ESRF	**Experiment title:** Structurally directed approaches to designing out cyanide from metal plating	**Experiment number**: CH 4239
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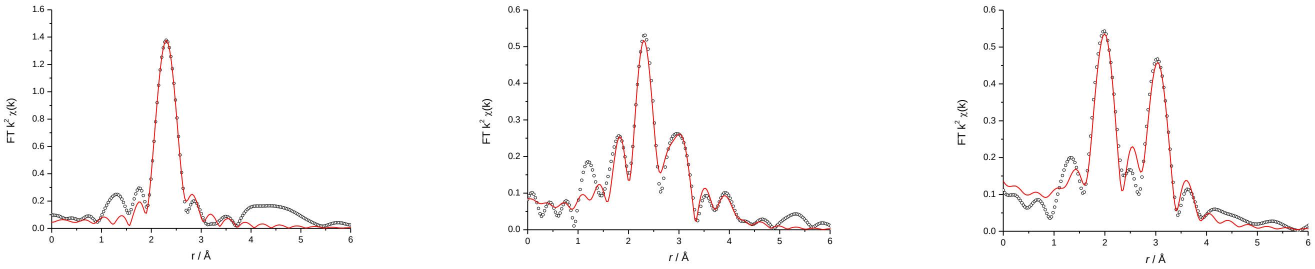
Report:

EXAFS spectra were acquired for gold, platinum, palladium and silver salts dissolved in eutectic mixtures created with choline chloride and hydrogen bond donors, such as urea or ethylene glycol, or in the ionic liquids 1-hexyl-3-methylimidazolium chloride and 1-ethyl-3-methylimidazolium thiocyanate. All samples were measured at room temperature. Solid salt samples were obtained for reference purposes.

Liquid samples were measured in both transmission and fluorescence mode, with the solid samples being measured in transmission mode and diluted in a cellulose matrix. The majority of the spectra were of good quality and glitch free, however major glitches were observed in two of the palladium spectra recorded with the fluorescence detector, at approx. 24410 and 24880-24950 eV. Small dips were present on gold transmission spectra before the edge at 11900 eV. These were not present in fluorescence data. Several of the metal salts under investigation were poorly soluble in the chosen solvents, however in the majority of cases, sufficient sample had dissolved in order to be measurable via EXAFS. Fluorescence data was generally noisier than transmission data. Large beam sizes (>2mm), which were tried to reduce the risk of radiation damage, significantly increased the noise level.

Metal-ligand distances were calculated to be 2.3 to 2.5 Å for M-Cl, 1.9 to 2.0 Å for M-C and 3.1 to 3.2 Å for M-N, which is consistent with both the solid reference samples and previous experimental data in comparable systems. Generally, as the initial proportion of cyanide present in the metal salt increased, a corresponding increase was observed in the amount of cyanide present in the metal species in solution. This occured in both the urea- and ethylene glycol-based liquids.

For the gold and silver samples, a coordination of 2 ligands was calculated, where speciation changed from $[MCl_2]^-$/$[MCl_3]^{2-}$ to [MCl(CN)] to $[M(CN)_2]^-$ with increasing cyanide concentration in solution. Changes in speciation are reflected in the electrochemical behaviour. With dicyanometallate sample, no ligand exchange was observed, despite the high chloride concentration in the ionic liquid.



Fourier transforms of the EXAFS data (black circles) and fits (red line) for AuCl (left), AuCN (middle) and $KAu(CN)_2$ (right) in 1:2 choline chloride :ethylene glycol.

Platinum(II) salts behaved in a similar manner to gold and silver, in that cyanide remained an integral component of the speciation of the metal salt in solution. The coordination was determined to be 4, where the proposed species are $[PtCl_4]^{2-}$, $Pt(CN)_2$ (poorly soluble) and $[Pt(CN)_4]^{2-}$. The only Pt(IV) salt studied, $PtCl_4$, could be fitted with 5xCl in both solvents.

Discrepancies were observed for the palladium cyanide salts. With 1:2 choline chloride : ethylene glycol as a solvent, three peaks are observed in the FT, similar to the Au, Ag, and Pt salts, which can be fitted to a coordination of 2xCl + 2xCN. In 1:2 choline chloride : urea, a single peak is observed, which can be fitted to a coordination of 4xCl.

In the ionic liquid Hmim-Cl metal salts exhibited lower coordination numerbs than in choline chloride based solvents. This may be explained with the lower polarity of the IL and is consistent with previous observations on copper salts.

These results have allowed us to understand how the proportion of cyanide in a metal salt has a direct effect on both the speciation and electrochemistry of the salt dissolved in DES media. Cyanide/chloride ligand exchange is no significant factor for the metal cyanide salts, despite the high (~5 M) chloride concentration in these solvents.