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Physicochemical characteristics of 2-, 3- and 4-methylpyridinium tetrachloroferrates(III)

Research Article

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Abstract: The crystal structure of 2-methylpyridinium tetrachloroferrate(III) was determined. The iron cation is tetracoordinated by chloride anions, and it adopts a slightly distorted tetrahedral coordination with three angles smaller, two almost equal and one larger than the tetrahedral. The compound is isostructural with its 3-, and 4-methylpyridinium analogues. The thermal properties of 2-, 3- and 4-methylpyridinium tetrachloroferrates(III) have been studied using TG and DSC techniques. The compounds exhibit a high stability in the melt.

Keywords: *Tetrachloroferrate(III) • Crystal structure • Thermal properties*

1. Introduction

We have been interested in tetrahalogenoferrate(III) ions since it has been found that they can be part of the structure of magnetic molecular conductors. These conductors have crystals which comprise planar electron donors, such as bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF) or its modification and a pair of paramagnetic inorganic anions, *e.g.* $[FeCl_4]^-$ and $[FeBr_4]^-$. These compounds are considered as novel, potentially attractive magnetic materials [1-3].

Recently, much attention has also been focused on designing tetrahalogenoferrate(III) salts as a new class of ionic liquids (*i.e.*, magnetic ionic liquids or MILs). Structural units of these compounds contain anions of transition metal complexes, *e.g.* $[FeCl_4]^-$ and ammonium, pyridinium, phosphonium or imidazolium cations [4,5]. Numerous applications can be found for magnetic ionic liquids, *e.g.* as magnetic fluids based on nanoparticles [6], transport and separation materials [7,8] as well as in the field of organic synthesis [9].

Our interest in tetrahalogenoferrates(III) has been directed towards their structure [10], magnetic properties [11,12] and thermal behavior [13,14]. We have recently reported magnetic properties of series of methylpyridinium salts, namely [2-Me(Py)H][$FeCl_4$], [3-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$] and the crystal structure only of 4-methylpyridinium tetrachlroroferrate(III), [4-Me(Py)H][$FeCl_4$] [15]. With the remaining two compounds, [2-Me(Py)H][$FeCl_4$], [3-Me(Py)H][$FeCl_4$], not enough quality crystals could be obtained and only their X-ray powder diagrams could be taken. In the present study we have been making an effort to investigate whether tetrachloroferrate(III) anions with methylpyridinium cations can be considered as a new class of magnetic ionic liquids.

In this paper, the crystal structure of 2-methylpyridinium tetrachlroroferrate(III), [2-Me(Py)H][$FeCl_4$], is presented. Knowledge of the crystal structure of [2-Me(Py)H][$FeCl_4$] may be useful for elucidation of physicochemical properties of tetrachloroferrate(III) anions with methylpyridinium cations. Thermal properties of [2-Me(Py)H][$FeCl_4$], [3-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$] are also reported. Knowledge of their thermal properties would allow verification of whether the compounds under investigation could be treated as ionic liquids.

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2. Experimental procedure

2.1. Synthesis

The synthesis of $[2\text{-Me(Py)H}][FeCl_4]$, $[3\text{-Me(Py)H}][FeCl_4]$ and $[4\text{-Me(Py)H}][FeCl_4]$ was carried out using a procedure reported earlier [15]. $[2\text{-Me(Py)H}][FeCl_4]$ specimens for crystallographic investigation were obtained by recrystallization from an acetone-ethanol (1:1) mixture at ambient temperature. After approximately three weeks, yellow-orange crystals appeared.

2.2. X-ray structure analysis of $[2\text{-Me(Py)H}][FeCl_4]$

A yellow needle-shaped crystal was used to collect X-ray intensity data with an Oxford Diffraction Gemini R Ultra diffractometer with a Ruby CCD detector. Data was collected with a graphite monochromated Mo Kα radiation (λ = 0.71073 Å) at 295.0(2) K, with ω scan mode. A 30 s exposure time was used and all reflections inside the Ewald sphere were collected up to $2\theta = 50.0°$. Details of the crystal data and refinement are given in Table 1. During data reduction multi-scan [16] absorption corrections were applied. The structure was solved by direct methods. All the non-hydrogen atoms were refined anisotropically using full-matrix, least-squares technique on F^2. All the hydrogen atoms were positioned geometrically, and constrained to ride on their parent atoms with isotropic temperature factors equal to 1.2 or 1.5 (for methyl group) times the value of the equivalent temperature factor of the parent atom. *SHELXS97*, *SHELXL97* [17] programs were used for data reduction and structure refinement. *PLATON* [18] program was used for computation of interactions and the *ORTEP-3* [19] program was used for molecular graphics.

