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Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

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Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

![ESRF logo]	**Experiment title:** Using NEXAFS spectroscopy to probe metal speciation in solution: to what extent does competitive complexation occur?	**Experiment number**: CH-4360
Beamline: BM25A	**Date of experiment**: from: 08 July 2015 at 08:00 to: 12 July 2015 at 08:00	**Date of report**: 05/09/2016
Shifts: 12	**Local contact(s)**: German Rafael CASTRO	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr Kevin Lovelock* Imperial College London

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Report:

The speciation of a metal solute in a solvent is crucial to its dissolution and potential performance in many applications, *e.g.* catalysis. We investigated the effect of the anions on the speciation of a metal cation solute using NEXAFS spectroscopy for a carefully-selected series of transition metal (TM) salts in ionic liquid solvents.
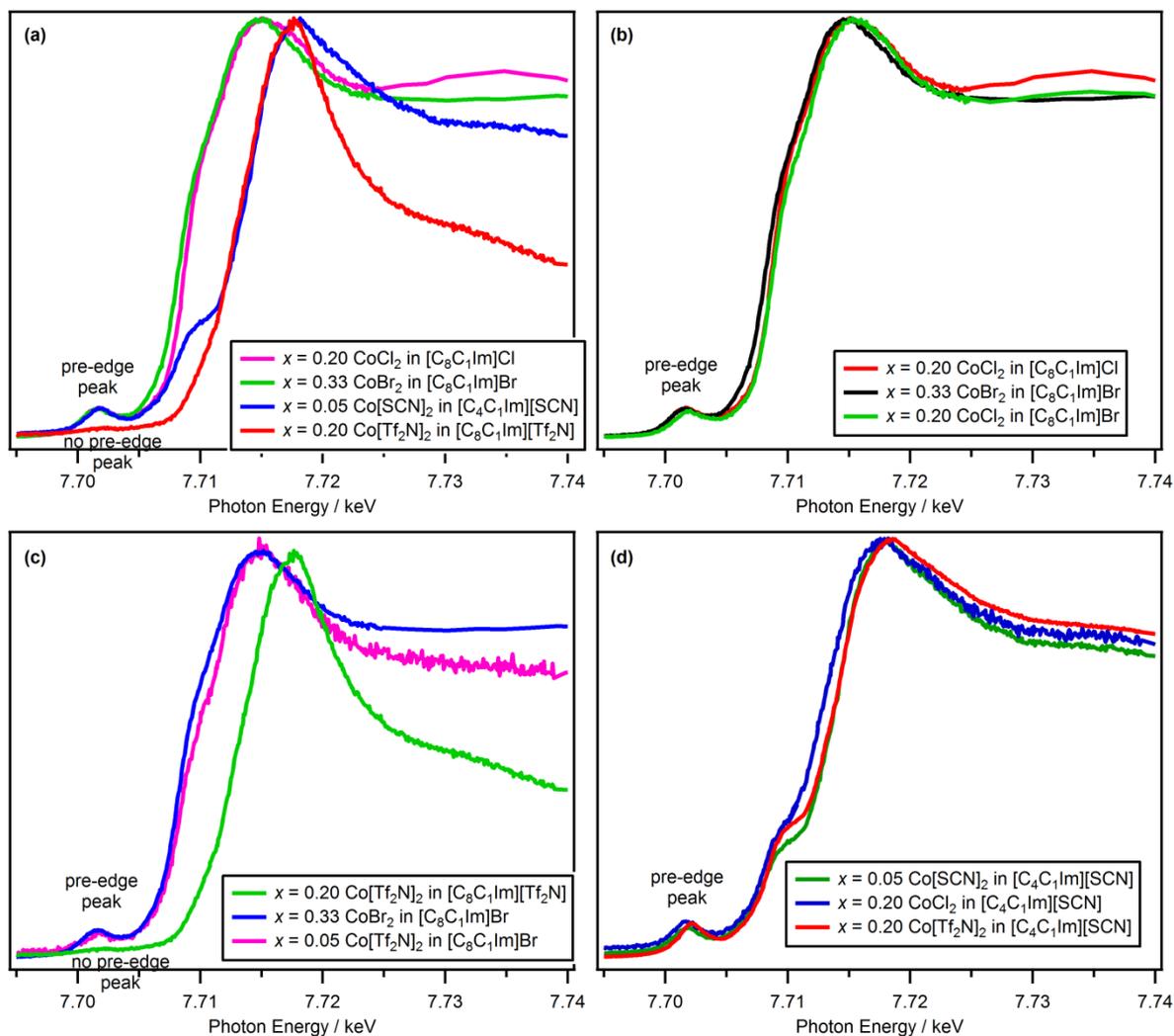
Figure 1a shows four solutions where only one anion was present in solution, as both the ionic liquid and the metal salt contain the same anion, *e.g.* $Co[SCN]_2$ and $[C_4C_1Im][SCN]$. Therefore, for these four solutions it is known which anion complexes to the Co^{2+}. Consequently, these four solutions represent fingerprint reference NEXAFS spectra for the cobalt complexes in solution.

