Ionic Liquids for Inorganic and Materials Synthesis

Workshop Rostock

20. February 2015

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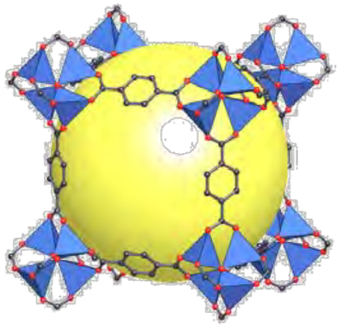
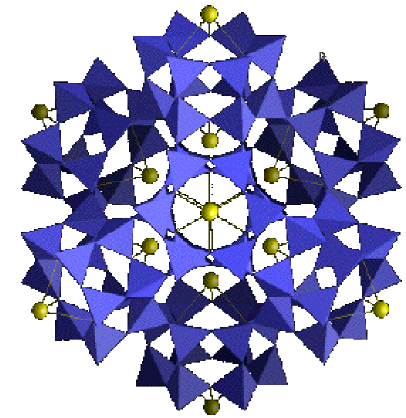
Introduction to Ionic Liquids

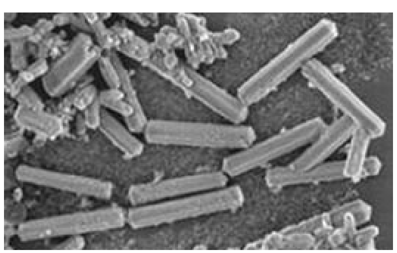
Applications of ILs in inorganic & materials chemistry



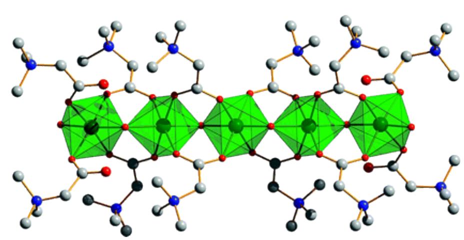
Metal-organic frameworks



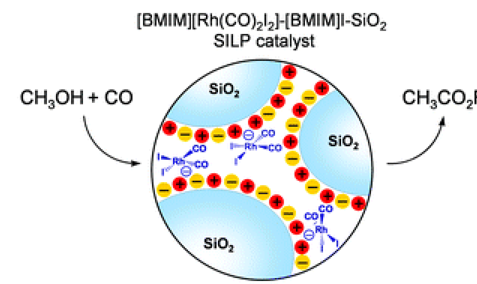
Zeolithe synthesis



Shaped nanoparticles



Coordination chemistry

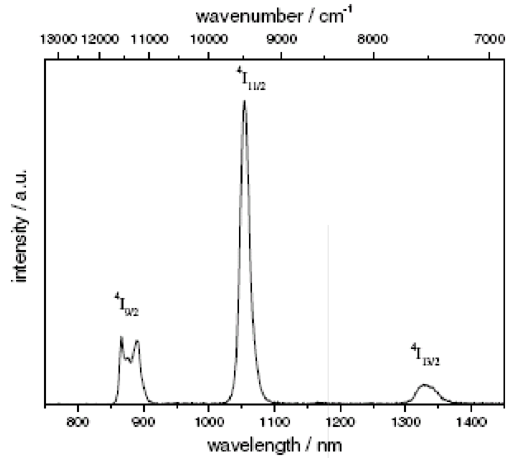


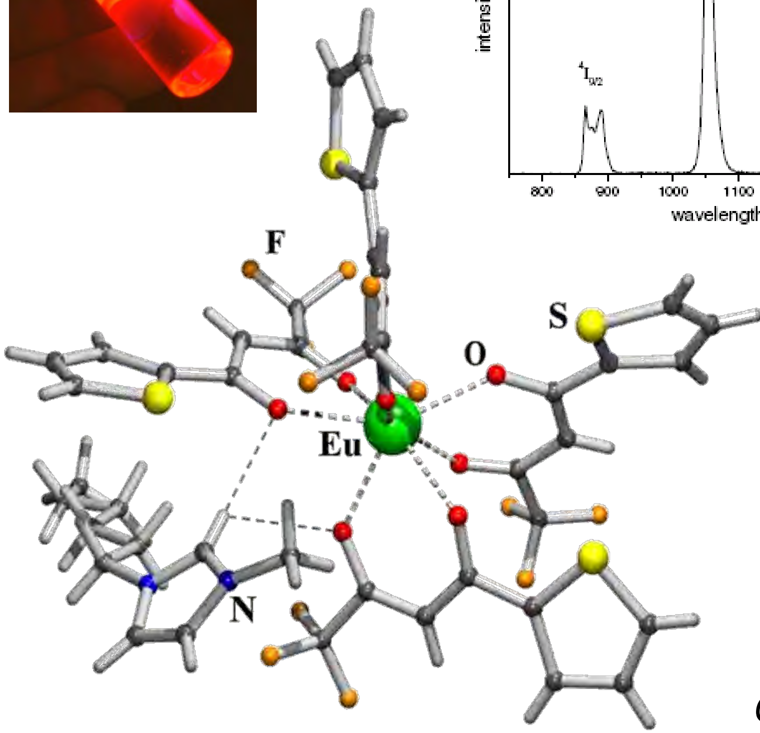
Catalysis

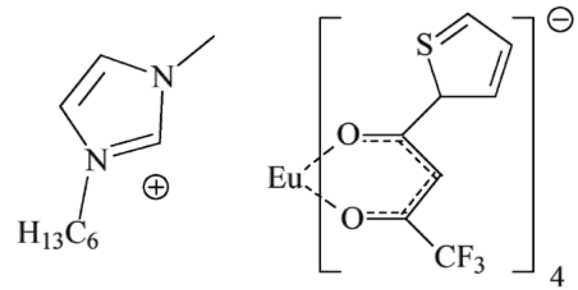
Outline

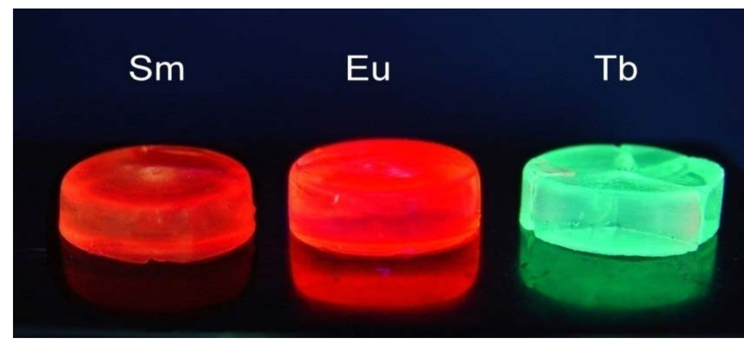
1. Coordination Chemistry in Ionic Liquids
2. Ionic Liquids for Materials Synthesis
3. Metal-Containing Ionic Liquids
4. Ionic Liquid Applications
5. Conclusions

Lanthanide & actinide spectroscopy in ionic liquids









Ionogels: hybrid materials consisting of an ionic liquid confined inside the nano-sized pores of a silica matrix

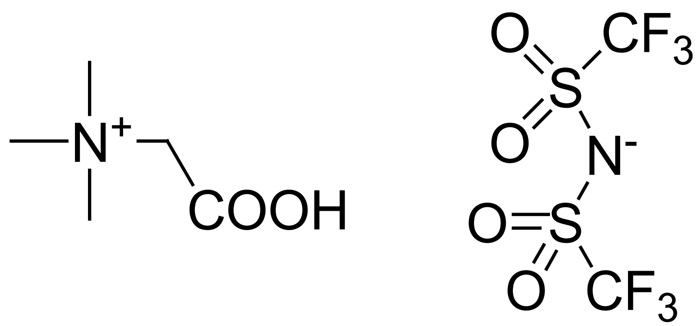
Chem. Commun., **2005**, *34*, 4354-4356.

Inorganic Chemistry, **2007**, *46*, 11335-11344.

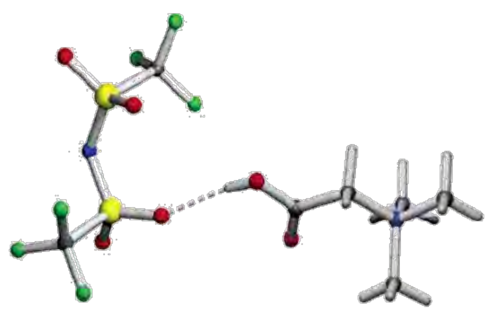
Queen's University Belfast

QUILL

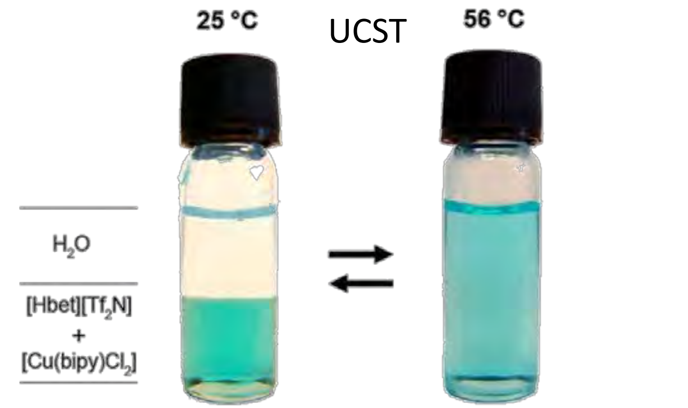
Ionic Liquids for Inorganic and Materials Chemistry



Betainium ionic liquid [Hbet][Tf_2N]

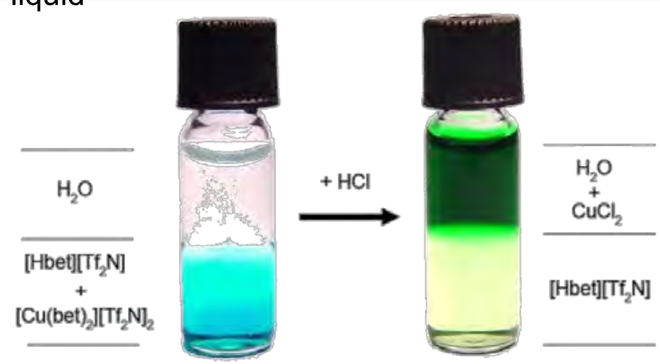


[Hbet][Tf_2N] can solubilize large quantities of metal oxides



“Catalytic Hydrogenolysis of Aromatic Ketones in Mixed Choline-Betainium Ionic Liquids“, *ChemSusChem*, **2008**, 1, 997-1005.

Stripping of metal ions from the ionic liquid

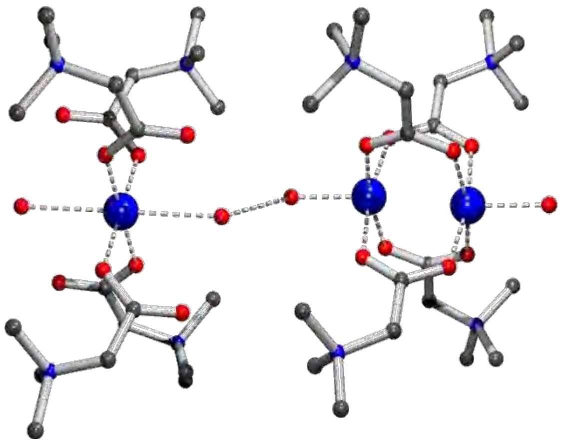


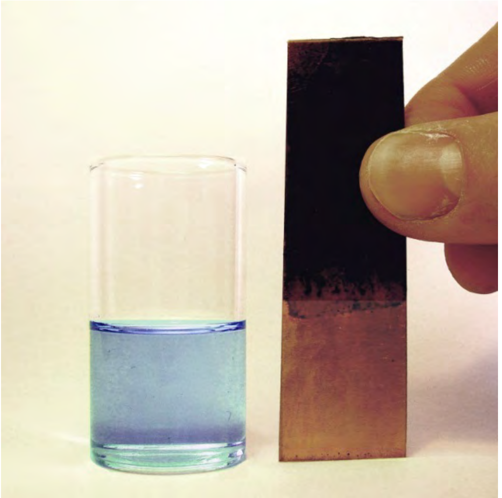
J. Phys. Chem. B, ***2006***, *110*, 20978 – 20992.

Inorg. Chem., **2008**, *47*, 9987 - 9999.

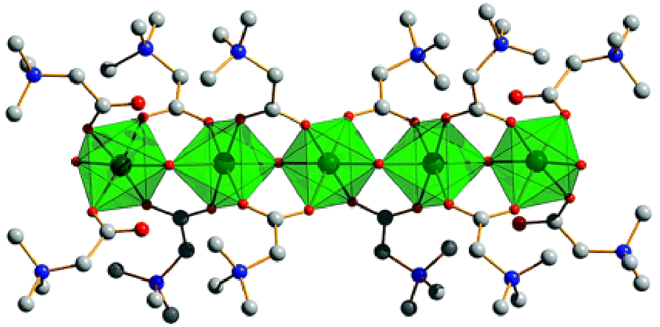
Solubility of metal oxides in the task-specific ionic liquid $[Hbet][Tf_2N]$

$[Cu_3(bet)_8(H_2O)_4][Tf_2N]_6$





$[Ni_5(bet)_{12}(H_2O)_6][Tf_2N]_{10}$

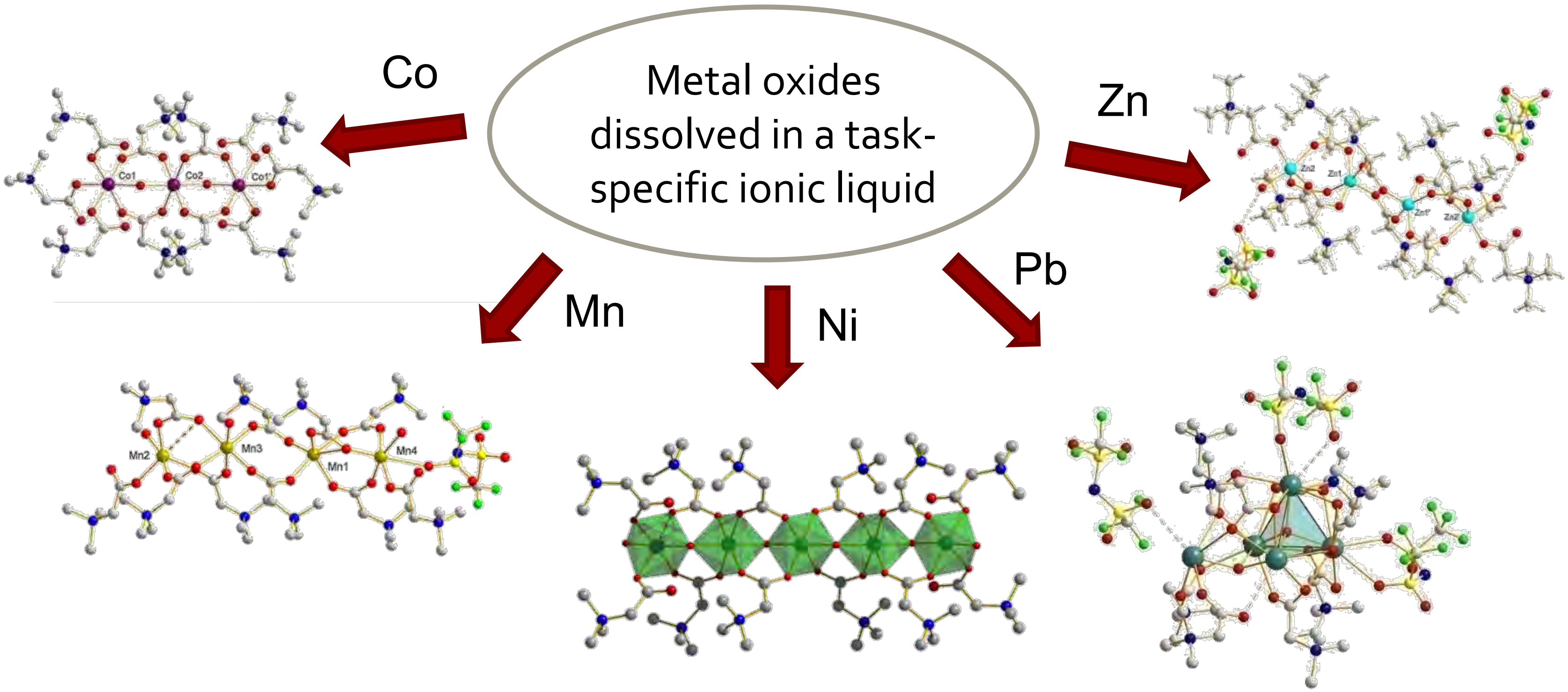


P. Nockemann *et al.*, *Crystal Growth & Design*, **2008**, *8*, 1353 – 1363.

- formation of pentameric Ni-clusters
- potential magnetic material
- high solubility of the complexes in ionic liquids

Ionic Liquids for Inorganic and Materials Chemistry

Pathway provides access to new classes of compounds and materials

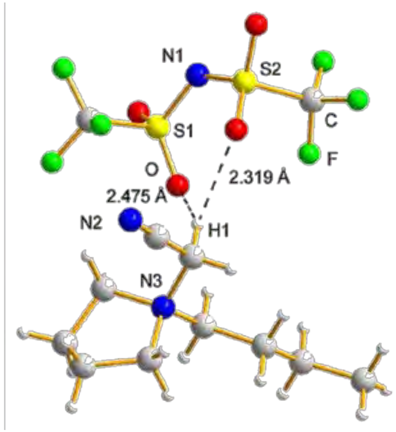


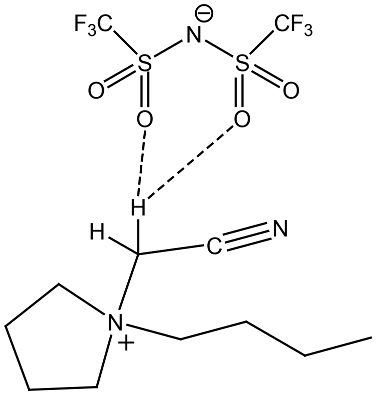
Indication for the high potential of synthesis from ionic liquids

Crystal Growth & Design, **2008**, *8*, 1353 – 1363.
Inorg. Chem., **2008**, *47*, 9987 - 9999.