Full crystallographic details, excluding structural features, have been deposited (CCDC deposition No. 811965) with the Cambridge Crystallographic Data Centre. These data may be obtained, on request, from the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK. Tel. +44 1223 336408, Fax +44 1223 336033, E-mail: deposit@ccdc.cam.ac.uk.

2.3. TG-DSC measurements

The TG-DSC measurements in argon (Ar 5.0) were run on a STA 449 *F3 Jupiter*® thermal analyzer (Netzsch), (range 308-873 K, Al crucible, empty crucible as a reference, sample mass 4-8 mg, heating rate 15 K min^{-1}, flow rate of the carrier gas 20 mL min^{-1}).

2.4. DSC measurements

The DSC measurements were carried out in argon (Ar 5.0) in a model DSC 204 Netzsch calorimeter (range 283-488 K, Al crucible, empty Al crucible as a reference,

Table 1. Crystal data and structure refinement for $[2\text{-Me(Py)H}][FeCl_4]$.

Empirical formula	$C_6H_8Cl_4FeN$
Formula weight	291.78
Temperature (K)	295.0(2)
Wavelength, λ (Mo Kα) (Å)	0.71073
Crystal system, space group	orthorhombic, *Pbca*
Unit cell dimensions (Å)	
A	9.2427 (7)
B	13.6862 (6)
C	18.3894 (14)
Volume (Å³)	2326.2 (3)
Z, Calculated density (Mg m^{-3})	8, 1.666
Absorption coefficient (mm^{-1})	2.165
F (000)	1160
Crystal size (mm)	0.6 × 0.1 × 0.1
θ Range for data collection (°)	2.98–25.00
Index ranges	$-9 \le h \le 10$, $-16 \le k \le 16$, $-20 \le l \le 21$
Reflections collected/unique [R_{int}]	17076/2045 [0.054]
Completeness to $2\theta = 50.0°$ (%)	99.9
Refinement method	full-matrix least-squares on F^2
Data/restrains/parameters	2045 / 0 / 110
Goodness-of-fit on F^2	0.833
Final R indices [$I>2\sigma(I)$]	$R_1 = 0.0409$, $wR_2 = 0.1100$
R indices (all data)	$R_1 = 0.0890$, $wR_2 = 0.1205$
Largest difference in peak and hole (e Å^{-3})	0.453 and -0.233

sample mass 4-6 mg, heating rate 10 K min^{-1}, flow rate of the carrier gas 20 mL min^{-1}). The DSC calorimeter had been calibrated earlier using standard materials (In, Sn, Bi, Zn, CsCl) provided by a manufacturer of the calorimeter (the Netzsch Company). At least two measurements were run (heating and cooling) for each sample.

3. Results and discussion

3.1. Crystal structure description

The crystal structure of the [2-Me(Py)H][FeCl$_4$] compound including the atom-labeling scheme is shown in Fig. 1. The asymmetric unit of the compound contains a 2-methylpyridinium cation, [2-Me(Py)H]$^+$, and the tetrachloroferrate(III) anion, [FeCl$_4$]$^-$. The iron cation is four-coordinated by chlorine anions, and it adopts a slightly distorted tetrahedral coordination with three angles smaller, two almost equal and one larger than the tetrahedral. This distortion is caused by two hydrogen bonds – the N1–H1···Cl4 and the C3–H3···Cl3 (Table 2, Fig. 2). The Fe–Cl bond lengths fall in the range of 2.177(1) – 2.187(1) Å. With an average deviation from the planarity of 0.004 Å, the pyridinium ring is planar. The intramolecular C$_{ar}$–C$_{ar}$ bond lengths of the [2-Me(Py)H]$^+$ pyridine ring fall in the range of 1.292(10) Å - 1.426(8) Å and are similar to these found in other similar structures [20-22]. The N1–C2 and N1–C6 bond lengths equal 1.360(7) Å and 1.410(9) Å, respectively. The supramolecular structure is stabilized by two of the hydrogen bonds previously mentioned, namely N1-H1···Cl4 and C3-H3···Cl3 [23] that link the cations and the anions into corrugated sheets running parallel to the *c* axis and packed alternately along the crystallographic *a* axis.

