# Using ionic liquids to trap unique coordination environments: polymorphic solvates of $ErCl_3(OH_2)_4 \cdot 2([C_2mim]Cl)$

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**Two polymorphs of $ErCl_3(OH_2)_4 \cdot 2([C_2mim]Cl)$ solvates were isolated from the same solution of 1-ethyl-3-methylimidazolium chloride when HCl(aq) was added, while $[C_2mim]_3[ErCl_6]$ was isolated without HCl addition, illustrating how ionic liquids can be used to trap unusual coordination environments in the solid state.**

Ionic liquids (ILs) provide the opportunity to explore metal ion coordination in totally ionic media at relatively low temperatures, compared to the dissolution of metal salts in high-temperature molten salts or in molecular solvents. In addition, because the metal ions are dissolved in ionic melts at lower temperatures, the effects of molecular solvents (including water) and organic or inorganic coordinating ligands can be studied. Such solvents or ligands would not survive the harsh conditions often used to generate high-temperature molten salts. Additionally, the broad interest in using ILs in metal ion separations (including f-elements) and in electrochemistry calls for a better understanding of coordination and solvation of metal ions in the presence of ILs.

We,[1] and others,[2] have recently focused on using the tunable ionic liquid media to trap unusual coordination numbers, modes, or geometries in the solid state by dissolution of f-element metal salts in a variety of ionic liquids. The high relative concentration of 'free' ions combined with the often flexible conformations of one or both ions in the IL can result in a variety of unique packing forces, thereby increasing the likelihood of polymorphs. Interestingly, these features have generated much interest in the field of f-element solvation, separation, and coordination.[3] Nonetheless, the IL community has only begun to truly exploit the unique characteristics that set ILs apart from conventional solvents, where for example, it has been found that the chemistry of certain lanthanides and actinides are similar in aqueous systems, but are quite different in IL environments, possibly becoming advantageous in separating lanthanides and actinides.[4] Other examples include an IL used to stabilize a divalent europium species,[5] and the utilization of a water-stable IL to spectroscopically observe non-octahedral, higher chloride complexes of Np(IV) and Pu(IV).[6]

In general, the coordination number of the lanthanide(III) halides in solution is around nine,[7] where with increasing *Z*, the inner coordination sphere decreases as the lanthanide ionic radii and therefore the inner coordination sphere contracts, forcing displacement of donor ligands and molecules. The lanthanide(III) chloride hydrates exist most notably as $[LnCl_2(OH_2)_n]Cl$ ($n$ = 6–8) in the solid state, where one chloride resides in the second coordination sphere, bridging $[LnCl_2(OH_2)_n]^+$ cations *via* hydrogen bonds.[8]

Solvation of lanthanide(III) ions in acidic aqueous media varies from nine water molecules in the early lanthanides to eight and lower in the later lanthanides (Tb–Lu), decreasing further with increasing $Cl^-$ concentration. However, even at 14 M LiCl, only partial dehydration has been observed.[9] These studies have focused on acidic aqueous media in the strictest sense, where chloride concentration, as well as ionic strength are inherently limited to the systems that have been chosen. This could be problematic in modeling such metal ions in the natural environment or in nuclear tank waste,[10] where essentially a 'sea of ions' exists, resulting in conditions that may not be accurately simulated by conventional molecular solvents.

To begin trying to model the complex high ionic strengths in nuclear tank wastes, we have chosen to investigate the dissolution of f-element salts in ILs with a common anion, with and without the addition of aqueous acid. Our initial efforts have focused on the smaller lanthanides, such as Er(III) situated in the second half of the lanthanide series, where the high charge and smaller size might lead to unusual coordination effects. We first dissolved $ErCl_3 \cdot 6H_2O$ directly into the IL 1-ethyl-3-methylimidazolium chloride ($[C_2mim]Cl$) resulting in the isolation of $[C_2mim]_3[ErCl_6]$ (determined by single-crystal X-ray diffraction[12]) with the hexacoordinate $[ErCl_6]^{3-}$ and three $[C_2mim]^+$ cations balancing the charge. This result is in common with other structurally characterized $[LnCl_6]^{3-}$ ions isolated from IL media.[11]

