)	0.195627	0.206940		
	0.229088	0.231072		
	0.299917	0.269119		
C2	0.251628	-0.196193		
C3	0.107606	0.097795		
H(C3)	0.213613	0.215400		
C4	0.199610	0.216580		
C5	-0.050021	0.209922		
H(C5)	0.240249	0.209059		
O	-0.299674	-0.284670		
N1	-0.379741	-0.375571		
H(N1)	0.462000	0.463488		
N2	-0.229319	-0.230732		
N3	-0.747691	-0.768472		
H(N3)	0.419477	0.405115		
	0.426170	0.427813		
Sum of ligand charges	+0.941	+0.727		

Table 6 Mulliken spin densities for the title compound

Fe	3.564672			
Cl	0.134318	0.129960	0.132276	0.137988
C1	0.004704	-0.001021		
H(C1)	0.000108 -0.000030 -0.000380	-0.000095 -0.000001 0.000098		
C2	-0.043301	-0.002435		
C3	0.006052	-0.063474		
H(C3)	0.000101	0.003921		
C4	-0.011103	-0.032509		
C5	0.033472	-0.004123		
H(C5)	0.000078	0.000518		
O	0.000884	-0.000024		
N1	0.000091	0.001320		
H(N1)	0.000157	0.000209		
N2	0.000496	0.015133		
N3	0.000962	0.007264		
H(N3)	0.000008 0.000003	-0.000063 0.000216		

The data gathered in Table 5 show that, in the $[\text{FeCl}_4]^-$ anion, one chlorine atoms has an atomic charge distribution of -0.0667 a.u, very different from the three others, which vary between -0.3397 and -0.3510 a.u. The sum of charges of the tetrachloroferrate (III) complex is -1.67 a.u. For the ligands, the most important feature is that the C2 and C5 carbons have very different charges, these charges compensating each other. The sum of charges of the two ligands is $0.941 + 0.727 = +1.668$ a.u, which equilibrate the negative charge of $[\text{FeCl}_4]^-$.

The results of Mulliken spin densities given in Table 6 show, as expected, that the atomic densities of spin are localized on the iron and a little on the chlorine atoms linked to it.

Molecular electrostatic potential

The molecular electrostatic potential (MEP) is used to predict the molecular reactive behavior towards electrophilic and nucleophilic attack and defined electrophile (electron-

deficient positively charged species) and nucleophile (an electron rich, negatively charged species) sites. The negative regions of the MEP which represent high electron density appear in red and are related to the electrophilic reactivity while the positive (blue) regions are related to nucleophilic reactivity. As it can be seen on Fig. 8, the red region is located around the FeCl_4^- anion which can be considered as electrophilic, while the positive region is localized on the organic cation which will be the reactive sites for nucleophilic attack.

Fig. 8 Molecular Electrostatic Potential maps of $(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O})_2[\text{FeCl}_4]$

Vibrational study

Infrared absorption spectroscopy was used to verify the functional groups present in the crystal and to investigate their vibrational behavior in the solid state. The IR spectrum of the title crystalline compound is shown in Fig. 9-a. The characteristic vibrational modes of this complex can be compared to those of similar materials [25-27]. In the high-frequency region, the very large band spreading between 3600 and 2800 cm^{-1} corresponds to the valence vibrations of C-H and N-H groups interconnected by a system of hydrogen bonds in the crystal [28]. The bands observed in the 1600 to 1050 cm^{-1} region can be assigned to the N-H and C-H bending vibrations and to the valence vibrations of C=C, C-C, C-N and C-N groups [29]. The

observed bands in the range $1000\text{--}600\text{ cm}^{-1}$ can be attributed to the out of plane bending modes of skeleton of amino-pyrimidine rings [30].

Fig. 8 Molecular Electrostatic Potential maps of $(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O})_2[\text{FeCl}_4]$

The infrared spectrum of $(\text{C}_5\text{H}_{7.50}\text{N}_3\text{O})_2[\text{FeCl}_4]$ was also calculated by DFT. The resulting IR spectrum is shown on Fig. 9-b and is very similar to the experimental one. A close agreement between the experimental and theoretical wave numbers is mostly achieved as shown in Fig.

10. Thus, the precision is well-sufficient to assign the experimental frequencies and to confirm the attributions proposed above.

Fig. 9 Infrared absorption spectrum experimental (a) and calculated (b) of $(C_5H_{7.50}N_3O)_2[FeCl_4]$

4. Conclusion

We have reported synthesis, crystal structure, physicochemical study and the Hirshfeld surface analysis of new tetrachloro-ferrate(III) salt. The results of single crystal X-ray diffraction analysis of this compound show that the tetrachloro-ferrate (III) anions form layers parallel to the (a, b) plane between which the organic cations are inserted. After formation of the $FeCl_4$ anion, the crystal structure is mainly stabilized by N-H...Cl, N-H...N and C-H...Cl hydrogen bonds and shows also significant pyrimidinium cycle stacking (C...C contacts). DFT calculations allow the attribution of the experimental IR bands. Frontier molecular orbitals study shows a low bond gap (1.15 eV) confirming a semiconductor character for the reported compound.

