Chemistry of polynuclear transition-metal complexes in ionic liquids

Ejaz Ahmed^{a,b} and Michael Ruck^{*a,b}

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Transition-metal chemistry in ionic liquids (IL) has achieved intrinsic fascination in the last few years. The use of an IL as environmental friendly solvent, offers many advantages over traditional materials synthesis methods. The change from molecular to ionic reaction media leads to new types of materials being accessible. Room-temperature IL have been found to be excellent media for stabilising transition-metal clusters in solution and to crystallise homo- and heteronuclear transition-metal complexes and clusters. Furthermore, the use of IL as solvent provides the option to replace high-temperature routes, such as crystallisation from the melt or gas-phase deposition, by convenient room- or low-temperature syntheses. Inorganic IL composed of alkali metal cations and polynuclear transition-metal cluster anions are also known. Each of these areas will be discussed briefly in this contribution.

Introduction

Ionic liquids (IL), defined as molten salts with melting points below 100 °C, have received a lot of attention from both academia and industry during the last decade.^{1–3} They exhibit intrinsically promising characteristics such as wide liquid range,

negligible vapour pressure, large electrochemical window, and high electric conductivity.⁴ These molten salts are being applied extensively as convenient solvents for organic and inorganic synthesis,⁴ for crystal engineering of coordination compounds,^{5–11} for liquid–liquid extraction,¹² for electrodeposition,¹³ for spectroscopic studies,¹⁴ as electrolyte in photovoltaic devices (solar cells)¹⁵ and as a constituent in hybrid materials.¹⁶ Moreover, transition-metal containing IL are regarded as potential materials that combine the properties of IL with additional inherent magnetic, optical or catalytic properties.^{17–21} A significant and distinctive feature of IL is the tunability of their chemical and physical

^aDepartment of Chemistry and Food Chemistry, Dresden University of Technology, D-01062, Dresden, Germany

^bMax Planck Institute for Chemical Physics of Solids, Nöthnitzer Str. 40, 01187, Dresden, Germany. E-mail: Michael.Ruck@tu-dresden.de

Ejaz Ahmed

Ejaz Ahmed obtained his first degree in Chemistry in 2004 and an M.Phil in analytical and inorganic chemistry in 2006 under the supervision of Prof. Muhammad Mazhar at Quaid-i-Azam University, Pakistan. In 2007, he was awarded a PhD scholarship by the Higher Education Commission of Pakistan (HEC) and the German Academic Exchange Service (DAAD); then he joined the research group of Prof. Michael Ruck at Dresden University of Technology, Germany. His current research is focused on the synthesis and crystal engineering of polynuclear metal clusters, low-dimensional conductors, and main-group polycations from room-temperature ionic liquids.

Michael Ruck

Michael Ruck obtained his diploma in chemistry in the group of Hartmut Bärnighausen at the University of Karlsruhe (Germany) in 1989. Then he joined the group of Arndt Simon at the Max Planck Institute for Solid State Research working on cluster compounds of the rare-earth metals and completing his doctoral degree at the University of Stuttgart in 1991. He returned to Karlsruhe, where he completed his habilitation on ternary bismuth subhalogenides in 1997. Since 2000 he held the Chair for Inorganic Chemistry at Dresden University of Technology. In 2010, he became a Fellow of the Max Planck Society. His research interests concern subvalent compounds, low-dimensional systems, metastable phases, low-temperature syntheses of inorganic materials, and pseudo-symmetry in crystal structures.

properties by selecting an appropriate combination of cation and anion.

There are several classical routes available to synthesise polynuclear transition-metal compounds. Mostly, they had been synthesised employing either higher temperature reactions (crystallisation from melt or chemical vapour transport)^{22–31} or by treating the precursors in some organic solvents (non-polar, *e.g.* ether or benzene, or polar, *e.g.* dichloromethane or acetonitrile)^{32–34} or inorganic solvents (*e.g.* water or aqueous HCl).³⁵

In the late 1980s, Hussey and co-workers introduced room-temperature ionic liquids (RTIL) for stabilising both monomeric and polymeric chlorido complexes of transition metals.³⁶ In many cases, RTIL proved to be superior to conventional molecular solvents such as water or acetonitrile, because the solvation and solvolysis pathways that are often available to these complexes in molecular solvents are absent in RTIL. Moreover, Hussey *et al.* also managed to investigate the spectroscopic and electrochemical properties of some of the transition-metal chloride clusters.^{37–39} Later, Hughbanks *et al.* reported a novel procedure, using RTIL to isolate the centred hexanuclear zirconium halogenide cluster compounds and studied their spectroscopic, electrochemical and structural properties.^{40–43} Following the same procedure, Köckerling *et al.* and Saito *et al.* synthesised some new centred hexanuclear zirconium halogenide clusters and trinuclear rhenium halogenide clusters, respectively.^{44,45} Mudring and co-workers synthesised a number of new salt-like structures from IL, containing lanthanides in the anionic network and investigated their structural and physical properties.^{8–11} Dyson *et al.*, Raubenheimer *et al.*, Xia *et al.*, and Xiao *et al.* used IL as reagent and solvent to prepare several new organometallics.⁴⁶ Dyson *et al.* also studied catalytic properties of transition-metal carbonyl clusters in IL.^{46a,47} Nockemann and co-workers obtained some polynuclear metal complexes from task-specific or functionalised IL.⁴⁸

In our recent articles, we have demonstrated a facile and convenient room-temperature route for the synthesis of transition-metal clusters and main group clusters employing RTIL as the reaction media.^{49–53} With respect to cluster chemistry, RTIL proved to be especially useful because of their good solubility for ionic compounds, redox stability, and thereof resulting opportunity to use reducing agents of various strengths. Moreover, controllable parameters, such as solvent acidity, oxidizing/reducing agents, and halide acceptors facilitate to produce transition-metal cluster compounds. The synthesis at room-temperature also widely eliminates the risk of product decomposition.

Although there are some interesting reviews or perspectives focused on selected topics in materials synthesis using IL,^{54–59} an updated account on polynuclear transition-metal complexes is still lacking, especially considering that the field is progressing relatively fast. Therefore, the main focus of this contribution is to highlight systematically some recent advances with some relevant past in the synthesis of discrete polynuclear transition-metal clusters and complexes in IL and to outline new research on transition-metal chemistry. Briefly, the modes of synthesis and the structures of the well characterised compounds will be discussed. For convenience, metal clusters or complexes are categorised and discussed with respect to the number of metal atoms present in the structure. This perspective does not intend to be extensive or all-inclusive, but aims to provide a general overview of the field and to prompt future research efforts.

Binuclear complexes

Nockemann and co-workers developed carboxyl-functionalised IL that are able to dissolve considerable amounts of a wide range of metal oxides, including rare-earth oxides.^{48,60} Such IL are of particular interest for applications in the nuclear fuel cycle, especially, for the extraction of uranium from ores and for the processing of spent nuclear fuel rods.^{59,61} Nockemann *et al.* reported different metal complexes formed upon dissolution of corresponding metal oxides and hydroxides in different IL, functionalised with a carboxyl group, *e.g.* [Hbet][Tf₂N], [HbetmIm][Tf₂N], [HbetmMor][Tf₂N] and [HbetmPyr][Tf₂N]. X-Ray diffraction studies on single crystals of the metal complexes revealed a rich structural variety with strong dependence on the cationic core attached to the carboxylate groups. The task-specific betainium IL produced a number of polynuclear complexes. All these complexes were incorporated with zwitterionic carboxylate ligands and [Tf₂N][–] counterions. Besides, the structural determination of single crystals of the complexes crystallised from these IL, the measurement of absorption and luminescence spectra of the metal complexes were also carried out. Task-specific IL were used to synthesise different binuclear complexes, *e.g.* [(UO₂)₂(bet)₆(H₂O)₂][Tf₂N]₄, [Cu₂(betmMor)₄][Tf₂N]₄, [Eu₂(betmMor)₆(H₂O)₂][Tf₂N]₆, [Cu₂(betmPyr)₄(H₂O)₂][Tf₂N]₄, [Cu₂(betmIm)₄(H₂O)₂][Tf₂N]₄·H₂O, [Cd₂(betPy)₂(H₂O)₂][Tf₂N]₂, [Eu₂(bet)₈(H₂O)₄][Tf₂N]₆, [Eu₂(bet)₈(H₂O)₂][Tf₂N]₆·2H₂O or [Y₂(bet)₆(H₂O)₄][Tf₂N]₆.^{48,60}

The crystal structure of [(UO₂)₂(bet)₆(H₂O)₂][Tf₂N]₄ consists of the binuclear complex cation [(UO₂)₂(bet)₆]⁴⁺ with six coordinating betaine zwitterions and two water molecules, surrounded by four non-coordinating bistriflimide [Tf₂N][–] counterions (Fig. 1). Two of the carboxyl functionalised betaine zwitterions are μ_2 -bridging. The other four betaine zwitterions exhibit monodentate coordination to each of the two uranyl cations in the asymmetric unit. Four of the coordinating betaine ligands and one water molecule form slightly distorted pentagonal-bipyramidal oxygen coordination around each of the uranium(VI) atoms.^{60a} Spectroscopic studies revealed that the uranyl complex was decomposed in aqueous solution, while in acetonitrile and in the IL [Hbet][Tf₂N], the carboxylate groups remained coordinated.

