IONIC LIQUIDS
DFG – SPP 1191

Magnetic Ionic Liquids - Properties and Structures

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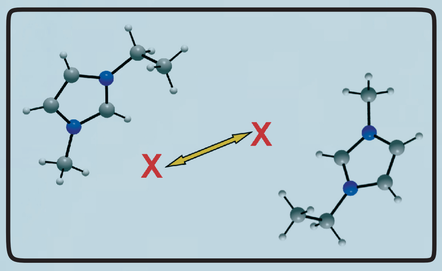
Magnetic Ionic Liquids: Goals

The goal of this research project is to contribute to the understanding of structure-property relations (interactions) of components of IL's with special emphasis on magnetic interactions as sketched in the enclosed figure. This goal shall be achieved through the synthesis, structure determination and thorough physico-chemical characterization (including theoretical calculations) of new IL's.



Magnetic Ionic Liquids: General Work Procedure

Three-step procedure:

1. **Synthesis of a variety of new IL's with magnetically prospective singly charged mononuclear complex anions of selected 3d metals and different cations.**
2. **Thorough physicochemical and structural characterization: Single crystal X-ray structure determination, magnetic measurements, melting point measurements, IR-, NMR-, mass-spectroscopy, elemental analysis, viscosity, surface-tension, density, vapour pressure measurements.**
3. **Quantum-chemical calculations to rationalize structure-property relations ("understanding"). Methods: quantum mechanical and Car-Parinello molecular dynamic simulations will be used to improve the *understanding*.**

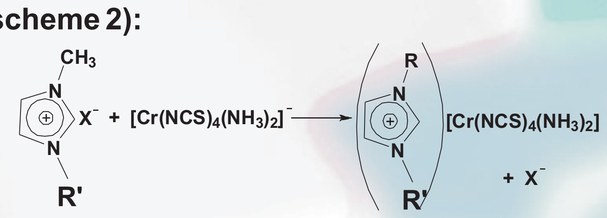
Synthesis of new IL's

Preparative work to synthesize new magnetic IL's has been focused on three groups of compounds:

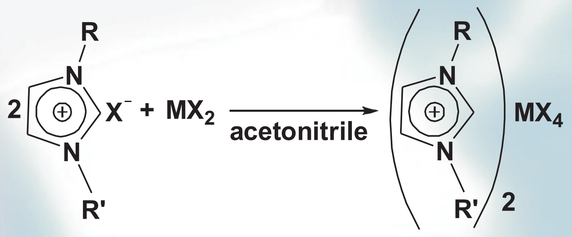
1) Derivatives of Reinecke salt with a variety of imidazolium-monocations
2)Tetrahalidesof Ni and Co with a variety of imidazolium-monocations
3) Tetrahalides of Ni and Co with a variety of imidazolium-dications

Schemes 1 and 2 show the principal synthetic procedures for group 1 (scheme 1) and group 2 and 3 (scheme 2):

Scheme 1:

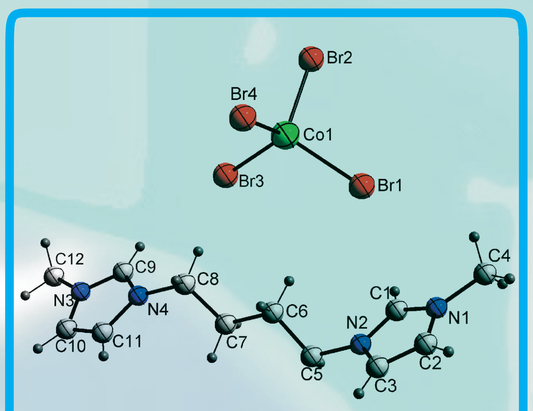


Scheme 2:

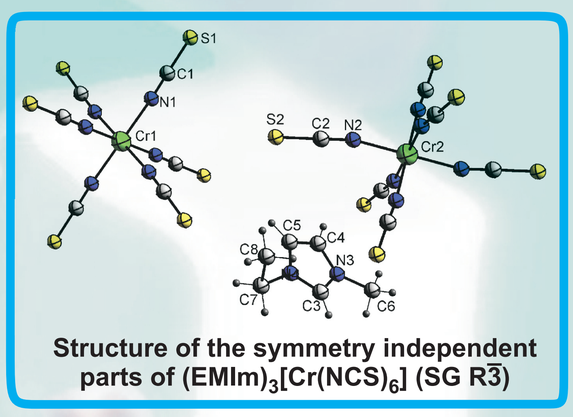


Crystal structures

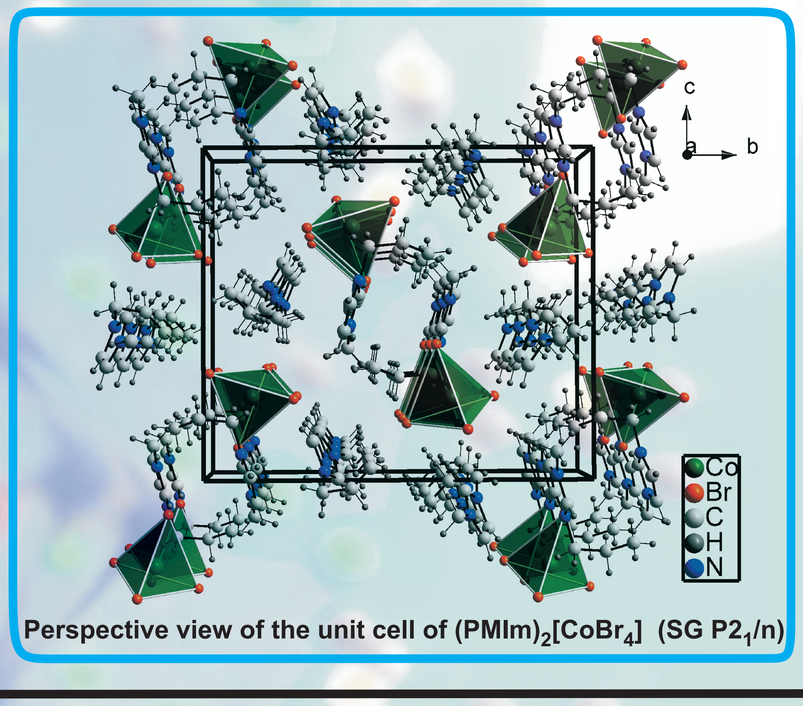
Continously (at low temperature) X-ray structures are determined, as soon as suitable single-crystals are availabale. Selected results are depicted below:



Structure of the symmetry independent parts of $(BMDIm)[CoBr_4]$ (SG $P2_1/c$)



Structure of the symmetry independent parts of $(EMIm)_3[Cr(NCS)_6]$ (SG $R\bar{3}$)



Perspective view of the unit cell of $(PMIm)_2[CoBr_4]$ (SG $P2_1/n$)

List of new IL's with paramagnetic metal-complexes

Group 1:

- **$NH_4[Cr(NCS)_4(NH_3)_2]$ (Reinecke salt, anhydrous)**
- **$(EMIm)_3[Cr(NCS)_6]$**
- **$(EMIm)[Cr(NCS)_4(bipy)]$, (bipy: 2,2'-bipyridine)**
- **$(BMIm)[Cr(NCS)_4(bipy)]$**
- **$(BenzMIm)[Cr(NCS)_4(bipy)]$**
- **(-picH)$[Cr(NCS)_4($ -picH$)_2]\cdot($ -pic), (-pic: -picoline)**
- **$(EMIm)[Cr(NCS)_4($ -picH$)_2]$**
- **$(BMIm)[Cr(NCS)_4($ -picH$)_2]$**

Group 2:

- **$(cation)_2[NiBr_4]$, with cation: EMIm, PMIm, BMIm**
- **$(cation)_2[CoBr_4]$, with cation: EMIm, PMIm, BMIm**

Group 3:

- **$(cation)[NiCl_4]$, with cation: EMDIm (3,3'-(ethane-1,2-diyl)-bis(1-methyl-imidazolium), PMDIm, HexMDIm, OctMDIm**
- **$(cation)[NiBr_4]$, with cation: EMIm, BMIm**
- **$(cation)[CoCl_4]$, with cation: EMDIm, PMDIm, HexMDIm, OctMDIm**
- **$(cation)[CoBr_4]$, with cation: EMDIm, BMDIm**

Magnetic Ionic Liquids: Properties

Of each of the synthesized materials UV/Vis-, IR-, and NMR-data, as well as melting points were measured.

Magnetic Ionic Liquids: Next steps

- **Magnetic measurements and their evaluation is in progress.**
- **IR- and Raman data in the FIR-region are planned.**
- **Theoretical calculations aiming for charge-distributions have been started on selcted members of this group of materials in order to correlate melting points with structural parameters.**

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