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ABSTRACT: [C₂mim][FeCl₄] behaves like a paramagnetic liquid at room temperature. Specific heat measurements indicate that there is a magnetic ordering below 3.8 K. The released entropy is far from the expected value for a J = 5/2 system, implying that the magnetic state is partly disordered. Full magnetic polarization was reached in fields above 4 T, and the anomaly in the magnetic susceptibility can be fully suppressed in higher B fields. Hence, the suggested magnetic ground state is superparamagnetic. In order to better understand the magnetic nature of this compound, structural investigations were carried out. Raman and IR-spectroscopy as well as UV–vis absorption measurements reveal the features characteristic for isolated [FeCl₄]⁻ anions in the liquid and solid state. The formation of dimeric [Fe₂Cl₇]⁻ units can not be evidenced. Thermal investigations show that the compound melts at 283 K. A solid—solid phase transition is observed at 261 K. [C₂mim][FeCl₄] decomposes above 623 K. By in situ crystal growth, it was possible to trap the two solid polymorphs of [C₂mim][FeCl₄]. The high temperature form of [C₂mim][FeCl₄] (1) crystallizes in the centric, monoclinic space group P2₁/c (No. 14) (a = 9.4124(19) Å, b = 14.645(3) Å, c = 12.444(4) Å, β = 129.84(18)°, V = 1317.1(6) Å³, Z = 4, ρ = 1.557 mg/m³), and the low temperature modification (2) in the non-centrosymmetric, monoclinic space group P2₁ (No. 4) (a = 6.1337(12) Å, b = 14.362(3) Å, c = 7.1111(14) Å, β = 91.33(3)°, V = 626.3(2) Å³, Z = 2, ρ = 1.636 mg/m³). Both polymorphs show the characteristic structural features of the [C₂mim]⁺ cation and isolated [FeCl₄]⁻ anions. However, they deviate in the conformation of the ethyl-chain of the cation and more importantly the relative arrangements of cation and anion. Interestingly, the low temperature modification shows only weak hydrogen bonds, whereas the high temperature modification shows an extended hydrogen-bonding network.

INTRODUCTION

Ionic liquids (ILs) have been in the focus of chemistry and materials science over the past few decades because of their outstanding properties. As salts, ILs are composed of distinct cations and anions which render them widely tunable. Indeed, they may be specifically designed for particular applications by the right choice of the respective cation and anion. Properties and property combinations which are often found for ILs — aside from often being liquid at room temperature and below — include comparatively low viscosities (especially at elevated temperature), negligible vapor pressures, wide liquidus ranges, good thermal stabilities, considerable electric conductivities, and wide electrochemical windows, which are interesting for a large number of applications.¹

Metal-containing ILs are promising new materials that allow adding further features to the typical properties of ILs such as magnetic, photophysical/optical, or catalytic behavior that are due to the incorporated metal.²⁻³ Solutions of lanthanide compounds in ILs have been shown to be promising novel soft luminescent materials for use in photochemistry and spectroscopy.⁴ However, trivalent lanthanides are not only of interest because of their luminescent behavior but also because of their magnetism. Especially the trivalent ions of Gd—Tm have high local magnetic moments, ranging from 8 to 11 μB. And indeed, it is possible to synthesize magnetic, luminescent ILs, for example, [C₄mim]₃·[Dy(SCN)₈]·(H₂O)ₓ (x = 0–2).³ Such a liquid can be manipulated by external magnetic fields. Traditionally, magnetic fluids (or ferrofluids) consist of nanoparticles of magnetic materials (e.g., iron-oxides) embedded in a carrier liquid, such as water or long chain hydrocarbons.⁵ In that context, ILs also offer advantages as liquid nanoparticle support.⁶ However, the magnetic ILs discussed here are single component materials where the magnetic ion does not get incorporated as small (nano)particles but as charged metal complex ions. The prerequisite is a large number of unpaired electrons in the valence shell of the metal cation.

