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Thermal analysis of quinolinium tetrachloroferrate(III)

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Abstract

Thermal decomposition of a compound consisting of a tetrachloroferrate(III) anion and a quinolinium cation, of general formula [QH][FeCl$_4$], has been studied using TG–FTIR, TG–MS, DTA and DTG techniques. The measurements were carried out in an argon atmosphere over the temperature range 20–800 °C. The solid products of the thermal decomposition were identified by IR, FIR and Mössbauer spectroscopy.
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1. Introduction

A number of complexes with a tetrahedral tetrachloroferrate(III) anion have been reported. Investigations have been focused on their spectroscopic characterization, structural analysis, magnetic properties [1] and, recently, their interaction with non-aqueous solvents [2].

The tetrachloroferrate(III) ions have a structure of a slightly distorted tetrahedron. The mean weighted Fe–Cl bond lengths and the Cl–Fe–Cl angles are 2.204 Å and 109.32°, respectively, for the non-associated [FeCl$_4$]$^-$ ion (a total of 164 structures) [3]. Owing to the presence of the high-spin d^5 Fe(III) in these compounds, they are likely to become new, attractive magnetic materials [4]. The tetrahaloferrate(III) anions are stable in aprotic and inert solvents. In amphiprotic solvents, due to the propensity of the solvents to form hydrogen bonds, the tetrahaloferrate(III) anions undergo dissociation.

However, in the chemical literature information of thermal behaviour of these compounds and resulting products are missing. For this reason, our interest has been concerned with the determination of the thermal stability of tetrahalogenoferrates(III) stabilized with cations of aliphatic and aromatic bases. The results presented here are a continuation of our efforts in this field [5]. In this paper, the synthesis and results of thermal analysis (TG, TG–FTIR, TG–MS, DTG and DTA) of a new salt, quinolinium tetrachloroferrate(III), are presented.

2. Experimental

2.1. Synthesis and chemical analysis

The synthesis of quinolinium tetrachloroferrate(III) was carried out using a procedure similar to that reported for the preparation of other tetrachloroferrates(III) [2]. Thus, an ethanolic solution of anhydrous ferric chloride was first prepared by dissolving FeCl$_3$ (0.05 mol) in 96% ethanol (25 mL). Then, to this solution a stoichiometric quantity of a 12 M HCl solution was added followed by quinoline (0.05 mol). The compound crystallized directly from this mixture at a low temperature after approximately 14 days as yellow–orange crystals. The composition of the compound was confirmed by elemental analysis (C, H, N) and potentiometric titration of the chloride with a standardized 0.1 M AgNO$_3$ solution: anal. calc. for C$_9$H$_{10}$Cl$_4$FeN: C, 32.46; H, 2.44; Cl, 43.32; N, 4.27. Found: C, 32.76; H, 2.44; Cl, 43.55; N, 4.17%.

2.2. Instrumental

The IR spectra were recorded on a BRUKER IFS 66 spectrophotometer in a KBr pellet over the 4400–650 cm^{-1} range and the FIR spectra (700–50 cm^{-1} range) were taken in PE.

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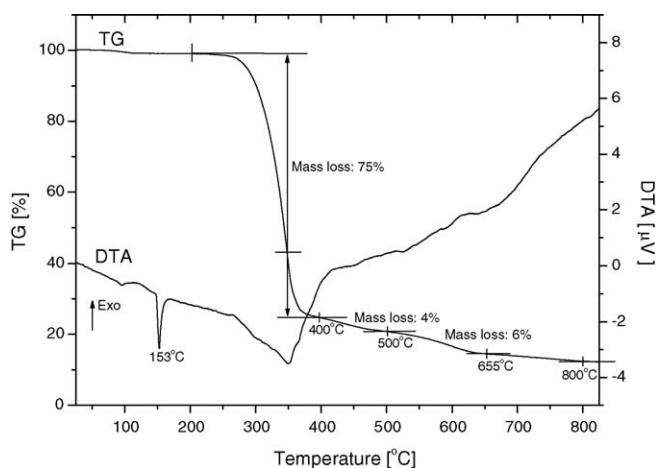Fig. 1. TG and DTA curves of thermal decomposition of [QH][FeCl$_4$] in argon.