These fingerprint NEXAFS spectra are generally very distinct for different metal complexes. The most important feature is the pre-edge peak at ~7701.8 eV, which results from excitation to molecular orbitals with primarily d-type character (with some p-character). Pre-edge transitions are forbidden if the cobalt atom is in a centrosymmetric environment; symmetry prevents d and p orbital mixing, and transitions to a purely d-type orbital are forbidden. Therefore the presence of a pre-edge peak suggests that $[CoCl_4]^{2-}$, $[CoBr_4]^{2-}$ and $[Co(NCS)_4]^{2-}$ complexes are non-centrosymmetric, and therefore most likely tetrahedral. For $[CoCl_4]^{2-}$ this finding is in agreement with UV spectra[1] and Co 1s NEXAFS spectra[2]. $Co[Tf_2N]_2$ dissolved in $[C_8C_1Im][Tf_2N]$ did not show a significant pre-edge peak at ~7701.8 eV (Figure 3a). Therefore, $Co[Tf_2N]_2$ dissolved in $[C_8C_1Im][Tf_2N]$ forms a centrosymmetric octahedral complex in solution, strongly suggesting that the metal complex in solution is $[Co(Tf_2N)_3]^-$.

NEXAFS spectra for $[CoBr_4]^{2-}$ in solution and $[CoCl_4]^{2-}$ in solution were similar in both shape and edge energy (Figure 1b). For the solution $x = 0.20$ $CoCl_2$ dissolved in $[C_8C_1Im]Br$, the anion formed could be $[CoBr_4]^{2-}$, $[CoCl_4]^{2-}$ or a mixture of Br and Cl ligands. Clearly, the Co 1s NEXAFS spectra cannot be used to determine ligand competition between Cl and Br (Figure 1b). It also appears that different x do not significantly impact upon the shape of the NEXAFS spectra, at least for halide ligands.

Co[Tf$_2$N]$_2$ dissolved in [C$_8$C$_1$Im]Br showed a very similar NEXAFS spectrum to the NEXAFS spectrum for [CoBr$_4$]$^{2-}$ in solution, and a very different NEXAFS spectrum to the NEXAFS spectrum for [Co(Tf$_2$N)$_3$]$^-$ in solution (Figure 1c); most importantly, there was no pre-edge peak for Co[Tf$_2$N]$_2$ dissolved in [C$_8$C$_1$Im]Br. Therefore, we can conclude that Co[Tf$_2$N]$_2$ dissolved in [C$_8$C$_1$Im]Br formed [CoBr$_4$]$^{2-}$ in solution, with free [Tf$_2$N]$^-$ anions. Therefore, Br$^-$ complexes more strongly to Co^{2+} than [Tf$_2$N]$^-$.

NEXAFS spectra for either CoCl$_2$ or Co[NTf$_2$]$_2$ dissolved in [C$_4$C$_1$Im][SCN] (x=0.2) were very similar, in both shapes and edge energies, to the NEXAFS spectrum for [Co(NCS)$_4$]$^{2-}$ in solution (Figure 1d). Therefore, [SCN]$^-$ complexes more strongly to Co^{2+} than [Tf$_2$N]$^-$, and [SCN]$^-$ complexes more strongly to Co^{2+} than Cl$^-$.

Figure 1. Co 1s NEXAFS spectra for: (a) $x = 0.20$ CoCl$_2$ dissolved in [C$_8$C$_1$Im]Cl, $x = 0.33$ CoBr$_2$ dissolved in [C$_8$C$_1$Im]Br $x = 0.20$ Co[SCN]$_2$ dissolved in [C$_4$C$_1$Im][SCN] and $x = 0.20$ Co[Tf$_2$N]$_2$ dissolved in [C$_8$C$_1$Im][Tf$_2$N]. (b) $x = 0.20$ CoCl$_2$ dissolved in [C$_8$C$_1$Im]Cl, $x = 0.33$ CoBr$_2$ dissolved in [C$_8$C$_1$Im]Br and $x = 0.20$ CoCl$_2$ dissolved in [C$_8$C$_1$Im]Br. (c) $x = 0.05$ Co[Tf$_2$N]$_2$ dissolved in [C$_8$C$_1$Im]Br, $x = 0.33$ CoBr$_2$ dissolved in [C$_8$C$_1$Im]Br and $x = 0.20$ Co[Tf$_2$N]$_2$ dissolved in [C$_8$C$_1$Im][Tf$_2$N]. (d) $x = 0.20$ Co[SCN]$_2$ dissolved in [C$_4$C$_1$Im][SCN], $x = 0.20$ CoCl$_2$ dissolved in [C$_4$C$_1$Im][SCN] and $x = 0.20$ Co[Tf$_2$N]$_2$ dissolved in [C$_4$C$_1$Im][SCN].

(**1**) S. Schaltin *et al.*, *Electrochem. Solid State Lett.*, 2007, **10**, D104.
(**2**) Y. T. Hsieh *et al.*, *Electrochim. Acta*, 2014, **117**, 217.