Fig. 1 The binuclear [(UO₂)₂(bet)₆(H₂O)₂]⁴⁺ complex cation. Hydrogen atoms are omitted for clarity as in the following figures.

The structure of the [Cu₂(betmIm)₄(H₂O)₂][Tf₂N]₄·H₂O complex also exhibits a dimeric core, consisting of four μ_2 -bridging

N-carboxymethyl-*N*-methylimidazolium ligands and two water molecules (Fig. 2). The surrounding anion network of four $[\text{TF}_2\text{N}]^-$ ions prefer hydrogen bonding with the acidic protons of imidazolium cations rather than with the coordinated water molecules. Both copper(II) ions show a distorted square-pyramidal coordination by oxygen atoms.^{60b}

Fig. 2 The binuclear $[\text{Cu}_2(\text{betmIm})_4(\text{H}_2\text{O})_2]^{4+}$ complex cation.

Ruck *et al.* applied the Lewis-acidic IL $[\text{BMIM}]\text{Cl}/\text{AlCl}_3$ to synthesise transition-metal clusters in high yields at room temperature. One example is the complex salt $[\text{Mo}_2\text{Te}_{12}]\text{I}_6$,⁵¹ which contains the heteropolycationic $[\text{Mo}_2\text{Te}_{12}]^{6+}$ cluster. $[\text{Mo}_2\text{Te}_{12}]\text{I}_6$ was obtained by reacting Mo, Te and I_2 in $[\text{BMIM}]\text{Cl}/\text{AlCl}_3$ at room temperature in only three days. This nicely demonstrates the versatility of IL in inorganic synthesis; the homeotypic $[\text{Mo}_2\text{Te}_{12}]\text{Br}_6$ has been synthesised by Beck through chemical vapour transport (CVT) at about 300 °C within four weeks yielding less product.⁶² Moreover, the CVT synthesis of the iodide analogue failed completely. In the crystal structure of $[\text{Mo}_2\text{Te}_{12}]\text{I}_6$, the cationic complexes $[\text{Mo}_2\text{Te}_{12}]^{6+}$ are surrounded by iodide ions, which connect them into a layer structure. In the complex cation $[(\text{Mo}^{3+})_2(\text{Te}_2^{2-})_2(\text{Te}_4^{2+})_2]^{6+}$, the two molybdenum atoms are connected by two bridging $\eta^2\text{-Te}_2^{2-}$ dumbbells (Fig. 3). In addition, each molybdenum atom is coordinated by a terminal Te_4^{2+} polycation in η^4 mode. As a result, both molybdenum atoms are in square-antiprismatic environment. Despite the short $\text{Mo} \cdots \text{Mo}$ distance of 297 pm, a paramagnetic moment of $3.53 \mu_{\text{B}}$ per molybdenum(III) atom was observed, which indicates that the magnetic moments are not coupled.

Raubenheimer *et al.* prepared several homonuclear and heteronuclear organometallic complexes employing IL as reagent and solvent as well, *e.g.*, binuclear cobalt complexes, $[\{\text{APIM}\}\text{Co}_2(\text{CO})_6]\text{PF}_6$ and $[\{\text{APIM}\}\text{Co}_2(\text{CO})_6]\text{B}(\text{C}_6\text{H}_5)_4$ were synthesised by reacting $\text{Co}_2(\text{CO})_8$ with freshly prepared IL $[\text{APIM}]\text{X}$ ($\text{X} = \text{PF}_6^-, \text{B}(\text{C}_6\text{H}_5)_4^-$) in dichloromethane. The former complex represents first example of an organometallic IL.^{46b}

The structure of the binuclear cobalt complex $[\{\text{APIM}\}\text{Co}_2(\text{CO})_6]\text{PF}_6$ consists of a pseudo-tetrahedral Co_2C_2 -

Fig. 3 The binuclear $[\text{Mo}_2\text{Te}_{12}]^{6+}$ complex cation.

core. The coordination of each cobalt atom is pseudo-octahedral, bridged by the alkyne ligand (Fig. 4). The imidazolium units are arranged in layers and face each other while the $\text{Co}_2(\text{CO})_6$ units face each other in the alternate layers.

Fig. 4 The binuclear cobalt $[\{\text{APIM}\}\text{Co}_2(\text{CO})_6]^+$ complex cation.

Dyson and co-workers synthesised several IL based, versatile ruthenium precursors like binuclear organometallic complex $[\text{RuCl}_2(\eta^6\text{-arene})]_2$ for aqueous and ionic liquid biphasic catalysis.^{47c}

Xia *et al.* prepared two organometallic heteronuclear complexes $[\text{bmim}]\text{K}[\text{Co}(\text{CO})_4]_2$ and $[\text{C}_4\text{Py}]\text{K}[\text{Co}(\text{CO})_4]_2$ by reacting a tetrahydrofuran solution of $\text{KCo}(\text{CO})_4$ with $[\text{bmim}]\text{Br}$ or $[\text{C}_4\text{Py}]\text{Br}$ dissolved in a minimum amount of methanol.^{46d}

The crystal structure of the heteronuclear complex $[\text{bmim}]\text{K}[\text{Co}(\text{CO})_4]_2$ shows two $[\text{Co}(\text{CO})_4]^-$ units, connected through one potassium cation, and a bulky organic cation $[\text{bmim}]^+$ as the counterion (Fig. 5). The molecular structure is represented as discrete ion pairs, with little affinity between the cations and the anions.

Xiao *et al.* synthesised an organometallic binuclear complex $[\text{PdBr}(\mu\text{-Br})(\text{bmiy})]_2$ ($\text{bmiy} = 1\text{-butyl-3-methylimidazol-2-ylidene}$) by reacting $\text{Pd}(\text{OAc})_2$ and $[\text{bmim}]\text{Br}$ in tetrahydrofuran and demonstrated it as an efficient catalyst precursor.^{46e}

Fig. 5 The heteronuclear complex anion $\text{K}[\text{Co}(\text{CO})_4]_2^-$.

Recently, Hagiwara *et al.* reported the binuclear molybdenum complex $[\text{BPy}]_2[\text{Mo}_2\text{O}_4\text{F}_6]$. It was obtained in an attempt to crystallise the low-melting salt BPyMoOF_5 , but single crystals of $[\text{BPy}]_2[\text{Mo}_2\text{O}_4\text{F}_6]$ resulted from the hydrolysis of BPyMoOF_5 with some traces of water during the crystal growth.⁶³

Trinuclear complexes

Saito *et al.* synthesised a trinuclear rhenium sulfide cluster from Lewis basic IL by treating $\text{Re}_3\text{S}_7\text{Cl}_7$ with a 1:1 mixture of EMIMBr and AlBr_3 at 70 °C for 2 days followed by refluxing in acetonitrile to get a viscous solution. After cooling and filtration, diethyl ether was layered and a black solid was obtained, which was recrystallised from acetonitrile–diethyl ether to obtain good quality single-crystals of $\text{Im}_3[\text{Re}_3(\mu_3\text{-S})(\mu\text{-S})_3\text{Br}_9]\text{Br}$. The structure of the cluster anion comprises an almost equilateral triangle of rhenium atoms with one $\mu_3\text{-S}^{2-}$, three $\mu\text{-S}^{2-}$ and nine terminal Br^- ligands (Fig. 6). The cation network is composed of three EMIM⁺ ions. This synthetic procedure has revealed that the IL EMIMBr/ AlBr_3 has the ability to remove one of the S atoms in the $\mu\text{-S}^{2-}$ ligands of the precursor complex $[\text{Re}_3(\mu_3\text{-S})(\mu\text{-S})_3\text{Cl}_6]\text{Cl}$, to exchange Cl^- for Br^- , and to coordinate extra bromido ligands to the Re_3S_4 core.⁴⁵

Fig. 6 (a) The $[\text{Re}_3(\mu_3\text{-S})(\mu\text{-S})_3\text{Br}_9]^{2-}$ cluster anion; (b) polyhedra representation emphasising the edge-sharing of coordination octahedra.