Quite a different result was obtained in the presence of 12.1 M HCl, and only for Er(III). When equimolar amounts of solid[13] $[C_2mim]Cl$ (0.9862 mmol) and solid $ErCl_3 \cdot 6H_2O$ (1.004 mmol) were added to stirring 12.1 M HCl (2.5 mL) and the solution partially evaporated quickly under dry ambient atmosphere, pink rod-like crystals of $[ErCl_3(OH_2)_4] \cdot 2([C_2mim]Cl)$ formed after *ca.* 12 h. Upon removal of the crystals of this complex for further study, the vial was sealed and allowed to sit for a total of 48 h, during which time a second polymorph of the solvate formed as hexagonal plates. Under these same conditions in conventional molecular solvents, standard hydrated metal salts are typically formed.[8]

Crystallographic examination of the rods and plates revealed two very similar polymorphs of $[ErCl_3(OH_2)_4] \cdot 2([C_2mim]Cl)$ solvates (Fig. 1).‡ In fact, the close similarity of the unit cell parameters was initially taken to mean the crystals were identical.

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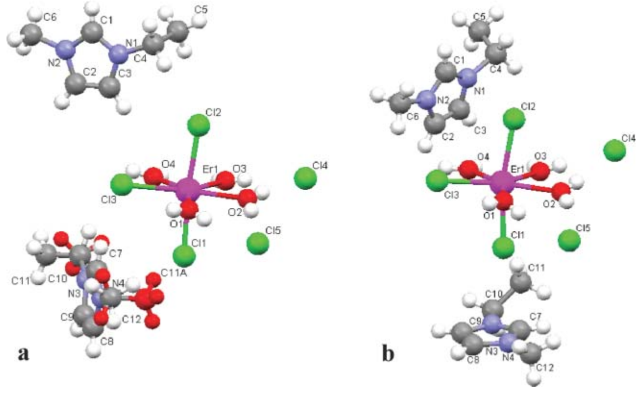

**Fig. 1** Crystal structures of $ErCl_3(OH_2)_4{\cdot}2([C_2mim]Cl)$, form **I** (kinetic (a)) and form **II** (thermodynamic (b)): Er–$OH_2$ 2.35(2) Å, Er–$Cl_{ax}$ 2.60(1) Å, Er–$Cl_{eq}$ 2.657(1) Å (form **I**) and Er–$OH_2$ 2.35(3) Å, Er–$Cl_{ax}$ 2.62(2) Å, Er–$Cl_{eq}$ 2.6440(8) Å (form II) (ethyl/methyl disorder in one of the cations in form **I** is shown in red).

Both complexes crystallize in the same triclinic space group and have similar unit cells, differing only by 27 Å$^3$.‡ However, it was not possible to use the coordinates from one form as a starting point in the refinement of the other; both crystal structures had to be independently solved and refined. Close examination of the packing environments revealed the nature of the polymorphism to be related to small rotations and disorder of the $[C_2mim]^+$ cations as discussed later.

While the isolation of polymorphic solvates is unique, we first focus on the reason for the study, a unique coordination environment for Er(III). The neutral, seven-coordinate Er(III) complexes consist of three $Cl^-$ and four $H_2O$ molecules directly coordinated to the metal center (Fig. 1), and is analogous to a recently postulated $[EuCl_y(H_2O)_{3-4}]^{3-y}$ hydrated metal center species existing in a 1-butyl-3-methlyimidazolium chloride aqueous solution.[14] These unique Er(III) moieties crystallize with two formula units of the IL $[C_2mim]Cl$ (which are found in the unit cell as discrete ions) in a 1 : 2 ratio. The observed coordination is unprecedented for non-chelated Er(III) and indeed for any lanthanide(III) halide.[7]

As evidenced by the close similarity in the unit cells of each form, both form **I** (kinetic) and form **II** (thermodynamic) are indeed almost the same (Fig. 2(a)). In fact, the $[ErCl_3(OH_2)_4]$ moieties are identical; differences in the two forms arise from the different packing orientations of the cations, each of which plays a separate role in the structure. One cation (the imidazolium ring comprised of N1–C1–N2–C2–C3, cation A) resides in the interstitial spaces between metal centers, stacking in crystallographically symmetric pairs (Fig. 3). These cation–cation pairs are slip aligned with interplanar distances and partial charge orientation that would indicate electrostatic interactions (closest ring–ring contacts obtained from the center of the C2–C3 bond are: form **I** = 3.48(8) Å; form **II** = 3.86(4) Å).[15] While these cations in Forms **I** and **II** are relatively similar, the positions of the pairs are somewhat twisted with respect to each other (Fig. 2(a)).

