

# Flexible coordination environments of lanthanide complexes grown from chloride-based ionic liquids†‡

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Hydrated lanthanide(III) chlorides,  $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$  ( $\text{Ln} = \text{La, Pr, Nd, Sm, Eu, Gd}$ ;  $x = 6-7$ ) readily dissolve in the low melting ionic liquid 1-ethyl-3-methylimidazolium chloride ( $[\text{C}_2\text{mim}]\text{Cl}$ ) in an open vessel at 110 °C, and upon cooling crystallize as the anhydrous  $[\text{C}_2\text{mim}]_3[\text{LnCl}_6]$ . The crystal structures exhibit a face-centered packing arrangement of the  $[\text{LnCl}_6]^{3-}$  anions, with the cations located as slip aligned pairs in the void spaces which participate in hydrogen-bonding to chlorides. A second crystalline form of the  $\text{Gd}^{3+}$  complex,  $\text{GdCl}_3(\text{OH}_2)_4 \cdot 2([\text{C}_2\text{mim}]\text{Cl})$ , was isolated when the above reaction was conducted in a sealed system. For comparison, a third  $\text{Gd}^{3+}$  compound was grown from the ionic liquid 1-butyl-3-methylimidazolium chloride ( $[\text{C}_4\text{mim}]\text{Cl}$ ) using the same unsealed conditions as above, and was found to be  $[\text{C}_4\text{mim}]_3[\text{GdCl}_6]$ . This compound exhibits a different packing arrangement to that observed for the  $[\text{C}_2\text{mim}]^+$  analogs. Based on these findings, ILs would appear to offer new crystallization process options based on their often high thermal stabilities and low to negligible vapor pressures.

## Introduction

It is only appropriate on the occasion of Professor Jerry L. Atwood's 65th birthday, that we, as his academic progeny, return to our roots to discuss the beauty of the crystalline state of matter. For one of us (R. D. R.), the first hand experience of learning chemistry, crystallography, teamwork, and collaboration, started while an undergraduate at The University of Alabama. After being given rather explosive liquid clathrate<sup>1</sup> reactions to undertake, it was a quick move to the relative safety of structural characterization of crystalline solids and a first paper.<sup>2</sup>

Ironically, it took almost 20 years to return to the scientific world of salts quite similar to those original liquid clathrates, the so-called 'ionic liquids' (ILs). Ionic liquids (defined as salts melting below 100 °C)<sup>3</sup> are now being used as neoteric solvents, organic directing agents in the synthesis of luminescent materials,<sup>4,5</sup> for stabilization of unique redox states free from hydrolysis and solvolysis,<sup>6</sup> for solvent extraction,<sup>7</sup> for structural chemistry,<sup>8</sup> and to provide unique solvation environments.<sup>9,10</sup>

Recently, we have started using ILs to investigate the possibilities of trapping unique metal coordination environ-

ments by dissolution, complexation, and subsequent recrystallization in ILs.<sup>11</sup> This has included modification of the IL and metal-ligand environments, as well as by tuning the amounts of water and acid available in the systems.<sup>12</sup> Here, we will discuss the combination of the rich chemistry of the rare-earth elements with the unique and complex solvent environments presented by ionic liquids.

The study of the coordination chemistry of lanthanides in and with ILs is interesting given the variety of possible outcomes when using multiple ion systems. For example, the lanthanide(III) halides can easily crystallize as 'solvates' with the isolation of a variety of anionic  $[\text{LnX}_n]^{(3-n)}$  moieties. In crystalline  $[\text{C}_4\text{mpyr}]_4[\text{LnI}_6][\text{NTf}_2]$  ( $\text{Ln} = \text{La},^{13} \text{Pr},^{14} \text{Nd},^{15} \text{Er},^{13}$   $\text{C}_4\text{mpyr} = 1\text{-butyl-1-methylpyrrolidinium}$ ;  $\text{NTf}_2 = \text{bis(trifluoromethanesulfonyl)imide}$ ), the incorporation of both IL component ions and the lanthanide complex anion were observed. Crystal structures such as  $[\text{C}_3\text{mpyr}]_2[\text{Yb}(\text{NTf}_2)_4]$  ( $\text{C}_3\text{mpyr} = 1\text{-propyl-1-methylpyrrolidinium}$ ) are also known, where the coordination of the 'non-coordinating'  $[\text{NTf}_2]^-$  anion<sup>16</sup> and other weakly coordinating IL anions show that even the most non-interacting ILs can help stabilize unique environments in both the solid and solution states. A recent paper has even suggested lanthanide-containing 'IL-like' materials are possible where the lanthanide complex anion serves as the IL counterion, as for example in  $[\text{C}_4\text{mim}]_{x-3}[\text{Ln}(\text{NCS})_x(\text{H}_2\text{O})_y]^{3-x}$  ( $\text{Ln} = \text{Y, La-Yb}$ ,  $x = 6-8$ ,  $y = 0-2$ ;  $\text{C}_4\text{mim} = 1\text{-butyl-3-methylimidazolium}$ ).<sup>17</sup>