Fig. 2. IR spectra of [QH][FeCl$_4$] (1) and of solid residue left after the first TG step of decomposition in argon (400 °C) (2).

The Mössbauer spectra were recorded at room (293 K) and low (80 K) temperatures by means of conventional spectrometer in transmission geometry using a ^{57}Co/Rh source. A gas flow cryostat was applied for low temperature measurements. The samples were prepared in pellets with thickness of ca.10 mg Fe/cm^2. The spectra were numerically analysed by a least-squares procedure assuming Lorentzian line shapes and isomer shifts are quoted relative to α-Fe.

The TG–DTG–DTA–MS measurements in argon (Ar 5.0) were run on a Setsys 16/18 thermalanalyzer (Setaram) coupled with a Thermostar quadrupole mass spectrometer (range 20–800 °C, corund crucible, sample mass 11 mg, Al$_2$O$_3$ as reference, heating rate 5 K/min, flow rate of carrier gas 15 mL/min). The TG–FTIR analyses in argon (Ar 5.0) were run on a Netzsch TG 209 apparatus coupled with a Bruker FTIR IFS66 spectrophotometer (range 25–800 °C, corund crucible, sample mass 11 mg, Al$_2$O$_3$ as reference, heating rate 5 K/min, flow rate of carrier gas 18 mL/min).

The course of thermal analysis was broken at points corresponding to the main steps of decomposition and the residues in the crucible were quickly cooled in the stream of argon. This enabled to analyze the residues at a strictly pre-determined step of decomposition. The analysis was carried out using the IR, FIR, and Mössbauer spectroscopic techniques, as well as elemental analysis (C, H, N).

3. Results and discussion

Results of thermal analysis of [QH][FeCl$_4$] are shown in Fig. 1. First effects are seen at ca. 95 and 153 °C (DTA), respectively, as two endothermic peaks. The first peak indicates phase transition rather than sample drying in spite of a small inflection in the TG curve. This conclusion is further supported by missing characteristic vibrations of H$_2$O in the IR spectrum of the volatiles (25–130 °C range) and of an $m/z = 18$ peak in the analysed ionic currents. The other one is due to melting of the sample.

The thermal decomposition of [QH][FeCl$_4$] occurs in two main steps and is preceded by melting of the compound. The first step is rapid with onse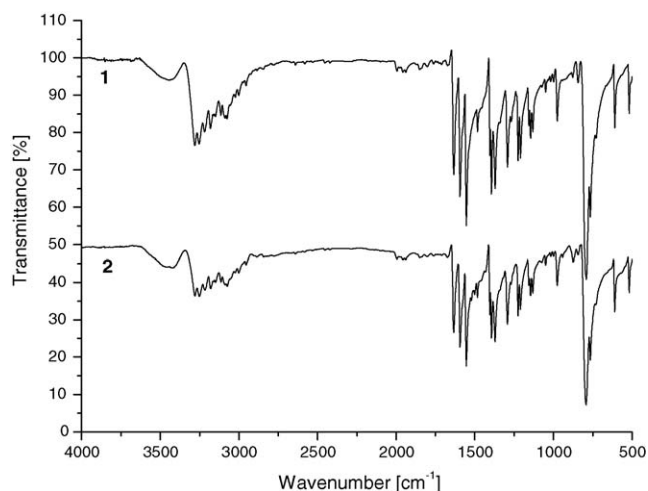t around 200 °C. The loss in mass accompanying this process amounts to ca. 75% at 400 °C (DTG$_{min}$: 347 °C). The second step is much slower. In the TG curve, in the range 400–800 °C there are, however, small inflections seemingly due to separate decomposition steps. The total loss in mass up to 800 °C is 87%.

Spectroscopic analysis (IR) of a solidified product of the first TG step of [QH][FeCl$_4$] decomposition, terminating at 400 °C, shows existence of the quinolinium cation in the same form as that present in the original sample (Fig. 2). Furthermore, the percentages of C (33.7%), H (2.44%) and N (4.34%) in the decomposition product suggest that the organic/inorganic matter ratio is almost identical as that in non-heated compound.