Supplementary data

Crystallographic data for the structural analysis have been deposited at the Cambridge Crystallographic Data Centre, CCDC No 1922466. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK: fax: (+44) 01223-336-033; e-mail: deposit@ccdc.cam.ac.

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The symmetry employed for this shelxl refinement is uniquely defined by the following loop, which should always be used as a source of symmetry information in preference to the above space-group names.

They are only intended as comments.

```

;
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 'x, y, z'

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 '-x, -y, -z'

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Reflections were merged by SHELXL according to the crystal class for the calculation of statistics and refinement.

_reflns_Friedel_fraction is defined as the number of unique Friedel pairs measured divided by the number that would be possible theoretically, ignoring centric projections and systematic absences.

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SHELXL-2014/7 (Sheldrick, 2014; WINGX (Farrugia, 1999)

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Cl2 Cl -0.34561(13) 0.24820(14) 0.78027(5) 0.0876(3) Uani 1 1 d . . . . .
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 H6C H -0.3836 0.6422 0.6891 0.092 Uiso 1 1 calc R U . . .
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 C8 C 0.4416(5) -0.3901(4) 0.90652(16) 0.0677(8) Uani 1 1 d
 H10 H 0.5032 -0.4587 0.8690 0.081 Uiso 1 1 calc R U . . .
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O2 0.0928(17) 0.0729(15) 0.0659(13) -0.0164(11) 0.0051(12) -0.0277(12)

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C4 0.0426(13) 0.0406(13) 0.0431(12) -0.0025(10) -0.0031(10) -0.0169(10)

C5 0.0675(18) 0.0570(17) 0.0633(17) -0.0231(14) 0.0032(14) -0.0187(14)

C6 0.080(2) 0.077(2) 0.0609(18) -0.0169(16) -0.0038(16) -0.0139(18)

C7 0.077(2) 0.0636(19) 0.0685(19) -0.0037(15) -0.0180(16) -0.0144(16)

C8 0.085(2) 0.0620(18) 0.0559(17) -0.0111(14) -0.0060(15) -0.0129(16)

C9 0.078(2) 0.0594(18) 0.0530(16) -0.0043(13) -0.0095(14) -0.0131(15)

C10 0.123(4) 0.096(3) 0.082(2) -0.026(2) 0.028(2) -0.044(3)

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All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes.

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Fe1 Cl1 2.1908(9) . ?

O1 C4 1.333(3) . ?

O1 C5 1.441(3) . ?

O2 C9 1.325(4) . ?

O2 C10 1.440(4) . ?

N1 C1 1.326(3) . ?

N1 C4 1.354(3) . ?
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N2 C2 1.365(3) . ?
N3 C2 1.323(3) . ?
N3 H1N 0.857(17) . ?
N3 H2N 0.868(18) . ?
N4 C6 1.328(5) . ?
N4 C9 1.355(4) . ?
N4 H6N 0.85(6) . ?
N5 C6 1.311(4) . ?
N5 C7 1.359(4) . ?
N6 C7 1.336(5) . ?
N6 H3N 0.872(18) . ?
N6 H4N 0.881(19) . ?
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C2 C3 1.397(3) . ?
C3 C4 1.362(3) . ?
C3 H4 0.9300 . ?
C5 H6A 0.9600 . ?
C5 H6B 0.9600 . ?
C5 H6C 0.9600 . ?
C6 H7 0.9300 . ?
C7 C8 1.392(5) . ?