The  $[\text{LnCl}_6]^{3-}$  anion can be prepared in high-temperature ionic melts composed of metal-metal chloride ( $\text{M}_3\text{LnCl}_6$ ) environments with the use of organic halide directing agents,<sup>18</sup> but in molecular solvents, the chloride ions are quickly replaced by water. Even in 14.0 M LiCl, only partial chloride complexation and further dehydration of the metal center is

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observed.<sup>19</sup> ILs have been reported to support the formation of the  $[\text{LnX}_6]^{3-}$  species in solution,<sup>10</sup> yet isolation of the complexes in the solid state from these ILs has been limited.

Crystallographic evidence has been reported in the form of  $[\text{C}_2\text{mim}]_3[\text{LaCl}_6]$  isolated from the dissolution of anhydrous  $\text{LaCl}_3$  in the tunable Lewis acid–base room temperature IL,  $[\text{C}_2\text{mim}]\text{Cl}/\text{AlCl}_3$  (40 mol%  $\text{AlCl}_3$ ;  $\text{C}_2\text{mim}$  = 1-ethyl-3-methylimidazolium).<sup>20</sup> In conventional solvents and using the more readily available hydrated metal chloride salts, however, the dehydration of the lanthanide metal centers is not favored due to the large energy of hydration and ionization inherent in this series of metal ions.<sup>21</sup>

In this commemorative paper, we present our current results in the isolation of crystalline lanthanide(III) chloride salts from the direct dissolution of  $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$  in the IL  $[\text{C}_2\text{mim}]\text{Cl}$ . This includes the isolation and structural characterization of  $[\text{C}_2\text{mim}]_3[\text{LnCl}_6]$  ( $\text{Ln}$  = La, Pr, Nd, Sm, Eu, Gd; all of which are isostructural with the  $\text{Ln}$  = La compound in ref. 20), one IL solvate,  $\text{GdCl}_3(\text{OH}_2)_4 \cdot 2([\text{C}_2\text{mim}]\text{Cl})$  prepared under different conditions, and for comparison,  $[\text{C}_4\text{mim}][\text{GdCl}_6]$  prepared by the same reaction as for the  $[\text{C}_2\text{mim}]^+$  analogs.

## Results and discussion

### Crystallization of complexes

Often the most difficult part of conducting a crystallization experiment from ILs is finding an IL in which the solute (in this case the lanthanide(III) chloride salts) dissolves. After that one must find the appropriate crystallization conditions, however, for the results presented here, the overall experiments were fairly straightforward. We chose two ILs,  $[\text{C}_2\text{mim}]\text{Cl}$  and  $[\text{C}_4\text{mim}]\text{Cl}$ , having both melting points above room temperature (82–87 °C and 65–69 °C, respectively),<sup>22</sup> and a common coordinating anion ( $\text{Cl}^-$ ). We also chose to study the more readily available hydrated  $\text{LnCl}_3$  salts, and conduct the studies in the open atmosphere, rather than utilize the stricter and more expensive anhydrous conditions previously studied.<sup>13–15,18,20</sup>

It was anticipated that the  $\text{Cl}^-$  anion would help solubilize the hydrated lanthanide salts and also provide a  $\text{Cl}^-$ -rich environment leading to higher coordination numbers. Evidence for this has come from spectroscopic investigations revealing the presence of non-octahedral f-element centers in solution,<sup>23</sup> as well as our own work with the isolation of unique coordination environments of f-element centers from ILs.<sup>12,24</sup> The higher melting point of the IL solvent chosen here for study was also thought to provide a crystallization event one way or another; either of a lanthanide complex or salt, or of the IL itself.

The salts  $\text{LnCl}_3 \cdot x\text{H}_2\text{O}$  ( $\text{Ln}$  = La, Pr, Nd, Sm, Eu, Gd;  $x$  = 6–7) were added to an open vial containing the solid salt,  $[\text{C}_2\text{mim}]\text{Cl}$  (in the case of  $\text{Gd}^{3+}$ ,  $[\text{C}_4\text{mim}]\text{Cl}$  was also used), in a 1 : 2  $\text{Ln}$  : IL molar ratio, and heated in the open atmosphere to 110 °C for 3 h. Slowly cooling the samples at 0.1 °C  $\text{min}^{-1}$  to a final temperature of 20 °C led to formation and isolation of crystals of anhydrous  $[\text{C}_2\text{mim}]_3[\text{LnCl}_6]$  and  $[\text{C}_4\text{mim}]_3[\text{GdCl}_6]$ .