The first example for such a liquid is [C₄mim][FeCl₄] (C₄mim = 1-butyl-3-methyl-imidazolium). Although the compound had been known for a while,⁶ its magnetic properties and potential application has been evaluated just recently.⁹ For [C₄mim][FeCl₄], a magnetic susceptibility of 40.6 × 10⁻⁶ emu/g, corresponding to a molar susceptibility μₘ₀ of 0.0137(7) emu/mol, was reported. The effective magnetic moment of μₑff = 5.8 μB is in accordance with a high-spin S = 5/2 state. Similar values are found for other

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tetrachloro- and tetrabromo-ferrate(III) liquids. Because of the high single ion magnetic moments, these ILs show a strong response to external magnetic fields. It has been shown that not only the liquid itself can be manipulated by a magnetic field but also that nonmagnetic (diamagnetic) materials can be transported and separated according to their density and magnetic susceptibility in these liquids. In consequence, there is a strong interest in paramagnetic ILs and especially in how such materials can be designed by choosing the right cation—anion combination.

However, in the context of magnetic ILs containing complex anions of metal cations with a large number of unpaired spins, the question about cooperative magnetic effects, complex anion interaction, and ion separation is quite important. The reported structures of [C\text{2mim}][\text{CoCl}_4] and [C\text{2mim}][\text{NiCl}_4] show isolated, discrete tetrahedral anions and no metal-bridging halides, and feature large distances between nearest neighboring metal centers.

However, it has been clearly established for [AlCl\textsubscript{4}]\textsuperscript{−} that dimers, [Al\textsubscript{2}Cl\textsubscript{7}]\textsuperscript{−}, can form. Similarly for [FeCl\textsubscript{4}]\textsuperscript{−} the formation of [Fe\textsubscript{2}Cl\textsubscript{6}]\textsuperscript{−} has been evidenced by Raman spectroscopy. The formation of a chloro bridged dimer would allow, in principle, the antiferromagnetic coupling of two Fe\textsuperscript{3+} ions. To investigate the structural behavior of such ILs in detail, we have looked at the structural and magnetic features of [C\text{2mim}][FeCl\textsubscript{4}] in detail. For [C\text{2mim}][FeCl\textsubscript{4}], a magnetic moment of 5.8 \mu\text{B} at 20 °C, a density of 1.42 g/cm\textsuperscript{3}, low viscosity of 14 cP at 30 °C, and high conductivity (1.8 \times 10\textsuperscript{−2} S cm\textsuperscript{−1} at 20 °C) were reported. Indeed, [C\text{2mim}][FeCl\textsubscript{4}] is currently one of the best studied paramagnetic ILs.

### EXPERIMENTAL DETAILS

1-Methyl-3-ethylimidazolium tetrachloroferrate(III), [C\text{2mim}][FeCl\textsubscript{4}]. Two grams of [C\text{2mim}][\text{Cl}] (0.014 mol) (Merck KGaA, Darmstadt, Germany, synthesis grade) and 3.69 g of FeCl\textsubscript{3}·6H\textsubscript{2}O (0.014 mol) are mixed without solvent and gently heated in an oil bath to 30 °C. Two liquid phases form. To increase the yield of the target compound, the aqueous phase was heated to decrease miscibility of the product with water. The segregated product phase was then dried in dynamic vacuum at 60 °C overnight. The product is obtained as a brown, oily liquid.

Elemental analysis (%) calcd for [C\text{2mim}][FeCl\textsubscript{4}]: C 23.00, H 3.56, N 9.07; found: C 22.89, H 3.48, N 8.96.

