

## 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 using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

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

Reports can now 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> Understanding gas-solid reactions involving nonporous crystals: a continuation		<b>Experiment number:</b> CH-3025
<b>Beamline:</b>  ID31	<b>Date of experiment:</b> from: 11Mar10 to: 15Mar10 from: 15Dec10 to: 20Dec10	<b>Date of report:</b>  30/08/12
<b>Shifts:</b>  33	<b>Local contact(s):</b> Dr Adrian Hill  Dr Caroline Curfs	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): *Prof. Lee BRAMMER, University of Sheffield, UK *Mr. Paul SMART, University of Sheffield, UK *Mr. Iñigo VITORICA-YREZABAL, University of Sheffield, UK *Mr Jason LOADER, University of Sheffield, UK		

## Report: Experiment CH-3025

The focus of the this experiment was the *in situ* monitoring of either gas sorption by porous materials or reactions of non-porous materials with gases.

The latter involves reactions two families of metal-organic coordination compounds with either HCl or HBr gas. These studies represent a continuation and extension of previous work<sup>[1-3]</sup> conducted at beamline ID31 and complements ongoing spectroscopic studies in Sheffield. The reactions themselves are quite unusual involving insertion of the HCl or HBr molecules into the Cu–N bonds of coordination compound of the form *trans*-[CuX<sub>2</sub>(n-Xpy)<sub>2</sub>] (X = Cl or Br and n = 3 or 4). The reactions are in fact reversible and represent a solid-gas equilibrium in which crystallinity of the non-porous solid is maintained. Current studies are aimed at addressing mechanistic questions, by exploiting small differences in behaviour between chloro and bromo compounds, between different isomers of the halopyridine ligands (n = 3 or 4) and between reactions with HCl and those with HBr gas.

A gas-handling apparatus designed and built at ESRF was used to connect a lecture bottle of HCl or HBr gas to a capillary containing the sample in each study, provding a sealed system. The apparatus allows for a limited (ca. 90 °) rotation of the capillary to minimise the effects of preferred orientation upon the pattern. This apparatus has undergone a number of design modifications during a series of visits we have made to ID31 to conduct experiments of this type.

Six separate reactions were studied in full, two involving reaction with HCl gas and four involving reaction with HBr gas. Reactions with HCl focussed on two aspects, firstly reaction with [CuCl<sub>2</sub>(4-Clpy)<sub>2</sub>], which enabled studies of the recation of HCl and it subsequent role in promoting a phase transition of the product to a new polymorph. The work has since been published in a special issue of the RSC journal *CrystEngComm* on solid-state reactions.<sup>[4]</sup> The second study involved reaction of [CuBr<sub>2</sub>(4-Clpy)<sub>2</sub>] with HCl gas leading to a product with mixed halides (Cl/Br) at the metal. Data quality was sufficient to establish that a non-random distribution of the halides was present at the four sites. The distribution could be rationalise do the basis of the strength of intermoelcular interactions involving these halide liagnds (hydrogen bonds and halogen

bonds). The reaction is accompanied by a colour change and a subsequent phase transition as illustrated in Figure 1.