It should be noted that all of these experiments started with fully hydrated lanthanide(III) chloride salts, yet none of the crystalline materials obtained contained any water. The combination of the high chloride content of the IL and open vessel heating above 100 °C, is obviously sufficient to completely dehydrate the metal ions, although other hydrated species may still exist in solution and cannot be ruled out.

The isostructural  $\text{Ln}$  = La analog,  $[\text{C}_2\text{mim}]_3[\text{LnCl}_6]$ , has previously been isolated by dissolving anhydrous  $\text{LaCl}_3$  in a strongly solvating<sup>22</sup>  $[\text{C}_2\text{mim}]^+/\text{chloroaluminate}^-$  IL; however, this class of IL is moisture sensitive and will react with any spurious water, leading to an anhydrous environment. This is in contrast to our current results which utilize hydrated metal salts and open bench top conditions. The hydrated salts and the  $[\text{C}_n\text{mim}]\text{Cl}$  ILs are easier to work with and are much cheaper.

It did occur to us that our methodology, using an open container and heating above 100 °C, might be the driver for dehydration of the system; thus while trying to re-grow crystals of the  $\text{Gd}^{3+}$  salt, the reaction mixture was heated to 110 °C for 3 h and slowly cooled as above, but this time the reaction was conducted in a sealed system. Interestingly, the unusual solvate,  $\text{GdCl}_3(\text{OH}_2)_4 \cdot 2([\text{C}_2\text{mim}]\text{Cl})$ , containing neutral  $\text{GdCl}_3(\text{OH}_2)_4$  and both of the IL ions was isolated. This complex is isostructural to the thermodynamic form of two polymorphic  $\text{Er}^{3+}$  structures isolated from the same IL, but with 12.1 M  $\text{HCl}$  added to increase the  $\text{Cl}^-$  ion concentration relative to the metal ion.<sup>12</sup> The present results now suggest that one could control the coordination environments of these metal centers by simple tuning of the IL and water content in the solution, rather than the addition or absence of acid or other ions.

### Crystal structures of $[\text{C}_2\text{mim}]_3[\text{LnCl}_6]$ ( $\text{Ln}$ = La, Pr, Nd, Sm, Eu, Gd)

All of the isolated  $[\text{LnCl}_6]^{3-}$  salts are isostructural with the one published analog,  $[\text{C}_2\text{mim}]_3[\text{LaCl}_6]$ .<sup>20</sup> The crystallographic data for these structures are provided in Table 1 and the  $\text{Ln}$  = Pr structure is depicted in Fig. 1. We did not attempt to re-determine the  $\text{La}^{3+}$  analog, but did confirm its isolation using our synthetic protocol by determining its unit cell parameters.

Each structure contains two crystallographically unique lanthanide metal centers residing on crystallographic centers of inversion, six unique chlorides (three per metal center), and three unique  $[\text{C}_2\text{mim}]^+$  cations. The  $[\text{LnCl}_6]^{3-}$  anions exhibit a face-centered packing arrangement (Fig. 1(a)), while the  $[\text{C}_2\text{mim}]^+$  cations fill the voids created between them, and are arranged in a triple cation motif suggesting weak electrostatic interactions (Fig. 1(b)).<sup>25</sup>

The two independent  $[\text{LnCl}_6]^{3-}$  anions do exhibit some differences. While all three unique chlorides complexed to the Ln2 position are essentially identical, in the Ln1 anion, asymmetry is observed for the Cl1 and Cl2 positions (Table 2). In each case the Ln1–Cl1 distance is the shortest and the Ln–Cl2 distance is the longest of the six unique Ln–Cl separations. In addition, the Cl1–Ln1–Cl2 angle is the sharpest of any Cl–Ln–Cl angles in each structure.

There are many contacts between the hydrogen atoms in each cation and the bound chlorides at distances less than