Inspection of the IR spectra of gaseous decomposition products released over the temperature range considered shows that the initial compound leaving the liquid phase, containing protonated quinoline, undergoes dissociation to quinoline and HCl. The broad 2750–2400 cm^{-1} band in the IR spectrum is probably due to N−H···Cl interaction occurring in products being released. The presence of quinoline and HCl in gaseous decomposition products is also evident from the curves of ionic currents (quinoline: $m/z = 51$, 64, 129; HCl: $m/z = 35$, 36, 38) recorded during TG–MS analysis. In the IR spectrum of the gaseous decomposition products of the compound, a fragment characteristic of CO$_2$ is seen (Fig. 3). Its occurrence is unclear in view of lack of the $m/z = 44$ peak in TG–MS. Most probably the quantity of CO$_2$ is small and might be attributed to oxidation of the volatiles with trace amounts of oxygen present in argon (5.0).

To identify the inorganic part of the first step of decomposition, FIR spectroscopy was used. The spectrum of the product of the first decomposition step is almost identical with that of the non-heated compound, [QH][FeCl$_4$] (Fig. 4). The frequencies: stretch ν_3(F$_2$), Fe–Cl and twist ν_4(F$_2$), Cl–Fe–Cl appear at ca. 376 and 138 cm^{-1}, respectively. These spectroscopic features are consistent with those of other tetrachloroferrates(III) [6–8] and confirm the presence of [FeCl$_4$]$^-$ ion in the product of the first decomposition step ($T_k = 400$ °C) of the compound.

Some additional information concerning the valence and spin state of iron in studied samples may be drawn from their
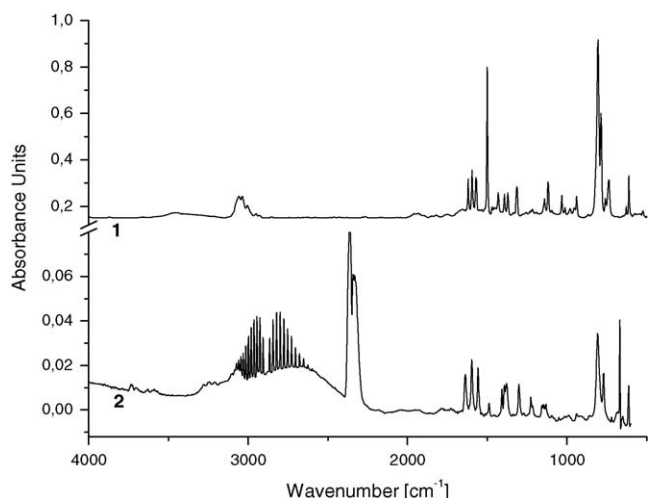
Fig. 3. IR spectra of gaseous quinoline (as a reference) (1) and gaseous products released during the first TG step of thermal decomposition of [QH][FeCl$_4$], recorded at 300 °C (2).
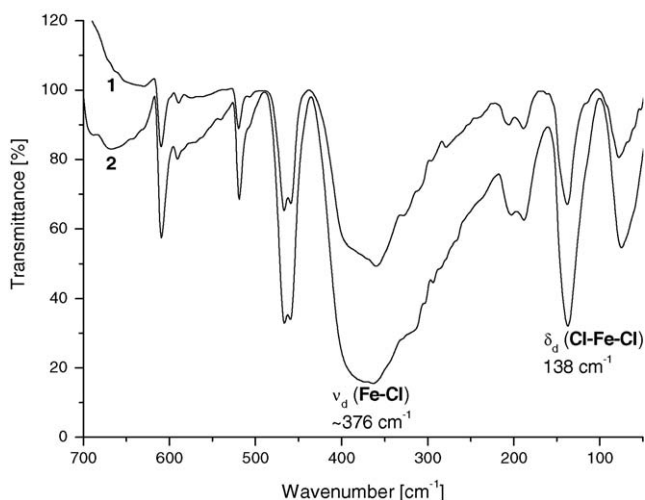

Fig. 4. FIR spectra of [QH][FeCl$_4$] (1) and of solid residue left after the first TG step of decomposition in argon (400 °C) (2).

