

## 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.**

Once completed, the report should be submitted electronically to the User Office via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

### ***Reports on experiments relating to long term projects***

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

### ***Published papers***

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

### **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.



	<b>Experiment title:</b> Using NEXAFS spectroscopy to probe cobalt speciation in solution: relating thermochromism to electronic structure	<b>Experiment number:</b> CH-5045
<b>Beamline:</b> BM28	<b>Date of experiment:</b> from: 24 June 2017 to: 27 June 2017	<b>Date of report:</b> 26/02/2018
<b>Shifts:</b> 9	<b>Local contact(s):</b> BOUCHENOIRE Laurence	<i>Received at ESRF:</i>

**Names and affiliations of applicants** (\* indicates experimentalists):

Dr. Kevin Lovelock\* (University of Oxford, now University of Reading)

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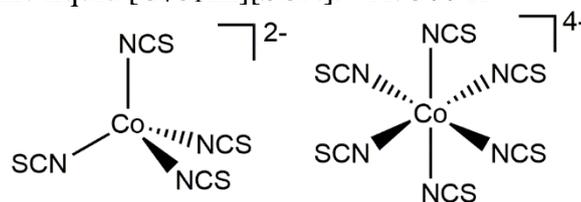
Rebecca Rowe (Imperial College London)

Dr. Tricia Hunt (Imperial College London)

Dr. Nick Besley (University of Nottingham)

**Report:**

Thermochromism, the property of a substance that changes colour due to a change in temperature,<sup>1</sup> has been demonstrated for the  $d^7$   $\text{Co}^{2+}$  salt,  $\text{Co}(\text{NCS})_2$ , dissolved in the ionic liquid  $[\text{C}_4\text{C}_1\text{Im}][\text{SCN}]$ .<sup>2</sup> At 300 K  $\text{Co}(\text{NCS})_2$  (mole fraction,  $x \leq 0.2$ ) dissolved in  $[\text{C}_4\text{C}_1\text{Im}][\text{SCN}]$  forms the tetrahedral metal complex  $[\text{Co}(\text{NCS})_4]^{2-}$ , giving a red colour (Figure 1). When cooled to  $\sim 233$  K, the octahedral metal complex  $[\text{Co}(\text{NCS})_6]^{4-}$  is formed, giving a blue colour (Figure 1). This system has been characterised using temperature-dependent UV-Vis absorption spectroscopy and magnetic susceptibility measurements, but not electronic structure measurements/calculations.<sup>2</sup> In these experiments, we have characterised the singly occupied and unoccupied molecular orbitals of both  $[\text{Co}(\text{NCS})_4]^{2-}$  and  $[\text{Co}(\text{NCS})_6]^{4-}$  in solution. These results form part of a larger collection of beamtime submissions and laboratory-based measurements on the electronic structure of cobalt complexes in solution. We are aiming to build up a complete picture of the electronic structure of both  $[\text{Co}(\text{NCS})_4]^{2-}$  and  $[\text{Co}(\text{NCS})_6]^{4-}$  in solution.



**Figure 1.** Structures of the two metal complexes to be investigated.

**Experimental.** Co 1s NEXAFS spectra were recorded at a wide range of temperatures,  $200 \text{ K} < T < 300 \text{ K}$ . Examples of low  $T$ , corresponding to  $[\text{Co}(\text{NCS})_6]^{4-}$ , and high  $T$ , corresponding to  $[\text{Co}(\text{NCS})_4]^{2-}$ , are given in Figure 2. These different complexes were readily differentiated from the NEXAFS spectra (Figure 2), but the expected colour changes were also observed. Due to the constraints in length of this report, the NEXAFS spectra for intermediate  $T$  values (showing the transition from tetrahedral to octahedral metal complexes) are not presented here, but were recorded. The clearest difference is presence of a significant pre-peak at  $\sim 7709$  eV for the  $[\text{Co}(\text{NCS})_4]^{2-}$  complex, which is not observed for  $[\text{Co}(\text{NCS})_6]^{4-}$ . These observations are discussed further below with regard to TD-DFT calculations. Due to apparatus constraints, an S 1s NEXAFS spectrum was recorded only at  $T = 300 \text{ K}$ , corresponding to  $[\text{Co}(\text{NCS})_4]^{2-}$ ; for comparison the S 1s NEXAFS spectrum

for the non-Co containing IL  $[\text{C}_4\text{C}_1\text{Im}][\text{SCN}]$  was also recorded. The S 1s NEXAFS spectra for these two ILs were subtly different (not shown here for space reasons), and TD-DFT calculations are currently being performed to understand these differences.