**Table 1** Crystallographic data

[C <sub>2</sub> mim] <sub>3</sub> [LnCl <sub>6</sub> ]								
Ln	La <sup>a</sup>	Pr	Nd	Sm	Eu	Gd	GdCl <sub>3</sub> (OH <sub>2</sub> ) <sub>4</sub> · 2[C <sub>2</sub> mim]Cl	[C <sub>4</sub> mim] <sub>3</sub> [GdCl <sub>6</sub> ]
Formula	C <sub>18</sub> H <sub>33</sub> Cl <sub>6</sub> N <sub>6</sub> La	C <sub>18</sub> H <sub>33</sub> Cl <sub>6</sub> N <sub>6</sub> Pr	C <sub>18</sub> H <sub>33</sub> Cl <sub>6</sub> N <sub>6</sub> Nd	C <sub>18</sub> H <sub>33</sub> Cl <sub>6</sub> N <sub>6</sub> Sm	C <sub>18</sub> H <sub>33</sub> Cl <sub>6</sub> N <sub>6</sub> Eu	C <sub>18</sub> H <sub>33</sub> Cl <sub>6</sub> N <sub>6</sub> Gd	C <sub>12</sub> H <sub>30</sub> Cl <sub>5</sub> N <sub>4</sub> O <sub>4</sub> Gd	C <sub>24</sub> H <sub>45</sub> Cl <sub>6</sub> N <sub>6</sub> Gd
<i>M<sub>r</sub></i>	685.11	687.11	690.44	696.55	698.16	703.45	628.90	787.61
<i>T</i> /K	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	15.566(10)	15.4637(11)	15.4590(12)	15.4235(10)	15.4175(10)	15.4112(11)	8.5556(5)	9.7573(8)
<i>b</i> /Å	12.664(10)	12.5622(9)	12.5543(10)	12.5234(8)	12.5250(8)	12.5133(9)	8.7213(5)	10.5481(8)
<i>c</i> /Å	15.046(2)	14.7103(11)	14.7119(11)	14.6633(10)	14.6565(9)	14.6384(10)	18.6748(11)	33.524(3)
$\alpha$ /°	90	90	90	90	90	90	76.743(1)	90
$\beta$ /°	90.46(6)	90.469(1)	90.499(2)	90.507(1)	90.508(1)	90.501(1)	87.775(1)	91.571(1)
$\gamma$ /°	90	90	90	90	90	90	61.121(1)	90
<i>V</i> /Å <sup>3</sup>	2965.89(5)	2857.5(4)	2855.1(4)	2832.2(3)	2830.1(3)	2822.8(3)	1183.4(1)	3449.0(5)
<i>Z</i>	4	4	4	4	4	4	2	4
<i>D<sub>c</sub></i> /g cm <sup>-3</sup>	1.534	1.597	1.606	1.634	1.639	1.655	1.765	1.517
Independent reflns.	—	6678	5807	6713	6681	6652	5318	8232
Obsd. reflns.	—	4499	4001	4365	4392	4800	4822	6557
<i>R</i> <sub>int</sub>	—	0.0367	0.0276	0.0345	0.0302	0.0298	0.0166	0.0334
GooF	—	1.059	1.011	1.013	0.997	1.015	1.022	1.020
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> <sup>b</sup>	—	0.0409,	0.0272,	0.0327,	0.0262,	0.0275,	0.0280,	0.0313,
[ <i>I</i> > 2σ( <i>I</i> )]	—	0.0569	0.0483	0.0521	0.0447	0.0488	0.0680	0.0572
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> <sup>b</sup> (all data)	—	0.0780,	0.0544,	0.0695,	0.0584,	0.0503,	0.0333,	0.0487,
		0.0637	0.0539	0.0585	0.0508	0.0547	0.0701	0.0605

<sup>a</sup> This study; unit cell matched only. <sup>b</sup>  $R = \sum \|F_o\| - |F_c| / \sum \|F_o\|$ ;  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum (w(F_o^2)^2)\}^{1/2}$ .

van der Waals radii (Table 3), as commonly observed for these ions.<sup>26</sup> There are 10 cations which exhibit 16 H···Cl–Ln1 (Fig. 1(c)) and 8 cations which exhibit 10 H···Cl–Ln2 (Fig. 1(d)) distances at least 0.1 Å less than the van der Waals contact distance. It is noted that Cl2 is the only bound chloride having three close contacts with the more acidic imidazolium ring hydrogen atoms, including one from the most acidic C2 position. This, or the more crowded cation environment around the Ln1 anion, may explain the asymmetry of this anion, and the fact that the Ln1–Cl2 separations are the longest of any such distances in all of the compounds examined.

### Crystal structure of [C<sub>4</sub>mim]<sub>3</sub>[GdCl<sub>6</sub>]

This complex crystallizes with only one unique [GdCl<sub>6</sub>]<sup>3–</sup> metal center (Fig. 2(a)) and three unique [C<sub>4</sub>mim]<sup>+</sup> cations. The range in Gd–Cl distances (2.6614(7)–2.6938(7) Å; average = 2.68(1) Å) and in Cl–Ln–Cl angles (86.07(2)–95.53(2)°; average = 90(3)°) reveal a distorted octahedral first coordination sphere for the lanthanide center, not unlike the Ln1 environment in the [C<sub>2</sub>mim]<sup>+</sup> analogs.