\textit{MIR.} ν [cm\textsuperscript{−1}] = 3145.4 (m), 3111.1 (m), 3099.7 (m, shoulder), 2979.7 (w), 2943.9 (w), 2938.2 (w), 1589.2 (m), 1564.9 (s), 1453.4 (m, shoulder), 1446.2 (m), 1424.8 (w), 1384.8 (w), 1346.2 (w, shoulder), 1331.9 (w), 1287.6 (w), 1163.3 (s), 1104.7 (m), 1084.7 (m), 1024.7 (w), 956.1 (w), 827.4 (s), 798.9 (w, shoulder), 738.8 (s), 698.8 (m), 644.5 (m), 618.8 (s), 594.5 (w), 464.5 (w), 374.4 (s)

\textit{Raman.} ν [cm\textsuperscript{−1}] = 3144.1 (w), 3095.9 (w), 3065.0 (w), 2974.4 (w, shoulder), 2951.2 (m, shoulder), 2916.5 (s, shoulder), 2891.5 (s), 2851.0 (s), 2772.5 (w), 1560.8 (w), 1454.7 (w, shoulder), 1437.4 (w), 1414.2 (w, shoulder). 1381.4 (w), 1355.1 (wve), 1300.4 (w), 1124.9 (w, shoulder), 1103.7 (w, shoulder), 1084.4 (w, shoulder), 1063.2 (w, shoulder), 1016.2 (w), 887.7 (w), 866.5 (w), 847.2 (w), 775–741 (w), 696.8 (wve), 658.2 (wve), 623.5 (w), 598.5 (w), 413.3 (w), 330.0 (wve), 231.6 (w), 181.5 (w, shoulder), 154.9 (w), 102.8 (w).

#### Elemental Analysis

Elemental analyses were obtained on a Vario EL (Elementar Analysensysteme GmbH, Hanau, D).

**Infrared Spectroscopy.** Infrared spectra were measured on a Bruker Alpha spectrometer with diamond ATR window (Bruker, Bremen, D).

**Raman Spectroscopy.** Raman spectra were recorded with a FRA 106-S Fourier Transform Raman spectrometer (Bruker Optik GmbH, Ettlingen, D) at 150 mW. Raman samples were measured in glass capillaries with an inner diameter of 0.1 cm and 0.15 mm wall thickness.

**UV–Visible Spectroscopy.** UV–visible absorption spectra were measured at room temperature and liquid nitrogen temperature on a Cary 5000 spectrometer (Varian, Palo Alto, USA). Samples were measured in a Q cell with a path length of 0.5 mm.

**Thermal Measurements.** Differential scanning calorimetry (DSC) was performed with a computer-controlled Phoenix DSC 204 F1 thermal analyzer (Netzsch, Selb, D) with argon as protection gas. The samples were placed in aluminum pans which were cold-sealed. 5 °C/min were chosen for the thermal ramp rate. Experimental data are displayed in such a way that exothermic peaks occur at negative heat flow and endothermic peaks at positive heat flow. Given temperatures correspond to the onset of the respective thermal process.

In order to analyze the thermal stability of [C\text{2mim}][FeCl\textsubscript{4}] thermogravimetric analysis (TGA) was carried out on a Shimadzu TG50 thermal analyzer. The sample was placed under inert conditions in an aluminum pan and heated to 400 °C with 10 °C/min. To ensure that full decomposition was reached at that temperature, the sample was kept for an additional 10 min at 400 °C.

Specific heat was measured with a physical properties measurement system (Quantum Design, PPMS) using a thermal relaxation method in the temperature range from 1.9 to 300 K. The addenda heat capacity was previously measured. Inside an argon glovebox, a droplet (1.9 mg) of [C\text{2mim}][FeCl\textsubscript{4}] was applied onto the cleaned sample plate. The sample holder was then quickly transferred to the helium-flooded sample chamber. The subsequent measurement took place in high vacuum. At high temperatures, the subtracted signal of the addenda is in the same order as the sample contribution, explaining the data noise above 200 K. However, approaching the magnetic transition temperature the relative sample contribution dominates.

**Magnetic Measurements.** A small amount (~2 mg) of the IL [C\text{2mim}][FeCl\textsubscript{4}] was placed in a polycarbonate ampule inside an argon filled drybox. To prevent any displacement of the liquid, the capillary force of corundum wool was used to fix the sample before sealing the ampule with an airtight lid. The amount of wool was optimized so that the wool was held in place by the lid. Magnetic susceptibility measurements in a field of up to 4.5 T and magnetization up to 7 T were performed in a squid MPMSXL (Quantum Design) in the temperature range 2–300 K.