Mössbauer spectra. The spectra of samples as prepared and decomposed at various temperatures were recorded at different conditions: at room temperature, at room temperature after degassing and at liquid nitrogen temperature. The Mössbauer spectra taken at room temperature are shown in Fig. 5. The hyperfine parameters obtained after the numerical analysis of all spectra are listed in Table 1.

The Mössbauer spectrum of sample as prepared (Fig. 5a) reveals the presence of iron(III) in form of [FeCl$_4$]$^-$ anion [5,6].

In the Mössbauer spectrum of the first step of decomposition product (Fig. 5b) a broad single (phase A) due to [FeCl$_4$]$^-$ prevails, what is consistent with the FIR spectra. There are also three doublets of different quadrupole splittings ascribed to three additional Fe(II) components (B–D) in this spectrum.

The Fe(II)/Fe(III) ratio estimated from the areas of appropriate doublets in the Mössbauer spectrum is equal to 35%:65%. Another situation was observed with the tetrachloroferrate(III)

Table 1
Mössbauer parameters for [QH][FeCl$_4$] as prepared and after decomposition in argon

T (K)	Phase	δ (mm/s)	Δ (mm/s)	Γ (mm/s)	A (%)	Species
[QH][FeCl$_4$] as prepared						
293, 293-vac	A	0.20(1)	0.23(1)	0.16(1)	100	[FeCl$_4$]$^-$
90	A	0.31(1)	0.25(1)	0.18(1)	100	[FeCl$_4$]$^-$
The product obtained after heating to 400 °C						
293	A	0.21(1)	0.24(1)	0.19(1)	67.0(6)	[FeCl$_4$]$^-$
	B	1.15(1)	2.26(1)	0.14(1)	13.8(9)	Fe^{2+}
	C	1.21(1)	3.00(1)	0.13(1)	15.4(8)	Fe^{2+}
	D	1.25(2)	0.90(3)	0.14(2)	3.8(6)	Fe^{2+}
293-vac	A	0.21(1)	0.24(1)	0.20(1)	66(1)	[FeCl$_4$]$^-$
	B	1.17(1)	2.30(1)	0.13(1)	32(1)	Fe^{2+}
	E	0.22(4)	1.28(8)	0.12^a	2.1(7)	Fe^{3+}
90	A	0.31(1)	0.24(1)	0.18(1)	78.1(4)	[FeCl$_4$]$^-$
	B	1.27(1)	2.60(1)	0.16(1)	19.1(3)	Fe^{2+}
	E	0.30(1)	1.38(2)	0.12(2)	2.8(3)	Fe^{3+}
The product obtained after heating to 500 °C						
293	B	1.15(1)	2.32(1)	0.15(1)	64(1)	Fe^{2+}
	H	1.07(1)	0.82(1)	0.14(1)	17(1)	[FeCl$_4$]$^{2-}$
	I	1.12(1)	1.56(2)	0.17(3)	11(2)	[FeCl$_5$]$^{3-}$
	F	0.41(1)	0.66(2)	0.12^a	8.5(5)	Fe^{3+}
293-vac	B	1.15(1)	2.32(1)	0.13(1)	61(1)	Fe^{2+}
	H	1.06(1)	0.84(2)	0.15(1)	14(1)	[FeCl$_4$]$^{2-}$
	I	1.09(1)	1.61(3)	0.19(3)	11(2)	[FeCl$_5$]$^{3-}$
	F	0.42(1)	0.66(2)	0.14(1)	14.6(7)	Fe^{3+}
90	B	1.27(1)	2.64(1)	0.19(1)	61(3)	Fe^{2+}
	H	1.20(1)	1.16(2)	0.19(1)	17(2)	[FeCl$_4$]$^{2-}$
	I	1.25(2)	2.00(4)	0.24(4)	17(4)	[FeCl$_5$]$^{3-}$
	F	0.45(1)	0.70(2)	0.14(2)	4.3(4)	Fe^{3+}
The product obtained after heating to 655 °C						
293	B	1.15(1)	2.31(1)	0.13(1)	50(1)	Fe^{2+}
	H	1.09(1)	0.76(1)	0.12(1)	19.5(8)	[FeCl$_4$]$^{2-}$
	I	1.09(1)	1.61(2)	0.25(3)	16(2)	[FeCl$_5$]$^{3-}$
	F	0.34^a	0.63(2)	0.25(1)	15.1(6)	Fe^{3+}
293-vac	B	1.15(1)	2.31(1)	0.13(1)	55.9(9)	Fe^{2+}
	H	1.10(1)	0.78(2)	0.14(1)	12.3(9)	[FeCl$_4$]$^{2-}$
	I	1.08(1)	1.60(4)	0.18(4)	6(2)	[FeCl$_5$]$^{3-}$
	F	0.34(1)	0.65(2)	0.22(1)	25.6(7)	Fe^{3+}
90	B	1.28(1)	2.62(1)	0.17(1)	54(1)	Fe^{2+}
	H	1.20(1)	1.14(1)	0.17(1)	14(2)	[FeCl$_4$]$^{2-}$
	I	1.26(1)	1.82(4)	0.28(5)	12(3)	[FeCl$_5$]$^{3-}$
	F	0.46(1)	0.70(1)	0.20(1)	20.1(5)	Fe^{3+}
The product obtained after heating to 800 °C						
293	B	1.15(1)	2.32(1)	0.14(1)	55.7(3)	Fe^{2+}
	F	0.38(1)	0.66(1)	0.20(1)	33.5(3)	Fe^{3+}
	G	0.19(1)	208.4(3)^a	0.13(1)	10.8(5)	Fe$_3$C
293-vac	B	1.14(1)	2.33(1)	0.13(1)	42.8(4)	Fe^{2+}
	F	0.38(1)	0.66(1)	0.19(1)	49.7(4)	Fe^{3+}
	G	0.21(1)	209.8(6)^a	0.13(1)	7.5(7)	Fe$_3$C
90	B	1.29(1)	2.61(1)	0.16(1)	50(3)	Fe^{2+}
	F	0.46(1)	0.62(1)	0.36(1)	41.6(3)	Fe^{3+}
	G	0.33(1)	246.6(6)	0.20(2)	9.0(6)	Fe$_3$C