As with the [C<sub>2</sub>mim]<sup>+</sup>-based structures, there are many close contacts less than van der Waals separation—a total of eight cations with 16 H···Cl contacts are observed. Nonetheless, the resulting ionic environment (Fig. 2(b)) is quite different from the [C<sub>2</sub>mim]<sup>+</sup> analogs. The cations labeled N1–C10 are interdigitated in a head-to-tail fashion forming cationic layers in the *ab* plane which separate double layers of the anions at every 0.5*c* distance. The other two cations (N1A–C10A and N1B–C10B) separate the anions in *a* and *b* and exhibit close cation–cation contacts at the C4–C5 bonds in each, the closest of which is C4A···C5B = 3.328(4) Å.

### Crystal structure of GdCl<sub>3</sub>(OH<sub>2</sub>)<sub>4</sub>·2([C<sub>2</sub>mim]Cl)

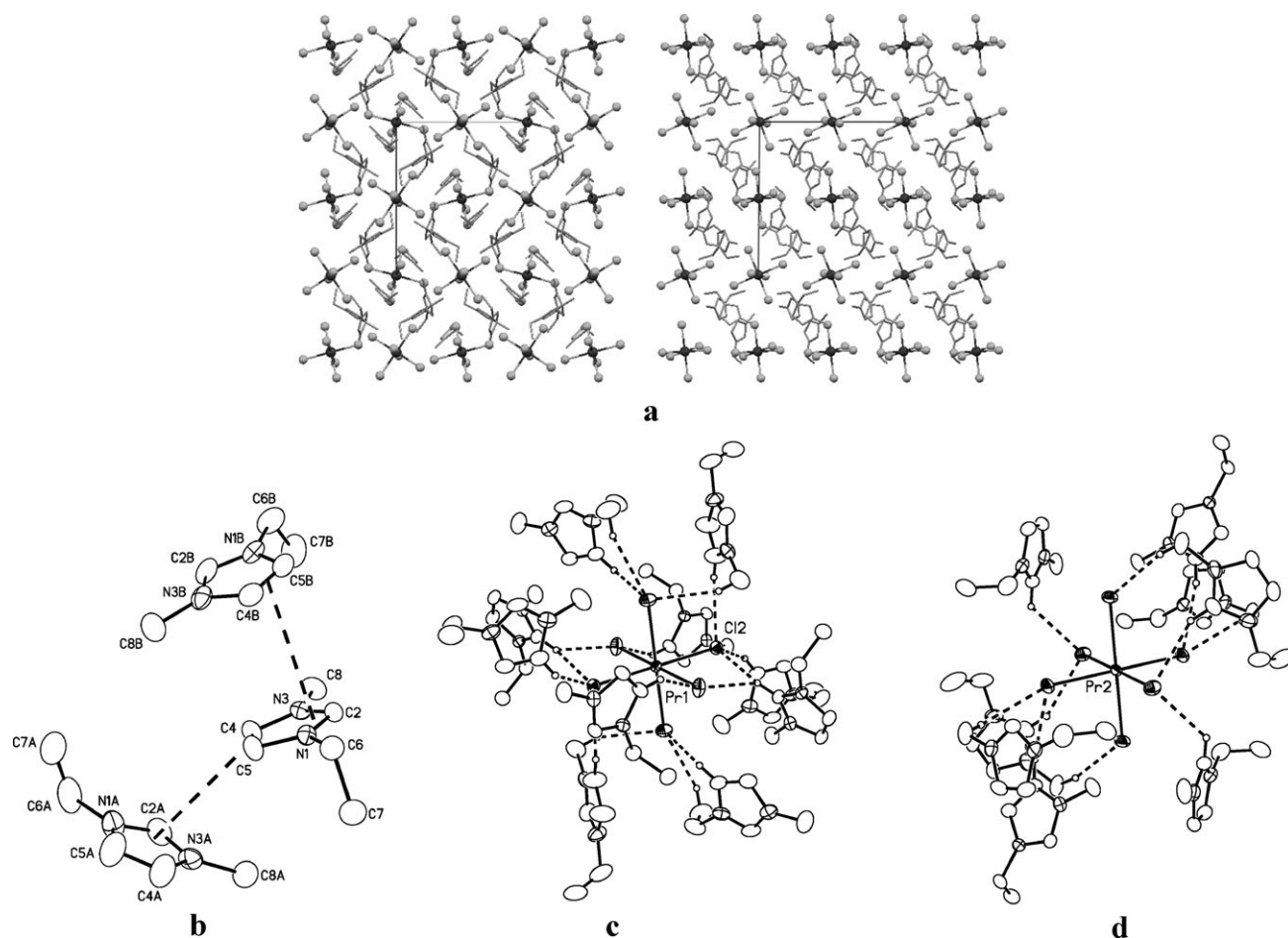
This compound (Fig. 3) is isostructural to the thermodynamic product (form II) of the Ln = Er analog.<sup>12</sup> It is surmised that by working in a closed system, and thus preventing the release of water, water was available to compete with the Cl<sup>–</sup> anions for metal coordination sites. The IL here plays a more dominant role in the stabilization of the neutral metal center, providing free chloride ions and free cations to stabilize the neutral metal center (Fig. 3(a)) and create 2D sheets in the crystal structure, Fig. 3(b).