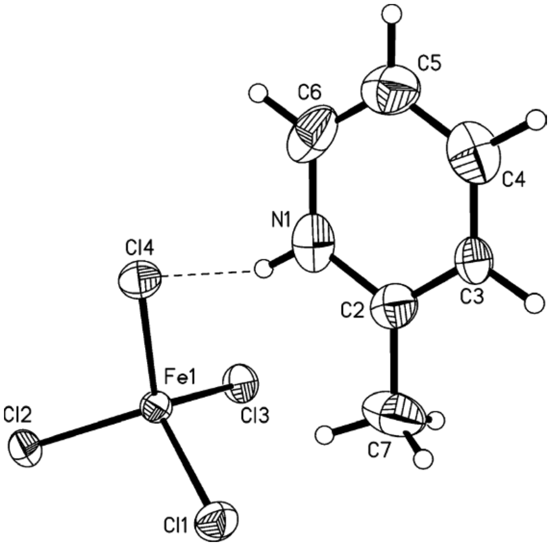

Figure 1. The molecular structure of [2-Me(Py)H][FeCl$_4$] showing the atom-labeling scheme. The N–H···Cl hydrogen bond is represented by dashed lines. The displacement ellipsoids are drawn at the 25% probability level, and H atoms are shown as small spheres of arbitrary radius.

Table 2. Hydrogen-bond geometry /Å, /° for [2-Me(Py)H][FeCl$_4$].

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1···Cl4	0.86	2.76	3.569 (6)	156
C3—H3···Cl3[a]	0.93	2.80	3.731 (6)	174

[a] Symmetry code: x, –y + 3/2, z + 1/2

In previous studies of the series of methylpyridinium tetrachloroferrates(III) it was found that they are isostructural [15]. Moreover, with increasing distance between the methyl group of the methylpyridiunium cation and the nitrogen atom, the intermolecular exchange parameter, ***zJ'***, slightly decreases, which means weaker antiferromagnetic interactions at low temperatures. Having established the structure of [2-Me(py)H][FeCl$_4$] we are now able to explain the slightly higher value of the ***zJ'*** parameter for [2-Me(py)H][FeCl$_4$] (***zJ'*** = -0.93 cm^{-1}) than that of [4-Me(py)H][FeCl$_4$] (***zJ'*** = -0.75 cm^{-1}) [15].

Bearing in mind the lack of free chloride ions in the crystal lattice of the compounds it was suggested that the most probable interaction pathway is likely to occur through orbitals of the chloride ligands of two tetrachloroferrate(III) ions, Fe-Cl···Cl-Fe [20]. This means that the interactions between magnetic centers of Fe(III) depends not only on Fe(III)···Fe(III) distance but also on the mutual orientation of two neighboring [FeCl$_4$]$^-$ coordination entities.

At this point, it is worth mentioning that the nearest Fe(III)···Fe(III) distance in the crystal lattice of [2-Me(py)H][FeCl$_4$] (6.497(2) Å) is a little longer than in [4-Me(py)H][FeCl$_4$] (6.390(2) Å) [15] but the coupling between electrons of Fe(III) ions is stronger for the former complex. Such behaviour can be explained by comparison of the nearest Fe–Cl···Cl–Fe distances in the crystal lattice of both compounds, which are much shorter in the case of [2-Me(py)H][FeCl$_4$] (3.634 Å) than they are for [4-Me(py)H][FeCl$_4$] (3.706 Å) [15]. This finding lends support to the suggestion that the strength of antiferromagnetic interactions depends strongly on the mutual arrangement of [FeCl$_4$]$^-$ structural units [24]. The arrangement of the Fe–Cl···Cl–Fe entities within the crystal lattice is affected by the position of the methyl group in the pyridine ring.