T: temperature of the measurement; vac: vacuum; δ: isomer shift vs. room temperature α-Fe; Δ: quadrupole splitting; Γ: absorber line width; A: relative contribution to the total spectrum.

^{a} Fixed parameter.

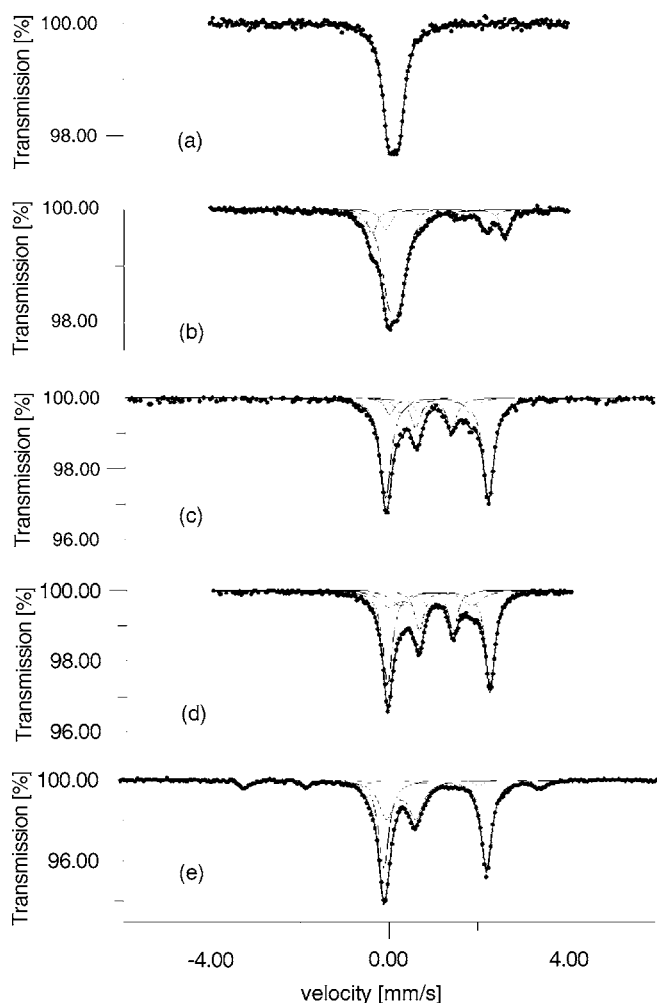Fig. 5. Room temperature Mössbauer spectra of [QH][FeCl$_4$] (a) and products of its thermal decomposition at 400 °C (b), 500 °C (c), 655 °C (d) and 800 °C (e).