### Conclusions

It is clear that ILs offer new crystallization process options based on their often high thermal stabilities and low to negligible vapor pressures. Here we have shown, for example, how easy it is to isolate anhydrous lanthanide complex anions even starting with hydrated starting materials. The crystallographic results also suggest that the [LnCl<sub>6</sub>]<sup>3–</sup> anions are readily formed in IL solution, supported by the ionic strength and other unique properties that the chloro-based ILs possess. Now, we will turn our attention toward tuning IL systems to specifically target currently unknown lanthanide coordination environments; an admittedly harder task.

### Experimental

The [C<sub>2</sub>mim]Cl and [C<sub>4</sub>mim]Cl used in this study were obtained as a gift from BASF (Florham Park, NJ) and used without further purification. The lanthanide salts LnCl<sub>3</sub>·*x*H<sub>2</sub>O (Ln = La, Pr, Nd, Sm, Eu, Gd; *x* = 6–7) were obtained from



**Fig. 1** Crystal structure of  $[\text{C}_2\text{mim}]_3[\text{PrCl}_6]$ : (a) packing diagram (down *a*, left; down *b*, right) with hydrogen atoms omitted for clarity; (b) cation–cation interactions ( $\text{N}3 \cdots \text{C}4\text{B}$  3.227(5) Å and  $\text{C}5 \cdots \text{N}3\text{A}$  3.546(5) Å; hydrogen atoms omitted for clarity); and all  $\text{H} \cdots \text{Cl}$  contacts less than 0.1 of the difference in van der Waals contact radii for (c) Pr1 and (d) Pr2 (only hydrogen atoms with short contacts shown). All thermal ellipsoids are shown at 50% probability.

**Table 2** Selected bond lengths (Å) and angles (°) in the  $[\text{LnCl}_6]^{3-}$  anions

Ln	La <sup>a</sup>	Pr	Nd	Sm	Eu	Gd
Ln1–Cl1	2.792	2.7216(9)	2.7095(9)	2.6789(9)	2.6670(7)	2.6604(7)
Ln1–Cl2	2.792	2.7631(9)	2.7471(8)	2.7184(7)	2.7081(7)	2.6957(7)
Ln1–Cl3	2.798	2.7483(9)	2.7339(8)	2.7046(8)	2.6949(7)	2.6821(7)
<b>Average</b>	<b>2.794(3)</b>	<b>2.74(2)</b>	<b>2.73(2)</b>	<b>2.70(2)</b>	<b>2.69(2)</b>	<b>2.68(2)</b>
Ln2–Cl4	2.807	2.7453(9)	2.7322(9)	2.7041(8)	2.6928(7)	2.6812(6)
Ln2–Cl5	2.790	2.7511(9)	2.7359(8)	2.7073(8)	2.6959(7)	2.6845(6)
Ln2–Cl6	2.766	2.750(1)	2.7359(9)	2.7030(8)	2.6922(7)	2.6827(8)
<b>Average</b>	<b>2.79(2)</b>	<b>2.749(3)</b>	<b>2.735(2)</b>	<b>2.705(2)</b>	<b>2.694(2)</b>	<b>2.683(2)</b>
Cl1–Ln1–Cl2	89.75	86.98(3)	86.99(3)	86.95(3)	87.07(2)	87.15(2)
Cl1–Ln1–Cl3	90.12	89.69(3)	89.76(3)	89.87(3)	89.81(2)	89.86(2)
Cl2–Ln1–Cl3	91.38	88.81(3)	88.95(2)	89.05(2)	89.05(2)	89.09(2)
<b>Average</b>	<b>90.4(9)</b>	<b>88(1)</b>	<b>89(1)</b>	<b>89(2)</b>	<b>89(1)</b>	<b>89(1)</b>
Cl4–Ln2–Cl5	91.31	89.81(3)	89.88(3)	89.81(3)	89.77(2)	89.83(2)
Cl4–Ln2–Cl6	92.88	88.80(3)	88.89(3)	88.99(3)	89.05(2)	89.10(2)
Cl5–Ln2–Cl6	89.41	90.52(3)	90.47(3)	90.49(3)	90.49(2)	90.48(2)
<b>Average</b>	<b>90(2)</b>	<b>89.7(9)</b>	<b>89.7(8)</b>	<b>89.8(8)</b>	<b>89.8(7)</b>	<b>89.8(7)</b>