## CuBr<sub>2</sub>(4-Clpy)<sub>2</sub> HCl uptake

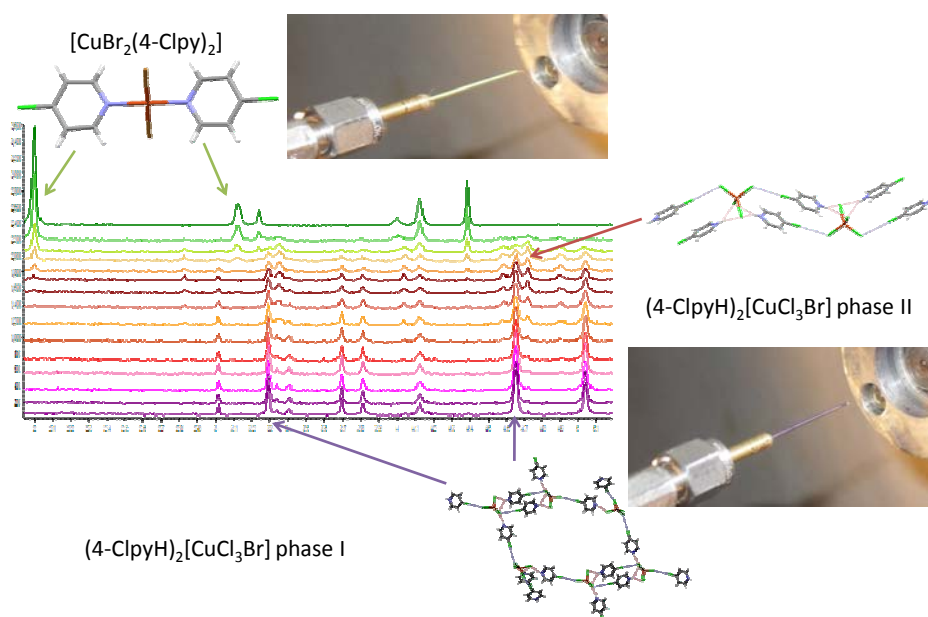


Figure 1. Summary of in situ XRPD study of gas-solid reaction between [CuBr<sub>2</sub>(4-Clpy)<sub>2</sub>] with HCl gas

The four studies involving HBr gas focussed on reactions with both chloride and bromide-containing coordination compounds and revealed that reactivity of HBr with metal chloride differs significantly from reaction of HCl with metal bromides.

Collectively, the studies are enabling us to build up a detailed understanding of these unusual gas-solid reactions, which is important in itself. More importantly, for the future, it allows us to apply this understanding to designing new reactions in other classes of materials and to take advantage of the experimental techniques and protocols developed in order to more effectively study a wider range of reactions. We hope in future to study such reactions *in situ* using the gas handling apparatus at ID31 and thereby further explore solid-state materials synthesis.

A number of *in situ* and *ex situ* studies of ligand addition and ligand replacement reaction in metal-organic frameworks were also undertaken. These resulted in a number of cases in data of sufficient quality to allow *ab initio* structure determination, which is very challenging for these periodic porous materials. Extensive model building has been required in order to establish the structures of a number of these materials. The work provides a significant portion of a PhD thesis chapter for Paul Smart and is currently being written up for publication.

[1] "Reversible extrusion and uptake of HCl molecules by crystalline solids involving covalent bond cleavage and formation," G. Mínguez Espallargas, L. Brammer, J. van de Streek, K. Shankland, A. J. Florence and H. Adams, *Journal of the American Chemical Society*, **2006**, 128, 9584-9585.

[2] "Reversible gas uptake by a non-porous crystalline solid involving multiple changes in covalent bonding," G. Mínguez Espallargas, M. Hippler, A. J. Florence, P. Fernandes, J. van de Streek, M. Brunelli, W. I. F. David, K. Shankland and L. Brammer\*, *Journal of the American Chemical Society*, **2007**, 129, 15606-15614.

[3] "Mechanistic Insights into a Gas-Solid Reaction in Molecular Crystals: The Role of Hydrogen Bonding," G. Mínguez Espallargas, J. van de Streek, P. Fernandes, A. J. Florence, M. Brunelli, K. Shankland and L. Brammer\*, *Angewandte Chemie International Edition*, **2010**, 49, 8892-8896.

[4] "Synthesis and polymorphism of (4-ClpyH)<sub>2</sub>[CuCl<sub>4</sub>]: solid-gas and solid-solid reactions," I. J. Vitorica-Yrezabal, R. A. Sullivan, S. L. Purver, C. Curfs, C. C. Tang and L. Brammer, *CrystEngComm*, **2011**, 13, 3189-3196.