Coordination Chemistry in Ionic Liquids

- Coordination of a cobalt(II) salt in a nitrile functionalised ionic liquid
- Example for tunable coordinating abilities and solvent interaction
- Cationic 'solvent coordination'

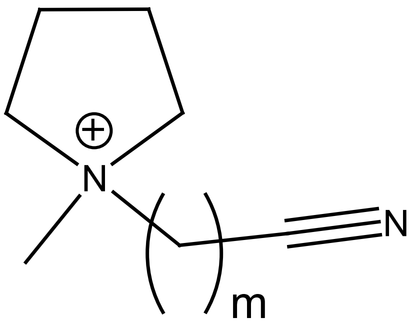


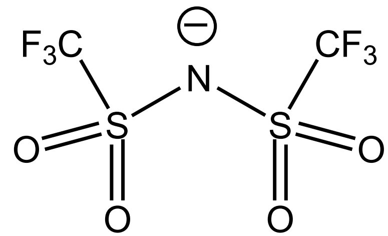


Chemistry – A European Journal **2010**, 16, 1849-1858.

Nitrile functionalized ionic liquids – ionic analogues of organic solvents

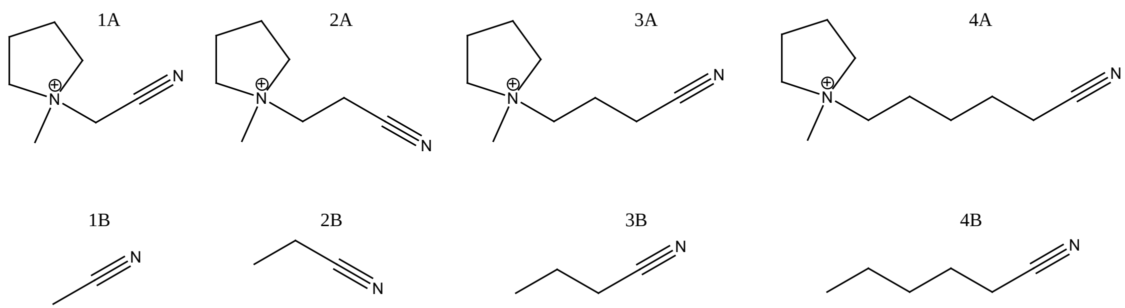
- Thermally robust
- Large electrochemical window
- High conductivity
- Low vapor pressure
- high solubilizing power for metal salts
- „Tuning“ of the coordinating abilities possible

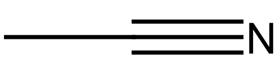




(m = 1,2,3,5)

“ionic” analogue of acetonitrile





acetonitrile

Coordination Chemistry in Ionic Liquids

$Co(Tf_2N)_2{\cdot}6H_2O$

+ ΔT
- H_2O

↓ $[C_1C_4Pyr][Tf_2N]$

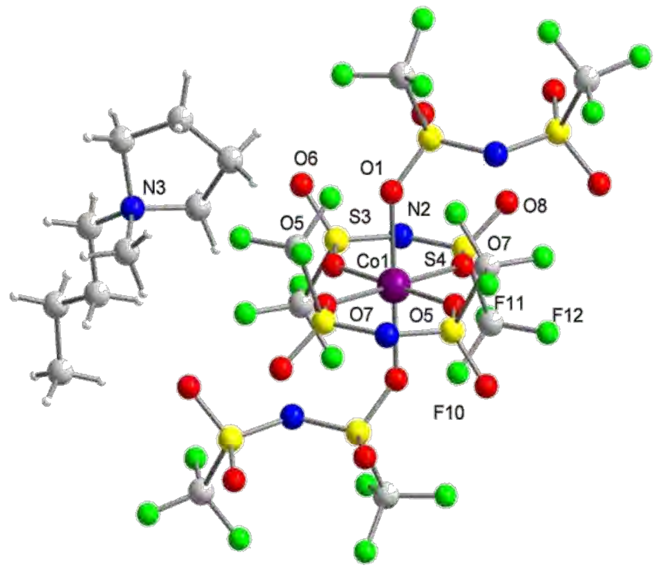
$[C_1C_4Pyr]_2[Co(Tf_2N)_4]$ (2)

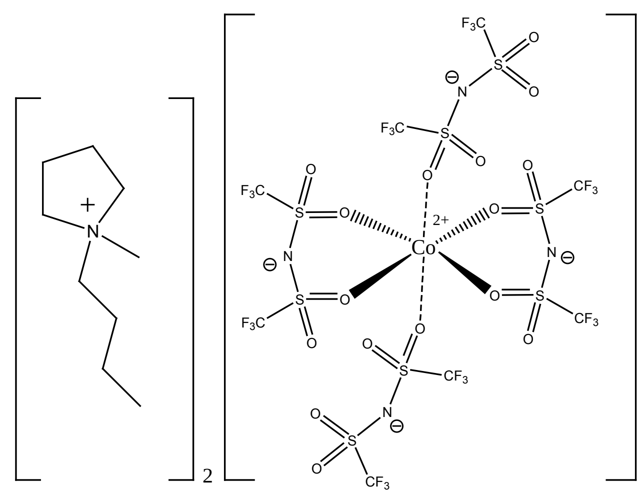
↓ $[C_1C_{1CN}Pyr][Tf_2N]$ (**1A**)

$[Co(C_1C_{1CN}Pyr)_2(Tf_2N)_4]$ (**3**)

↓ $[C_1C_{2CN}Pyr][Tf_2N]$ (**1B**)

$[Co(C_1C_{2CN}Pyr)_8][Tf_2N]_8$ (**4**)





Coordination Chemistry in Ionic Liquids

$Co(Tf_2N)_2 \cdot 6H_2O$

↓ $+ \Delta T$, $- H_2O$, $[C_1C_4Pyr][Tf_2N]$

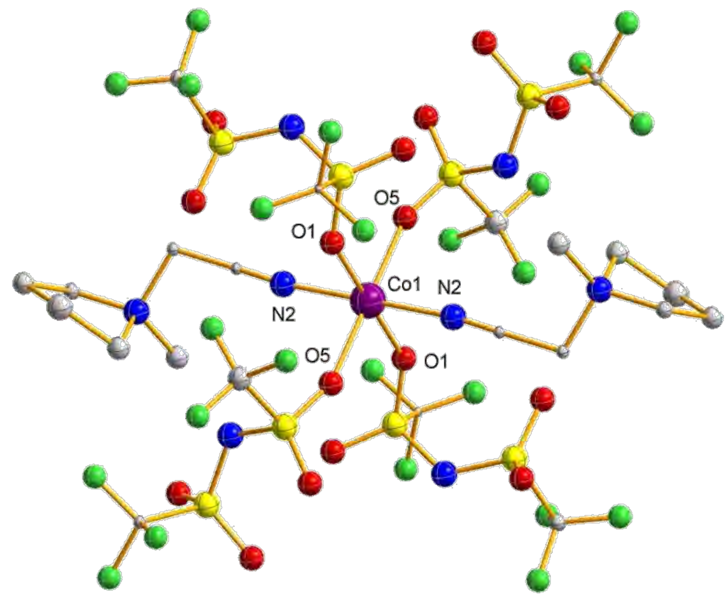
$[C_1C_4Pyr]_2[Co(Tf_2N)_4]$ **(2)**

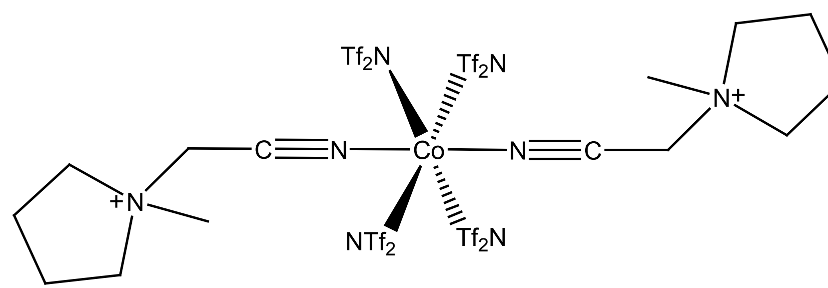
↓ $[C_1C_{1CN}Pyr][Tf_2N]$ **(1A)**

$[Co(C_1C_{1CN}Pyr)_2(Tf_2N)_4]$ **(3)**

↓ $[C_1C_{2CN}Pyr][Tf_2N]$ **(1B)**

$[Co(C_1C_{2CN}Pyr)_8][Tf_2N]_8$ **(4)**





Coordination Chemistry in Ionic Liquids

$Co(Tf_2N)_2 \cdot 6H_2O$

↓ $+ \Delta T$, $- H_2O$ — $[C_1C_4Pyr][Tf_2N]$

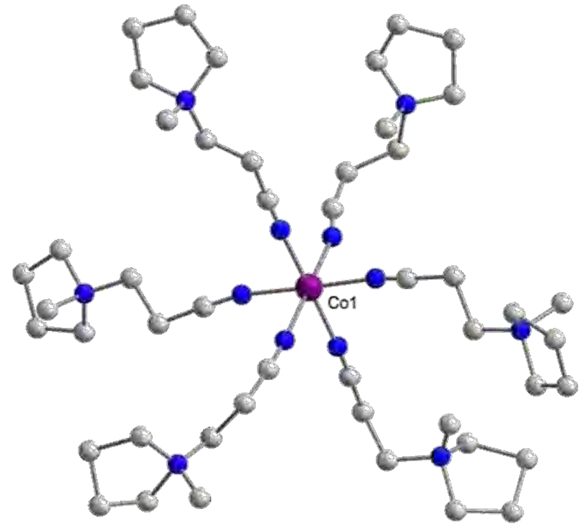
$[C_1C_4Pyr]_2[Co(Tf_2N)_4]$ **(2)**

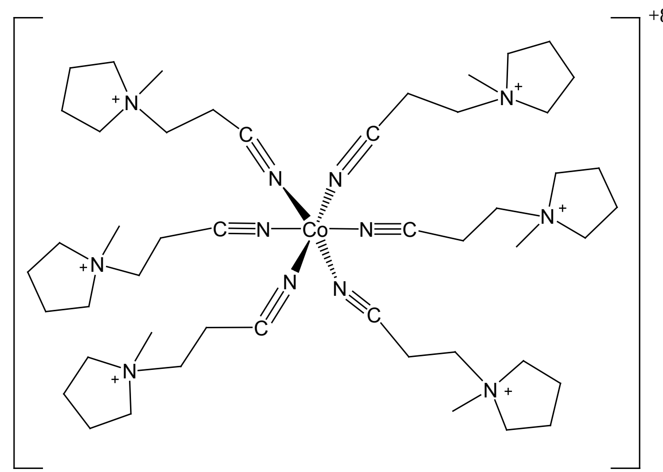
↓ $[C_1C_{1CN}Pyr][Tf_2N]$ **(1A)**

$[Co(C_1C_{1CN}Pyr)_2(Tf_2N)_4]$ **(3)**

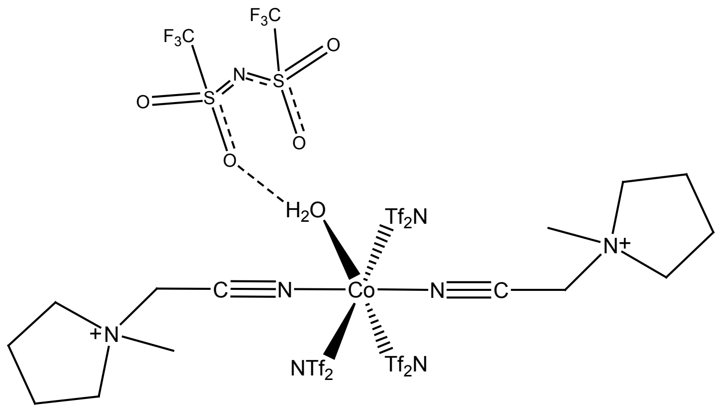
↓ $[C_1C_{2CN}Pyr][Tf_2N]$ **(1B)**

$[Co(C_1C_{2CN}Pyr)_8][Tf_2N]_8$ **(4)**





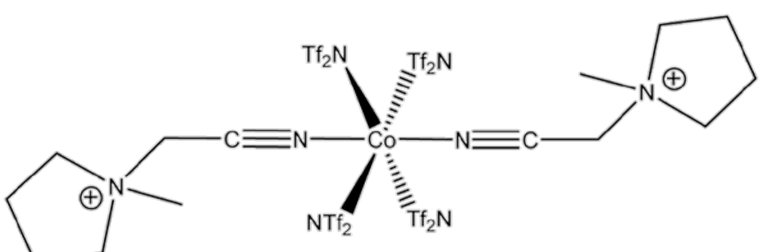
Hydration of a solvate – but reversible!

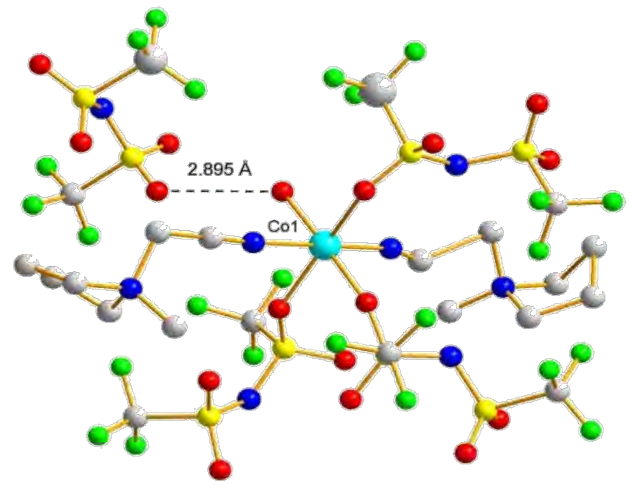


$[Co(C_1C_{1CN}Pyr)_2(Tf_2N)_{4-n}(H_2O)_n][Tf_2N]_n$ (**2B, 2C**)

$+ n\ H_2O$ ↑ ↓ ΔT, $-n\ H_2O$

$[Co(C_1C_{1CN}Pyr)_2(Tf_2N)_4]$ (**2**)





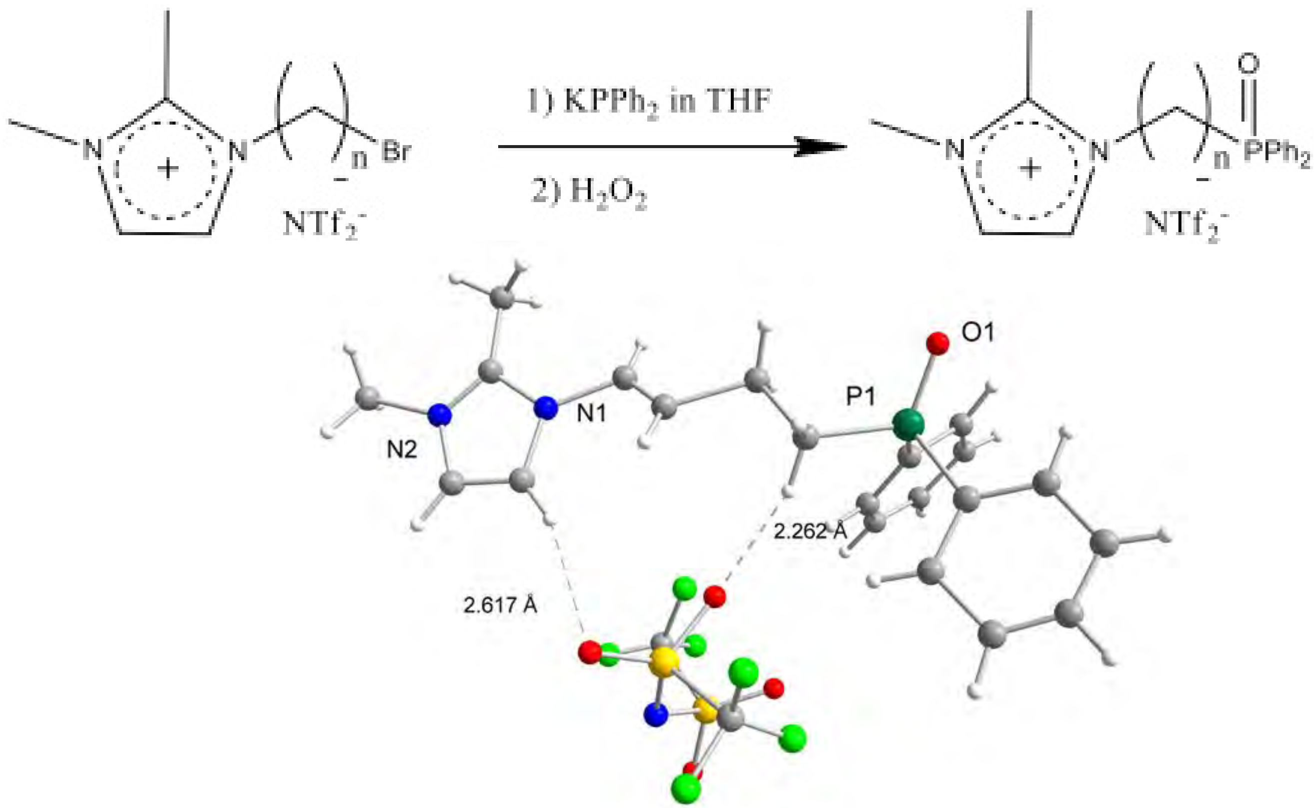
Crystal structure of $[Co(Tf_2N)_3(H_2O)(C_{2N}MPyr)_2](Tf_2N)$

Chemistry – A European Journal **2010**, 16, 1849-1858.