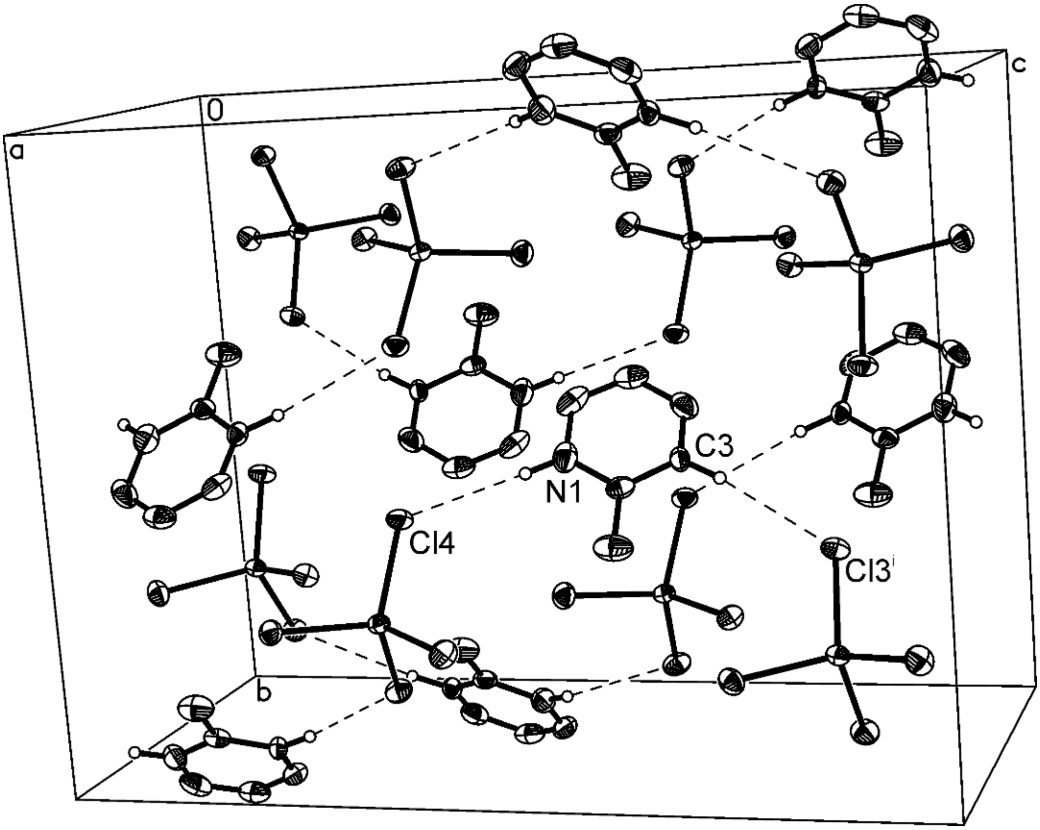

Figure 2. The crystal packing of [2-Me(Py)H][$FeCl_4$]. The N–H···Cl and C–H···Cl hydrogen bonds are represented by dashed lines. The displacement ellipsoids are drawn at the 25% probability level, and H–atoms not involved in interactions were omitted for clarity.

3.2. Thermal properties

Results of the thermal analysis of the compounds studied are compiled in Table 3, while the TG and DSC curves are presented in Fig. 3.

Decomposition of [2-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$] is preceded by solid-solid and solid-liquid phase transitions (Table 4). Upon cooling of [2-Me(Py)H][$FeCl_4$] two phase transitions occur as well. However, their peaks are shifted to lower temperatures. This finding can be explained in terms of super-cooling of the sample due to delayed formation of crystal nuclei of the new phase. The comparable value but different sign of enthalpy upon heating and cooling the sample means that the solid-solid phase transformation is reversible.

A slightly different behaviour is seen during DSC measurements of [4-Me(Py)H][$FeCl_4$]. Upon heating of [4-Me(Py)H][$FeCl_4$] two solid-solid and one solid-liquid phase transitions are observed. Then, upon cooling only two exothermic peaks are seen. The first is due to recrystallization of the compound and, similarly as with 2-methylpyridinium salt, is displaced towards lower temperatures. The second appears at a temperature *ca.* 4^{o}C lower than that observed upon heating of the sample. The lack of the third peak means that one of the solid-solid phase transitions preceding melting of [4-Me(Py)H][$FeCl_4$] is irreversible. In the case of [3-Me(Py)H][$FeCl_4$], only one peak emerges, due to melting of the sample.