Nockemann and co-workers demonstrated the preparation of the trinuclear cobalt complex $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2][\text{TF}_2\text{N}]_{10}[\text{Hbet}]_2$ from the task-specific IL $[\text{Hbet}][\text{TF}_2\text{N}]$.^{48a} The synthesis was accomplished by reacting $\text{Co}(\text{OH})_2$ with $[\text{Hbet}][\text{TF}_2\text{N}]$ in the presence of water. The crystal structure of $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2][\text{TF}_2\text{N}]_{10}[\text{Hbet}]_2$ contains discrete trimeric $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2]^{8+}$ units, eight non-coordinating $[\text{TF}_2\text{N}]^-$ anions as counter ions and two additional $[\text{Hbet}][\text{TF}_2\text{N}]$ ion pairs as

“solvent” molecules in the crystal structure. The three cobalt(II) atoms of the trimeric $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2]^{8+}$ units are connected by four μ_2 -bridging carboxylate groups of the betaine ligands and two bridging water molecules. The octahedral oxygen coordination of each cobalt atom is slightly distorted (Fig. 7).

Fig. 7 The trimeric $[\text{Co}_3(\text{bet})_8(\text{Hbet})_2(\text{H}_2\text{O})_2]^{8+}$ complex cation, highlighting the corner-sharing $[\text{CoO}_6]$ octahedra.

A trinuclear tungsten cluster compound was synthesised by Ruck *et al.* using a Lewis acidic IL as reaction medium. Dark brown, column-like crystals of $\text{Sn}[\text{SnCl}][\text{W}_3\text{Cl}_{13}]$ were obtained at room temperature by the reduction of WCl_6 with elemental tin in $[\text{BMIM}]\text{Cl}/\text{AlCl}_3$.⁵⁰ The structure of $\text{Sn}[\text{SnCl}][\text{W}_3\text{Cl}_{13}]$ contains a trinuclear $[\text{W}_3\text{Cl}_{13}]^{3-}$ cluster anion, a tin(II) cation, and a $[\text{SnCl}]^+$ cation. The cluster anion $[\text{W}_3\text{Cl}_{13}]^{3-}$ comprises an equilateral triangle of tungsten atoms, which are connected by one $\mu_3\text{-Cl}$ and three $\mu\text{-Cl}$ ligands. Each tungsten atom is further coordinated by three terminal Cl^- ions. Therefore, all tungsten atoms are found in slightly distorted octahedral environment (Fig. 8). The tin(II) cations, which are in trigonal-pyramidal and in distorted trigonal-antiprismatic coordination by terminal chloride ions, connect the clusters into a layer structure. Similar cluster compounds, $\text{A}_3[\text{W}_3\text{Cl}_{13}]$ with $\text{A} = \text{Li}, \text{Na}$ or K , have been obtained previously by Messerle *et al.* and Meyer *et al.* applying classical solid-state synthesis, which necessitated 240 to 500 °C and 6 to 7 days.^{64,65}

Fig. 8 (a) The trinuclear $[\text{W}_3(\mu_3\text{-Cl})(\mu\text{-Cl})_3\text{Cl}_9]^{3-}$ cluster anion; (b) polyhedra representation emphasising the edge-sharing of coordination octahedra.

Raubenheimer *et al.* prepared a heterotrinuclear gold ferrocenyl complex bis{1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)-2*H*-imidazol-2-ylidene}gold(I) tetrafluoroborate by the reaction of a freshly prepared mononuclear complex 1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)imidazolium tetrafluoroborate with Ag_2O , and

tetraethylammonium chloride in a mixture of CH_2Cl_2 and MeOH, followed by the addition of chlorido(dimethylsulfide)gold(I).^{46c}

The asymmetric unit in the heteronuclear compound contains the gold complex, a highly disordered BF_4^- anion, and a solvent molecule, CH_2Cl_2 . The structure reveals a linear coordination of the central gold(I) atom to the two carbene carbons. The cyclopentadienyl rings are almost parallel. The $\eta^5\text{-C}_5\text{H}_4$ rings and the phenyl rings are nearly parallel (Fig. 9).

Fig. 9 The trinuclear bis{1-[(*E*)-2-butenyl]-3-(4-ferrocenylphenyl)-2*H*-imidazol-2-ylidene}gold(I) complex cation.

Tetranuclear complexes

The first tetranuclear cobalt complex $[\{\text{DPIM}\}\{\text{Co}_2(\text{CO})_6\}_2]\text{BPh}_4$ was reported by Dyson and co-workers.⁶⁶ The synthesis was performed, employing 1,3-dialkyne-functionalised imidazolium IL derivatives, *e.g.* 1,3-dipentynylimidazolium tetraphenylborate, was treated with $\text{Co}_2(\text{CO})_8$ in dichloromethane. In the structure of the tetranuclear complex, the 1,3-dialkyne arms adopt a *trans* conformation. The Co–Co distances are found to be shorter than in the parent $\text{Co}_2(\text{CO})_8$ complex. The cobalt atoms are bridged by alkyne ligands (Fig. 10) and three different $\text{C-H}\cdots\pi$ interactions were observed in the structure. In addition, one of the H atoms in the CH_2 group is also involved in a $\text{C-H}\cdots\pi$ interactions with the phenyl ring of the counterion.

Fig. 10 The tetranuclear $[\{\text{DPIM}\}\{\text{Co}_2(\text{CO})_6\}_2]^+$ complex cation.

Nockemann *et al.* synthesised two tetranuclear complexes, $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4][\text{Tf}_2\text{N}]_8$ and $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2][\text{Tf}_2\text{N}]_8$, by applying the task-specific IL $[\text{Hbet}][\text{Tf}_2\text{N}]$.^{48a} The synthesis was performed by reacting the corresponding metal oxides with $[\text{Hbet}][\text{Tf}_2\text{N}]$ in the presence of water. The crystal structure of the tetranuclear manganese complex $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4][\text{Tf}_2\text{N}]_8$

consists of discrete tetrameric $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})]^{7+}$ units and seven non-coordinating $[\text{Tf}_2\text{N}]^-$ counterions (Fig. 11). The four manganese(II) atoms, which differ in their coordination, are connected by bridging carboxylate groups of the betaine ligands. The oxygen coordination environment of the manganese atoms Mn2 and Mn4 can be described as strongly distorted octahedra, while Mn1 and Mn3 are found in distorted square-based pyramidal coordination by five oxygen atoms. In addition to the bridging carboxylate groups of the ligands, water molecules complete the octahedral surrounding of Mn2 and Mn4.

Fig. 11 The tetranuclear $[\text{Mn}_4(\text{bet})_{10}(\text{H}_2\text{O})_4(\text{Tf}_2\text{N})]^{7+}$ complex cation.

In the tetrameric zinc complex $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2][\text{Tf}_2\text{N}]_8$, the discrete tetrameric cation $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2]^{8+}$ is surrounded by eight non-coordinating $[\text{Tf}_2\text{N}]^-$ anions (Fig. 12). The zinc(II) atoms are connected by bridging carboxylate groups of the betaine ligands. The crystal structure shows two independent zinc (Zn1 and Zn2) atoms which exhibit square-pyramidal coordination. Zn1 is coordinated by five carboxylate groups that are in μ -bridging to the adjacent zinc atoms Zn2 and Zn1', respectively. Zn2 is surrounded by one monodentate betaine ligand, three betaine ligands that are μ -bridging to Zn1 and one water molecule.

Fig. 12 The tetranuclear $[\text{Zn}_4(\text{bet})_{10}(\text{H}_2\text{O})_2]^{8+}$ complex cation.