In Situ Crystal Growth and Crystal Structure Analysis.

To determine the low temperature crystal structures of [C\text{2mim}][FeCl\textsubscript{4}], crystals of sufficient quality for single crystal X-ray structure analysis were grown from the melt in situ on an X-ray diffractometer using the method and experimental setup developed by Bose. This method already has been used successfully to grow crystals of low melting ionic liquids (RTIL – room temperature ionic liquids) for X-ray diffraction. For the in situ crystal growth, a small amount of liquid [C\text{2mim}][FeCl\textsubscript{4}] was introduced under inert gas atmosphere into a fused silica capillary (approx 2.5 cm long and 0.3 mm in diameter), sealed and mounted vertically on a Bruker-AXS SMART diffractometer in a nitrogen stream (Oxford Cryosystem). The sample was carefully cooled until [C\text{2mim}][FeCl\textsubscript{4}] solidified as a polycrystalline material. At this point, the zone-melting procedure was started using the optical heating and crystallization device (OHCD) to grow single crystals. A small section (~1 mm) of the lower portion of the capillary was heated with an IR laser to create a zone of molten material which was slowly moved along the capillary, while the laser power was adjusted to sufficiently melt the polycrystalline material. Then the laser beam was moved along the whole capillary from bottom to top in approximately 1 h. The laser power was then slowly reduced and the cycles were repeated several times until a single crystal of sufficient quality for structure analysis was grown. Crystal growth and intensity data were performed on a Bruker-AXS SMART diffractometer (Karlsruhe, Germany, and Madison, Wisconsin, USA; MoK\textsubscript{α} radiation, \( \lambda = 0.71073 \) \( \text{Å} \), \( \omega \) scan) at \( \sim 50 ^\circ \text{C} \) and \( \sim 30 ^\circ \text{C} \). The data were corrected for Lorentz and polarization effects. Data reduction was carried out with the program package XPRESS. A multiscan absorption correction was applied (SADABS).
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The structures were solved by direct methods (SIR-92) \(^{22}\) and refined by full-matrix least-squares against \(F^2\) with all measured reflections (SHELXL97). \(^{23}\) All non-hydrogen atoms were refined anisotropically and the hydrogen atoms were included riding on the respective parent atom with isotropic thermal displacement factors fixed at 1.2 times the \(U_{eq}\) of the parent atoms (1.5 times for methyl groups). Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: int. code +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk].

■ RESULTS AND DISCUSSION

Infrared and Raman Spectroscopy. In both the infrared (IR) and Raman spectrum of the IL [C\(_2\)mim][FeCl\(_4\)], the characteristic vibrations of the 1-ethyl-3-methylimidazolium cation are detected (Figure 1). In addition, the Raman spectrum shows the expected vibrations for the [FeCl\(_4\)]\(^-\) complex anion with \(T_d\) symmetry. The value of 334 cm\(^{-1}\) observed for the \(A_1\) mode is comparable to that found for the tetrachloroferrate anion in [C\(_4\)mim][FeCl\(_4\)]\(^-\) or [PR\(_4\)][FeCl\(_4\)]\(^-\).\(^{24}\) From the Raman spectrum, we can rule out the presence of [Fe\(_2\)Cl\(_7\)]\(^-\) dimers as no signals are found around 370 and 420 cm\(^{-1}\) where the vibrational frequency of the dimer typically appears.\(^{8}\)