Ionic liquids for extraction / separation of lanthanides

Phosphine Oxide Functionalised Ionic Liquids

- Tuning of the spacer length of these ion-tagged phosphine oxides affects the donor properties of the functional group



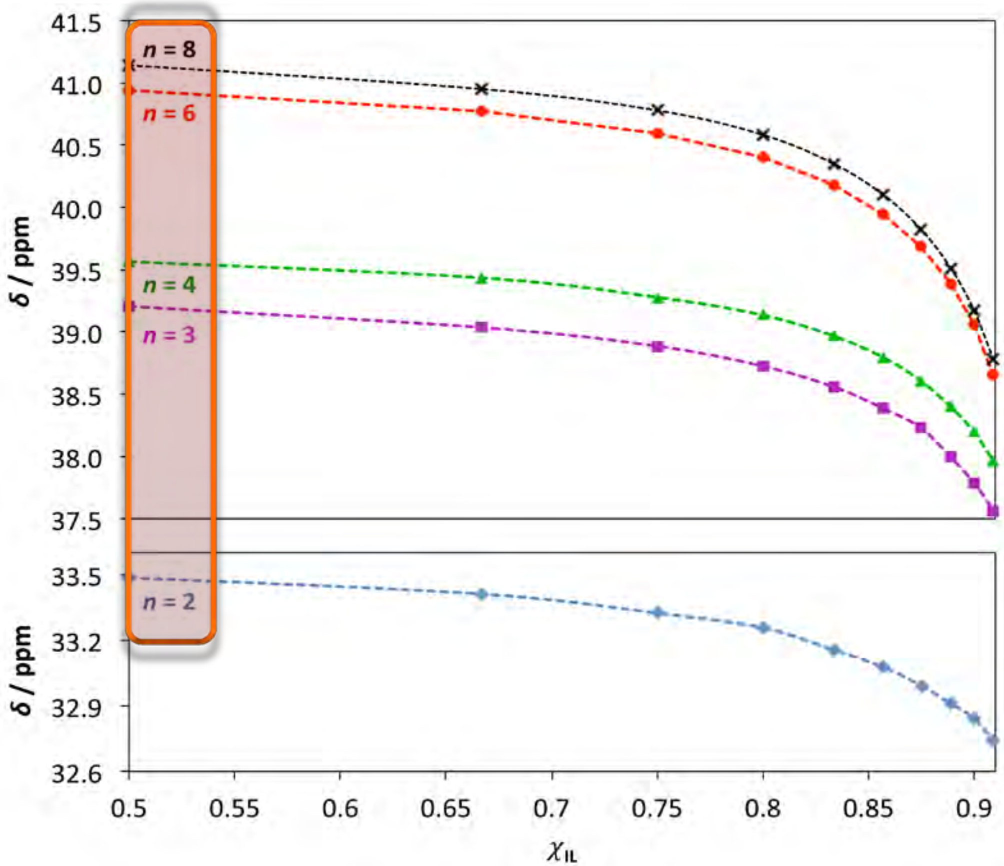
Chem. Commun., 2012, *48*, 6115.

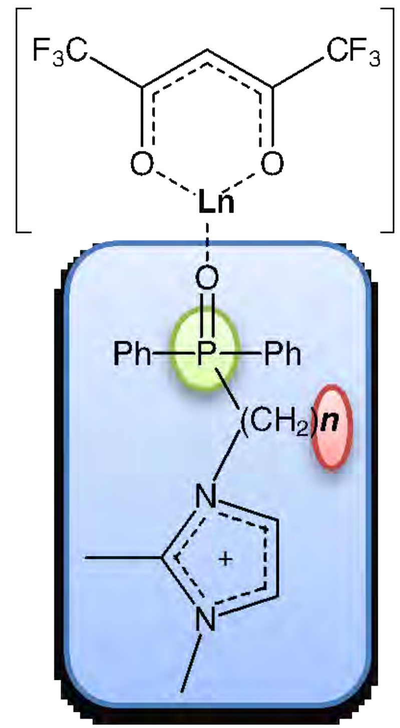
Ionic liquids for extraction / separation of lanthanides

Phosphine oxide functionalised imidazolium ionic liquids as tuneable ligands for Lanthanide complexation

^{31}P NMR shifts in a complexometric titration

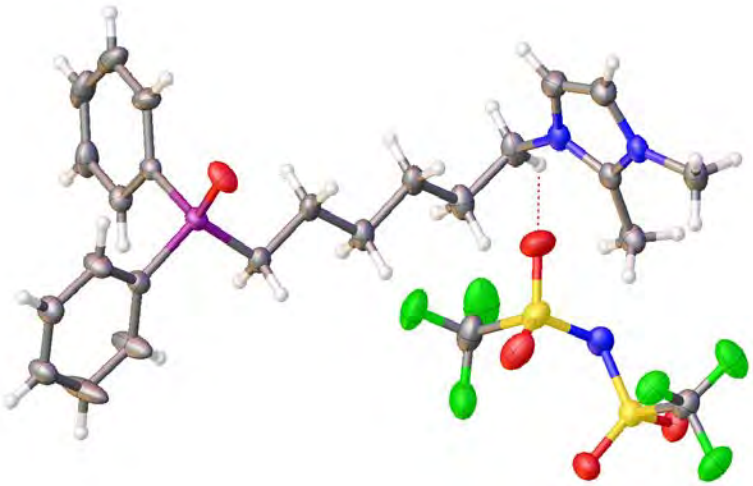
^{31}P NMR shift

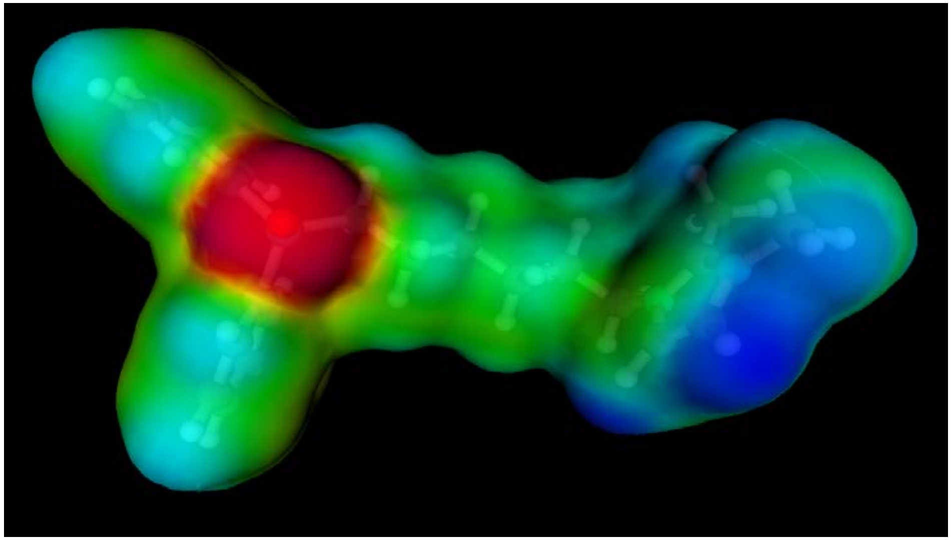


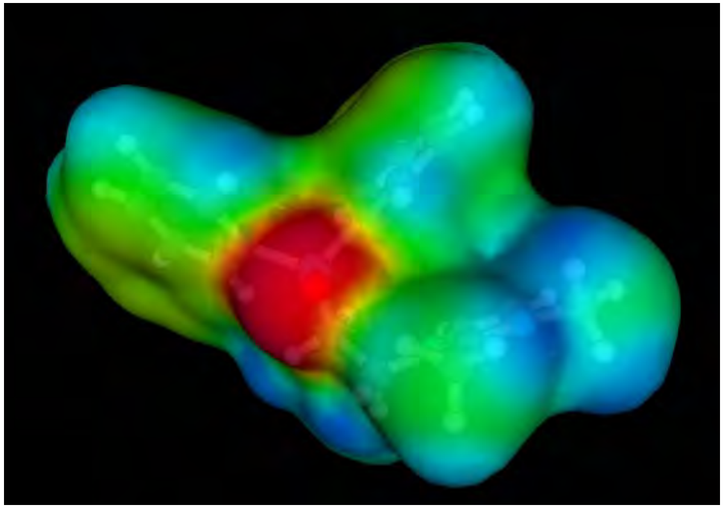


molar ratio of IL

Chem. Commun., 2012, *48*, 6115.



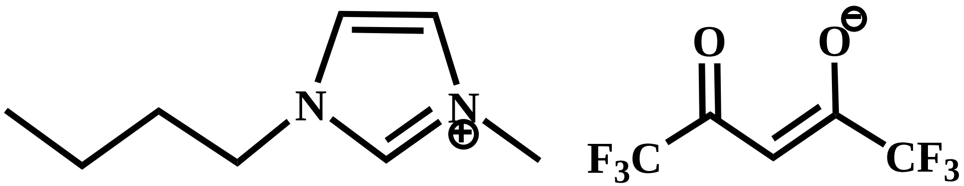




1-hexyl-diphenylphosphine-oxide-2,3-dimethylimidazolium $[Tf_2N]^-$

Coordination Chemistry in Ionic Liquids

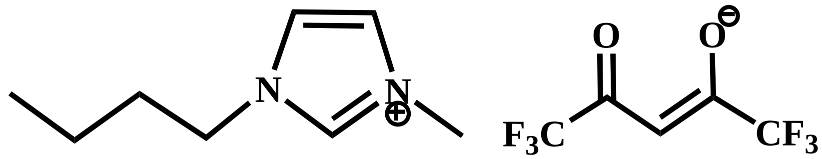
- Coordination in an ionic liquid with a strongly coordinating anion
- Dissolved metal complexes form anionic species
- Conceptually suitable for extraction of metals



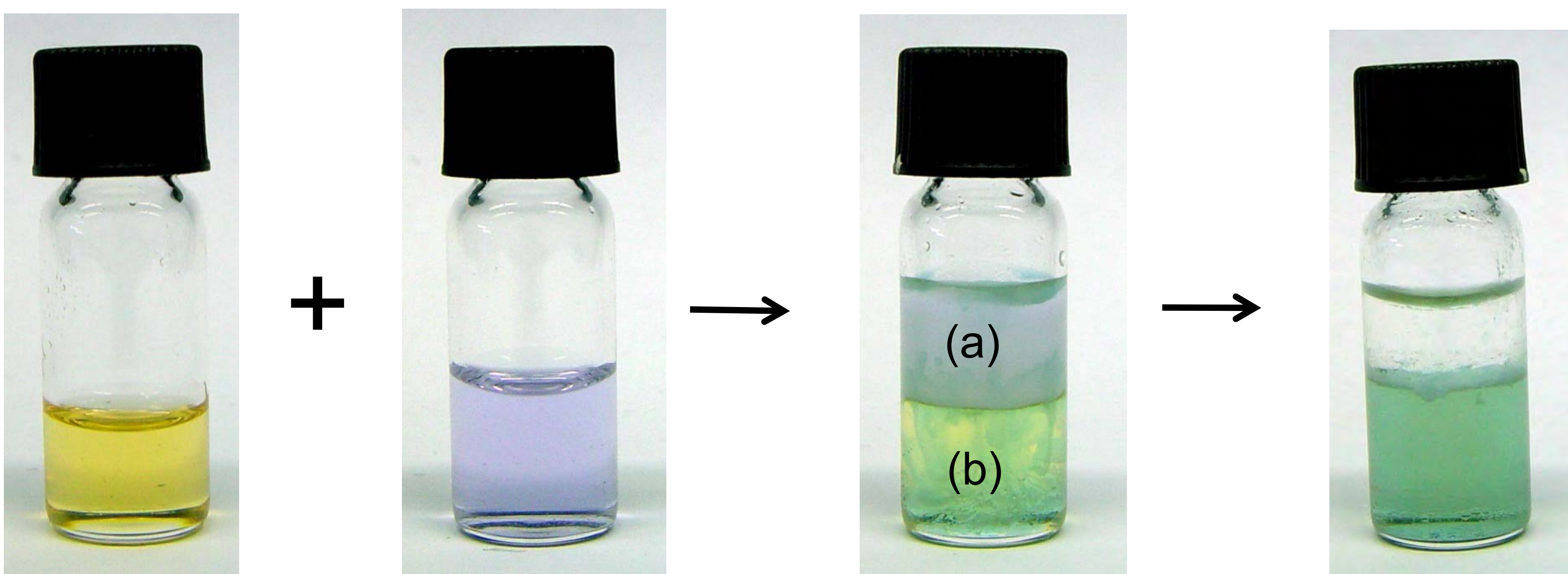
H. Mehdi *et al.*, *Chem. Commun.*, **2010**, *113,* 234-236.

Neodymium extraction using an ionic liquid

Aqueous solution of $Nd(Tf_2N)_3$



[BMIM][hfac]

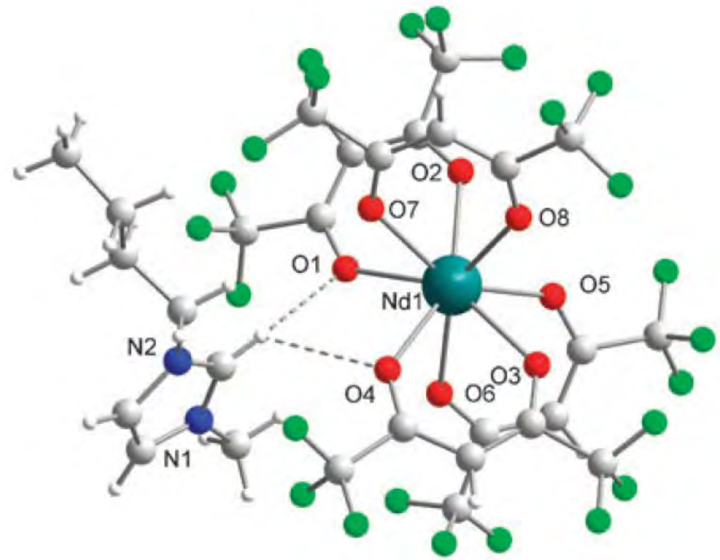


(b) Ionic liquid (a) $Nd(Tf_2N)_3$ in H_2O

H. Mehdi *et al.*, *Chem. Commun.*, **2010**, *113,* 234-236.

Structure of a neodymium(II) complex obtained after extraction

$Nd(Tf_2N)_{3,aq}$ + $4[C_4mim][hfac]_{org}$
-> $[C_4mim][Nd(hfac)_4]_{org}$ + $3[C_4mim][Tf_2N]_{org}$



$[C_4mim][Nd(hfac)_4]$

Crystallised from a concentrated solution

Chem. Commun., **2010**, *113*, 234-236.

Outline

1. Coordination Chemistry in Ionic Liquids
2. Ionic Liquids for Materials Synthesis
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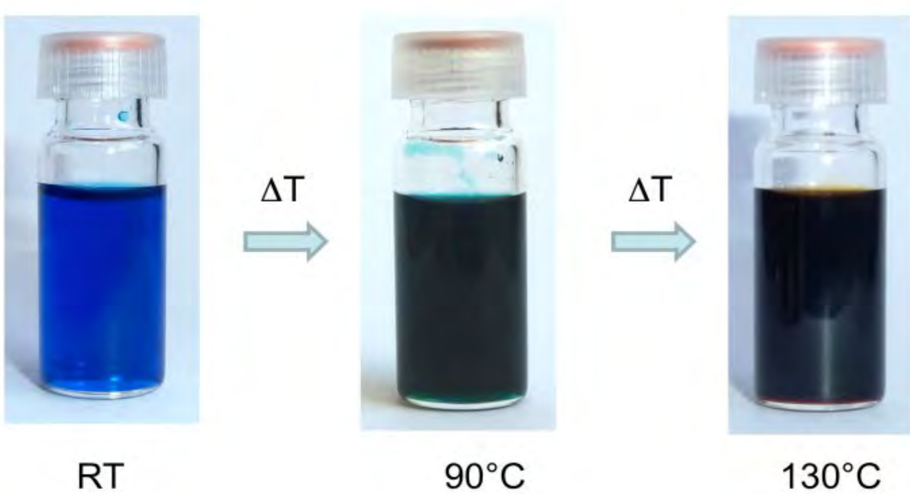
5. Conclusions

Ionic Liquid Based Nanofluids

metal oxide NPs formation

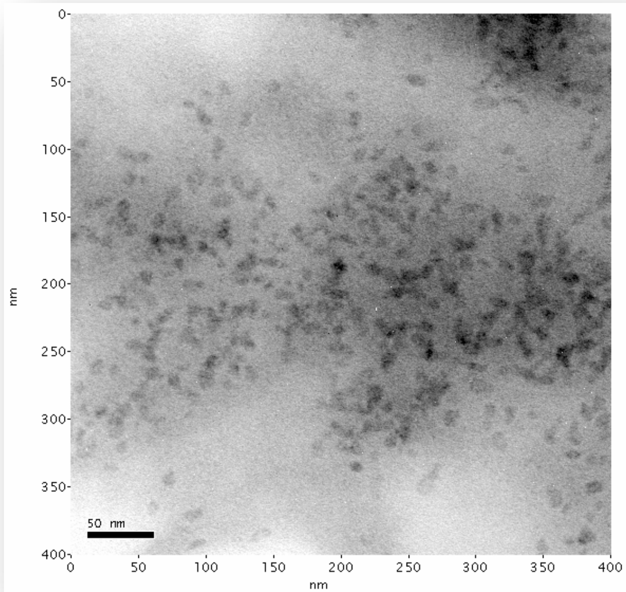
$Cu_2(OAc)_4{\cdot}2H_2O + 2\,[P_{8\,8\,8\,12}][OAc] \rightarrow [P_{8\,8\,8\,12}]_2[Cu_2(OAc)_4(OH)_2] + 2\,HOAc$
$\rightarrow\; 2\,CuO + 2\,[P_{8\,8\,8\,12}][OAc] + 4\,HOAc$