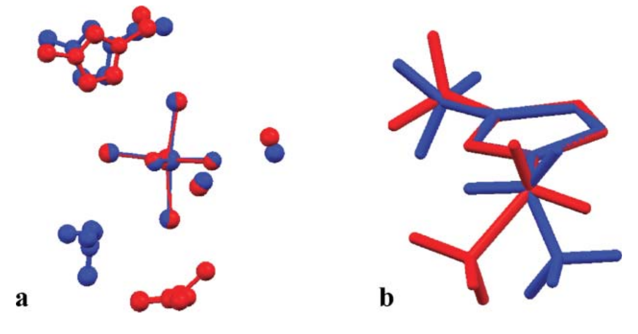

**Fig. 2** (a) Structural overlay of the asymmetric units of the polymorphs where the metal center and three bound chlorides serve as the overlay points: form **I** (blue); form **II** (red) (hydrogen atoms are omitted for clarity). (b) Overlay of the N3/N4 $[C_2mim]^+$ cations (cation B) in the two structures, showing a bending of the ethyl chain toward a coplanar position for form **II**.

The second cation (the imidazolium ring comprised of N3–C7–N4–C8–C9, cation B) shows the most distinguishable difference between the two structures, highlighting how the flexibility in position and in conformation of these alkylated-imidazolium cations provide a media adaptable to both polymorph and solvate formation. In form **I**, this cation is rotationally disordered about a line bisecting the C8–C9 positions and through C7 (C10, C11, C11A and C12 are each half occupied, the latter two atoms have methyl and methylene groups, respectively; Fig. 1(a)).

In form **II**, the corresponding cation ring is facially positioned above a bound chloride (cation B: Cl1 to N3, N4, C7 = 3.639(3), 3.698(3), 3.521(3) Å), and in addition is facing a free chloride on the opposite side of the ring (cation B: Cl4 to N3, N4, C7 = 3.628(3), 3.613(3), 3.539(3) Å). Such an open-faced interaction of this cation is possible because the alkyl chain (N3–C10–C11) is bent towards the imidazolium ring in form **II**, but not in form **I**, indicated by the difference in torsion angles: C7–N3–C10–C11: form **I** = 92(1)°, 110(1)° *vs.* form **II** = 40.2(5)° (Fig. 2(b)).

The ring face interactions in cation B with both bound (Cl1) and free (Cl4) chloride in form **II** connect the layers of hydrogen bonded sheets present in both forms (Fig. 3). It is clear that in the nucleation of these crystalline materials, the hydrogen-bonded networks comprised of the $[ErCl_3(OH_2)_4]$ and $Cl^-$ anions (which are essentially the same in both forms) are dominant. The other

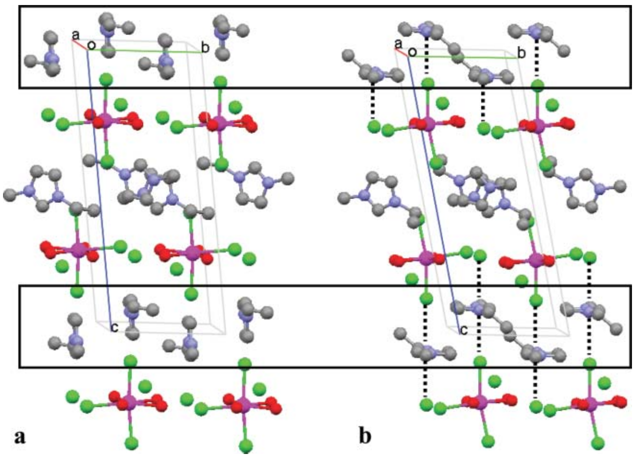

**Fig. 3** Packing diagrams of form **I** (a) and form **II** (b) looking down *a*. The distance between metal centers is slightly larger in form **I** (Er–Er 8.81(9) Å) than in form **II** (Er–Er 8.66(11) Å). Cation B in form **II** interacts with both a coordinated and a free chloride with the electron deficient portion of the imidazolium ring.