UV-vis Spectroscopy. UV-vis spectra of a liquid sample of [C\(_2\)mim][FeCl\(_4\)] at room temperature as well as of a solid sample frozen in liquid nitrogen were measured (Figure 2). Both spectra show absorption bands in the region of 450–500 nm which are typical for the [FeCl\(_4\)]\(^-\) anion. The \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^E(a)\)\(^{4T_1}(b)\), \(\varepsilon\)\(^{T_2}(b)\)\(^{2A_1}\) transition is observed at 515 nm, the \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^{T_1}(b)\), \(\varepsilon\)\(^{E}(b)\) transition at 533 nm \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^{2T_2}(b)\) and at 575 nm the \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^{2A_1}(a)\), at 602 nm the \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^{4A_2}\) at 687 nm \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^{2T_2}(a)\) and at 737 nm \(\varepsilon\)\(^{A_1}A_1 \rightarrow \varepsilon\)\(^{4T_1}(a)\) transitions occur. These are the typical absorption characteristics of the tetrahedral [FeCl\(_4\)]\(^-\) anion.\(^{25}\) The spectra of the two samples show the same features, indicating that the tetrahedral structure of the anion is the same in the solid and the liquid.

Crystal Structure. [C\(_2\)mim][FeCl\(_4\)] is found to crystallize in two polymorphs. Modification 1 crystallizes in the centric, monoclinic space group \(P2_1/c\) (No. 14) \(a = 9.4124(19)\) \(\text{\AA}\), \(b = 14.645(3)\) \(\text{\AA}\), \(c = 12.444(4)\) \(\text{\AA}\), \(\beta = 129.841(18)^\circ\), \(V = 1317.1(6)\) \(\text{\AA}^3\), \(Z = 4\), \(\rho = 1.557\) g/cm\(^3\), \(T = -50\) °C). Modification 2 crystallizes in the non-centrosymmetric, monoclinic space group \(P2_1\) (No. 4) \(a = 6.1337(12)\) \(\text{\AA}\), \(b = 14.362(3)\) \(\text{\AA}\), \(c = 7.1111(14)\) \(\text{\AA}\), \(\beta = 91.33(3)^\circ\), \(V = 626.3(2)\) \(\text{\AA}^3\), \(Z = 2\), \(\rho = 1.638\) g/cm\(^3\), \(T = -30\) °C).

As can already be seen from Figure 3, the structures 1 and 2 deviate with respect to the cation–anion arrangement as well as in the conformation of the [C\(_2\)mim] cation. In 1, the ethyl group forms a dihedral angle of 52.58(2)^\circ\) (\(\angle(C6-C5-N2-C4)\)) to the imidazolium ring, and in 2 the angle amounts to −29.35(2)^\circ\) (\(\angle(C6-C5-N2-C4)\)). All interatomic distances (C–C and C–N) lie in the expected range comparable to those found in other [C\(_2\)mim] compounds, as for example in [C\(_2\)mim][AsF\(_6\)].\(^{26}\) For detailed structural information, see Supporting Information.

Figure 1. IR (top) and Raman spectra (bottom and inset) of [C\(_2\)mim][FeCl\(_4\)].

Figure 2. UV-vis spectra of [C\(_2\)mim][FeCl\(_4\)] (bold line: liquid sample at room temperature; fine line: solid sample at 77 K).
The complex \([\text{FeCl}_4]^{-}\) anion in 1 and 2 forms a slightly distorted tetrahedron, with Fe–Cl distances between 2.197(1) and 2.227(5) Å (mean value 2.209 Å) for 1 and 2.120(8) to 2.161(2) Å (mean value 2.141 Å) for 2. The Cl–Fe–Cl angles in 1 are between 107.59(1)° and 112.59(1)° with a mean value of 109.35°, close to the ideal tetrahedral angle at ~50 °C. In 2 Cl–Fe–Cl angles are found between 108.21(1)° and 112.78(1)° (mean value 109.90°) are observed. However, the values are in the expected range as found for similar containing \([\text{FeCl}_4]^{-}\), such as methyliatriphenylphosphonium tetrachloroferrate(III)\(^{27}\) or alkali metal tetrahaloferrates.\(^{28}\) The shortest Fe–Cl distance in 1 is 6.229(2) Å and in 2 6.134(1) Å.