Heating a solution of $Cu_2(OAc)_4{\cdot}2H_2O$ in $[P_{8\,8\,8\,12}][OAc]$



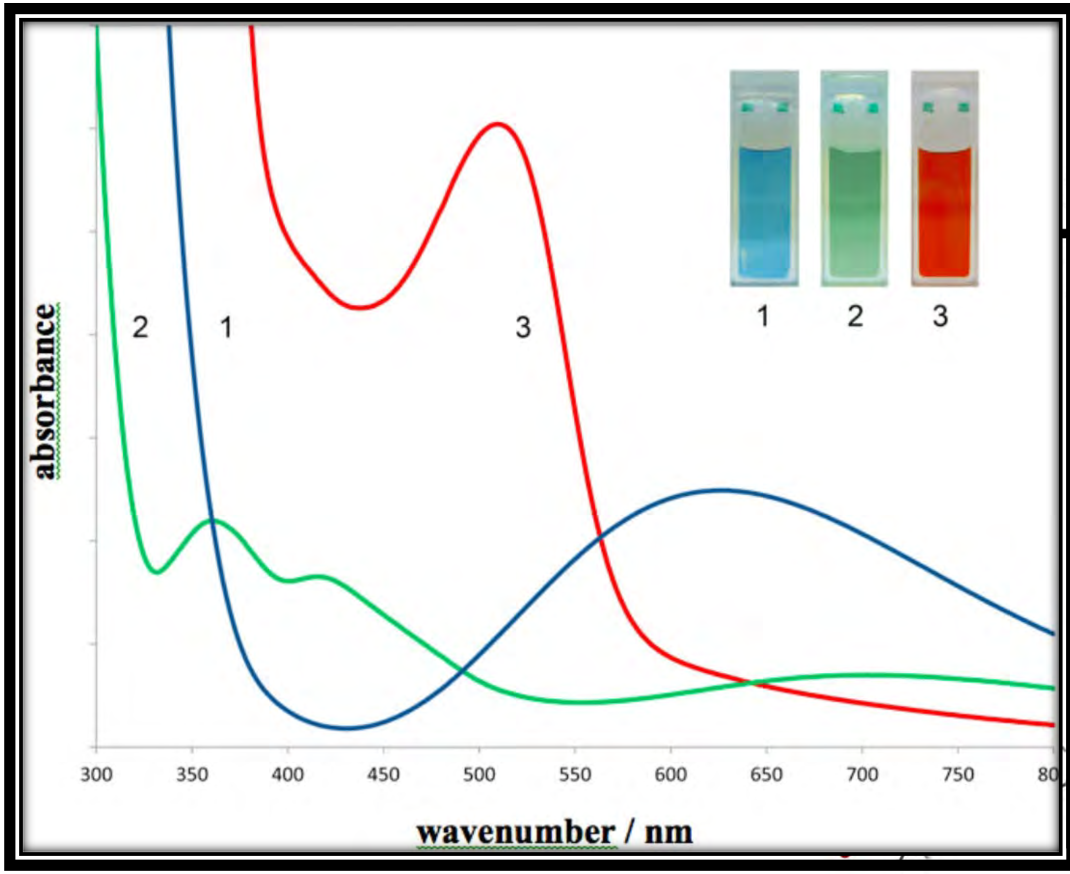
In-situ synthesis of a copper(II)oxide dispersion

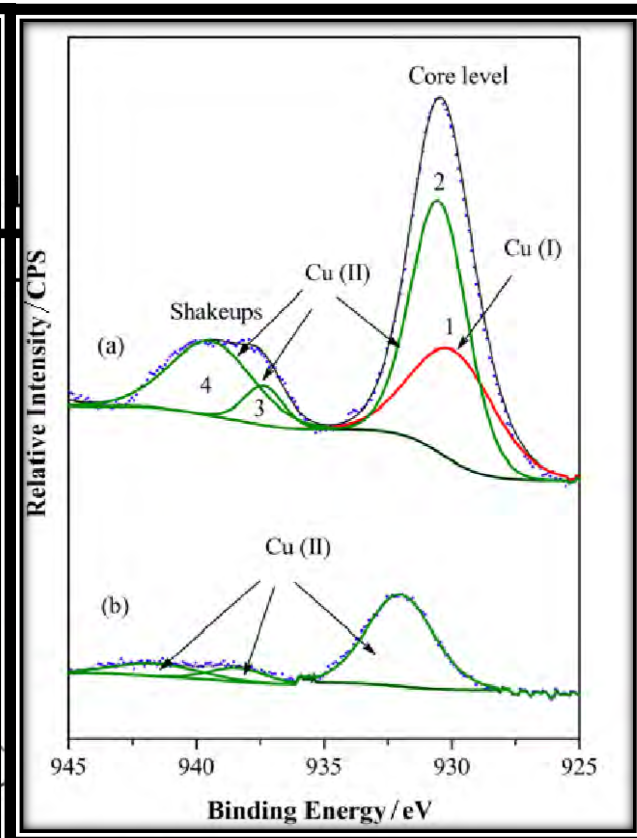
TEM - EDX



Dalton Trans, 2012, **41**, 219 **(Hot Paper)**.

Facile *in situ* synthesis of nanofluids based on ionic liquids and copper oxide clusters and nanoparticles

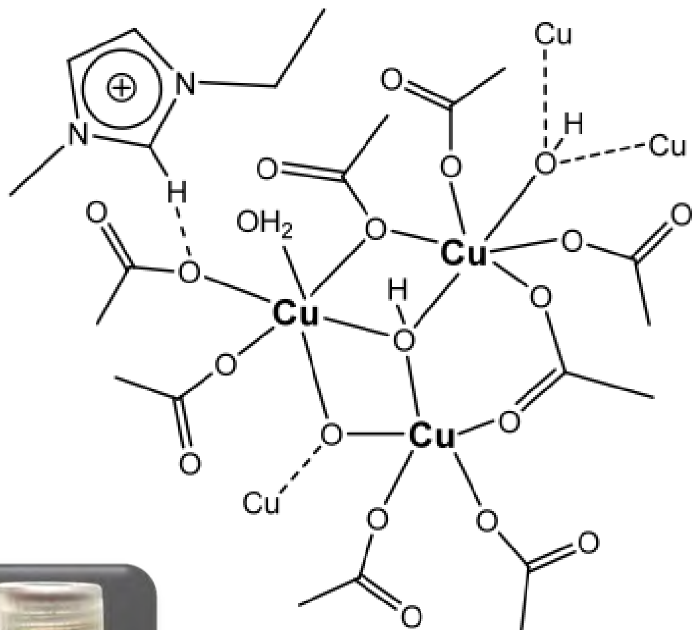


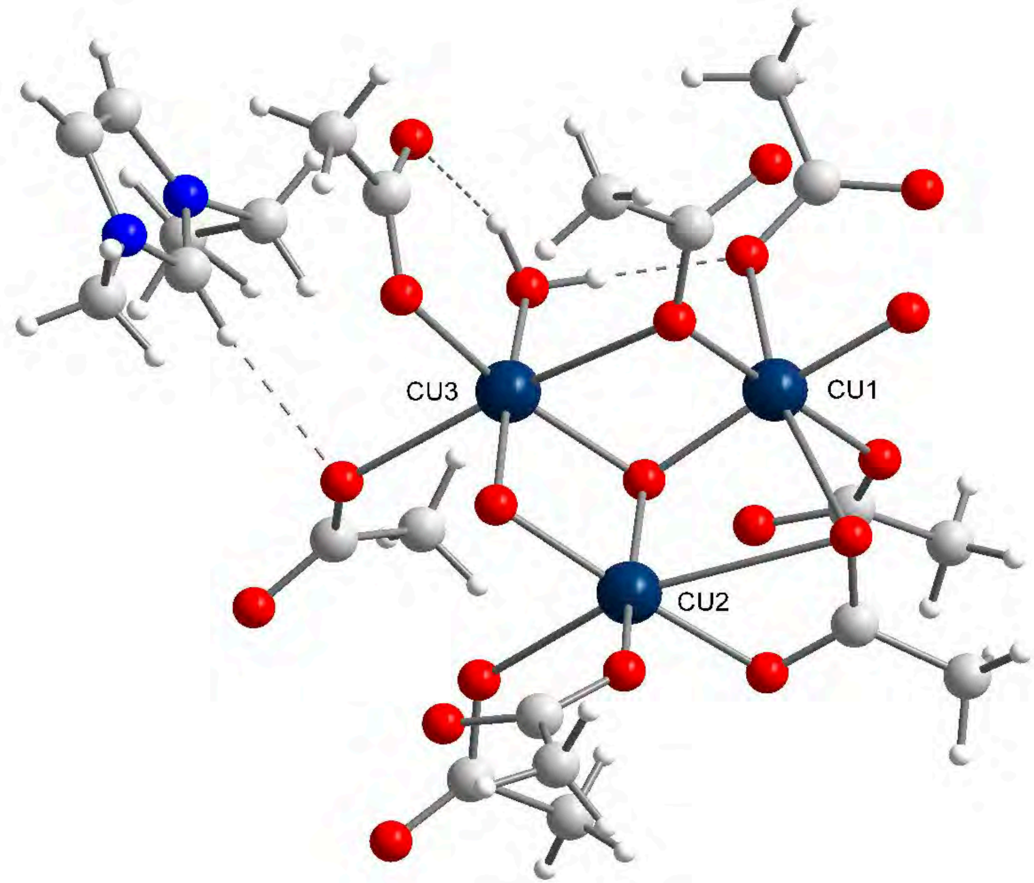


Cu(I/II)oxide clusters

Dalton Trans, 2012, **41**, 219 **(Hot Paper)**.

Ionic Liquid Based Nanofluids: *In-Situ* Synthesis and Physical Properties of Stable and Liquid Nanocomposite Materials

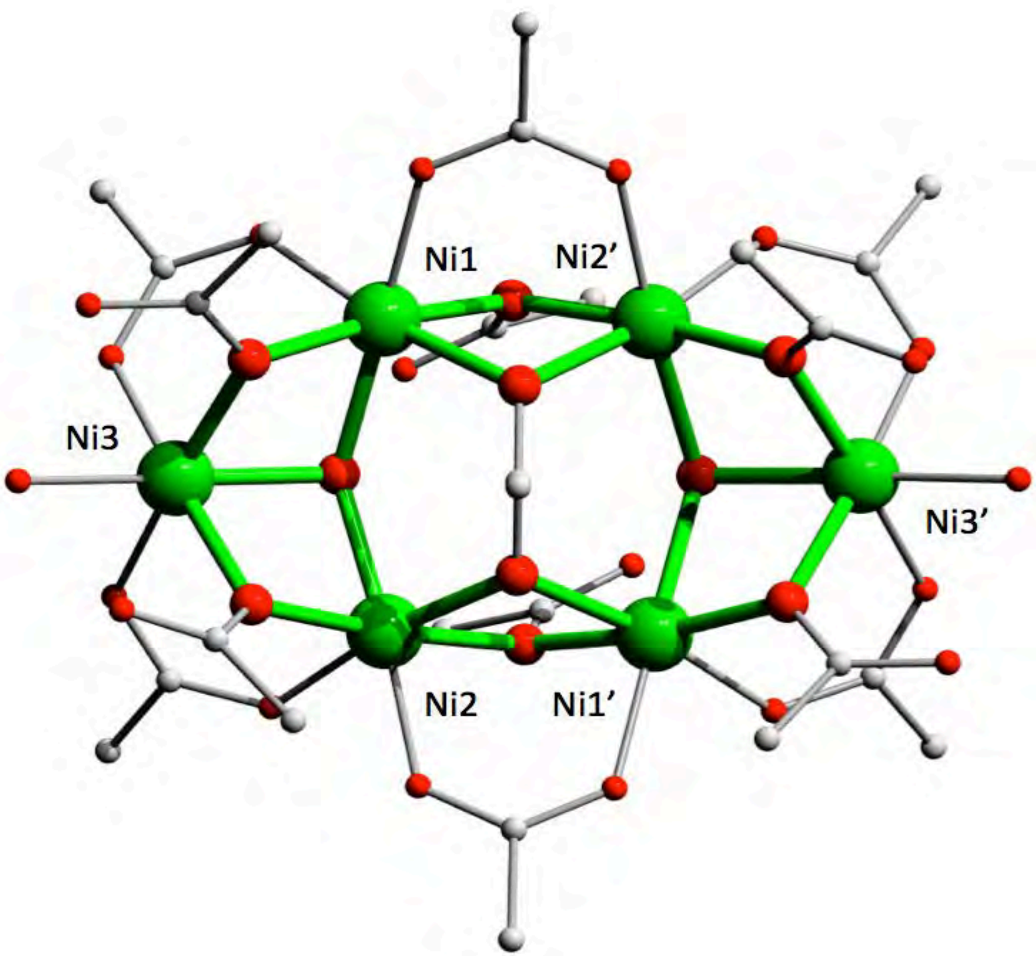


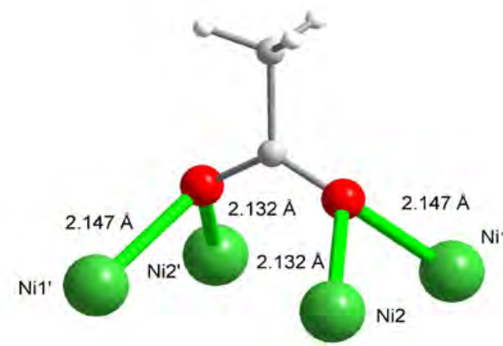


[Emim][$Cu_3(OAc)_5(H_2O)(OH)_2$]H_2O

Ionothermal Synthesis of Polynuclear Metal Clusters in Acetate Ionic Liquids

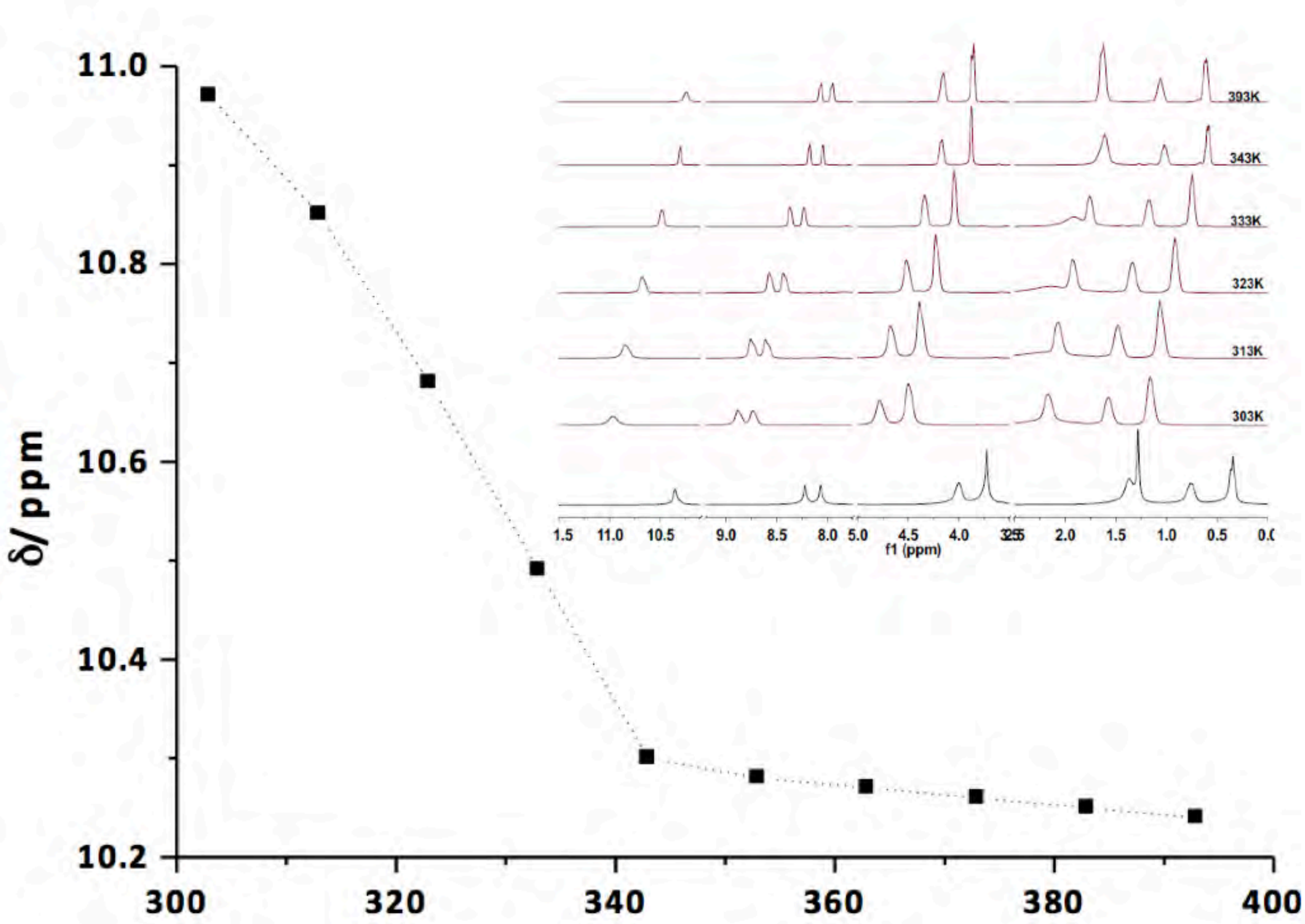
$[C_2mim]_4[Ni_6(OAc)_{13}(OH)_2(H_2O)_2](OAc)(HOAc)$