C8 C9 1.367(4) . ?
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 O1 C4 C3 126.8(2) . . ?
 N1 C4 C3 120.9(2) . . ?
 O1 C5 H6A 109.5 . . ?
 O1 C5 H6B 109.5 . . ?
 H6A C5 H6B 109.5 . . ?
 O1 C5 H6C 109.5 . . ?
 H6A C5 H6C 109.5 . . ?
 H6B C5 H6C 109.5 . . ?
 N5 C6 N4 126.8(3) . . ?
 N5 C6 H7 116.6 . . ?
 N4 C6 H7 116.6 . . ?

N6 C7 N5 116.5(4) . . ?

N6 C7 C8 121.5(3) . . ?

N5 C7 C8 122.0(3) . . ?

C9 C8 C7 117.8(3) . . ?

C9 C8 H10 121.1 . . ?

C7 C8 H10 121.1 . . ?

O2 C9 N4 112.4(3) . . ?

O2 C9 C8 127.6(3) . . ?

N4 C9 C8 120.1(3) . . ?

O2 C10 H12A 109.5 . . ?

O2 C10 H12B 109.5 . . ?

H12A C10 H12B 109.5 . . ?

O2 C10 H12C 109.5 . . ?

H12A C10 H12C 109.5 . . ?

H12B C10 H12C 109.5 . . ?

loop_

_geom_hbond_atom_site_label_D

_geom_hbond_atom_site_label_H

_geom_hbond_atom_site_label_A

_geom_hbond_distance_DH

_geom_hbond_distance_HA

_geom_hbond_distance_DA

_geom_hbond_angle_DHA

_geom_hbond_site_symmetry_A

C1 H1 Cl4 0.93 2.84 3.623(3) 142.5 2_556

C3 H4 Cl1 0.93 2.95 3.780(2) 148.9 1_455

C5 H6B Cl4 0.96 2.91 3.707(3) 140.8 1_565
 C8 H10 Cl2 0.93 2.80 3.694(3) 162.5 1_645
 C10 H12B Cl5 0.96 2.93 3.822(4) 155.1 1_655
 N3 H1N Cl1 0.857(17) 2.88(2) 3.688(3) 159(3) 1_455
 N3 H1N Cl4 0.857(17) 2.84(3) 3.363(2) 121(2) 1_455
 N3 H2N N2 0.868(18) 2.203(19) 3.069(3) 175(3) 2_456
 N6 H3N Cl5 0.872(18) 2.77(3) 3.368(4) 127(3) 1_545
 N6 H4N N5 0.881(19) 2.14(2) 3.018(5) 174(4) 2_547
 N1 H5N N1 0.81(4) 1.89(4) 2.695(4) 176(5) 2_566

_refine_diff_density_max 0.634

_refine_diff_density_min -0.467

_refine_diff_density_rms 0.052

_shelx_res_file

;

shelx.res created by SHELXL-2014/7

TITL kk

CELL 0.71073 6.6406 7.4042 19.6212 88.3500 87.0050 77.2100

ZERR 2 0.0002 0.0003 0.0007 0.0025 0.0026 0.0024

LATT 1

SFAC Fe Cl C H N O

DISP Fe 0.34630 0.84440

DISP Cl 0.14840 0.15850

DISP C 0.00330 0.00160
 DISP H 0.00000 0.00000
 DISP N 0.00610 0.00330
 DISP O 0.01060 0.00600
 UNIT 2 8 20 30 12 4
 LIST 4
 ACTA
 BOND \$H
 FMAP 2
 PLAN -20 .5 .5
 omit -3 54.
 htab
 L.S. 12
 EQIV \$1 -x, -y, -z+1
 HTAB C1 CI4_\$1
 EQIV \$2 x-1, y, z
 HTAB C3 CI1_\$2
 EQIV \$3 x, y+1, z
 HTAB C5 CI4_\$3
 EQIV \$4 x+1, y-1, z
 HTAB C8 CI2_\$4
 EQIV \$5 x+1, y, z
 HTAB C10 CI5_\$5
 HTAB N3 CI1_\$2
 HTAB N3 CI4_\$2
 EQIV \$6 -x-1, -y, -z+1
 HTAB N3 N2_\$6

EQIV \$7 x, y-1, z
 HTAB N6 CI5_\$7
 EQIV \$8 -x, -y-1, -z+2
 HTAB N6 N5_\$8
 EQIV \$9 -x, -y+1, -z+1
 HTAB N1 N1_\$9
 dfix 0.88 0.02 n3 H1n
 dfix 0.88 0.02 n3 H2n
 dfix 0.88 0.02 n6 H3n
 dfix 0.88 0.02 n6 H4n
 WGHT 0.046000 0.378800
 FVAR 0.75481
 FE1 1 -0.017770 0.178351 0.749233 11.00000 0.04701 0.05203 =
 0.04983 -0.00817 0.00521 -0.01378
 CL1 2 0.089186 0.427123 0.715303 11.00000 0.07168 0.05694 =
 0.09778 0.00119 0.01889 -0.01958
 CL2 2 -0.345607 0.248198 0.780266 11.00000 0.05629 0.09514 =
 0.10914 -0.01907 0.02908 -0.01707
 CL4 2 0.025741 -0.011737 0.664278 11.00000 0.09023 0.10745 =
 0.08567 -0.05279 0.03578 -0.05491
 CL5 2 0.158138 0.051987 0.835989 11.00000 0.10535 0.09123 =
 0.09091 0.02019 -0.03732 -0.03261
 O1 6 -0.254776 0.643881 0.595843 11.00000 0.05574 0.04997 =