Pentanuclear complexes

Nockemann and co-workers continued their efforts to build even higher nuclearity metal complexes and were successful in isolating two pentanuclear complexes, $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6][\text{Tf}_2\text{N}]_{10}$ and $[(\text{Pb}_2\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3][\text{Tf}_2\text{N}]_4\cdot\text{MeOH}$, by applying the same synthetic strategy of reacting metal oxides with $[\text{Hbet}][\text{Tf}_2\text{N}]$ in the presence of water or methanol.^{48a}

The crystal structure of the pentanuclear complex $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6][\text{Tf}_2\text{N}]_{10}$ consists of discrete pentameric $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6]^{10+}$ units and non-coordinating $[\text{Tf}_2\text{N}]^-$ anions as counterions. The three symmetrically independent nickel(II) atoms of the pentameric $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6]^{10+}$ unit are connected by eight μ_2 -bridging carboxylate groups of the betaine ligands and four bridging water molecules. Each Ni atom is coordinated

by oxygen atoms of four betaine ligands and two water molecules to give slightly distorted octahedral coordination polyhedron. The terminal betaine ligands and water molecules are coordinated to Ni1 atoms in a monodentate fashion (Fig. 13).

Fig. 13 The pentanuclear $[\text{Ni}_5(\text{bet})_{12}(\text{H}_2\text{O})_6]^{10+}$ complex cation, the chain of corner-sharing $[\text{NiO}_6]$ octahedra is prominent.

The pentanuclear lead complex $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3][\text{Tf}_2\text{N}]_4 \cdot \text{MeOH}$ contains an oxo-hydroxo cluster inside the discrete pentameric $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3]^{4+}$ unit. The cation is surrounded by four non-coordinating $[\text{Tf}_2\text{N}]^-$ counter ions and one methanol molecule. The cationic unit $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3]^{4+}$ is composed of an oxo-centred $[\text{OPb}_4]^{6+}$ tetrahedron, which is connected to an additional lead atom through a μ_3 -bridging hydroxide and chelating-bridging carboxylate groups of betaine ligands. The $[\text{Pb}_4(\mu_4\text{-O})\text{Pb}(\mu_3\text{-OH})]^{7+}$ moiety is surrounded by eight betaine ligands and two coordinating $[\text{Tf}_2\text{N}]^-$ anions (Fig. 14). The $\mu_4\text{-O}$ atom tetrahedrally bridges Pb2, Pb3, Pb4 and Pb5 atoms while the $(\mu_3\text{-OH})$ -ligand bridges Pb1, Pb2 and Pb3 in a pyramidal shape (Fig. 14).

Fig. 14 The pentanuclear $[(\text{Pb}_4\text{O})\text{Pb}(\text{OH})(\text{bet})_8(\text{Tf}_2\text{N})_3]^{4+}$ complex cation.

Ruck *et al.* synthesised a pentanuclear molybdenum cluster compound $\text{Bi}[\text{Mo}_5\text{Cl}_{13}]\text{Cl}$ by the reduction of MoCl_5 with elemental bismuth in Lewis-acidic $[\text{BMIM}]\text{Cl}/\text{AlCl}_3$ at room

temperature.^{52,53} The resulting bismuth(III) cations are included in the product.

The crystal structure of $\text{Bi}[\text{Mo}_5\text{Cl}_{13}]\text{Cl}$ is a defect variant of the $\text{Pb}[\text{Mo}_6\text{Cl}_{14}]$ type.⁶⁷ One of the molybdenum atoms of the Mo_6 cluster core is missing, resulting in a $[\text{Mo}_5\text{Cl}_{13}]^{2-}$ cluster and a chloride ion that is not bonded to the cluster. In the $[\text{Mo}_5\text{Cl}_{13}]^{2-}$ cluster anion, the molybdenum atoms form a square pyramid, where each metal atom is coordinated by four Cl^{i} ligands and one Cl^{a} ligand ($^{\text{i}}$ = inner, $^{\text{a}}$ = apical or outer, according to the notation of Schäfer and Schnering⁶⁸). As a result, the Mo_5 core is surrounded by eight inner Cl^{i} ligands in the form of a cube. Out of these eight inner Cl^{i} , four are present as μ_3 -bridging ligands above the faces of the pyramid and the other four as μ -bridging ligands to the basal Mo atoms. The bismuth cations are surrounded by the five apical Cl^{a} and the non-cluster-bonded chloride ion in a slightly distorted octahedral environment (Fig. 15). $\text{Bi}[\text{Mo}_5\text{Cl}_{13}]\text{Cl}$ is paramagnetic with an effective magnetic moment of $1.67 \mu_{\text{B}}$, which indicates an unpaired electron in the $[\text{Mo}_5\text{Cl}_{13}]^{2-}$ anion corresponding to the odd number of 19 electrons in cluster core.

Fig. 15 A characteristic unit of the structure of $\text{Bi}[\text{Mo}_5\text{Cl}_{13}]\text{Cl}$, where each molybdenum atom is coordinated by four inner Cl^{i} and one apical Cl^{a} and bismuth is in octahedral surrounding.

Hexanuclear and high-nuclearity complexes

Hughbanks and co-workers introduced a new synthetic scheme, using room-temperature Lewis-basic IL to isolate centred hexanuclear zirconium halogenide cluster compounds and studied their spectroscopic, electrochemical, and structural properties.^{40–43} Room-temperature chloridoaluminate molten salts, mixtures of $\text{EMImCl}/\text{AlCl}_3$ were used as solvents to excise and isolate centred hexanuclear zirconium halogenide clusters from their solid-state precursors, *e.g.* $\text{Zr}_6\text{Br}_{14}\text{Fe}$, $\text{Li}_2\text{Zr}_6\text{Cl}_{15}\text{Mn}$, or $\text{Rb}_2\text{Zr}_6\text{Cl}_{18}\text{B}$. Compounds that include the cation of the IL, such as $\text{Im}_5[(\text{Zr}_6\text{Mn})\text{Cl}_{18}] \cdot 1.5\text{CH}_3\text{CN}$, $\text{Im}_4[(\text{Zr}_6\text{C})\text{Cl}_{18}]$, $\text{Im}_4[(\text{Zr}_6\text{Fe})\text{Cl}_{18}]$, $\text{Im}_5[(\text{Zr}_6\text{Mn})\text{Cl}_{18}] \cdot \text{C}_6\text{H}_5\text{CH}_3 \cdot 2\text{CH}_3\text{CN}$ or $\text{Im}_5[(\text{Zr}_6\text{B})\text{Cl}_{18}] \cdot \text{C}_6\text{H}_5\text{CH}_3 \cdot 2\text{CH}_3\text{CN}$, were isolated in good yield.

The molecular cluster anions consist of octahedral (Zr_6Z) ($\text{Z} = \text{Fe}, \text{Mn}, \text{B}$ or C) units with the 12 edges bridged by inner chloride ligands. Six terminal (outer) chloride ions occupy the apical positions (Fig. 16).⁶⁸

It was assumed that in basic molten salts, the chloride nucleophilicity is sufficient, which could serve as a reagent for excising these centred clusters from highly cross-linked solid-state compounds. They were also successful to carry out exchange of halogenides in the basic molten salts. This approach was found

Fig. 16 A typical heptanuclear cluster anion $[(Zr_6Z)Cl_{18}]^{n-}$ ($Z = Fe, Mn, Be$ or B and $n = 4$ or 5).

to be effective for several compounds that resist dissolution in acetonitrile or are unstable in aqueous solution. Later, Köckerling *et al.* followed the same route and isolated cluster phases $(EMIm)_4[(Zr_6Fe)Br_{18}]$ and $(EMIm)_4[(Zr_6Be)Br_{18}]$ from their solid-state precursors $Na_4[(Zr_6Be)Cl_{16}]$ and $K[(Zr_6Fe)Cl_{15}]$ by dissolving in Lewis-basic $EMIMBr/AlBr_3$. In the bromide-based IL, a complete exchange of all the outer and inner chlorides by bromide took place.⁴⁴

A hexanuclear molybdenum cluster compound $BiCl[Mo_6Cl_{14}]$ was prepared by Ruck and co-workers by reacting bismuth and $MoCl_5$ in Lewis acidic $[BMIM]Cl/AlCl_3$ at room temperature.⁵³ The crystal structure, which shows no noteworthy difference to the compound previously synthesised by a high-temperature method,^{22c} consists of $[Mo_6Cl_8^{14}Cl_6]^{2-}$ units containing an almost regular octahedral Mo_6 cluster core. The clusters are bonded *via* Cl^a to $[BiCl]^{2+}$ dumbbells (Fig. 17).

Fig. 17 The hexanuclear $[Mo_6Cl_{14}]^{2-}$ cluster anion.