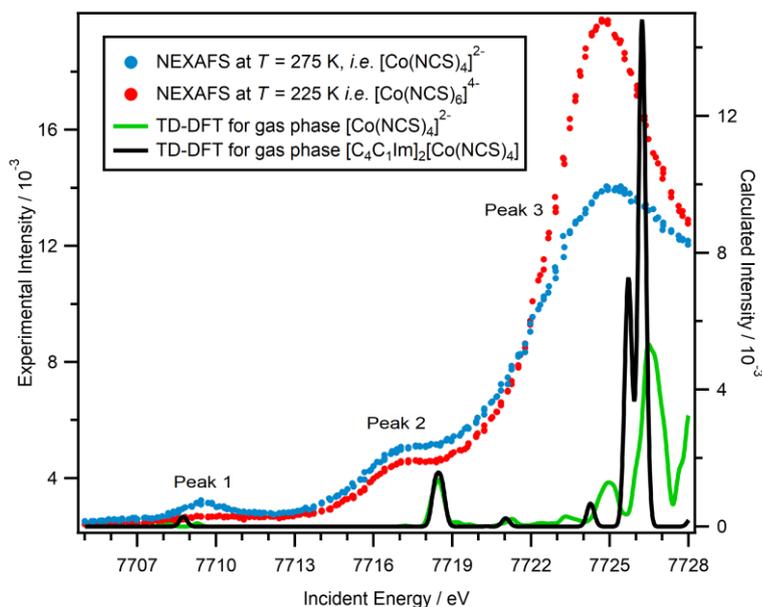
**TD-DFT calculations.** Structural calculations for the  $[\text{Co}(\text{NCS})_4]^{2-}$  complex were performed by the group of Tricia Hunt and TD-DFT calculations were performed on these structures by Nick Besley (TD-DFT calculations for the  $[\text{Co}(\text{NCS})_6]^{4-}$  complex are on-going). The overall match to the experimental data is excellent; no energy-scale shifts were applied to the calculated NEXAFS spectra. In particular, the peak-to-peak energy separations in the experimental and calculated NEXAFS spectra match very well, demonstrating the high quality of the TD-DFT calculations performed. Peak 1 corresponds to excitation of beta 1s electrons to singly occupied orbitals. These orbitals are predominantly localised on Co and have d character (Figure 3).

However, these orbitals also have some p character. Pre-edge transitions are forbidden if the Co atom is in a centrosymmetric environment; symmetry prevents d and p orbital mixing, and transitions to a purely d-type orbital are forbidden. The  $[\text{Co}(\text{NCS})_4]^{2-}$  complex is tetrahedral, and therefore non-centrosymmetric, allowing such transitions and giving rise to a pre-peak. The intensity of this pre-peak for the  $[\text{Co}(\text{NCS})_6]^{4-}$  complex is very small (Figure 2), as expected for this highly centrosymmetric octahedral complex. Peak 2 was observed for both  $[\text{Co}(\text{NCS})_4]^{2-}$  and  $[\text{Co}(\text{NCS})_6]^{4-}$  complexes. For the TD-DFT calculations, this peak was observed both with and without the presence of cationic counterions. Peak 2 corresponds to excitation to unoccupied orbitals composed of a mixture of Co d and ligand  $\pi^*$  orbitals. For the isolated anion (*i.e.* those without cationic counterions), peak 3 has two distinct components. These two bands correspond to excitation to the same unoccupied orbitals; the lower energy band arises from excitation of alpha electrons while the higher energy band corresponds to excitation of the beta electrons. The unoccupied orbitals contain contributions from both ligand  $\sigma^*$  and Co p orbitals. The significant contribution of Co p orbitals explains the relatively large calculated intensities.

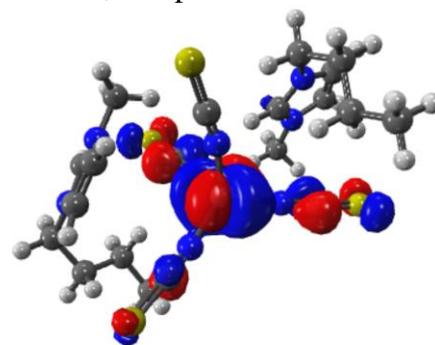
Our experimental results provide a fundamental benchmark for NEXAFS calculations, which is currently lacking. For our TD-DFT calculations, the addition of explicit counteranions change details of the outputs, but not the big picture, demonstrating that, once experimental NEXAFS data has been recorded TD-DFT calculations on one gas phase ion is sufficient to capture the electronic environment of the metal complex, at least to a first approximation.

During this beamtime we also measured NEXAFS spectra for a range of Pd-containing catalysts. These results have already led to a publication.<sup>3</sup>

(1) M. A. White, *et al.*, *J. Chem. Educ.*, 1999, **76**, 1201. (2) S. J. Osborne, *et al.*, *Dalton Trans.*, 2015, **44**, 11286. (3) S. Doherty, *et al.*, *Catal. Sci. Technol.*, 2018, DOI: 10.1039/C7CY02557B.



**Figure 2.** Experimental Co 1s NEXAFS spectra for  $[\text{Co}(\text{NCS})_4]^{2-}$  and  $[\text{Co}(\text{NCS})_6]^{4-}$ . Calculated TD-DFT Co 1s NEXAFS spectra for gas phase  $[\text{Co}(\text{NCS})_4]^{2-}$  and gas phase  $[\text{C}_4\text{C}_1\text{Im}]_2[\text{Co}(\text{NCS})_4]$  (*i.e.* 3 ions). No shifts were applied to the calculated NEXAFS spectra.



**Figure 3.** An MO that gives rise to peak 1, with significant Co d orbital contributions.