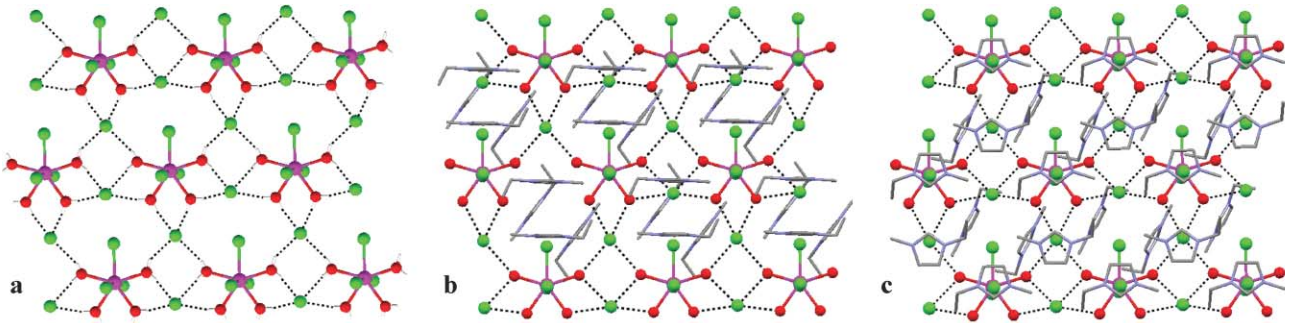

**Fig. 4** (a) Hydrogen bonded network responsible for the bulk structural characteristics in the crystal structures (form **II** represented). (b), (c): Hydrogen-bonded network viewed down *c* with cations located in the interstitial spaces. Rows of hydrogen-bonded metal center···free chloride sheets are interpenetrated by cations in two alternating conformations (form **I** (b), form **II** (c)).

cations in form **II**, and both types of cations in form **I**, appear to merely provide charge balance and appropriate packing to allow building of clay-like layers (Fig. 4).

It is clear that ILs can be used to trap unusual coordination modes, numbers, and geometries. The very nature of the IL pair and flexible ions inherent in ILs allow for many different possible structural motifs. The challenge will lie in gaining sufficient control of IL complexity, to make it worth utilizing them as a unique crystallization tool.

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## Notes and references

‡ Data were collected on a Bruker CCD area detector-equipped diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda$ = 0.71073 Å) and structures solved using SHELXTL.[16] Absorption corrections were made with SADABS.[17] All non-hydrogen atoms were readily located and refined anisotropically. The structures were refined by full-matrix least squares on $F^2$. In cases of disorder, alternate positions were found and refined with alternating least-squares cycles. Hydrogen atoms on bound water molecules were found from difference Fourier maps and all other hydrogen atoms were placed in calculated positions. Figures were created using the Mercury CSD 1.5 program.[18]

*Crystal data*: form **I** (CCDC 656211): $C_{12}H_{30}N_4O_4Cl_5Er$, $M$ = 638.91, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 8.7022(6), $b$ = 8.8756(6), $c$ = 18.183(1) Å, $\alpha$ = 78.342(1), $\beta$ = 83.510(1), $\gamma$ = 60.517(1)°, $U$ = 1197.2(1) Å$^3$, $T$ = 173(2) K, $Z$ = 2, $\mu$(Mo-Kα) = 4.086 mm$^{-1}$, 7812 reflections measured, 5240 unique ($R_{\text{int}}$ = 0.0255) which were used in all calculations. The final $R_1$ and $wR(F^2)$ were 0.0315 [($I > 2\sigma(I)$], 0.0838 (all data). Form **II** (CCDC 656212): $C_{12}H_{30}N_4O_4Cl_5Er$, $M$ = 638.91, triclinic, space group $P\bar{1}$ (no. 2), $a$ = 8.5226(5), $b$ = 8.6848(5), $c$ = 18.598(1) Å, $\alpha$ = 76.775(1), $\beta$ = 87.976(1), $\gamma$ = 61.221(1)°, $U$ = 1170.0(1) Å$^3$, $T$ = 173(2) K, $Z$ = 2, $\mu$(Mo-Kα) = 4.180 mm$^{-1}$, 8053 reflections measured, 5326 unique ($R_{\text{int}}$ = 0.0145) which were used in all calculations. The final $R_1$ and $wR(F^2)$ were 0.0253 [$I > 2\sigma(I)$], 0.0661 (all data).

For crystallographic data in CIF or other electronic format see DOI: 10.1039/b711679a

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