Hydrogen bonding is very important for ILs. However, in 1 only weak (long) hydrogen bonds are found. None of the interatomic distances (Table 1) lie in the generally accepted range for typical hydrogen bonding.\(^{29}\) For 2, significantly stronger, hence shorter hydrogen bonds, are found (Table 1). Most astonishing, the most acidic hydrogen atom in the 2-H position of the imidazolium ring is not involved in the hydrogen bonding network (Figure 4). Compared to \([\text{C}_4\text{mim}]_2[\text{FeCl}_4]^{-}\)\(^{30}\) which contains divalent iron, the C–H…Cl hydrogen bonds in 1 and 2 are weaker. Possibly because in \([\text{C}_4\text{mim}]_2[\text{FeCl}_4]^{-}\) the complex anion bears two negative charges compared to only one in \([\text{C}_2\text{mim}]_2[\text{FeCl}_4]^{-}\). Unlike in \([\text{C}_4\text{mim}]_2[\text{FeCl}_4]^{-}\), no cation–cation interaction, as for example interaction of the aromatic rings through \(\pi\)-stacking could be observed in either of the polymorphs of \([\text{C}_2\text{mim}]_2[\text{FeCl}_4]^{-}\). Similar observations have been made for \([\text{C}_2\text{mim}]_2[\text{BF}_4]^{-}\)\(^{31}\) and the tetrafluoroborate, hexafluorophosphate, and hexafluoroantimonate salts of 1-butyl-2,3-dimethylimidazolium.\(^{32}\)

The crystal structure of both modifications is formed by a layer of cations and anions, alternating along the unique \(b\) axis. Although the general spatial arrangement of anions and cations roughly stays the same in both polymorphs, subtle changes are present. Both in 1 and 2, the \([\text{FeCl}_4]^{-}\) tetrahedra form 4 nets in the \(a_c\) plane. In 1, the \([\text{FeCl}_4]^{-}\) tetrahedra have the same orientation along \(a\) but are twisted along \(c\) by a rotation of about 28°. In 2, the \([\text{FeCl}_4]^{-}\) tetrahedra point in the same direction within one anion layer, but change orientation from layer to layer. In 1 and 2, one anion layer is shifted with respect to the next one so that the \([\text{FeCl}_4]^{-}\) tetrahedra come to lie above the open (distorted) squares of the neighboring layer. The cations also form 4 nets in the \(a_c\) plane but are stacked nearly identically above one another. The orientation of the cations in the stacking direction is related by the 21 axis running along \(b\). In 1, the cations are oriented parallel to each other along \(a\), while along \(c\) they are...
rotated by 180°. The C$_2$ mim cations in 2 lie parallel to each other along $a$ and $b$. Altogether the density of 2 is higher compared to 1, and the symmetry of 2 is lower than that of 1. From this, it can be anticipated that 1 is the low temperature phase.

**Thermal Analysis.** The thermal properties of [C$_2$mim][FeCl$_4$] were examined by differential scanning calorimetry (DSC) and thermogravimetry (TG) and specific heat capacity measurements. In contrast to previous reports, where a single melting point at about 291 K was found, the phase behavior is more complex as already evidenced by X-ray structure analysis.

The DSC trace recorded between 223 and 313 K of [C$_2$mim][FeCl$_4$] is displayed in Figure 6, left. When cooling from the melt, crystallization of [C$_2$mim][FeCl$_4$] is observed at 283 K. Upon subsequent heating [C$_2$mim][FeCl$_4$] from 223 K, one solid–solid phase transition at 261 K occurs before [C$_2$mim][FeCl$_4$] finally melts at 289 K. Repeated cooling and heating cycles show the same thermal behavior for [C$_2$mim][FeCl$_4$]. In order to check whether the last phase transition before melting belongs to a crystalline-plastic crystal transition, the fusion entropy $\Delta S_f$ has been calculated. According to Timmerman’s criterion,

Figure 5. Projections of the crystal structure of 1 (left) and 2 (right).
\( \Delta S_f \) for such a phase transition should be about 20 J mol\(^{-1}\) K\(^{-1}\). The final entropy of fusion for [C\(_2\)mim][FeCl\(_4\)] was calculated to be \( \Delta S_f = 49.4 \text{ J mol}^{-1} \text{ K}^{-1} \), which is significantly higher than Timmerman’s criterion. However, larger entropies of fusion up to 43 J K\(^{-1}\) mol\(^{-1}\) have been observed quite a few times for plastic crystals of ionic liquids. Thermogravimetric (TGA) experiments indicate that [C\(_2\)mim][FeCl\(_4\)] starts to decompose at about 623 K (Figure 6, right).