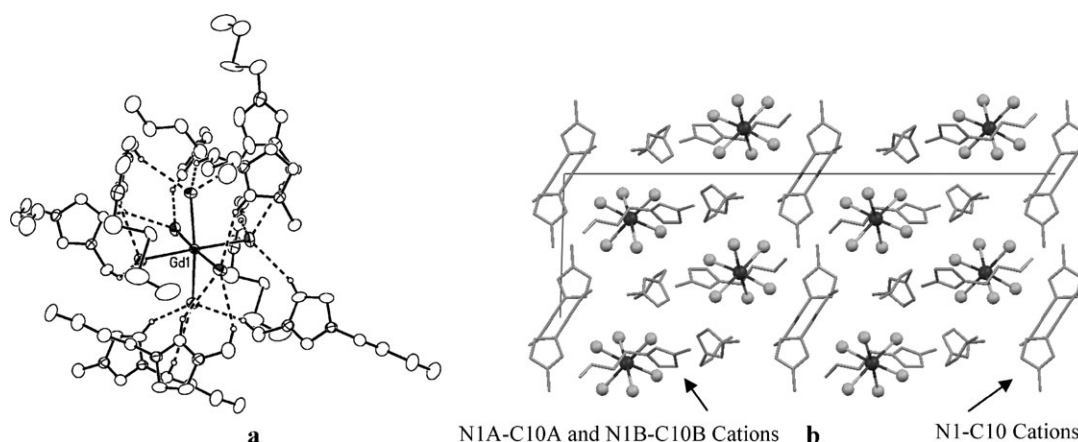
<sup>a</sup> Data collected at 20 °C (ref. 20); note that in the cell setting chosen in that study Ln2–Cl4 corresponds to Ln1–Cl2 in the current study.

**Table 3** Contacts at least 0.1 Å shorter than the van der Waals separation in  $[\text{C}_2\text{mim}]_3[\text{PrCl}_6]$

Atoms	D–H/ Å	H...A/ Å	D...A/ Å	ΔvdW/ Å	D–H...A/°
<b>Ln1</b>					
C8A–H8AC...Cl1 <sup>a</sup>	0.98	2.68	3.473(5)	–0.272	138.4
C2–H2A...Cl2	0.95	2.70	3.555(4)	–0.255	150.8
C4A–H4AA...Cl2 <sup>b</sup>	0.95	2.72	3.554(5)	–0.230	146.9
C5B–H5BA...Cl1 <sup>c</sup>	0.95	2.73	3.497(4)	–0.221	138.5
C5–H5A...Cl3 <sup>d</sup>	0.95	2.77	3.580(4)	–0.180	143.8
C7B–H7BC...Cl1 <sup>e</sup>	0.98	2.78	3.655(5)	–0.165	148.4
C2–H2A...Cl3	0.95	2.79	3.346(4)	–0.159	118.2
C4B–H4BA...Cl2 <sup>e</sup>	0.95	2.82	3.635(4)	–0.131	144.5
<b>Ln2</b>					
C8A–H8AA...Cl5	0.98	2.62	3.583(4)	–0.327	166.5
C2B–H2BA...Cl6	0.95	2.73	3.423(4)	–0.222	130.5
C4–H4A...Cl4 <sup>f</sup>	0.95	2.73	3.589(4)	–0.217	150.5
C2A–H2AA...Cl6 <sup>g</sup>	0.95	2.73	3.552(4)	–0.216	144.6
C8B–H8BC...Cl4 <sup>h</sup>	0.98	2.83	3.655(4)	–0.124	142.8

<sup>a</sup>  $-x + 1, -y, -z$ . <sup>b</sup>  $x, y - 1, z$ . <sup>c</sup>  $-x + 1, y - 1/2, -z + 1/2$ . <sup>d</sup>  $-x + 1, y + 1/2, -z + 1/2$ . <sup>e</sup>  $-x + 1, -y + 1, -z$ . <sup>f</sup>  $x + 1, y + 1, z$ . <sup>g</sup>  $-x, -y, -z$ . <sup>h</sup>  $-x, y + 1/2, -z + 1/2$ .





**Fig. 2** Crystal structure of [C<sub>4</sub>mim]<sub>3</sub>[GdCl<sub>6</sub>]: (a) H...Cl contacts at least 0.1 Å shorter than the van der Waals separation (only hydrogen atoms with short contacts shown, 50% probability thermal ellipsoids) and (b) packing diagram (down *b*) of the structure (hydrogen atoms omitted), showing a different supramolecular arrangement when compared to the [C<sub>2</sub>mim]<sup>+</sup> analog.

Strem Chemicals (Newburyport, MA) and used without any prior treatment.