 0.05559 -0.01487 0.00490 -0.02611
 O2 6 0.676872 -0.183337 0.902552 11.00000 0.09281 0.07290 =
 0.06585 -0.01638 0.00510 -0.02771
 N1 5 -0.152176 0.415229 0.521663 11.00000 0.04073 0.04994 =

0.04857 -0.00917 0.00727 -0.02415
 N2 5 -0.325056 0.173724 0.507126 11.00000 0.05028 0.04565 =
 0.05356 -0.00961 0.00653 -0.02492
 N3 5 -0.620085 0.163531 0.571277 11.00000 0.06206 0.05840 =
 0.07176 -0.01205 0.01960 -0.03769
 N4 5 0.419913 -0.143739 0.982007 11.00000 0.07979 0.06333 =
 0.05776 -0.01307 -0.00706 -0.01714
 N5 5 0.174393 -0.330106 0.995902 11.00000 0.07951 0.07723 =
 0.07026 -0.01307 -0.00493 -0.01987
 N6 5 0.194429 -0.577113 0.926090 11.00000 0.10043 0.08305 =
 0.09221 -0.02067 0.00038 -0.03620
 C1 3 -0.176183 0.262011 0.492836 11.00000 0.04348 0.05182 =
 0.05320 -0.01446 0.00972 -0.02087
 AFIX 43
 H1 4 -0.077754 0.211904 0.459088 11.00000 -1.20000
 AFIX 0

 C2 3 -0.466333 0.247936 0.557454 11.00000 0.04466 0.04372 =
 0.04572 0.00136 0.00193 -0.02028
 C3 3 -0.450343 0.406524 0.591770 11.00000 0.04431 0.04635 =
 0.04218 -0.00504 0.00764 -0.01773
 AFIX 43
 H4 4 -0.544473 0.454438 0.626989 11.00000 -1.20000
 AFIX 0
 C4 3 -0.291825 0.488407 0.571755 11.00000 0.04262 0.04060 =
 0.04313 -0.00248 -0.00306 -0.01688
 C5 3 -0.388422 0.729205 0.651684 11.00000 0.06750 0.05698 =

0.06332 -0.02310 0.00324 -0.01871

AFIX 133

H6A 4 -0.527583 0.766250 0.637131 11.00000 -1.50000

H6B 4 -0.343111 0.835998 0.665998 11.00000 -1.50000

H6C 4 -0.383591 0.642200 0.689119 11.00000 -1.50000

AFIX 0

C6 3 0.256135 -0.192596 1.012358 11.00000 0.08018 0.07746 =

0.06091 -0.01687 -0.00382 -0.01394

AFIX 43

H7 4 0.192786 -0.121839 1.049145 11.00000 -1.20000

AFIX 0

C7 3 0.271256 -0.432695 0.942515 11.00000 0.07656 0.06361 =

0.06853 -0.00371 -0.01795 -0.01443

C8 3 0.441553 -0.390117 0.906523 11.00000 0.08463 0.06205 =

0.05590 -0.01114 -0.00601 -0.01293

AFIX 43

H10 4 0.503212 -0.458680 0.869018 11.00000 -1.20000

AFIX 0

C9 3 0.515065 -0.244151 0.928169 11.00000 0.07769 0.05939 =

0.05301 -0.00429 -0.00950 -0.01309

C10 3 0.782793 -0.272699 0.842461 11.00000 0.12304 0.09567 =

0.08239 -0.02558 0.02843 -0.04382

AFIX 133

H12A 4 0.830325 -0.402689 0.851896 11.00000 -1.50000

H12B 4 0.898866 -0.219428 0.829641 11.00000 -1.50000

H12C 4 0.689781 -0.255535 0.805796 11.00000 -1.50000

AFIX 0

H1N 4 -0.713825 0.208341 0.601689 11.00000 0.06178

H2N 4 -0.629505 0.068721 0.547660 11.00000 0.06586

H3N 4 0.263494 -0.647301 0.893995 11.00000 0.08837

H4N 4 0.093157 -0.609180 0.950891 11.00000 0.10648

H5N 4 -0.064962 0.470529 0.508626 10.50000 0.02427

H6N 4 0.467751 -0.050434 0.991662 10.50000 0.07042

HKLF 4

REM kk

REM R1 = 0.0394 for 2999 $F_o > 4\sigma(F_o)$ and 0.0594 for all 4036 data

REM 232 parameters refined using 4 restraints

END

WGHT 0.0443 0.3969

REM Instructions for potential hydrogen bonds

HTAB C1 Cl4_\$1

HTAB C3 Cl1_\$2

HTAB C5 Cl4_\$3

HTAB C8 Cl2_\$4

HTAB C10 Cl5_\$5

HTAB N3 Cl1_\$2

HTAB N3 Cl4_\$2

HTAB N3 N2_\$6

HTAB N6 CI5_\$7

HTAB N6 N5_\$8

HTAB N1 N1_\$9

EQIV \$10 -x+1, -y, -z+2

HTAB N4 N4_\$10