The specific heat of [C\(_2\)mim][FeCl\(_4\)] shows two prominent features close to 285 K (the melting point) and 3.8 K (Figure 7). The high temperature anomaly is typical for a first-order phase transition (inset in Figure 7), as the drastic release of entropy is completed within approximately 1 K. This agrees with the solidification of the paramagnetic IL. The low temperature entropy release resembles a second-order phase transition, which is known from long-range magnetic ordering. For magnetic fluids without outer magnetic fields, the magnetic ground-state is under debate. Possible ferromagnetic and superparamagnetic states differ in their zero-point (\( T = 0 \) K) entropy, where the former has none but the latter a finite “rest” entropy. Hence, the order parameter can be estimated by comparing the theoretical entropy of a \( S = S/2 \) ferromagnet with the integrated magnetic specific heat of [C\(_2\)mim][FeCl\(_4\)] at low temperatures. By subtracting an empirical estimation of the minor phononic background, the magnetic heat capacity was extracted (inset in Figure 7). The amount of entropy below 1.9 K cannot be estimated without further low temperature data. However, a large part of the magnetic entropy is missing in comparison with the theoretical value of \( R \ln(2f+1) \). Depending on how much entropy has been neglected in the range 0–1.9 K, the total entropy can vary but it is not possible to reach the theoretical value for a fully ordered system. Hence, the magnetic system has to be at least partly disordered. This contradicts the suggestion recently made by de Pedro et al., based on magnetic measurements for [C\(_2\)mim][FeCl\(_4\)], where a fully ordered ferromagnetic magnetic

Figure 6. DSC thermogram of [C\(_2\)mim][FeCl\(_4\)], heating rate 5 K/min (left). TGA of [C\(_2\)mim][FeCl\(_4\)]. The solid line indicates the weight loss, and the dotted line represents the temperature (initial mass: 9.8 mg), right.

Figure 7. Specific heat of [C\(_2\)mim][FeCl\(_4\)] in a temperature range of 1.9 to 300 K. Lower right inset: magnification of the high temperature transition range, upper left inset: magnetic specific heat vs temperature \( c_{\text{mag}}/T \) (J mol\(^{-1}\) K\(^{-1}\)) and its integral, that is, the entropy \( S \) compared with the theoretical expectation (full line) for spin-only Fe\(^{3+}\).
The magnetic susceptibility of [C2mim][FeCl4] as a function of temperature at different fields, emphasizing the low temperature region. The upper right inset shows in detail the shifting of the freezing temperature at different fields, emphasizing the low temperature region. The vertical dashed line indicates a minor anomaly present in all curves. The dashed line represents the Curie–Weiss fit for the temperature region 200–300 K. The upper left inset shows the first-order phase transition close to 290 K, where the arrows show the direction of each measurement. The magnetization at 2 K as function of field is shown in the lower right inset.

**Figure 8.** The temperature-dependent inverse magnetic susceptibility of [C2mim][FeCl4]. The dashed line represents the Curie–Weiss fit for the temperature region 200–300 K. The upper left inset shows the first-order phase transition close to 290 K, where the arrows show the direction of each measurement. The magnetization at 2 K as function of field is shown in the lower right inset.

**Figure 9.** The magnetic susceptibility of [C2mim][FeCl4] as a function of temperature at different fields, emphasizing the low temperature region. The upper right inset shows in detail the shifting of the freezing temperature (Tf) depending upon the field strength. The vertical dashed line indicates a minor anomaly present in all curves. The dashed line represents the Curie–Weiss fit for the temperature region 200–300 K. The upper left inset shows the first-order phase transition close to 290 K, where the arrows show the direction of each measurement. The magnetization at 2 K as function of field is shown in the lower right inset.