It is worth mentioning that the melting points of [3-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$] are above 373 K and that of [2-Me(Py)H][$FeCl_4$] is close to 373 K. This means that the compounds studied can not be considered as ionic liquids [25]. On the other hand, it is interesting to note that the liquid phase persists up to *ca.* 493 K (depending on which kind of methylpyridinium cation) and in this phase the complexes undergo degradation. These relatively high decomposition points indicate a high stability of [2-Me(Py)H][$FeCl_4$], [3-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$] in the melt.

The thermal decomposition of the complexes occurs in several steps and is different for each compound (Fig. 3). Our previous studies [13] as well as other reports in the literature [26,27] show that thermal decomposition of the tetrachloroferrates(III) is complex. The iron ions undergo many non-stoichiometric transformations which are accompanied by complicated redox reactions. For these reasons it is difficult to suggest definite equations describing the processes.

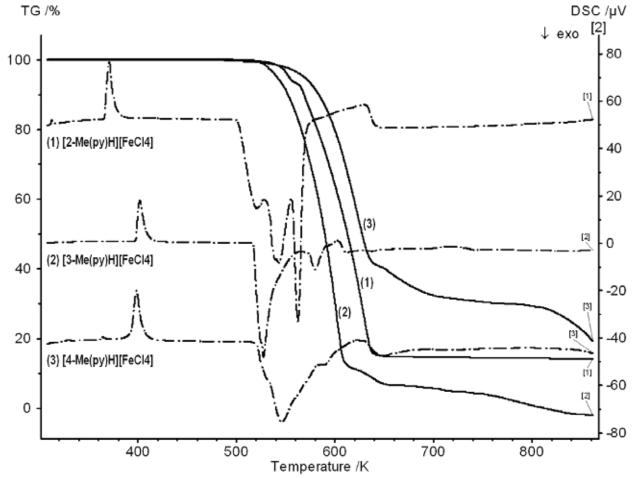

Figure 3. TG and DSC curves of the thermal decomposition of [2-Me(Py)H][$FeCl_4$] (1), [3-Me(Py)H][$FeCl_4$] (2) and [4-Me(Py)H][$FeCl_4$] (3) in argon.

Table 3. Thermal characteristics of [2-Me(Py)H][$FeCl_4$], [3-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$] in argon.

Formula	Range of decomposition/ K	Peak temperature [a] /K		Mass loss/ %
		DTG	DSC	
[2-Me(Py)H][$FeCl_4$]	501 – 559	552	520, 543, 562	6.5
	559 – 651	629	629 (endo)	78.6
[3-Me(Py)H][$FeCl_4$]	515 – 619	601	527, 580, 602 (endo)	86.3
	619 – 663	639	-	4.8
	663 – 858	-	721 (endo)	8.5
[4-Me(Py)H][$FeCl_4$]	513 – 640	622	546, 576	58.4
	640 – 773	654	648	11.4

[a] Peak temperature – the temperature at which a maximum of the thermal effect emerges

Table 4. Temperature /K and enthalpy changes /kJ mol^{-1} for physical transformations of [2-Me(Py)H][$FeCl_4$], [3-Me(Py)H][$FeCl_4$] and [4-Me(Py)H][$FeCl_4$].

Formula	Heating		Cooling	
	T /K [a]	ΔH /kJ mol^{-1}	T /K [a]	ΔH /kJ mol^{-1}
[2-Me(Py)H][$FeCl_4$]	310.5	0.94	303.0	- 0.91
	367.5	10.61	329.5	- 10.56
[3-Me(Py)H][$FeCl_4$]	402.3	15.17	343.5	- 14.33
[4-Me(Py)H][$FeCl_4$]	329.2	0.29	325.2	- 0.35
	364.8	0.38	-	-
	398.9	12.48	357.9	- 11.40

[a] Peak temperature – temperature at which a maximum of the thermal effect emerges

4. Conclusions

In conclusion, we successfully obtained enough quality crystals of a new iron(III) complex salt, 2-methylpyridinium tetrachloroferrate(III), [2-Me(Py)H][$FeCl_4$]. Its crystal structure was determined by X-ray crystallography. The compound is isostructural with its 3- and 4-methylpyridinium analogues. The arrangement of the Fe–Cl···Cl–Fe entities within the crystal lattice is affected by the position of methyl group in the pyridine ring and has an influence on interactions between magnetic centers of Fe(III) at low temperatures. The melting points of the compounds studied are close to 373 K. However, in the melt these compounds are extremely stable. Their degradations occur at temperatures ca. 100 K higher than the melting points.

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