Mudring and co-workers isolated a number of new salt-like structures from IL, containing lanthanides in the anion network. Besides mononuclear complexes,^{8–10} they also synthesised an octanuclear europium cluster compound $[bmpyr]_6[Eu_8(\mu_4-O)(\mu_3-OH)_{12}(\mu_2-OTf)_{14}(\mu-OTf)_2] \cdot 1.5HOTf$ from the IL $[bmpyr][OTf]$.

The structural characterisation revealed an Eu_8 cluster unit, which is centred by an oxide anion.¹¹ Moreover, they also prepared some low-melting IL, *e.g.* $[C_3mim][Eu(Tf_2N)_4]$ ($mp = 81.0^\circ C$), $[C_4mim][Eu(Tf_2N)_4]$ ($mp = 67.9^\circ C$), and $[C_4mpyr]_2[Eu(Tf_2N)_5]$ ($mp = 92.1^\circ C$). The dimeric europium units of the composition $[Eu_2(Tf_2N)_8]^{2-}$ were confirmed in the first two substances through crystallographic studies. These low-melting IL possess excellent photophysical properties (high lifetimes at high europium(III) concentration, small linewidth, and high colour purity), which might render them particularly valuable for various optical applications.^{9a}

Coordination polymers

Recently, Morris and co-workers introduced the concept of ionothermal synthesis, the use of an IL as solvent and potential template or structure directing agent in the preparation of crystalline solids, which offers several advantages over conventional hydrothermal and solvothermal materials synthesis methods.⁶⁹ This new strategy was further conveniently exercised by Yu *et al.*, Zhai *et al.*, Bu *et al.*, and many others to synthesise metal organic frameworks or coordination polymers.^{69–73}

Morris and co-workers demonstrated that the homochiral frameworks SIMOF-1 $(BIMIm)_2[Ni(TMA-H)_2(H_2O)_2]$ and SIMOF-2 $(BIMIm)_2[Ni_3(TMA-H)_4(H_2O)_2]$ could be achieved by using achiral building blocks in the chiral IL $[BIMIm][L-AspH]$.^{69b}

The structure of SIMOF-1 consists of octahedrally coordinated nickel(II) atoms. Each nickel atom is bound to four trimesate (TMA) anions and two water molecules (Fig. 18). The spatial arrangement of the four linking TMA anions around each nickel atom leads to a pseudo-tetrahedral building unit, which in turn connects to four other metal atoms to form a diamond-type network. The chirality in the structure is represented by a 4_1 screw axis. The pseudotetrahedral units, all of which have the same handedness, form helices and are linked into a three dimensional framework by the bridging ligands. The IL cations are strongly held inside the pores of the substructure.

Later, Zhai *et al.* reported a novel three-dimensional ferroelectric metal–organic framework, $\{(EMI)_2[Zn_3(1,2,4,5-BTC)_2] \cdot 2H_2O\}_n$ ($1,2,4,5-BTC = 1,2,4,5-benzenetetracarboxylate$) by ionothermal synthesis, which defined a new strategy to ferroelectric materials. The ionothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and 1,2,4,5-BTC ligands in IL $[EMI]Br$ was carried out at $160^\circ C$ for 7 days to yield colourless block crystals of the product.⁷⁰

The three-dimensional anionic porous framework is constructed from zinc(II) atoms and μ_6 -1,2,4,5-BTC ligands. The asymmetric unit consists of three crystallographically unique zinc atoms, two 1,2,4,5-BTC ligands, two unique $[EMI]^+$ cations, and two lattice water molecules, respectively. The three zinc atoms are in distorted tetrahedral environment defined by four carboxylic oxygen atoms from four different 1,2,4,5-BTC ligands. Two independent 1,2,4,5-BTC ligands adopt the μ_6 -bridging mode with two *para*-carboxylate groups in a bidentate fashion, while the other two *para*-carboxylate groups are monodentate (Fig. 18). As a result, the zinc atoms are interconnected through μ_6 -1,2,4,5-BTC ligands to generate a three-dimensional anionic porous framework.

Bu *et al.* further extended the scope of ionothermal synthesis by developing a generalized approach to synthesise homochiral zeolite-like low-connectivity framework materials in which highly

Fig. 18 The substructure of the anionic network of chiral SIMOF-1 showing the octahedral coordination by oxygen atoms around each nickel atom.

Fig. 19 The polymeric $\{[Zn_3(1,2,4,5-BTC)_2] \cdot 2H_2O\}_n^{2-}$ anion, highlighting the distorted tetrahedral environment around each zinc atom.

coordinated metal atoms (coordination number ≥ 8) are joined into homochiral three-dimensional tetrahedral frameworks by a templated synthesis. They treated enantiopure D-camphoric acid (D-H₂cam) and achiral 4,4'-oxybis(benzoic acid) (H₂obb) with indium(III) nitrate in two different ionic liquids, [EMIm]Es and [BMIm]Ms. This updated synthetic procedure resulted in a number of new open-framework materials that contain eight-coordinated indium(III) atoms as the tetrahedral nodes. Both 4-connected and to a smaller extent 3-connected homochiral frameworks were successfully synthesized, e.g., ALF-1 (EMIm)[In(D-cam)₂], ALF-3 (EMIm)₃[In(obb)₂]₂Es₂·H₂O, ALF-4 (EMIm)₂[In₂(D-cam)₃(D-Hcam)₂] and ALF-5 (BMIm)₂[In₂(D-cam)₃(D-Hcam)₂].⁷¹

Yu *et al.* represented three new open-framework metal borophosphates, [Na₆Co₃B₂P₅O₂₁Cl]·H₂O (JIS-4), K₅Mn₂B₂P₅O₁₉(OH)₂ (JIS-5) and (NH₄)₈[Co₂B₄P₈O₃₀(OH)₄] (JIS-6), synthesised under ionothermal conditions using the ionic liquid [Emim]Br as the solvent. These are the first examples of metalborophosphate prepared by the ionothermal method.⁷²

IL with polyoxometallate (POM) anions are also known. The first POM-based IL was reported by Giannelis *et al.*⁷⁴ The

synthesis was performed by combining a partially deprotonated heteropolyacid [H_{3-x}PW₁₂O₄₀]^{x-} with quaternary ammonium ions (CH₃)(C₁₈H₃₇)N⁺[(CH₂CH₂O)_nH][(CH₂CH₂O)_mH] ($m + n = 15$). This new family of materials was characterised by electrochemical and thermal analysis. The fluid character and proton transport properties under anhydrous conditions make these IL possible candidates for fuel cell and catalytic applications. Later, Dietz *et al.* carried out further investigations for the preparation and preliminary characterisation of the other members of this family of aprotic, POM-based IL, and described their potential as organic–inorganic hybrid materials.⁷⁵ Hou *et al.* and many others promoted this class of materials by adding IL to the list that exhibited excellent catalytic performance in organic synthesis.^{76–80}

Shan *et al.* synthesised several new inorganic IL⁸¹ consisting of an inorganic polyoxometallate anion with the Keggin structure⁸² and sodium cations, e.g. Na₁₃[Ln(TiW₁₁O₃₉)₂]·xH₂O (Ln = La, Ce, Pr, Sm, Gd, Dy, Er, Tm or Yb, $x = 27.1–43.7$), Na₅[MTiW₁₁O₃₉]·xH₂O and Na₆[MTiW₁₁O₃₉]·xH₂O (M = Cr, Mn, Fe, or Zn, $x = 27.2–30.2$). These inorganic IL were characterised by NMR, IR spectroscopy and by elemental analysis. Moreover, their physicochemical properties were also investigated. It was concluded that these IL are almost immiscible with water below room temperature, but the solubility of the IL increases sharply with an increase in temperature. The most significant feature of these IL is that water is their indispensable component and the role of the water molecules in IL is similar to that of crystalline water in hydrated compounds.