Fig. 6. FIR spectra of solid residue left after heating [QH][FeCl$_4$] to 500 °C (1), 655 °C (2) and 800 °C (3) in argon.

ion stabilized with tetrabutylammonium cation. In that case, after heating at 410 °C, complete reduction of Fe(III) to Fe(II) took place [5]. Degassing of quinolinium tetrachloroferrate(III) sample and its repeated measurement at ambient temperature results in transformation of two less stable Fe(II) species (C and D) into a third one (B) which is the most stable form. The Mössbauer parameters of a doublet assigned to phase B reveal the presence of Fe(II) as bichloride-bridged ions capable of formation of larger chain-like polymeric systems [9]. A weak temperature dependence of the quadrupole splitting of this doublet suggests existence of a strong ligand field around the iron ions. The Debye temperature for the iron state attributed to phase B was estimated as equal to ~200 K. In addition, there is a small amount of Fe(III) species (phase E) in the sample. The relatively large quadrupole splitting (QS) of doublet attributed to phase E may indicate that it originates from the Fe(III) species of very low co-ordination symmetry.

It is remarkable that the Mössbauer parameters of the Fe(II) doublet (phase B) match those of an external doublet assigned to the more stable Fe(II) species present in the product of the first decomposition step of the previously studied compound,
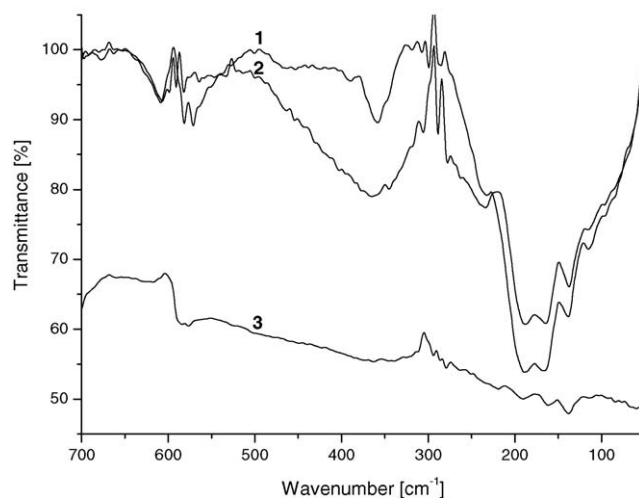
[(C$_4$H$_9$)$_4$N][FeCl$_4$] (T = 410 °C). It can thus be concluded that irrespective of using either the tetrabutylammonium or quinolinium ion for stabilization of the tetrachloroferrate(III), the degradation pathway at 400 °C leads to identical co-ordination form of Fe(II). Again, thermal stability of Fe(III) in the tetrahedral environment of the chloride ions is much higher when protonated quinoline is a cation.

Further, it should be mentioned that during thermal decomposition of [(C$_4$H$_9$)$_4$N][FeCl$_4$], the reduction of Fe(III) to Fe(II) was accompanied by oxidation of the chloride ions to afford small amounts of Cl$_2$ (m/z = 70, 72). However, in the decomposition products of [QH][FeCl$_4$] gaseous Cl$_2$ was missing (TG–MS). This was probably due either to low sensitivity of the TG–MS analyzer when recording trace amounts of chlorine or to liberation of the chloride ions exclusively as HCl. Consequently, an electron that reduces Fe(III) might be of organic origin. It is also probable that the HCl gas is produced through a free-radical mechanism as suggested previously [10]. In this case, an electron retained in the chloroferrate matrix might participate in the reduction of Fe(III). However, at this stage of investigation, the origin of the electron is difficult to be elucidated.