Ground state was assumed. We propose a superparamagnetic ground state, which fits well with the magnetic observations. **Magnetism.** The IL [C2mim][FeCl4] exhibits a paramagnetic behavior above 4 K (Figure 8). The Weiss constant (θ(CW)), extrapolated from the high temperature (200–300 K) region, is positive, showing a tendency toward parallel spin arrangement in the fluctuating state. This contradicts observation for similar compounds where almost perfectly decoupled spins are reported.

The calculated magnetic moment for Fe[FeCl4] (5.71 μB) is reasonably close to the spin-only value of Fe[FeCl4] (5.9 μB); the reason for the minor discrepancy could be an error in the exact weighing of the 2 mg sample. In the temperature range 285–295 K, there is a difference in χ if this range is passed on cooling or heating (see upper left inset in Figure 8). Such a behavior was already noticed for [C2mim][FeCl4] and [C2mim][FeBr4] and is a typical indication of a first-order phase transition, due to its hysteretic nature: this is interpreted as the melting/solidification of [C2mim][FeCl4] and fits to the DSC and specific heat data.

The magnetization, at the lowest measured temperature (lower right inset in Figure 9), reaches about 5.1 μB at 7 T and follows the expected ordered moment of a S = 5/2 ion, that is, about 5 μB. It proved possible to shift Tf to lower temperature by increasing the field (Figure 9). At the highest field of 4.5 T, Tf was suppressed to temperatures below 2 K and χ(T) is no longer superimposed with the curves obtained at other fields. This is a sign for a partly saturated system, agreeing with the magnetization measurement (inset in Figure 9). Obviously, it is possible to reach this partial saturation already far above Tf.

Combining the magnetic observations with the thermodynamic data, an explanation would be that ferromagnetism dominates the ground state of [C2mim][FeCl4]. If tendencies toward superparamagnetism are present, the disordered part is significant according to the specific heat measurement. Neutron diffraction would reveal the spin coherence lengths and is, hence, the next investigation needed to clear this matter. At relatively high temperatures, small fluctuating ferromagnetic clusters form (positive θ(CW)) and grow upon cooling. Below 4 K (Tf), the large ferromagnetic domains must freeze with a random orientation as the susceptibility declines. The Tf shift with field and the easily reached saturation of the magnetization of [C2mim][FeCl4] are consistent with a superparamagnet, although with relatively large domains.

**CONCLUSIONS**

[C2mim][FeCl4] is a room temperature IL which melts at 283 K and only shows a small degree of supercooling when cooled from the melt. However, upon reheating a solid–solid phase transition is observed at 261 K. Above 623 K, [C2mim][FeCl4] decomposes.

Magnetic measurements show that [C2mim][FeCl4] is a superparamagnet with a global spin freezing temperature of 3.8 K. The magnetism is due to the d5–Fe3+ ion of the complex anion. Below 3.8 K, [C2mim][FeCl4] is a ferromagnet approximant, meaning that, within detection limits, a large part of the spins order at low temperature. However, there must be spin clusters present, because the magnetic susceptibility decreases below the ordering temperature, whereas a classical ferromagnet would behave differently.

To reveal possible magnetic interactions between the magnetic units, structural investigations were carried out. Vibrational as well as optical spectroscopy show the presence of isolated [FeCl4]− anions. By in situ crystal growth on the X-ray diffractometer, it was possible to trap the two solid polymorphs of [C2mim][FeCl4]. The structure of both solid modifications is characterized by 4+ nets of isolated [C2mim]2+ cations and [FeCl4]− anions. In the two polymorphs, the conformation of the C2mim cation is different. Most importantly, the two polymorphs deviate in the relative arrangements of cations and anions. As a consequence, in the high temperature modification a strong hydrogen-bonding network is found, whereas in the low temperature polymorph only weak supramolecular interactions are found. However, the distances between two Fe3+ cations are larger than 6 Å and therefore too large to allow for significant magnetic exchange interactions.