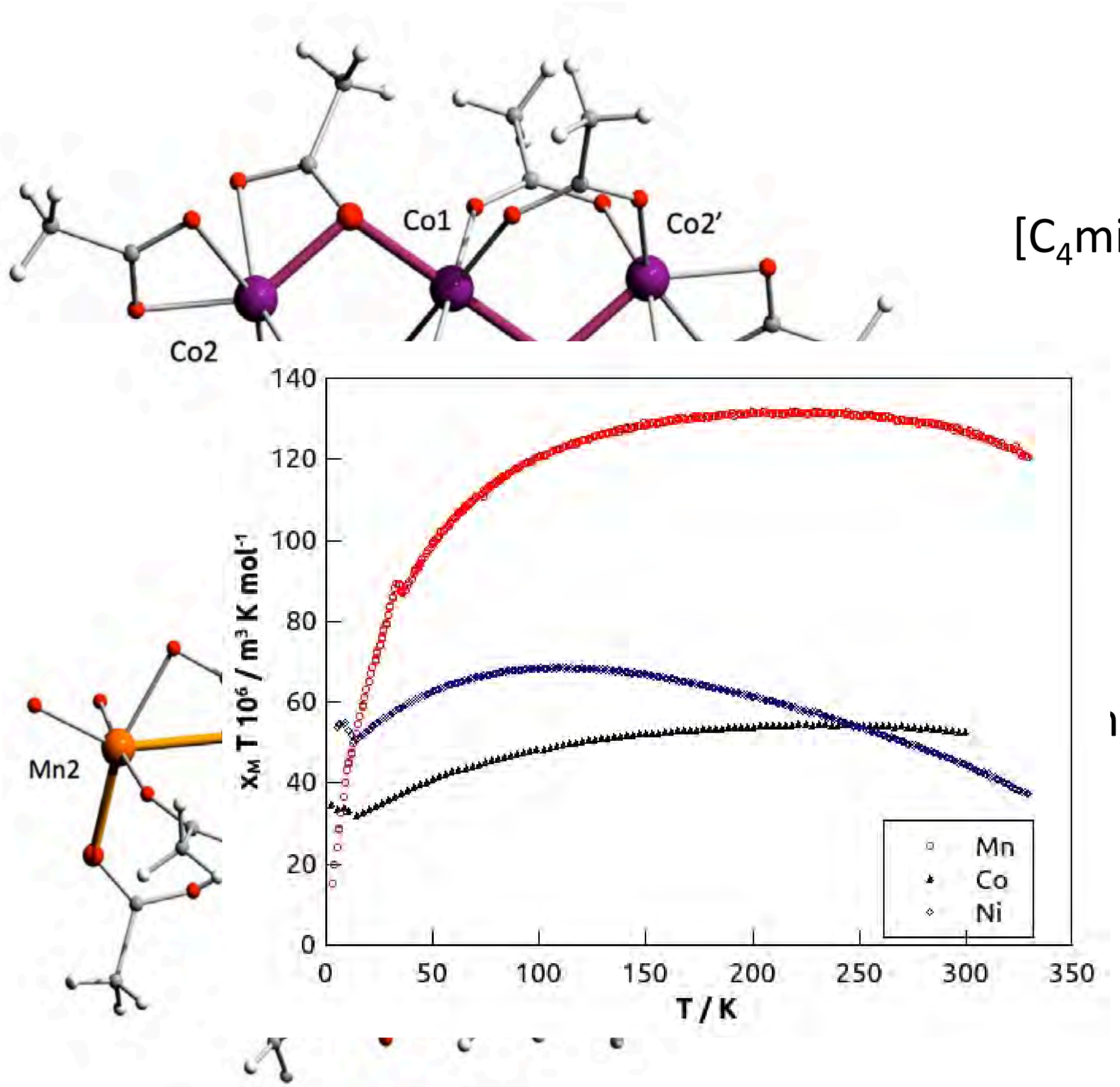


μ-η^2:η^2 acetate binding mode

Ionothermal Synthesis of Polynuclear Metal Clusters in Acetate Ionic Liquids



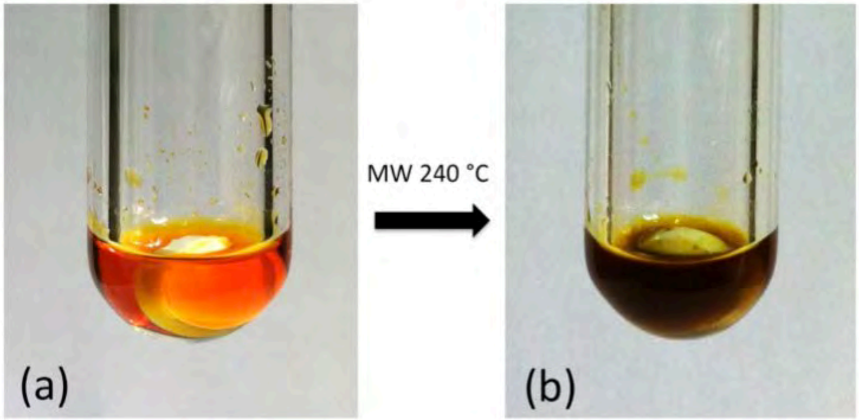
Ionothermal Synthesis of Polynuclear Metal Clusters in Acetate Ionic Liquids



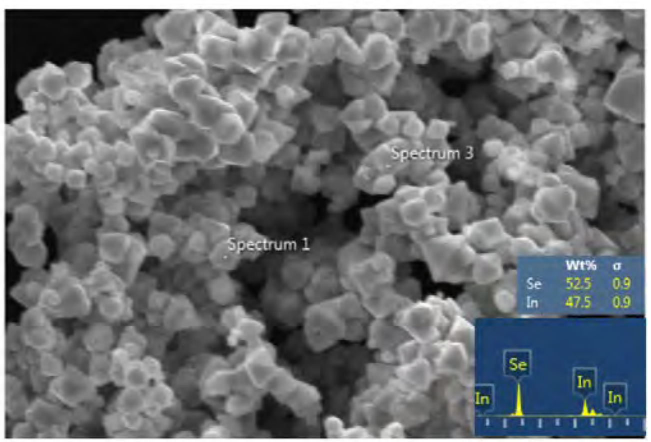
$[C_4mim]_2[Co_3(OAc)_8]$

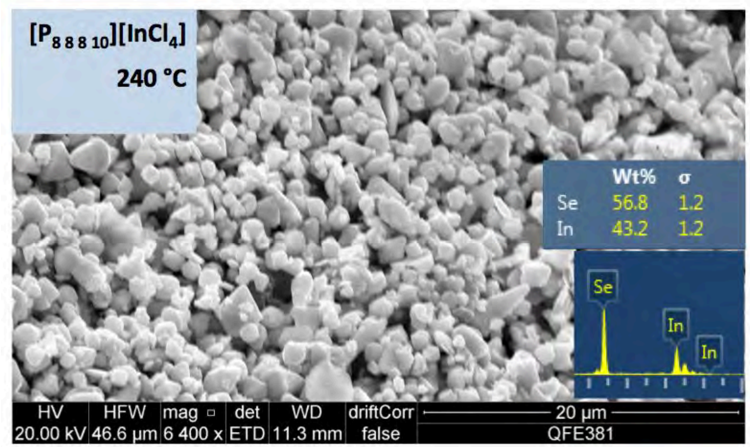
$\text{ıim}]\{Mn_3(OAc)_7\}_n$

Ionothermal, Microwave-Assisted Synthesis of Indium(III) Selenide



No.	ionic liquid	morphology (by SEM) 240 °C	280 °C
1	$[P_{8\,8\,8\,10}][InCl_4]$	Uniform spherical product, 0.5-3 µm	non-uniform 1-3 µm, 10-30 µm
2	$[P_{6\,6\,6\,14}][InCl_4]$	Uniform product, 2-5 µm	non-uniform, 10-30 µm, affected by laser, no clear image
3	$[P_{6\,6\,6\,17}][InCl_4]$	1-3 µm, clear uniform product	1-3 µm, clear uniform product
4	$[C_8mim][InCl_4]$	0.05-1 µm, clear uniform spherical product	1-5 µm, unclear, non uniform product

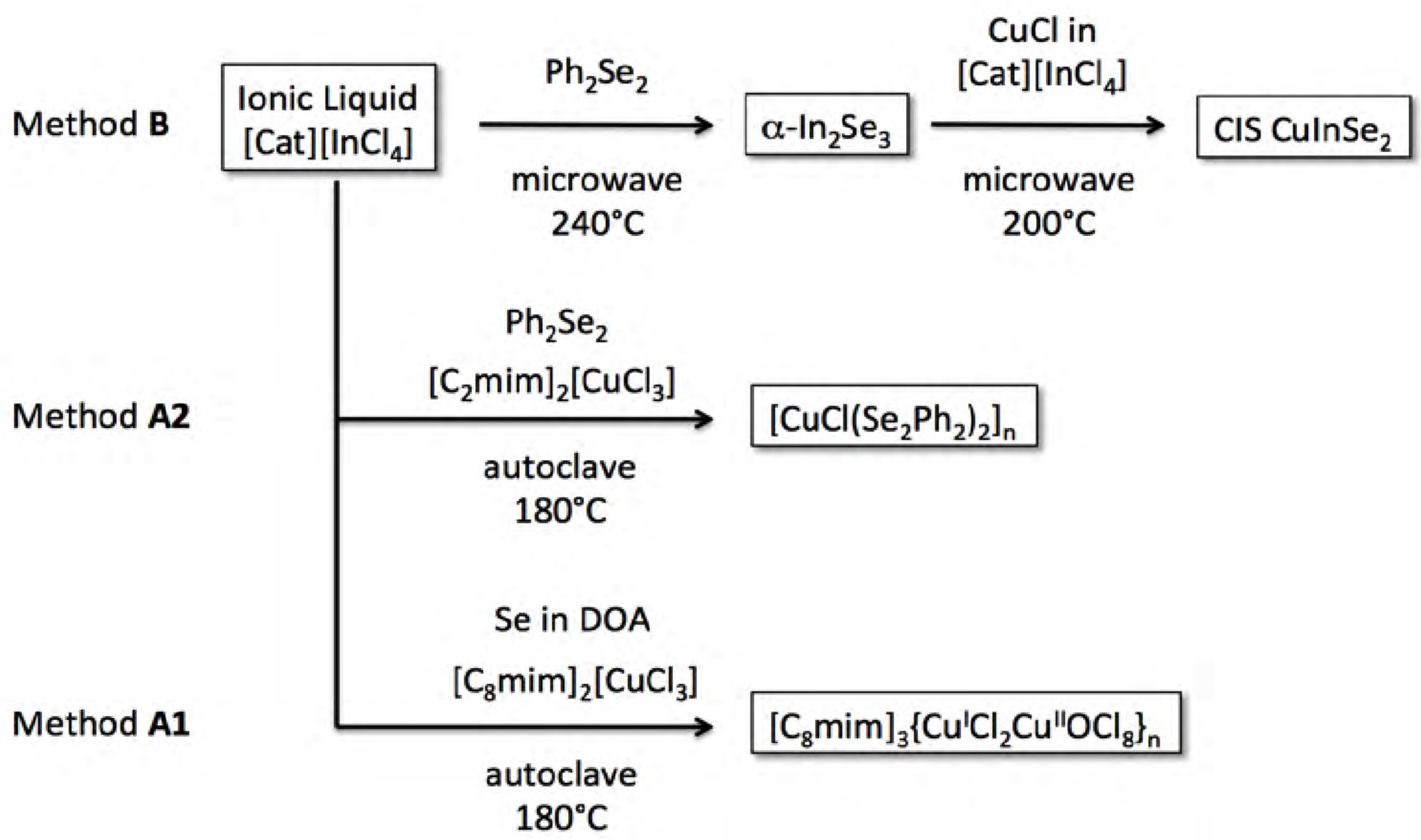




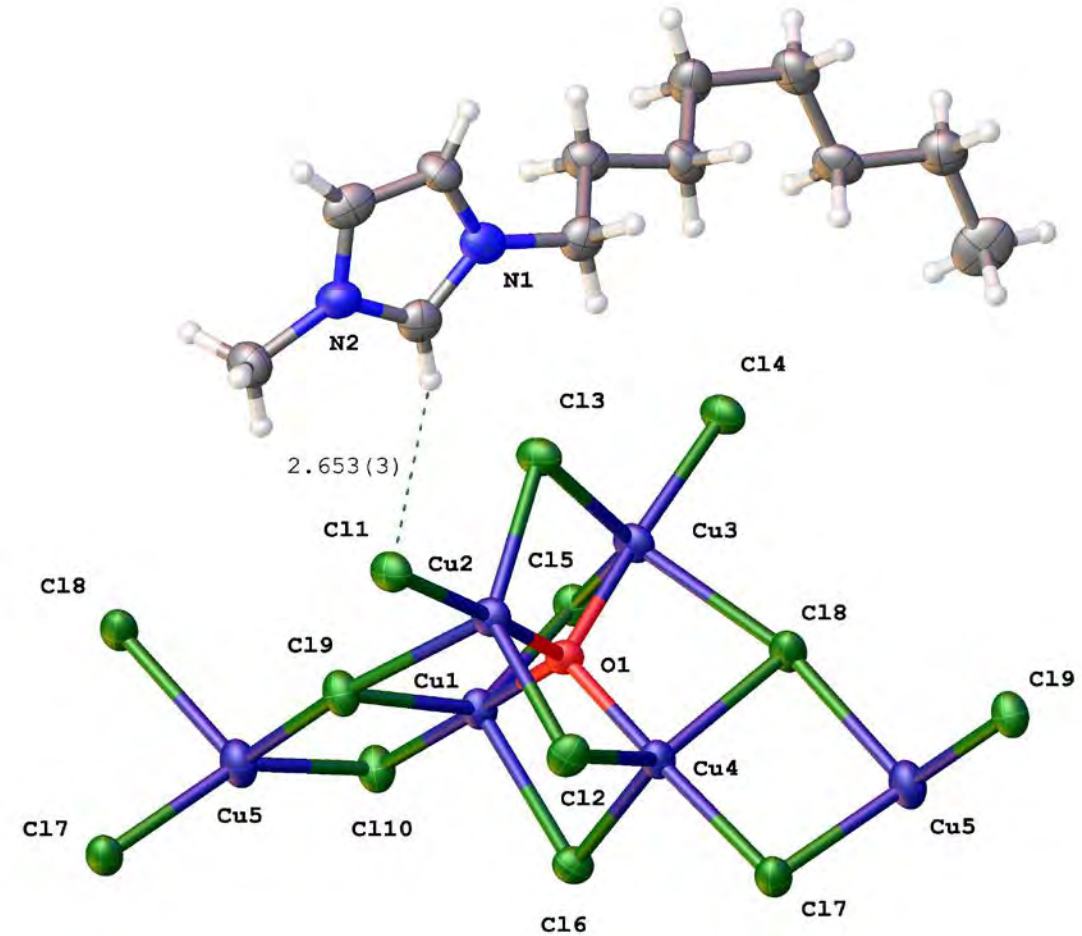
J. Mat. Chem. A, 2014, accepted.