Above 400 °C the decomposition is much slower and the loss in mass at particular steps is small. The structure of the quinolinium cation undergoes degradation as indicated by missing characteristic bands in the IR spectrum of the solid product obtained at 500 °C. Elemental analysis reveals relatively high percentages of C (24.8%), H (1.15%) and N (3.04%) in the analyzed material. The organic fraction is likely to occur as a cation stabilizing the inorganic anion, as a neutral molecule (ligand) capable of co-ordination to iron(II) through the nitrogen atom, or both. Under these conditions also an irregular polymer, C$_c$H$_h$N$_n$, or elemental carbon can be formed [10,11].

In the FIR spectrum of the decomposition product obtained at 500 °C, the Fe–Cl stretching band in the [FeCl$_4$]$^-$ ion is displaced towards lower wavenumbers, whereas the Cl–Fe–Cl band is narrower and weaker (Fig. 6(1)). Thus, inspection of the FIR spectrum of the material has shown that the [FeCl$_4$]$^-$ ion is absent in the decomposition product obtained at 500 °C.

There emerge, however, new bands most probably ascribable to a system with lower symmetry owing either to a partial or complete suppression of degenerate vibrations. The degeneration may be due either to exchange of the chloride ligand at the iron atom or to formation of a new bond by the chlorine atom.

The bands around 115 and 286 cm^{-1} may be due to the presence of the $[FeCl_4]^{2-}$ ion [12], whereas those around 234, 287, 359 and 391 cm^{-1} might be assigned to the edge-sharing bitetrahedral $[Fe_2Cl_6]^{2-}$ species [13]. The co-existence of both entities cannot be rule out, as well. This hypothesis is supported by inspection of the Mössbauer spectra. At 500 °C there is an almost complete reduction of Fe(III) to Fe(II). The tetrachloroferrate(III) ion (phase A) is converted to phase B [Fe(II)] which already appeared in the product of the first step of decomposition ($T = 400$ °C). There are also two new phases, H and I, of Fe(II) (Table 1) but of another co-ordination environment than in phases C and D. It is worth mentioning that the Mössbauer parameters of phase H (IS = 1.07 mm/s and QS = 0.82 mm/s) correspond to a less thermodynamically stable Fe(II) phase occurring in the product of the first TG step of the tetrabutylammonium tetrachloroferrate(III) thermal decomposition ($T = 410$ °C, in Ar) [5]. The quadrupole splitting of the doublet assigned to phase H indicates a symmetry resembling that of $[FeCl_4]^{2-}$, whereas a doublet of phase I suggests the existence of Fe(II) in the form of a more complex system, namely $[FeCl_5]^{3-}$ [14,15]. There is also a small quantity of Fe(III) (phase F) in the sample but of another co-ordination environment than in the starting material and in phase E. The origin of phase F is obscure. It might be formed by oxidation of any of the Fe(II) phases. Degassing of the sample and its repeated measurement at ambient temperature resulting only in the increase of the F phase content confirms this suggestion (IS and QS values remain the same).

A comparison of the IR and FIR spectra of the solid residues left at 500 and 600 °C does not reveal any significant differences. It can thus be expected that at this step quantitative changes occur rather than qualitative ones induced by structural modifications of the organic and inorganic fragments of the material. This is supported by Mössbauer results. The same phases as those present in the sample obtained at 500 °C are observed in the spectrum of the sample decomposed at 655 °C. Here also phase B prevails (50%). Its contribution is, however, smaller than that in the 500 °C sample. The contribution of the remaining phases of iron (H, I and F) is larger. Degassing of the sample followed by measurements at ambient temperature reveals increased contents of phases B and F at the expense of the remaining two.

The FIR spectra of the residue left at 800 °C (the final decomposition product of [QH][FeCl$_4$]) differ considerably from those of the 500 and 655 °C samples (Fig. 6). Considering a small loss in mass (ca. 2%) accompanying this step (655–800 °C) it can be concluded that it is only due to a qualitative change in the phases of iron present in the sample, as supported by inspection of the Mössbauer spectrum (Fig. 5). It shows that Fe(II) occurs in phase B only. There is also an increase in the Fe(III) content in phase F. Again, the stable phases of Fe(II), H and I, disappear. Degassing of the sample followed by measurement at ambient temperature reveals an increase in the amount of Fe(III) at the expense of Fe(II). The reason for the change of the Fe(II)/Fe(III) ratio upon

degassing remains obscure. Most probably, the Fe(II)-attributed phase B is characterized by enhanced volatility resulting in partial elimination of this phase during degassing. Furthermore, in the Mössbauer spectrum of the final product appears a sextet that parameters correspond to a new phase of Fe$_3$C (phase G) (Fig. 5e).