Summary and outlook

The presently known discrete homo- and heteropolynuclear transition-metal complexes and cluster compounds have been reviewed combining the most relevant past and recent developments (see Appendix). A concise description regarding the most recent (ionothermal) synthesis of coordination polymers from IL have also been included. It is concluded that halogenido-aluminate IL could be exploited as an efficient alternative reaction medium for the synthesis of polynuclear metal clusters under mild conditions, which were previously obtained by high-temperature methods. In case of the task-specific IL, the zwitterionic nature of the betaine ligand and the weakly coordinating ability of the bistriflimide anion facilitate the isolation of polynuclear complexes, presumably these structural features give rise to highly favourable lattice energy. Some of the organometallic complexes synthesised from IL were found to be intermediate catalyst precursors. For example, the binuclear palladium complex [PdBr(μ-Br)(bmiy)]₂ acts as an intermediate to synthesise mononuclear [PdBr₂(bmiy)]₂, which can catalyse Heck reactions. Similarly, the ruthenium complex [RuCl₂(η⁶-arene)]₂ represents an ideal precursor for both aqueous and ionic liquid biphasic catalysis.

IL perform multiple roles for the ionothermal synthesis of coordination polymers, independently in three different ways: (i) solvent and cationic structure-directing agent, (ii) solvent only, and (iii) solvent and anionic structure-directing agents. These three different functions of IL further extend the applicability of this approach and make it possible to synthesise a variety of homochiral and achiral metal organic frameworks with various compositions and structures.

From this review, we anticipate that the reader will get the general impression that the synthesis of polynuclear transition-metal complexes using or in the presence of IL has already showed some promise, but substantial work still lies ahead. We believe that the present achievements and many projected future prospects in this area will have fundamental and practical impacts on transition metal chemistry.

Appendix

Table 1 List of abbreviations for different ionic liquids

Ionic liquid	Abbreviation
Betainium bis(trifluoromethyl)sulfonylimide	[Hbet][Tf ₂ N]
1-Carboxymethyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	[HbetmIm][Tf ₂ N]
<i>N</i> -Carboxymethyl- <i>N</i> -methylmorpholinium bis(trifluoromethyl)sulfonylimide	[HbetmMor][Tf ₂ N]
<i>N</i> -Carboxymethyl- <i>N</i> -methylpyrrolidinium bis(trifluoromethyl)sulfonylimide	[HbetmPyr][Tf ₂ N]
1- <i>n</i> -Butyl-3-methylimidazolium tetrachloridoaluminate	[BMIM]Cl/AlCl ₃
<i>N</i> -Butylpyridinium oxopentafluoridomolybdate	[BPY]MoOF ₅
1-Ethyl-3-methylimidazolium tetrabromidoaluminate	[EMIm]Br/AlBr ₃
1-Butyl-1-methylpyrrolidinium trifluoromethanesulfonate	[bmpyr][OTf]
1-Propyl-3-methylimidazolium bis(trifluoromethyl)sulfonylimide	[C ₃ mim][Tf ₂ N]
1-Butyl-3-methylpyrrolidinium bis(trifluoromethyl)sulfonylimide	[C ₄ mpyr][Tf ₂ N]
1-Butyl-3-methylimidazolium <i>L</i> -aspartate	[BMIm][L-AspH]
1-Ethyl-3-methylimidazolium ethylsulfate	[EMIm]Es
1-Butyl-3-methylimidazolium methylsulfate	[BMIm]Ms
<i>N</i> -Butylpyridinium bromide	[C ₄ Py]Br
1,3-Dipentynylimidazolium tetraphenylborate	[DPIM]BPh ₄
3-Allyl-1-(prop-2-ynyl)-3 <i>H</i> -imidazol-1-ium bromide	[APIM]Br

Table 2 Selected discrete homo- and heteropolynuclear transition-metal complexes and clusters synthesised from IL

Complex	Nuclearity	Ref.
[(UO ₂) ₂ (bet) ₆ (H ₂ O) ₂][Tf ₂ N] ₄	2	60a
[Cu ₂ (betmMor) ₄][Tf ₂ N] ₄	2	60b
[Eu ₂ (betmMor) ₆ (H ₂ O) ₂][Tf ₂ N] ₆	2	60b
[Cu ₂ (betmPyr) ₄ (H ₂ O) ₂][Tf ₂ N] ₄	2	60b
[Cu ₂ (betmIm) ₄ (H ₂ O) ₂][Tf ₂ N] ₄ ·H ₂ O	2	60b
[Cd ₂ (betPy) ₂ (H ₂ O) ₂][Tf ₂ N] ₂	2	60b
[Eu ₂ (bet) ₈ (H ₂ O) ₄][Tf ₂ N] ₆	2	48b
[Eu ₂ (bet) ₈ (H ₂ O) ₂][Tf ₂ N] ₆ ·2H ₂ O	2	48b
[Y ₂ (bet) ₆ (H ₂ O) ₄][Tf ₂ N] ₆	2	48b
[Mo ₂ Te ₁₂]I ₆	2	51
[BPY] ₂ [Mo ₂ O ₄ F ₆]	2	63
[{APIM}Co ₂ (CO) ₆]PF ₆	2	46b
[{APIM}Co ₂ (CO) ₆]B(C ₆ H ₅) ₄	2	46b
[RuCl ₂ (η ⁶ -arene)] ₂	2	47c
[bmim]K[Co(CO) ₄] ₂	2	46d
[C ₄ Py]K[Co(CO) ₄] ₂	2	46d
[PdBr(μ-Br)(bmiy)] ₂	2	46e
Im ₃ [Re ₃ (μ ₃ -S)(μ-S) ₃ Br ₉]Br	3	45
[Co ₃ (bet) ₈ (Hbet) ₂ (H ₂ O) ₂][Tf ₂ N] ₁₀ [Hbet] ₂	3	48a
Sn[SnCl][W ₃ Cl ₁₃]	3	50
Bis{1-[(<i>E</i>)-2-butenyl]-3-(4-ferrocenylphenyl)-2 <i>H</i> -imidazol-2-ylidene}gold(i) tetrafluoroborate	3	46c
[{DPIM}{Co ₂ (CO) ₆ }] ₂ BPh ₄	4	66
[Mn ₄ (bet) ₁₀ (H ₂ O) ₄][Tf ₂ N] ₈	4	48a
[Zn ₄ (bet) ₁₀ (H ₂ O) ₂][Tf ₂ N] ₈	4	48a
[Ni ₅ (bet) ₁₂ (H ₂ O) ₆][Tf ₂ N] ₁₀	5	48a
[(Pb ₄ O)Pb(OH)(bet) ₈ (Tf ₂ N) ₃][Tf ₂ N] ₄ ·MeOH	5	48a
Bi[Mo ₂ Cl ₁₃]Cl	5	53
Im ₄ [(Zr ₆ Cl) ₁₈]	6	43b
Im ₃ [(Zr ₆ B)Cl ₁₈]-C ₆ H ₅ CH ₃ ·2CH ₃ CN	6	41
BiCl[Mo ₆ Cl ₁₄]	6	53
Im ₄ [(Zr ₆ Fe)Cl ₁₈]	7	40
Im ₅ [(Zr ₆ Mn)Cl ₁₈]-1.5CH ₃ CN	7	40
Im ₅ [(Zr ₆ Mn)Cl ₁₈]-C ₆ H ₅ CH ₃ ·2CH ₃ CN	7	43b
[EMIm] ₄ [(Zr ₆ Fe)Br ₁₈]	7	44
[EMIm] ₄ [(Zr ₆ Be)Br ₁₈]	7	44
[bmpyr] ₆ [Eu ₈ (μ ₄ -O)(μ ₃ -OH) ₁₂ (μ ₂ -OTf) ₁₄ (μ-OTf) ₂]-1.5HOTf	8	11