Ionothermal Syntheses of Nano- and Microstructured Ternary Copper-Indium-Chalcogenides

Overview of the reaction pathways and methods used



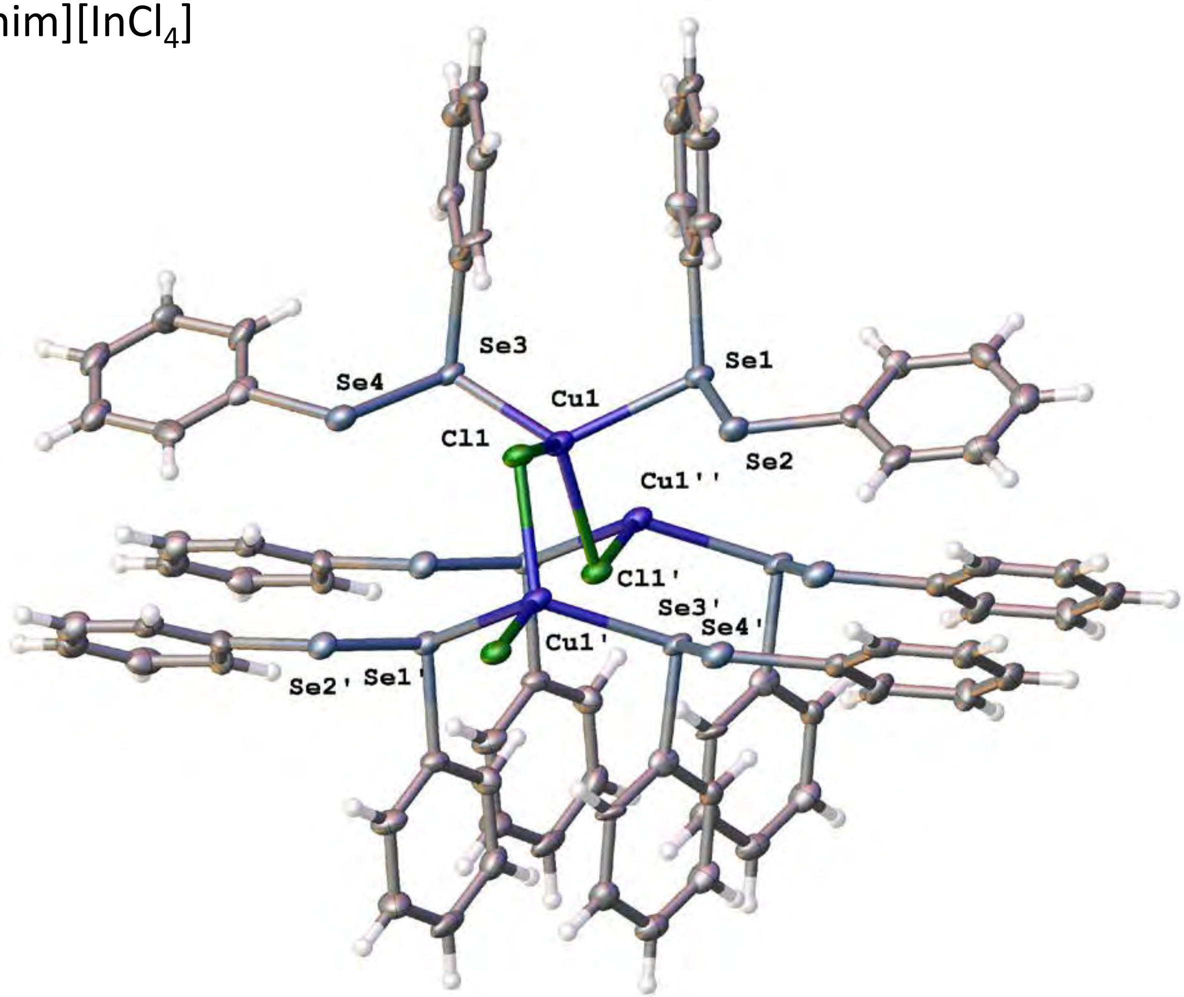
Ionothermal Syntheses of Nano- and Microstructured Ternary Copper-Indium-Chalcogenides



Crystal structure of $[C_8mim]_3\{Cu^ICl_2Cu^{II}OCl_8\}_n$

Ionothermal Syntheses of Nano- and Microstructured Ternary Copper-Indium-Chalcogenides

Formed by the reaction of $[C_2mim][CuCl_2]$, Ph_2Se_2 and $[C_2mim][InCl_4]$



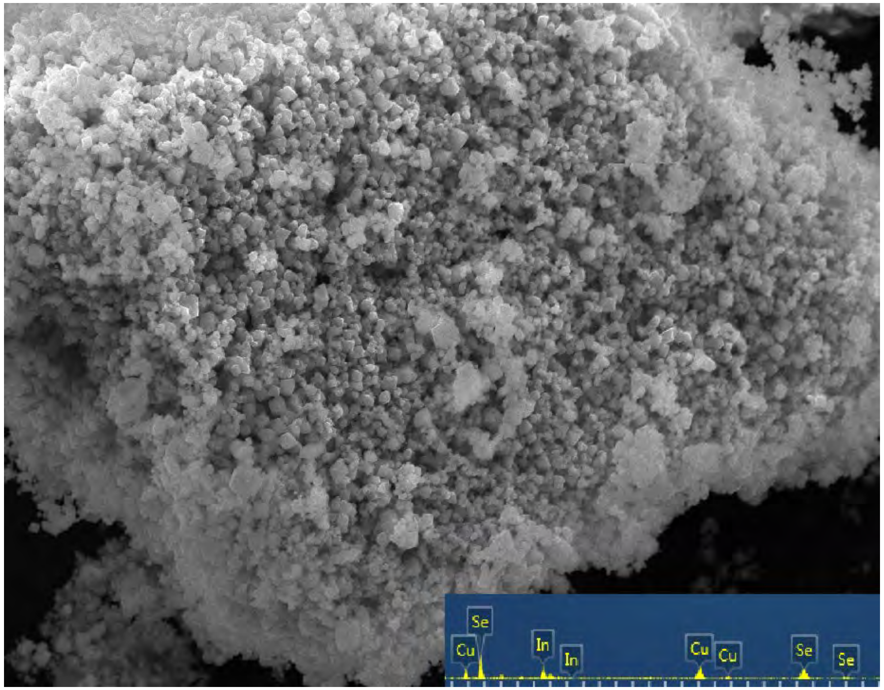
Part of the crystal structure of the polymeric $[CuCl(Se_2Ph_2)_2]_n$

Ionothermal Syntheses of Nano- and Microstructured Ternary Copper-Indium-Chalcogenides

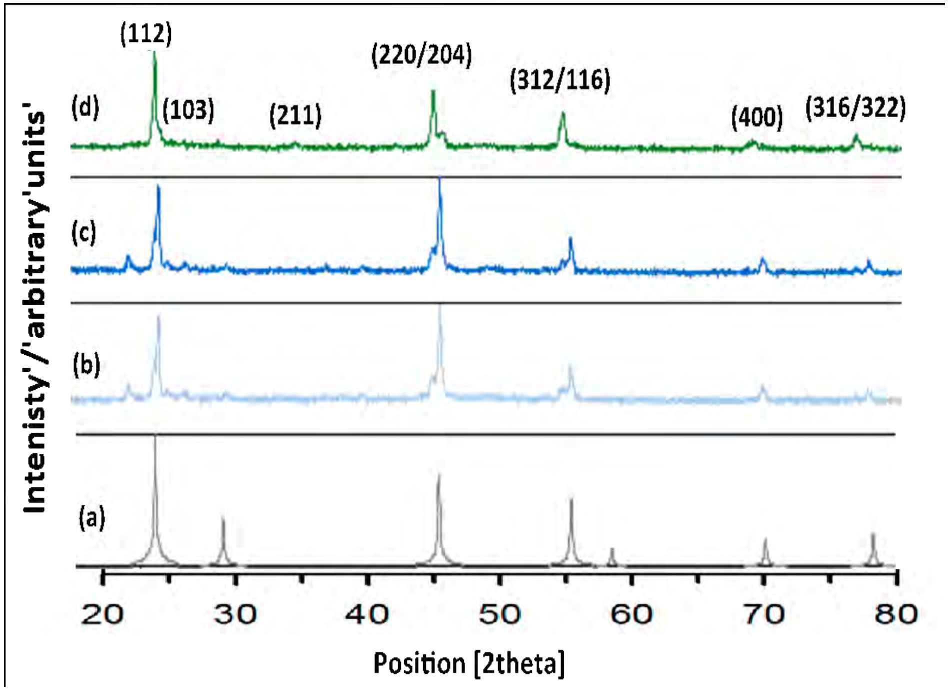
No.	Ionic liquid	Reaction conditions/ order of reagents		Elemental composition (by EDX)
1	$[P_{6\,6\,6\,14}][InCl_4]$	a) IL + Ph_2Se_2 + CuCl	All together and reacted at 240°C	Cu_2Se/ CuSe
		b) In_2Se_3 formed + CuCl	In_2Se_3 formed at 240°C Cu^ICl added and heated to 240°C Cu^ICl added and heated to 200°C	$CuInSe_2$
2	$[C_8mim][InCl_4]$	a) IL + Ph_2Se_2 + CuCl	All together and reacted at 240°C	Cu_2Se/CuSe
		b) In_2Se_3 formed + CuCl	In_2Se_3 formed at 240°C, Cu^ICl added and heated at 200°C	$CuInSe_2$ and Cu_2Se

Ionothermal Syntheses of Nano- and Microstructured Ternary Copper-Indium-Chalcogenides

SEM for $CuInSe_2$



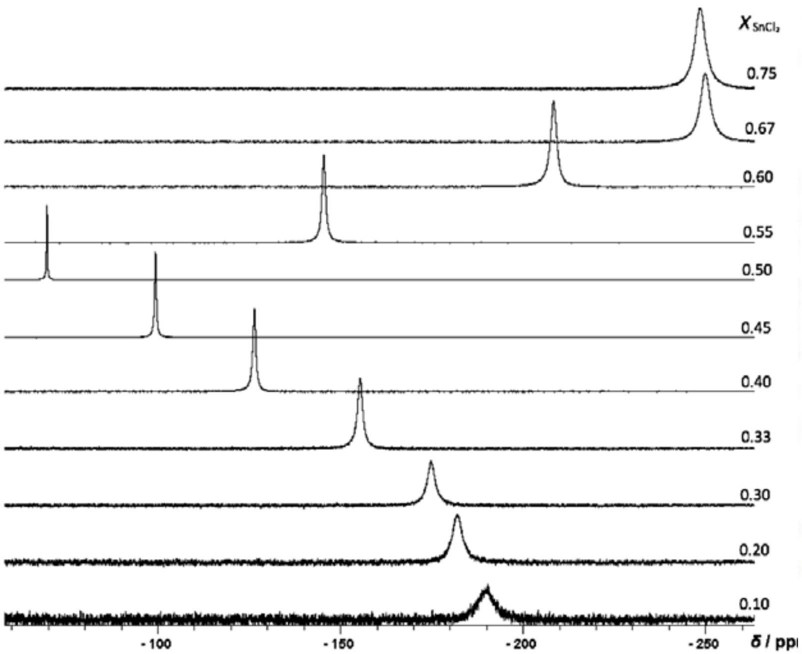
PXRD for $CuInSe_2$



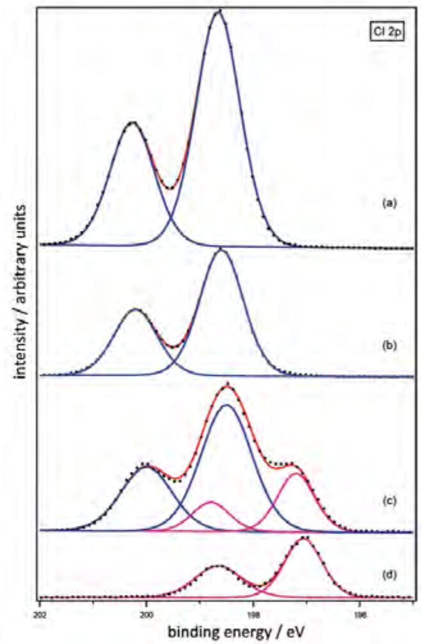
Outline

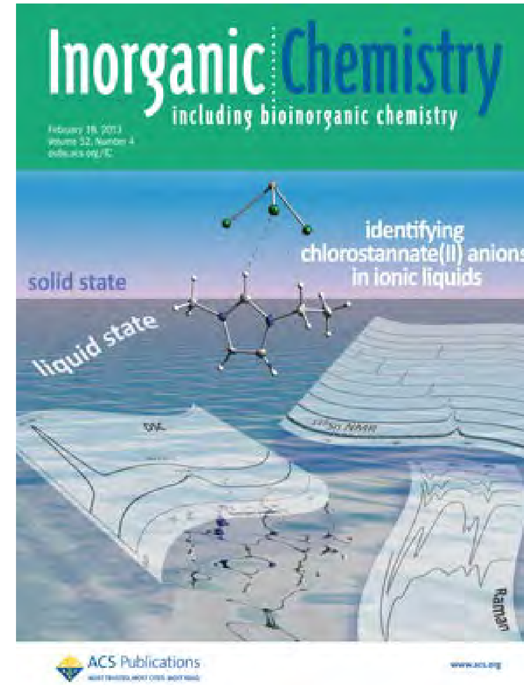
1. Coordination Chemistry in Ionic Liquids
2. Ionic Liquids for Materials Synthesis
3. Metal-Containing Ionic Liquids
4. Ionic Liquid Applications
5. Conclusions

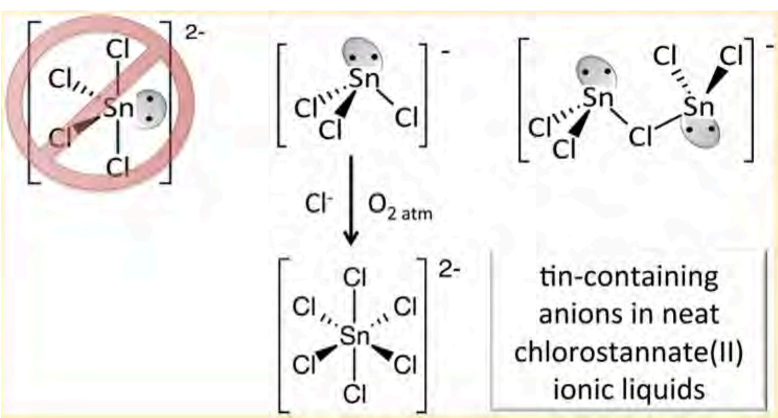
Chlorostannate(II) Ionic Liquids: Speciation, Lewis Acidity, and Oxidative Stability

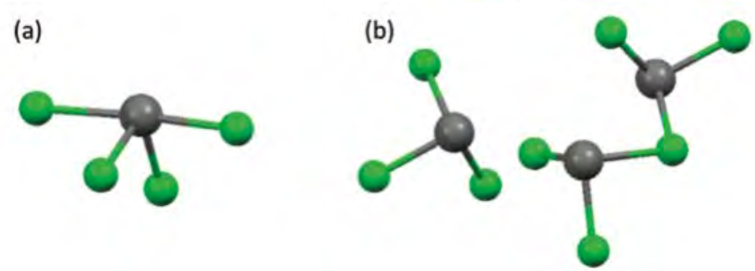


^{119}Sn NMR spectra (186.48 MHz, 80 °C, neat liquid.





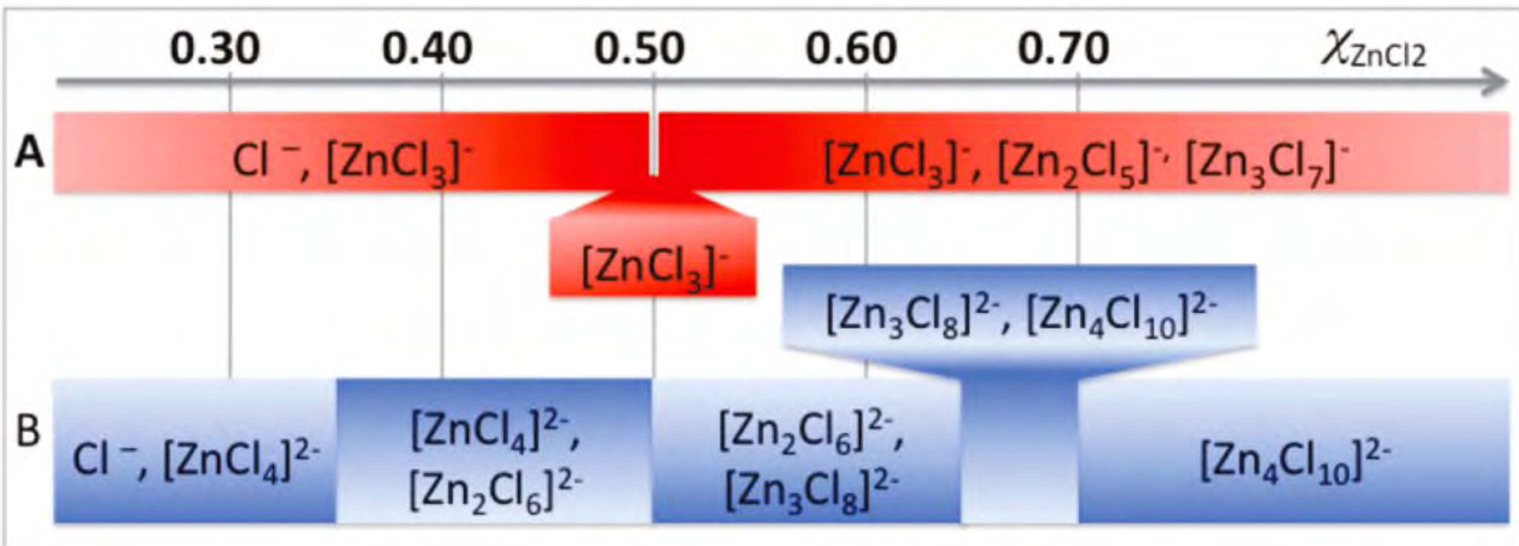




Inorg. Chem. 2013, 52, 1710–1721.

Validation of Speciation Techniques

- Chlorozincate ionic liquids with imidazolium cations
- Chlorometallate ionic liquids are lewis acidic catalysts
- Tunable – control of the catalytic activity
- Applications in catalysis, electrodeposition and batteries



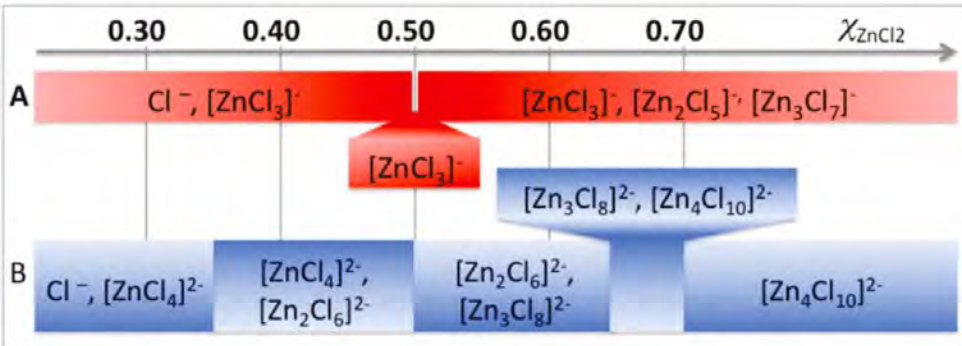
Why is speciation so important?