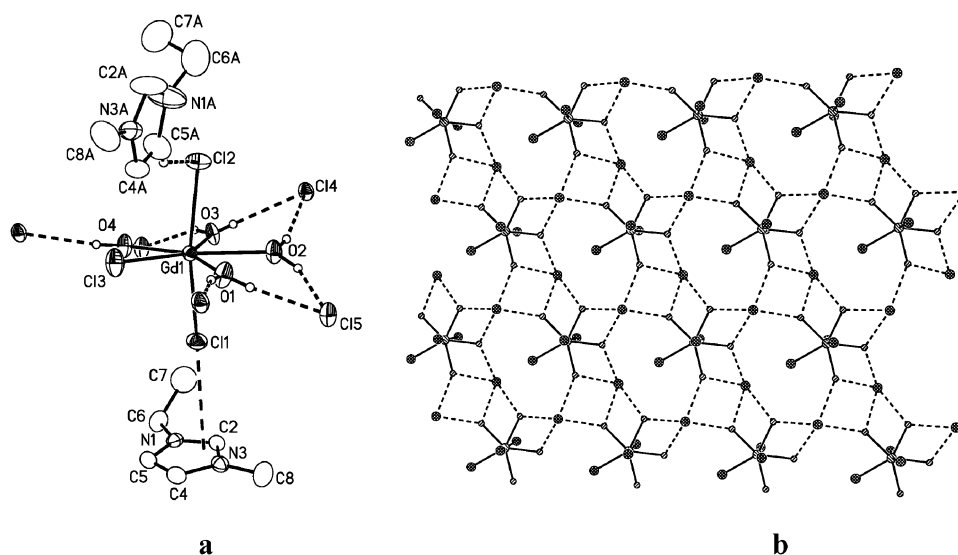
In individual open vials, LnCl<sub>3</sub>·*x*H<sub>2</sub>O (1.0 mmol; Ln = La, Pr, Nd, Sm, Eu, Gd; *x* = 6–7) was added to solid [C<sub>2</sub>mim]Cl (2.0 mmol; a 1 : 2 Ln : IL molar ratio) and heated unsealed to 110 °C for 3 h with intermittent vortexing for 30–60 s (in the case of Gd<sup>3+</sup>, this reaction was also conducted using [C<sub>4</sub>mim]Cl). An Isotemp<sup>®</sup> Programmable Muffle Furnace (Model 650-58, Fisher Scientific, Waltham, MA) was employed to slowly cool the samples at 0.1 °C min<sup>-1</sup> to a final temperature of 20 °C. In an attempt to prepare better crystals of [C<sub>2</sub>mim]<sub>3</sub>[GdCl<sub>6</sub>], a reaction mixture containing GdCl<sub>3</sub>·*x*H<sub>2</sub>O and IL was prepared as above, but in a sealed vial.

Single-crystal X-ray diffraction data were collected on a Bruker CCD area detector-equipped diffractometer (Madison, WI) with graphite-monochromated Mo-Kα radiation (*λ* = 0.71073 Å). Crystals were cooled to -100 °C under a nitrogen

gas stream during data collection. Absorption corrections were made with SADABS.<sup>27</sup>

The structure of [C<sub>2</sub>mim]<sub>3</sub>[PrCl<sub>6</sub>] was solved by Patterson methods using SHELXTL.<sup>28</sup> The coordinates from this structure were then used in the refinement of the other isostructural complexes. All hydrogen atoms were placed in calculated positions for each of the isolated complexes with thermal parameters fixed at 1.5 (methyl) or 1.2 (aromatic, methylene) times that of the bonded atom.

The structure of GdCl<sub>3</sub>(OH<sub>2</sub>)<sub>4</sub>·2([C<sub>2</sub>mim]Cl) was refined starting with the non-hydrogen coordinates from one polymorph (form II) of the analogous Er<sup>3+</sup> complex.<sup>12</sup> All bound water hydrogen atoms were located from difference Fourier maps and refined isotropically, while all other hydrogen atoms were placed in calculated positions with thermal parameters fixed at 1.5 (methyl) or 1.2 (aromatic, methylene) times that of the bonded atom.



**Fig. 3** Crystal structure of GdCl<sub>3</sub>(OH<sub>2</sub>)<sub>4</sub>·2([C<sub>2</sub>mim]Cl): (a) close contacts between the neutral metal center bound water molecules and free chloride, as well as the bound chloride...ring-H and chloride...π(ring) interactions (only hydrogen atoms with short contacts shown, 50% probability thermal ellipsoids) and (b) hydrogen-bonding framework responsible for the overall structural features (hydrogen atoms and cations omitted).

The structure of  $[\text{C}_4\text{mim}]_3[\text{GdCl}_6]$  was solved by Patterson methods using SHELXTL.<sup>28</sup> Disorder in the  $n$ -alkyl chains of the organic cations was observed, and additional partially occupied atoms were located, and refined using alternating least squares cycles. All hydrogen atoms were placed in calculated positions with thermal parameters fixed at 1.5 (methyl) or 1.2 (aromatic, methylene) times that of the bonded atom.

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