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References

- 1 T. Welton, *Chem. Rev.*, 1999, **99**, 2071–2084.
- 2 P. Wasserscheid and W. Keim, *Angew. Chem.*, 2000, **112**, 3926–3945; P. Wasserscheid and W. Keim, *Angew. Chem., Int. Ed.*, 2000, **39**, 3772–3789.
- 3 K. R. Seddon, *J. Chem. Technol. Biotechnol.*, 1997, **68**, 351–356.
- 4 P. Wasserscheid and T. Welton, *Ionic Liquids in Synthesis*, Wiley-VCH, New York, 2007.
- 5 W. M. Reichert, J. D. Holbrey, K. B. Vigour, T. D. Morgan, G. A. Broker and R. D. Rogers, *Chem. Commun.*, 2006, 4767–4779.
- 6 J. D. Holbrey, K. B. Vigour, W. M. Reichert and R. D. Rogers, *J. Chem. Crystallogr.*, 2006, **36**, 799–804.
- 7 K. Jin, X. Huang, L. Pang, J. Li, A. Appel and S. Wherland, *Chem. Commun.*, 2002, 2872–2873.
- 8 A. Babai and A. V. Mudring, *Chem. Mater.*, 2005, **17**, 6230–6238.
- 9 (a) S. Tang, A. Babai and A. V. Mudring, *Angew. Chem.*, 2008, **120**, 7743–7746; S. Tang, A. Babai and A. V. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7631–7634; (b) A. Babai and A. V. Mudring, *Inorg. Chem.*, 2006, **45**, 4874–4876; (c) A. Getsis, S. Tang and A. V. Mudring, *Eur. J. Inorg. Chem.*, 2010, 2172–2177.
- 10 A. Babai and A. V. Mudring, *J. Alloys Compd.*, 2006, **418**, 122–127.
- 11 A. Babai and A. V. Mudring, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1956–1958.
- 12 A. E. Visser, R. P. Swatloski, W. M. Reichert, R. Mayton, S. Sheff, A. Wierzbicki, J. H. Davis and R. D. Rogers, *Environ. Sci. Technol.*, 2002, **36**, 2523–2529.
- 13 F. Endres, M. Bukowski, R. Hempelmann and H. Natter, *Angew. Chem.*, 2003, **115**, 3550–3552; F. Endres, M. Bukowski, R. Hempelmann and H. Natter, *Angew. Chem., Int. Ed.*, 2003, **42**, 3428–3430.
- 14 (a) H. T. Sun, Y. Sakka, H. Gao, Y. Miwa, M. Fujii, N. Shirahata, Z. Bai and J. G. Li, *J. Mater. Chem.*, 2011, **21**, 4060–4063; (b) H. T. Sun, Y. Sakka, M. Fujii, N. Shirahata and H. Gao, *Opt. Lett.*, 2011, **36**, 100–102.
- 15 N. Papageorgiou, Y. Athanassov, M. Armand, P. Bonhôte, H. Pettersson, A. Azam and M. Grätzel, *J. Electrochem. Soc.*, 1996, **143**, 3099–3108.
- 16 K. Lunstroo, K. Driesen, P. Nockemann, C. Görrler-Walrand, K. Binnemans, S. Bellayer, J. L. Bideau and A. Vioux, *Chem. Mater.*, 2006, **18**, 5711–5715.
- 17 P. Nockemann, B. Thijs, N. Postelmans, K. Van Hecke, L. Van Meervelt and K. Binnemans, *J. Am. Chem. Soc.*, 2006, **128**, 13658–13659.
- 18 Y. Yoshida, J. Fujii, G. Saito, T. Hiramatsu and N. Sato, *J. Mater. Chem.*, 2006, **16**, 724–727.
- 19 I. J. B. Lin and C. S. Vasam, *J. Organomet. Chem.*, 2005, **690**, 3498–3512.
- 20 M. Hasan, I. V. Kozhevnikov, M. R. H. Siddiqui, A. Steiner and N. Winterton, *Inorg. Chem.*, 1999, **38**, 5637–5641.
- 21 (a) R. E. D. Sesto, T. M. McCleskey, A. K. Burrell, G. A. Baker, J. D. Thompson, B. L. Scott, J. S. Wilkes and P. Williams, *Chem. Commun.*, 2008, 447–449; (b) S. Pitula and A. V. Mudring, *Chem.–Eur. J.*, 2010, **16**, 3355–3365; (c) B. Mallick, B. Balke, C. Felser and A. V. Mudring, *Angew. Chem.*, 2008, **120**, 7747–7750; B. Mallick, B. Balke, C. Felser and A. V. Mudring, *Angew. Chem., Int. Ed.*, 2008, **47**, 7635–7638.
- 22 (a) F. W. Koknat, J. A. Parson and A. Vongvusharintra, *Inorg. Chem.*, 1974, **13**, 1699–1702; (b) Y. Park and M. G. Kanatzidis, *Chem. Mater.*, 1991, **3**, 781–783; (c) J. Beck and M. Hengstmann, *Z. Anorg. Allg. Chem.*, 1998, **624**, 433–437.
- 23 M. Ruck, *Z. Anorg. Allg. Chem.*, 1995, **621**, 2034–2042.
- 24 M. Ruck, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1535–1541.
- 25 M. Ruck, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1583–1590.
- 26 M. Ruck, *Z. Anorg. Allg. Chem.*, 1997, **623**, 1591–1598.
- 27 M. Ruck and R. M. Heich, *Z. Anorg. Allg. Chem.*, 2000, **626**, 2449–2456.
- 28 A. Günther, F. Steden and M. Ruck, *Z. Anorg. Allg. Chem.*, 2008, **634**, 423–430.
- 29 B. Wahl, L. Kloos and M. Ruck, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1979–1985.
- 30 M. Ruck, *Solid State Sci.*, 2001, **3**, 369–375.
- 31 (a) B. Wahl, L. Kloos and M. Ruck, *Angew. Chem.*, 2008, **120**, 3996–3999; B. Wahl, L. Kloos and M. Ruck, *Angew. Chem., Int. Ed.*, 2008, **47**, 3932–3935; (b) B. Wahl and M. Ruck, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2267–2275.
- 32 (a) R. D. Adams, J. E. Babin and M. Tasi, *Angew. Chem.*, 1987, **99**, 691–692; R. D. Adams, J. E. Babin and M. Tasi, *Angew. Chem., Int. Ed. Engl.*, 1987, **26**, 685–686; (b) M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1984, **106**, 1495–1496.
- 33 (a) G. Schmid, N. Klein, L. Korste, U. Kreibitz and D. Schöner, *Polyhedron*, 1988, **7**, 605–608; (b) F. W. Vergeer, P. Matousek, M. Towrie, P. J. Costa, M. J. Calhorda and F. Hartl, *Chem.–Eur. J.*, 2004, **10**, 3451–3460.
- 34 (a) E. J. Welch, N. R. M. Crawford, R. G. Bergman and J. R. Long, *J. Am. Chem. Soc.*, 2003, **125**, 11464–11465; (b) S. Cordier, K. Kirakci, D. Mery, C. Perrin and D. Astruc, *Inorg. Chim. Acta*, 2006, **359**, 1705–1709.
- 35 (a) H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 1995, **621**, 921–924; (b) B. Jung and G. Meyer, *Z. Anorg. Allg. Chem.*, 1992, **610**, 15–19; (c) X. Zhao, Y. G. Li, Y. H. Wang and E. B. Wang, *Transition Met. Chem.*, 2007, **33**, 323–330; (d) S. Chang, Y. F. Qi, E. B. Wang and Z. Zhang, *Inorg. Chim. Acta*, 2009, **362**, 453–457.
- 36 C. L. Hussey, *Pure Appl. Chem.*, 1988, **60**, 1763–1772.
- 37 C. L. Hussey, R. Quigley and K. R. Seddon, *Inorg. Chem.*, 1995, **34**, 370–377.
- 38 P. A. Barnard, I. W. Sun and C. L. Hussey, *Inorg. Chem.*, 1990, **29**, 3670–3674.
- 39 R. Quigley, P. A. Barnard, C. L. Hussey and K. R. Seddon, *Inorg. Chem.*, 1992, **31**, 1255–1261.
- 40 C. E. Runyan and T. Hughbanks, *J. Am. Chem. Soc.*, 1994, **116**, 7909–7910.
- 41 Y. Tian and T. Hughbanks, *Inorg. Chem.*, 1995, **34**, 6250–6254.
- 42 J. D. Harris and T. Hughbanks, *J. Am. Chem. Soc.*, 1997, **119**, 9449–9459.
- 43 (a) D. Sun and T. Hughbanks, *Inorg. Chem.*, 1999, **38**, 992–997; (b) D. Sun and T. Hughbanks, *Inorg. Chem.*, 2000, **39**, 1964–1968.
- 44 J. B. Willems, H. W. Rohm, C. Geers and M. Köckerling, *Inorg. Chem.*, 2007, **46**, 6197–6203.
- 45 H. Sakamoto, Y. Watanabe and T. Saito, *Inorg. Chem.*, 2006, **45**, 4578–4579.
- 46 (a) P. J. Dyson, *Transition Met. Chem.*, 2002, **27**, 353–358; (b) H. Schottenberger, K. Wurst, U. E. I. Horvath, S. Cronje, J. Lukasser, J. Polin, J. M. McKenzie and H. G. Raubenheimer, *Dalton Trans.*, 2003, 4275–4281; (c) U. E. I. Horvath, G. Bentivoglio, M. Hummel, H. Schottenberger, K. Wurst, M. J. Nell, C. E. J. van Rensburg, S. Cronje and H. G. Raubenheimer, *New J. Chem.*, 2008, **32**, 533–539; (d) F. G. Deng, B. Hu, W. Sun and C. G. Xia, *Dalton Trans.*, 2008, 5957–5961; (e) L. Xu, W. Chen and J. Xiao, *Organometallics*, 2000, **19**, 1123–1127.
- 47 (a) P. J. Dyson, *Coord. Chem. Rev.*, 2004, **248**, 2443–2458; (b) T. J. Geldbach, G. Laurenczy, R. Scopelliti and P. J. Dyson, *Organometallics*, 2006, **25**, 733–742; (c) T. J. Geldbach and P. J. Dyson, *J. Am. Chem. Soc.*, 2004, **126**, 8114–8115.
- 48 (a) P. Nockemann, B. Thijs, K. Van Hecke, L. Van Meervelt and K. Binnemans, *Cryst. Growth Des.*, 2008, **8**, 1353–1363; (b) P. Nockemann, B. Thijs, K. Lunstroo, T. N. Parac-Vogt, C. Görrler-Walrand, K. Binnemans, K. Van Hecke, L. Van Meervelt, S. Nikitenko, J. Daniels, C. Hennig and R. Van Deun, *Chem.–Eur. J.*, 2009, **15**, 1449–1461.
- 49 E. Ahmed, D. Köhler and M. Ruck, *Z. Anorg. Allg. Chem.*, 2009, **635**, 297–300.
- 50 E. Ahmed, M. Groh and M. Ruck, *Eur. J. Inorg. Chem.*, 2010, 5294–5297.
- 51 E. Ahmed, E. Ahrens, M. Heise and M. Ruck, *Z. Anorg. Allg. Chem.*, 2010, **636**, 2602–2606.
- 52 E. Ahmed, E. Ahrens, M. Heise and M. Ruck, *Z. Anorg. Allg. Chem.*, 2010, **636**, 2053.
- 53 E. Ahmed, E. Ahrens, M. Heise and M. Ruck, *Z. Anorg. Allg. Chem.*, 2011, **637**, 961–964.
- 54 M. Antonietti, D. B. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem.*, 2004, **116**, 5096–5100; M. Antonietti, D. B. Kuang, B. Smarsly and Y. Zhou, *Angew. Chem., Int. Ed.*, 2004, **43**, 4988–4992.
- 55 (a) Z. Ma, J. Yu and S. Dai, *Adv. Mater.*, 2010, **22**, 261–285; (b) Y. Zhou, *Curr. Nanosci.*, 2005, **1**, 35–42.
- 56 A. Taubert, *Acta Chim. Slov.*, 2005, **52**, 183–186.
- 57 A. Taubert and Z. H. Li, *Dalton Trans.*, 2007, 723–727.
- 58 E. R. Parnham and R. E. Morris, *Acc. Chem. Res.*, 2007, **40**, 1005–1013.
- 59 K. Binnemans, *Chem. Rev.*, 2007, **107**, 2592–2614.
- 60 (a) P. Nockemann, R. Van Deun, B. Thijs, D. Huys, E. Vanecht, K. Van Hecke, L. Van Meervelt and K. Binnemans, *Inorg. Chem.*, 2010, **49**, 3351–3360; (b) P. Nockemann, B. Thijs, T. N. Parac-Vogt, K. Van Hecke, L. Van Meervelt, B. Tinant, I. Hartenbach, T. Schleid, V. T. Ngan, M. T. Nguyen and K. Binnemans, *Inorg. Chem.*, 2008, **47**, 9987–9999.