- **Lewis acidity**
  - depends on a metal
  - increases with increasing $\chi_{\mathbf{MCl}\boldsymbol{x}}$:
    - Cl^- is a Lewis base
    - polynuclear species, *e.g*. $[Al_2Cl_7]^-$, are Lewis acids
- **Coordination environment of metal affects its:**
  - catalytic properties
  - redox potential

Critical review of the existing literature

Looking for a hint

bibliographic study on chlorozincates, including molten salts



JRS

Raman spectroscopy of ionic liquids derived from 1-n-butyl-3-methylimidazolium chloride and niobium chloride or zinc chloride mixtures

Melquizedeque B. Alves, Vianney O. Santos Jr., Valerio C. D. Soares, Paulo A. Z. Suarez and Joel C. Rubim

INTRODUCTION

speciation technique	phase	model
FAB-MS	ionised gas	A
ESI-MS	ionised gas	A
Raman	neat liquid	B
^{1}H and ^{13}C NMR	solution	A
^{35}Cl NMR	neat supercooled liquid	A
^{1}H and ^{13}C solid state NMR	neat solid	A
X-Ray diffraction	neat solid	B
powder XRD	neat solid	A
EXAFS	neat solid or liquid	A
XANES	neat solid or liquid	A
cyclic voltammetry	neat liquid	A
Freezing point	neat solid/liquid	A
DSC	neat solid/liquid	B
DSC	neat solid/liquid	A
POM	neat solid	A

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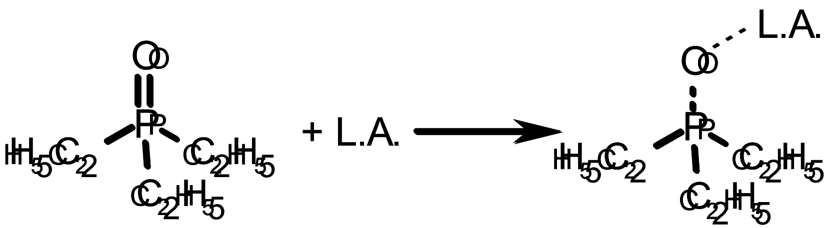
How we investigated...

Methodology

The acidity of these compounds were determined by measuring their Guttmann acceptor numbers (AN) via ^{31}P NMR

Which means:

- A probe $P(O)Et_3$ (tepo) is used and reacts with Lewis acid as follows:



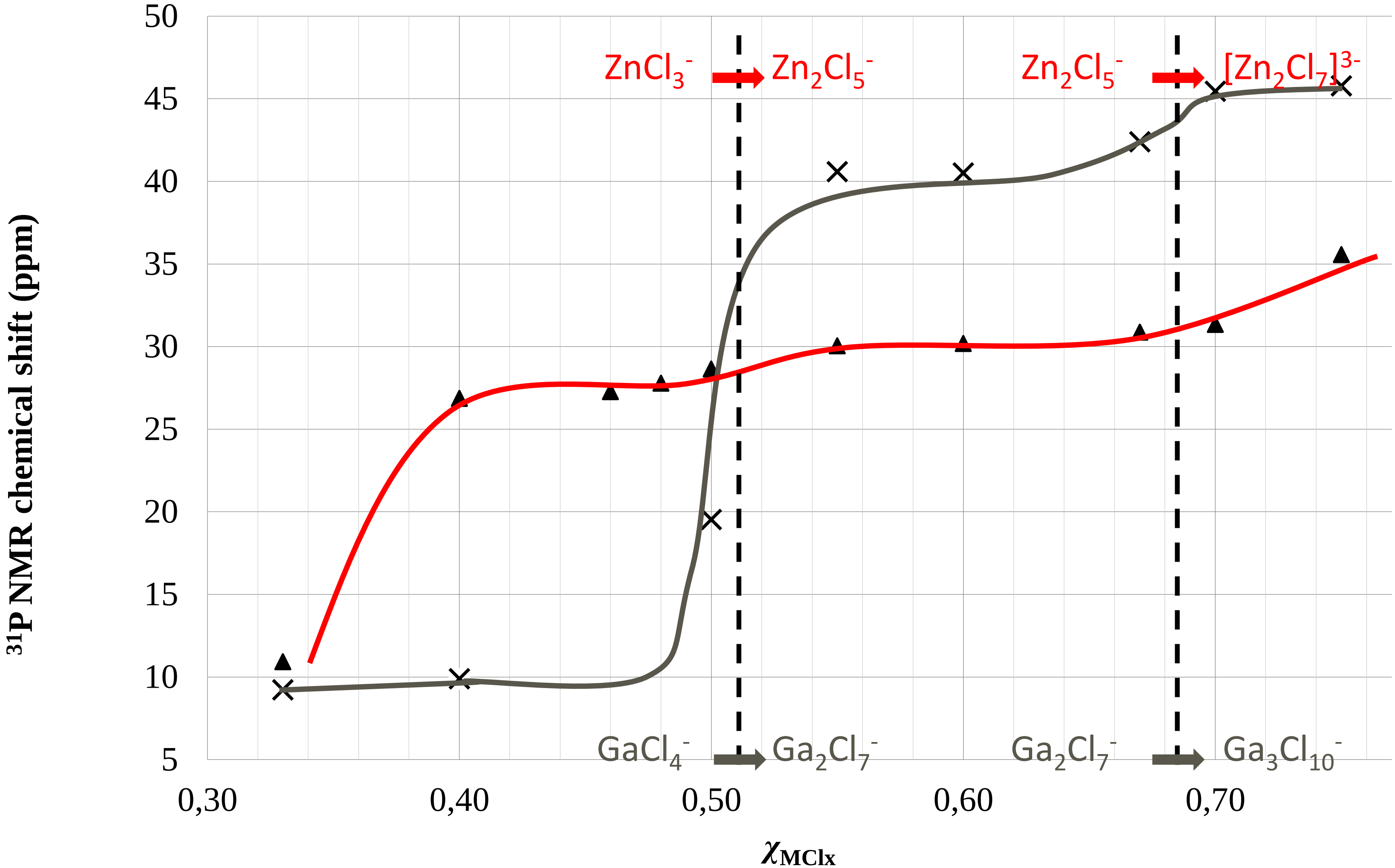
- The chemical shift of the probe is measured on ^{31}PNMR and directly proportional to their AN

- Concentration effect eliminated by extrapolation to infinite dilution

- Comparable to "classical" organic acids as AN are known for many acids or solvents

Inorganic chemistry, **2011**, 50, 5258-71.

Acidity of chlorozincate(II) ionic liquids



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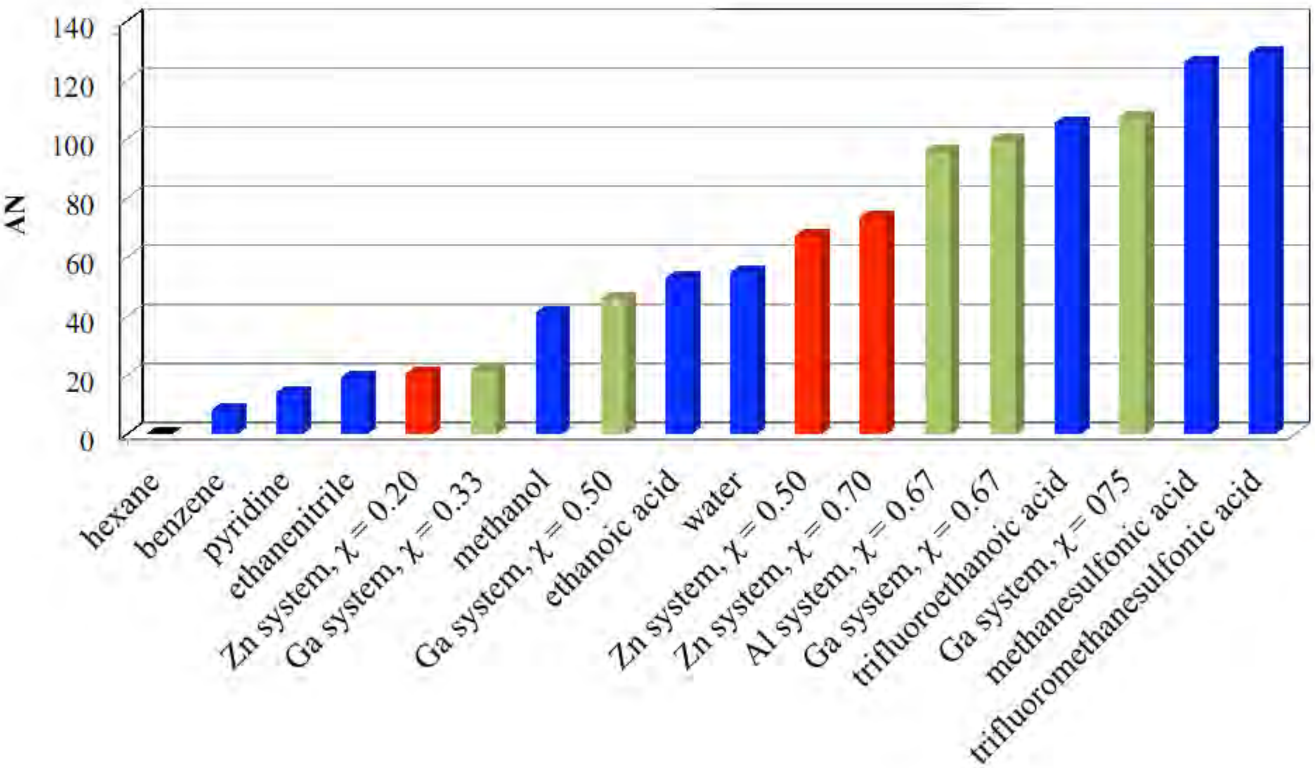
Inorganic chemistry, **2011**, 50, 5258-71.

Acidity of chlorozincate(II) ionic liquids - range of acidity

Our enlarged acidity scale

Results obtained for chlorozincate(II) ILs have been compared to others ILs



As expected, chlorozincate(II) ionic liquids possess a medium Lewis acidity.

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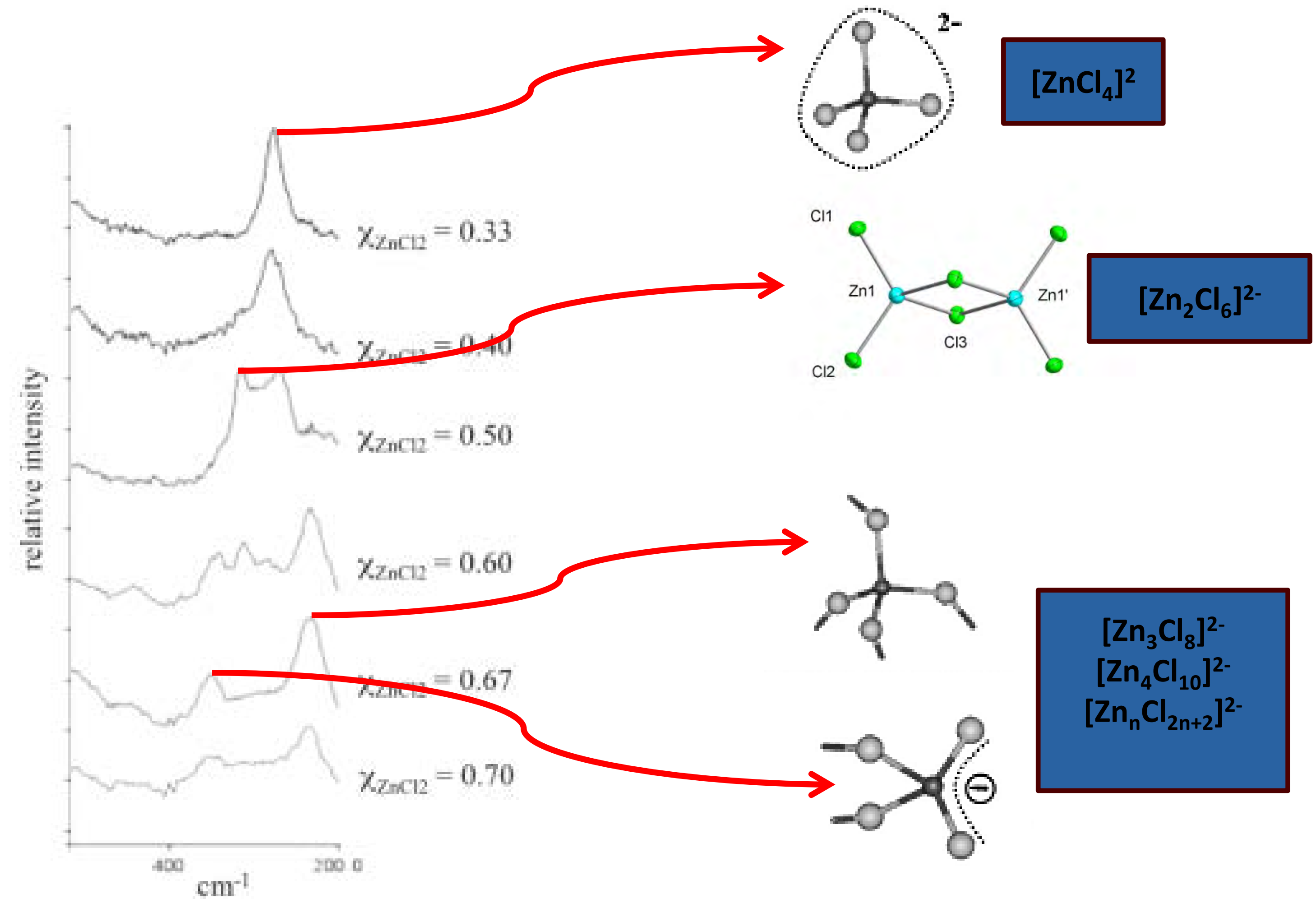
Inorganic chemistry, **2011**, 50, 5258-71.

One technique in the liquid phase: Raman spectroscopy



This Raman study confirms the results observed for the AN

Both of these techniques are carried out on the **liquid** phase

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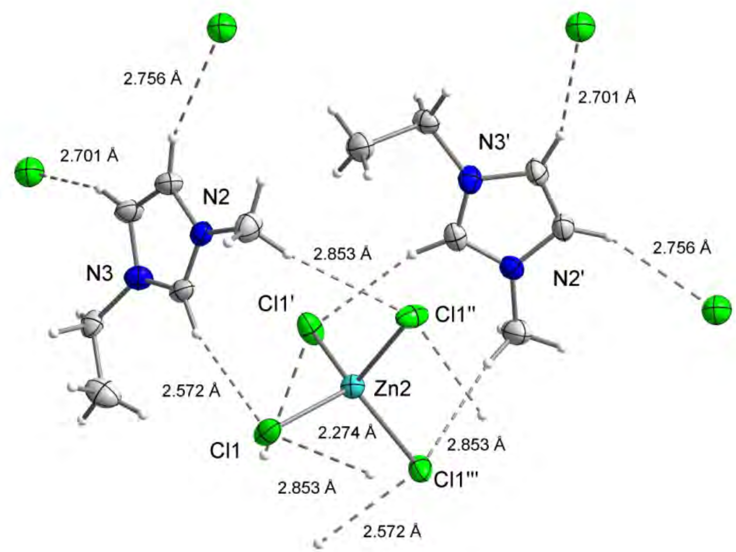
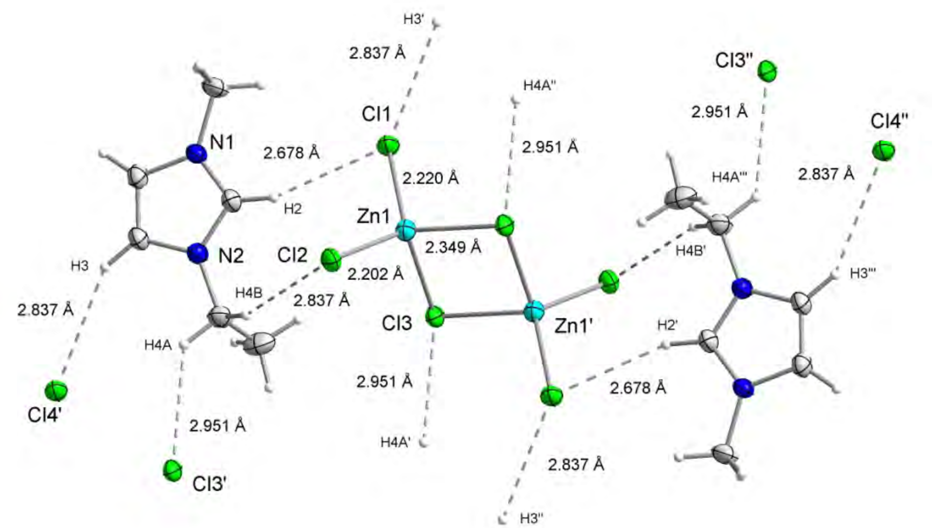
Inorganic chemistry, **2011**, 50, 5258-71.

The solid phase - A crystallographic study

Single crystal have been obtained for different composition of $[C_2mim]Cl\text{-}ZnCl_2$



$\chi_{ZnCl2} = 0.33$



$\chi_{ZnCl2} = 0.50$

Crystal structures give results equivalent to what is observed with Raman.

Here, speciation in the liquid and the solid states are equivalent.

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Inorganic chemistry, **2011**, 50, 5258-71.