4. Conclusions

Spectroscopic analysis of both the solid and gaseous products of the thermal decomposition of [QH][FeCl$_4$] shows the process to be complex and intricate. During the first TG step (200–400 °C), a partial decomposition of the tetrachloroferrate(III) takes place, whereas the organic part is released as quinoline. Above 400 °C there occurs a total decomposition of the cation resulting probably in a polymer, $C_cH_hN_n$, and a small amount of carbon. The chloride ions are released as HCl. It can also be hypothesized that part of the chloride ions is released as FeCl$_3$, which forms Fe$_2$Cl$_6$ dimers in the gas phase. Iron ions present in the sample undergo many non-stoichiometric transformations leading to less or more stable forms of iron in different co-ordination environments. These processes are accompanied by complicated redox reactions, which obscure thermal pathways of the compound transformations.

In view of the complexity of the processes which occur during thermal decomposition of [QH][FeCl$_4$] it is difficult to suggest definite equations describing the process. On the other hand, appearance of both the stable and unstable forms of iron during decomposition of the tetrachloroferrate(III), as well as the diversity of co-ordination forms, inspires for continuation of this study. To better understand the mechanism of the thermal processes it would be worthwhile to use a smaller cation stabilizing the $[FeCl_4]^-$ ion which would more readily escaper from the system. This would allow to answer the question what is the role of cation in thermal stabilization of the tetrachloroferrate(III) ion and how it affects transformations of iron present in the sample.

References

[1] See for example;
(a) K.D. Butcher, S.V. Didziulis, B. Briat, E.I. Solomon, J. Am. Chem. Soc. 112 (1990) 2231;
(b) B.D. James, M.B. Millikan, M.F. Mackay, Inorg. Chim. Acta 64 (1982) L55;
(c) R. Shaviv, C.B. Lowe, J.A. Zora, C.B. Aakeröy, P.B. Hitchcock, K.R. Seddon, R.L. Carlin, Inorg. Chim. Acta 198–200 (1992) 613.
[2] Z. Warnke, D. Wyrzykowski, G. Wawrzyniak, Polish J. Chem. 77 (2003) 1121.
[3] Cambridge Structural Database, Version 5.25, November 2003.
[4] U. Bentrup, M. Feist, E. Kemnitz, Prog. Solid State Chem. 27 (1999) 75.
[5] D. Wyrzykowski, T. Maniecki, A. Pattek-Janczyk, J. Stanek, Z. Warnke, Thermochim. Acta 435 (2005) 92.

[6] C.A. Clausen, M.L. Good, Inorg. Chem. 9 (1970) 220.

[7] A.P. Ginsberg, M.B. Robin, Inorg. Chem. 2 (1963) 817.

[8] R.J.H. Clark, F.B. Taylor, J. Chem. Soc. (A) (1967) 693.

[9] R.E. Greeney, C.P. Landee, J.H. Zhang, W.M. Reiff, Phys. Rev. B39 (1989) 12200.

[10] M. Feist, R. Kunze, D. Neubert, K. Witke, H. Mehner, E. Kemnitz, Thermochim. Acta 361 (2000) 53.

[11] M. Feist, S. Troyanov, A. Stiewe, E. Kemnitz, R. Kunze, Z. Naturforsch 52b (1997) 1094.

[12] A. Sabatini, L. Sacconi, J. Am. Chem. Soc. 86 (1964) 17.

[13] J. Sun, H. Zhao, X. Ouyang, R. Clérac, J.A. Smith, J.M. Clemente-Juan, C. Gómez-Garcia, E. Coronado, K.R. Dunbar, Inorg. Chem. 38 (1999) 5841.

[14] M. Feist, S.I. Troyanov, H. Mehner, K. Witke, E. Kemnitz, Z. Anorg. Allg. Chem. 625 (1999) 141.

[15] P.R. Edwards, C.E. Johnson, R.J.P. Williams, J. Chem. Phys. 47 (1967) 2074.