

	Experiment title: Copper containing ionic liquids for use in electrodeposition	Experiment number: 26-01 906		
Beamline: BM26A	Date of experiment: from: July 11 2010 to: July 15 2011	Date of report: December 2 2011		
Shifts: 9	Local contact(s): Sergey Nikitenko and Miguel Silveira	<i>Received at ESRF:</i>		
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Report:

We have been synthesising new metal containing ionic liquids that have the metal as part of the cation in view to using these liquids as electrolytes for electrodeposition of metals.^{1,2} The aim of this proposal was to investigate by XAS the structure of the copper cations in these ionic liquids.

Ionic liquids are solvents that consist entirely of ions. Typically they are low-melting organic salts and they can be liquid even at temperatures below room temperature. Ionic liquids have unique properties like an extremely low vapour pressure and an intrinsic electric conductivity. Because of their high electric conductivity and wide electrochemical window, ionic liquids are very suitable electrolytes that can be used for the electrodeposition of reactive metals that cannot be deposited from aqueous solution. For metals that can be electrodeposited from water ionic liquids offer nevertheless interesting possibilities because the morphology of a metal layer obtained in an ionic liquid is often different from one deposited from an aqueous solution. Moreover, it is possible to obtain from an ionic liquid alloys with compositions different from that formed in aqueous solution.

Due to problems of metal salt solubility in ionic liquids we are devising new metal containing ionic liquids. These have high metal ion concentrations and prove very good electrolytes for the electrodeposition of metals. For instance ionic liquids comprising a cation with a copper(I) centre ligated by four ligands in a tetrahedral arrangement can be considered as analogues of ammonium and phosphonium ionic liquids (see figure below). The rich variation in number and geometry of ligands around transition metal centres gives a large number of possible ionic liquids. In order to understand and characterise these fully, knowledge of the coordination geometry is particularly important.

Whilst we have crystal structures for some of these compounds others will not crystallise or are liquids so it is not possible to obtain information about the metal coordination sphere in this manner. This is where EXAFS is proving most useful. During our experimental time we were able to collect EXAFS data on over 20 samples despite a few setbacks with the machine crashing. So far our analysis has revealed that the spectra of the solid compounds of known structure compare well with that predicted from the coordination seen in the single crystal structure. For example in the compounds $[\text{Cu}(\text{BuIm})_4\text{Cl}][\text{Cl}]$ (black curve; BuIm = 1-butylimidazole) and $[\text{Cu}(\text{MeIm})_4][\text{Tf}_2\text{N}]_2$ (blue curve; MeIm = 1-methylimidazole, Tf_2N = bis(fluoromethyl)-sulfonylimide) the interatomic distances seen in the crystal structures (Figure 2) correspond well with the distances in the Fourier Transform (Figure 1). Thus, we are able to look at the compound $[\text{Cu}(\text{HexIm})_4][\text{Tf}_2\text{N}]_2$ (HexIm = 1-hexylimidazole), which is a liquid at room temperature, and compare the coordination environment to that of the known structures. These results are currently been written up to be submitted as a paper in the next 2-3 months.

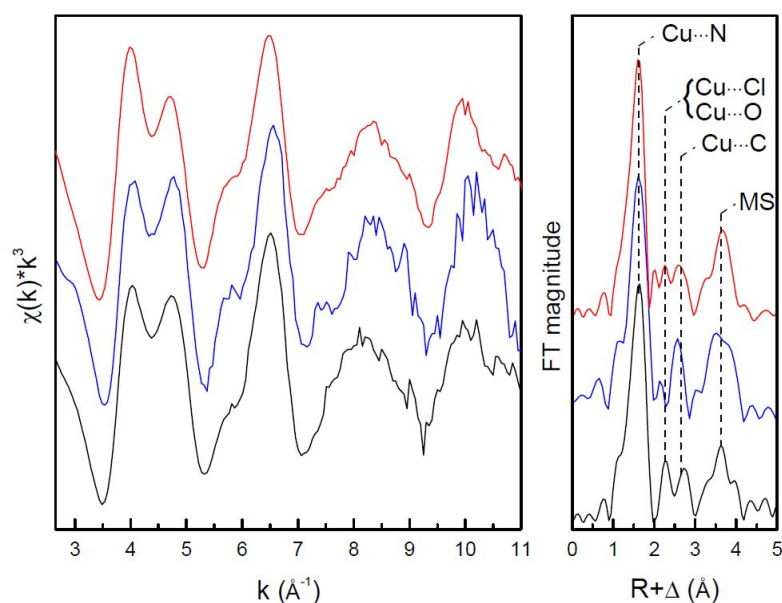


Figure 1: The graph shows three EXAFS spectra with corresponding Fourier Transforms of three Cu(II) imidazole complexes: $[\text{Cu}(\text{BuIm})_4\text{Cl}][\text{Cl}]$ (black curve), $[\text{Cu}(\text{MeIm})_4][\text{Tf}_2\text{N}]_2$ (blue curve) and $[\text{Cu}(\text{HexIm})_4][\text{Tf}_2\text{N}]_2$ (red curve).

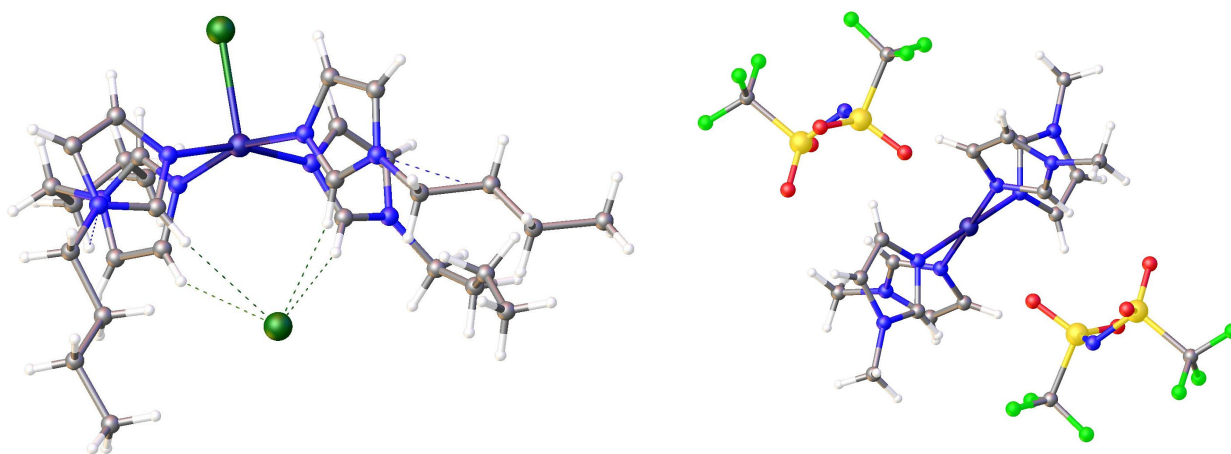


Figure 2: Solid state structures of $[\text{Cu}(\text{BuIm})_4\text{Cl}][\text{Cl}]$ (left) and $[\text{Cu}(\text{MeIm})_4][\text{Tf}_2\text{N}]_2$ (right).

References:

- [1] S. Schaltin, N. R. Brooks, K. Binnemans and J. Fransaer, *J. Electrochem. Soc.*, 2011, **158**, D21
- [2] N. R. Brooks, S. Schaltin, K. Van Hecke, L. Van Meervelt, K. Binnemans and J. Fransaer, *Chem. Eur. J.*, 2011, **17**, 5054