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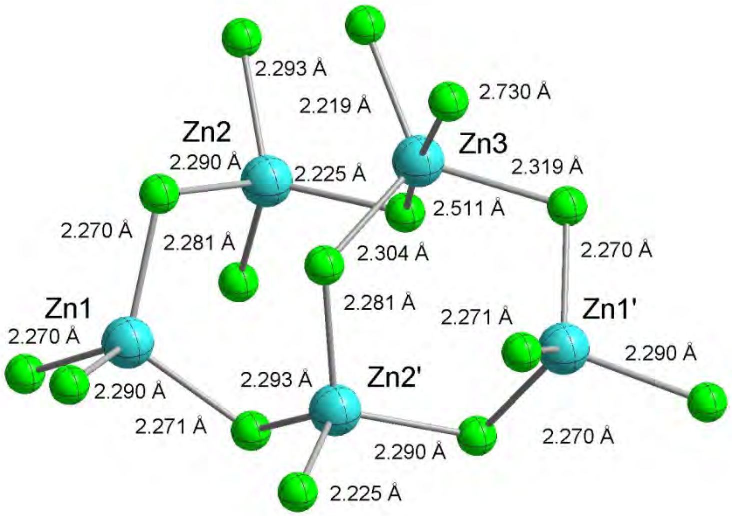
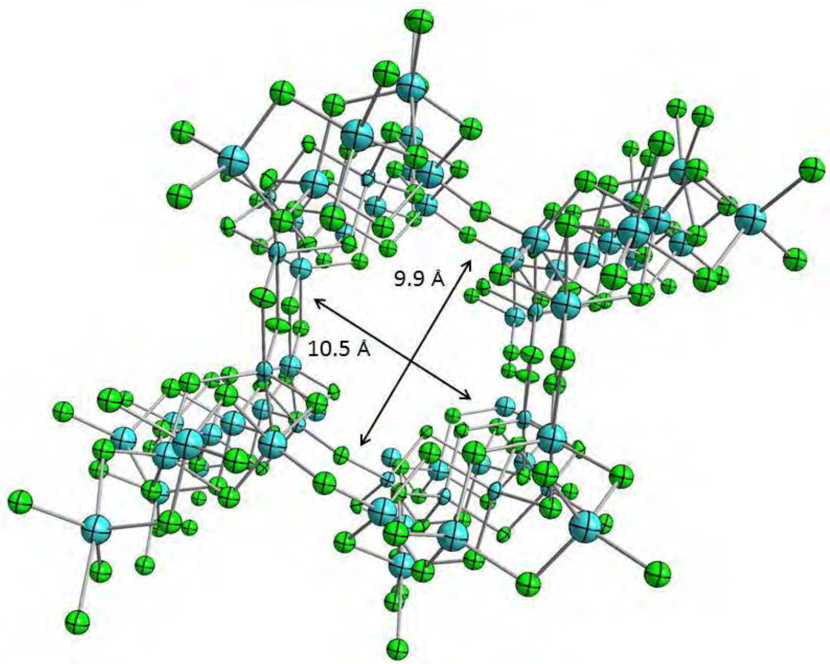
The solid phase - A crystallographic study

Single crystal have been obtained for different composition of $[C_2mim]Cl\text{-}ZnCl_2$



$\chi_{ZnCl2} = 0.33$



$\chi_{ZnCl2} = 0.75$

- First example of this type of zinc coordination
- Here, obvious difference of speciation in the liquid and the solid states

Inorganic chemistry, **2011**, 50, 5258-71.

Suggested liquid-phase speciation of chlorozincate(II) ionic liquids:

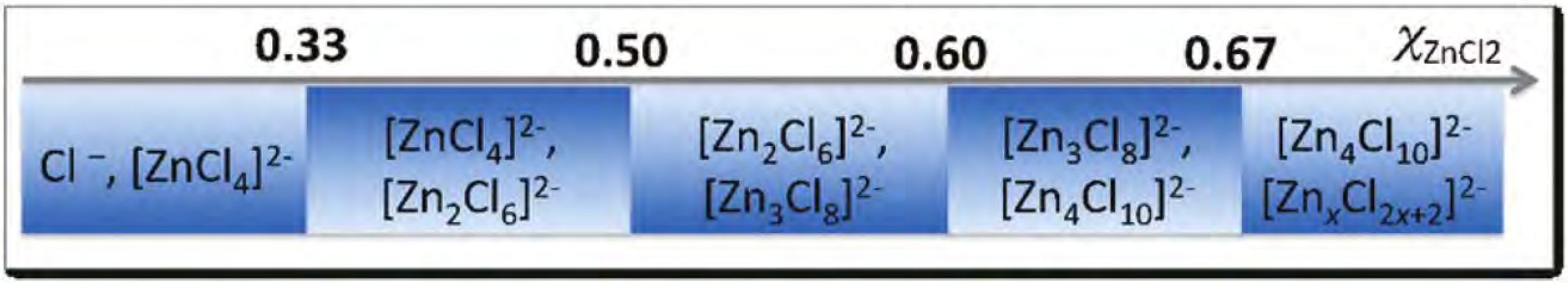


Figure 11. Suggested liquid-phase speciation of chlorozincate(II) ionic liquids, where $[Zn_xCl_{2x+2}]^{2-}$ $(x > 4)$ are postulated polynuclear species.

Inorganic chemistry, **2011**, 50, 5258-71.

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WO/2012/046057

An ionic liquid process for mercury removal from natural gas

$$2[CuCl_4]^{2-} + Hg(0) \rightarrow [HgCl_4]^{2-} + 2[CuCl_2]^- \quad (1)$$

$$2[Cu_2Cl_6]^{2-} + 2Hg(0) \rightarrow [Hg_2Cl_6]^{2-} + 2[CuCl_2]^- + 2CuCl(s) \quad (2)$$

$$[Cu_2Cl_6]^{2-} + Hg(0) \rightarrow HgCl_2(s) + 2[CuCl_2]^- \quad (3)$$

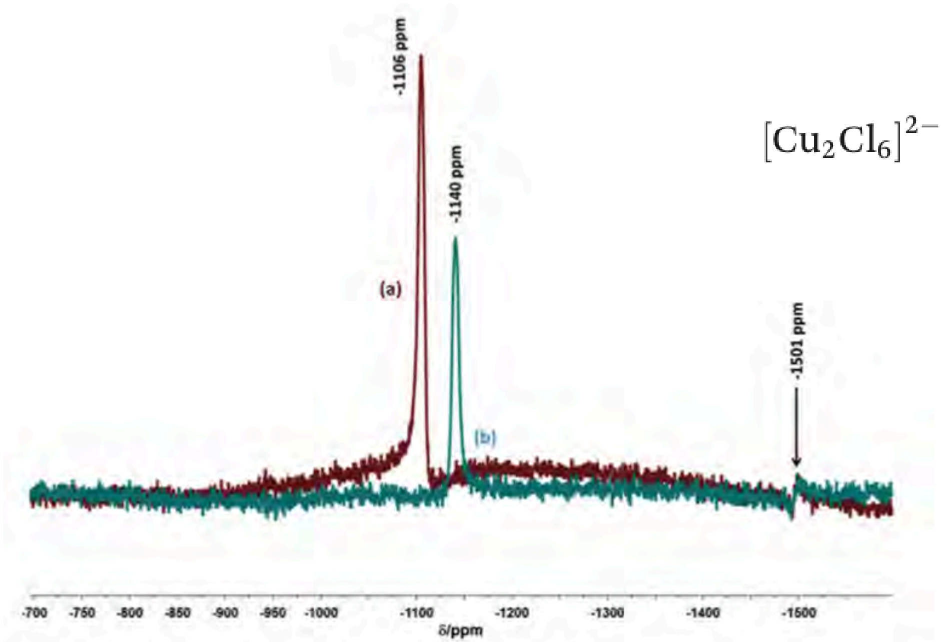
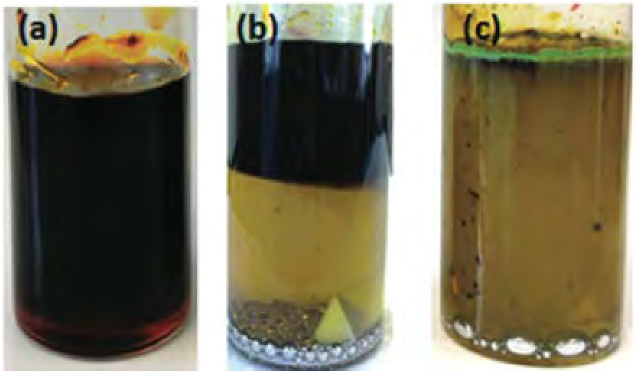
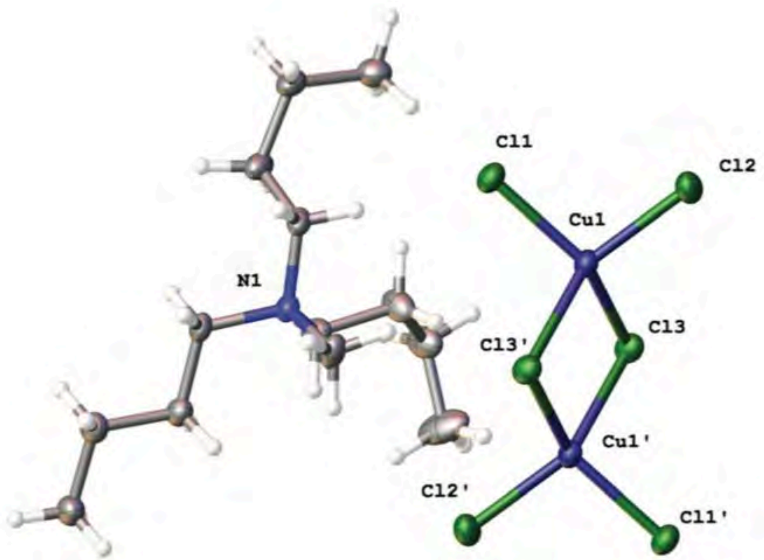


Fig. 4 ^{199}Hg NMR (23 °C, neat, 89.57 MHz) spectra of the ionic liquids obtained from the reaction mixtures of (a) $[C_4mim]_2[CuCl_4]$ + Hg(0) (red trace) and (b) $[C_4mim]_2[Cu_2Cl_6]$ + Hg(0) (blue trace). The peak at −1501 ppm is the reference peak.



An ionic liquid process for mercury removal from natural gas

$[N_{4\ 4\ 4\ 1}]_2[Cu_2Cl_6]$



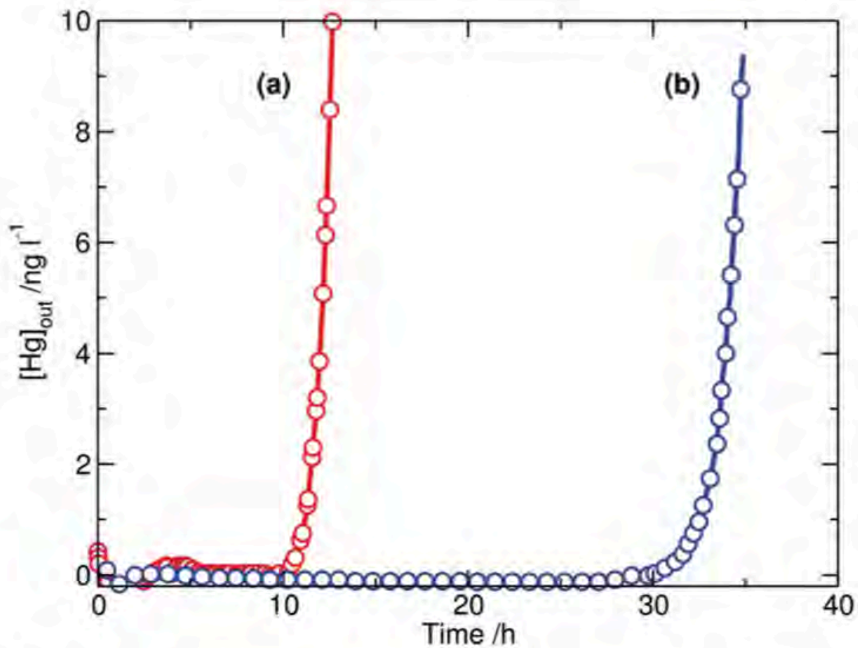


Fig. 7 Mercury breakthrough curves for the capture of mercury vapour from dinitrogen gas ($[Hg]_{in}$ = 2000 ng l^{-1}, flow rate = 600 cm^3 min^{-1}, *T* = 25 °C) using 0.10 g samples of (a) a sulfur-impregnated activated carbon and of (b) a 10 wt% $[N_{4441}]Cl-CuCl_2$ (χ_{CuCl_2} = 0.50) SILP on porous silica (135 m^2 g^{-1} surface area and 0.83 cm^3 g^{-1} pore volume). Similar results were obtained using methane as the carrier gas.

Dalton Trans. **2015**, DOI: 10.1039/c4dt03273j

Bench Scale Testing of Solid Supported Ionic Liquids (SSILs)

- Bench scale testing to determine:
  - Type of support
  - Adsorption capacity of the SSILs
  - Hg extraction efficiency and kinetics
  - Optimum ionic liquid composition

- Rapid screening to determine breakthrough of mercury on SSIL

WO/2012/046057

An ionic liquid process for mercury removal from natural gas

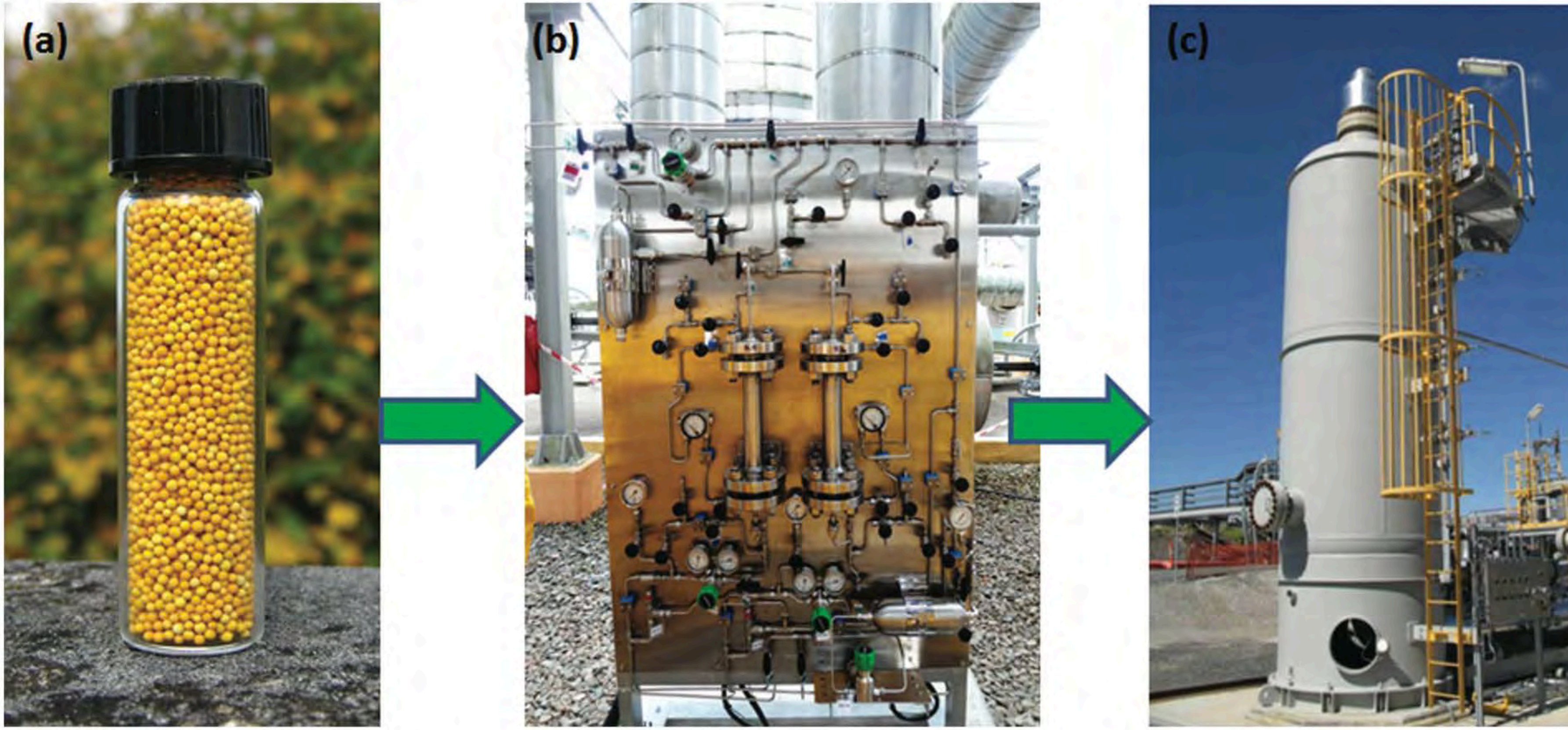


Fig. 11 Transformation from (a) lab-scale preparation of chlorocuprate(II) SILPs through to (b) pilot-scale using 100 cm^3 of SILP on production plant gas feeds to (c) full-scale mercury removal units with 20 m^3 of SILP at a gas processing plant site.[27]

Dalton Trans. **2015**, DOI: 10.1039/c4dt03273j

Towards *low temperature solid state chemistry* in ILs

A „temperature gap“

„Ionothermal Synthesis“

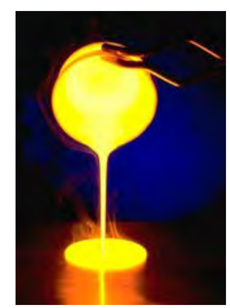
Solvent chemistry

Coordination chemistry

Solvothermal

Solid-state chemistry

Temperature



Novel inorganic synthetic pathways in coordination & materials chemistry

Advantages of ionic liquids for materials chemistry:

- Tuneable chemical and physical properties
- Negligible vapour pressure – e.g. water can be reversibly removed
- Large electrochemical window (some -4 V to +4 V) & chemical stability
- High temperature stability (for some up to 400°C)
- Stabilisation of new species, oxidation states etc.

Limitations of ionic liquids:

- Product separations / crystallisation
- High viscosities
- High manufacturing costs
- Purity of ionic liquids is crucial

Acknowledgement

- Queen's University Belfast
  - Dr. Małgorzata (Gosia) Swadźba-Kwaśny
  - Dr. Nimal Gunaratne
  - Collaborators: Dr. Johan Jacquemin, Dr John Holbrey, Prof. Martin Atkins, Prof. Ken Seddon

  - Jorge Alvarez Vicente, Sophie Tyrrell, Claire Boudie, Anne Schmidt
  - Sabine Möhle, Agata Mlonka, Stephen Osborne
  - Lisa Shearer, Matthew Currie, Ke Wang, Yiwen Xu

  - Collaboration with Prof. Rik Van Deun, Prof. Kristof Van Hecke, UGhent; Prof. Koen Binnemans, K.U. Leuven

  - Funding: EPSRC, Umicore, Petronas, DAAD, IAESTE, InvestNI

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