- 61 (a) V. A. Cocalia, K. E. Gutowski and R. D. Rogers, *Coord. Chem. Rev.*, 2006, **250**, 755–764; (b) W. R. Pitner, A. E. Bradley, D. W. Rooney, D. Sanders, K. R. Seddon, R. C. Thied and J. E. Ratter, *Green Ind. Appl. Ionic Liquids.*, 2003, **92**, 209–226; (c) P. R. V. Rao, K. A. Venkatesan and T. G. Srinivasan, *Prog. Nucl. Energy*, 2008, **50**, 449–455.
- 62 J. Beck, *J. Solid State Chem.*, 1996, **125**, 165–170.
- 63 T. Kanatani, K. Matsumoto and R. Hagiwara, *Eur. J. Inorg. Chem.*, 2010, 1049–1055.
- 64 V. Kolesnichenko, J. J. Luci, D. C. Swenson and L. Messerle, *J. Am. Chem. Soc.*, 1998, **120**, 13260–13261.
- 65 M. Weisser, S. Tragl and H.-J. Meyer, *Z. Anorg. Allg. Chem.*, 2006, **632**, 1885–1889.
- 66 Z. Fei, D. Zhao, R. Scopelliti and P. J. Dyson, *Organometallics*, 2004, **23**, 1622–1628.
- 67 S. Bösch and H.-L. Keller, *Z. Kristallogr.*, 1992, **200**, 305–315.
- 68 H. Schäfer and H. G. Schnering, *Angew. Chem.*, 1964, **76**, 833–849.
- 69 (a) E. R. Cooper, C. D. Andrews, P. S. Wheatley, P. B. Webb, P. Wormald and R. E. Morris, *Nature*, 2004, **430**, 1012–1016; (b) Z. Lin, A. M. Z. Slawin and R. E. Morris, *J. Am. Chem. Soc.*, 2007, **129**, 4880–4881; (c) R. E. Morris, *Angew. Chem.*, 2008, **120**, 450–452; R. E. Morris, *Angew. Chem., Int. Ed.*, 2008, **47**, 442–444; (d) R. E. Morris and X. Bu, *Nat. Chem.*, 2010, **2**, 353–361; (e) R. E. Morris, *Chem. Commun.*, 2009, 2990–2998.
- 70 W. J. Ji, Q. G. Zhai, S. N. Li, Y. C. Jiang and M. C. Hu, *Chem. Commun.*, 2011, **47**, 3834–3836.
- 71 J. Zhang, S. Chen and X. Bu, *Angew. Chem.*, 2008, **120**, 5514–5517; J. Zhang, S. Chen and X. Bu, *Angew. Chem., Int. Ed.*, 2008, **47**, 5434–5437.
- 72 T. Su, H. Xing, J. Xu, J. Yu and R. Xu, *Inorg. Chem.*, 2011, **50**, 1073–1078.
- 73 H. Fu, Y. Li, Y. Lu, W. Chen, Q. Wu, J. Meng, X. Wang, Z. Zhang and E. Wang, *Cryst. Growth Des.*, 2011, **11**, 458–465.
- 74 A. B. Bourlinos, K. Raman, R. Herrera, Q. Zhang, L. A. Archer and E. P. Giannelis, *J. Am. Chem. Soc.*, 2004, **126**, 15358–15359.
- 75 P. G. Rickert, M. R. Antonio, M. A. Firestone, K. A. Kubatko, T. Szreder, J. F. Wishart and M. L. Dietz, *J. Phys. Chem. B*, 2007, **111**, 4685–4692.
- 76 H. Li, Z. Hou, Y. Qiao, B. Feng, Y. Hu, X. Wang and X. Zhao, *Catal. Commun.*, 2010, **11**, 470–475.
- 77 H. Li, Y. Qiao, L. Hua, Z. Hou, B. Feng, Z. Pan, Y. Hu, X. Wang, X. Zhao and Y. Yu, *ChemCatChem*, 2010, **2**, 1165–1170.
- 78 W. Huang, W. Zhu, H. Li, H. Shi, G. Zhu, H. Liu and G. Chen, *Ind. Eng. Chem. Res.*, 2010, **49**, 8998–9003.
- 79 Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge and L. Shen, *Angew. Chem.*, 2008, **121**, 174–177; Y. Leng, J. Wang, D. Zhu, X. Ren, H. Ge and L. Shen, *Angew. Chem., Int. Ed.*, 2008, **48**, 168–171.
- 80 A. Corma, S. Iborra, F. X. L. Xamena, R. Montón, J. J. Calvino and C. Prestipino, *J. Phys. Chem. C*, 2010, **114**, 8828–8836.
- 81 L. Dai, S. Yu, Y. Shan and M. He, *Eur. J. Inorg. Chem.*, 2004, 237–241.
- 82 J. D. Peter, *J. Am. Chem. Soc.*, 1984, **106**, 7677–7687.