



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.



	Experiment title: Understanding gas-solid reactions involving nonporous crystals	Experiment number: CH-2700
Beamline: ID31	Date of experiment: from: 24Sep08 to: 27Sep08 from: 05Feb09 to: 09Feb09	Date of report: 29/03/10
Shifts: 12 + 12	Local contact(s): Dr Michela Brunelli and Prof. Andy Fitch	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):

- *Prof. Lee BRAMMER, University of Sheffield, UK
- *Dr. Guillermo MINGUEZ, University of Sheffield, UK
- *Mr. Charles MASON, University of Sheffield, UK
- *Mr. Paul SMART, University of Sheffield, UK
- *Mr. Iñigo VITORICA-YREZABAL, University of Sheffield, UK

Report: Experiment CH-2700

Two visits of 6 shifts each was requested to address the original project. This was extended to two visits, each of 12 shifts, through allocation of personal research time by principal scientist Prof Andy Fitch in conjunction with an EPSRC funded collaboration that supports a 4-year PhD studentship. Studies of reactions of molecular crystalline solids with HCl gas were conducted together with reactions of a silver(I) carboxylate coordination polymer. These studies occupied over half of the total time and represent the core experiments originally proposed. The remaining time was devoted to experiments that further extend the methodology used in these two model systems to a family of porous materials known as metal-organic frameworks (MOFs), which are highly actively studied worldwide for their potential applications in gas storage, chemical separations and catalysis.

In our earlier successes at ID31 where we were able to show that the molecular coordination compound *trans*-[CuCl₂(3-halopyridine)₂] on mild heating loses two equivalents HCl (g), requiring cleavage of Cu–Cl and N–H bonds, as well as N–H···Cl(Cu) hydrogen bonds, and formation of new Cu–N coordination bonds.¹

In experiment CH-2700 we tried to extend this approach to a range of simple organic compounds, and in particular made use of the gas handling apparatus at ID31 to expose samples to HCl gas and monitor changes in the powder pattern. However, none of the samples examined, although known to readily react with HCl in solution, showed changes associated with gas-solid reactions. Given the range of coordination compounds that we and others have now established as undergoing such gas-solid reactions, the lack of reaction was surprising and warrants further investigation. Our prior work involving coordination compounds will still result in a number of publications as we complete other (spectroscopic) studies that complement the powder diffraction work.² These results have specifically led to a number of invitations to speak at international conferences (in the USA, UK and South Africa in 2009) and recently resulted in the award of the Royal Society of Chemistry Dalton Young Investigator Award for Dr. Guillermo Mínguez Espallargas for his PhD work on these studies,³ which follows two other international awards he has received based upon this work.

The second family of compounds studied were a family of coordination polymers in which silver perfluorocarboxylate units are linked via tetramethylpyrazine (TMP) ligands. We reported that these materials were able to reversibly take up or extrude ethanol involving a change in coordination environment at silver centres, in part based upon powder diffraction studies at ID31.⁴ (Fig. 1). We have since been able to extend these studies to include analogous reactions involving different alcohols. Our studies during CH-2700 focussed on further developing this work and trying to understand the scope of these reactions, through a series of co-grinding reactions (mechanochemistry) in the presence or absence of vapours of different alcohols.

Similar co-grinding studies in the presence of other ligands. Formation of a mixture of products, some of which could be identified from the diffraction data provided useful information on the solid-state behaviour of these materials.

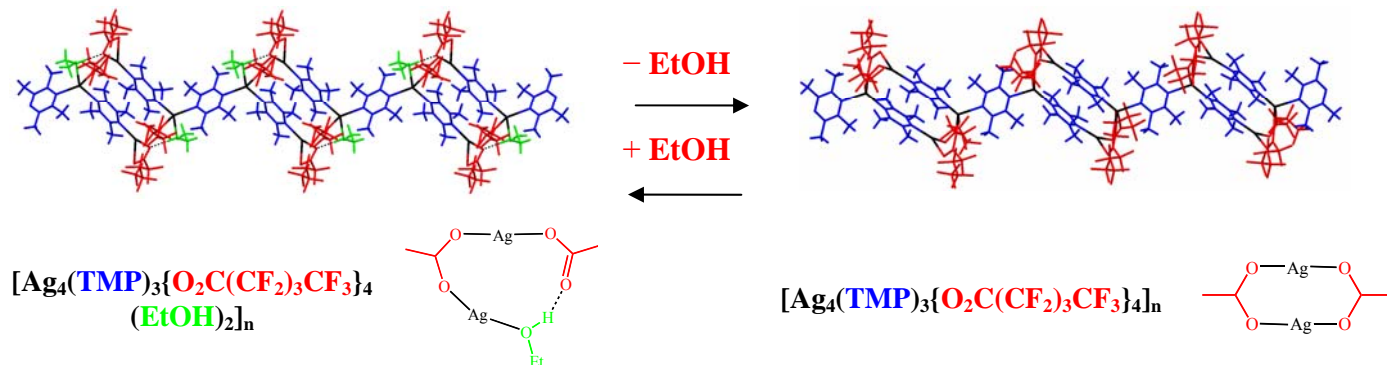


Fig. 1. Reversible insertion/deinsertion of ethanol into/from the Ag–O bond of a non-porous crystalline coordination polymer.

The final family of compounds studied were metal-organic frameworks based upon layers comprising Zn^{2+} ions linked via dicarboxylate ligands. In particular we investigated a series of reactions that enable new ligands to be inserted into MOFs and show promise for future synthesis of more complex and diverse MOFs. These studies follow up on laboratory powder diffraction and spectroscopic studies we have conducted. A highlight of these studies was that we were able to demonstrate clearly by powder diffraction that such reactions take place. We were also able to index the pattern of the product and with the aid of computational modelling were able to solve its structure and conduct a successful Rietveld refinement (Fig. 2).

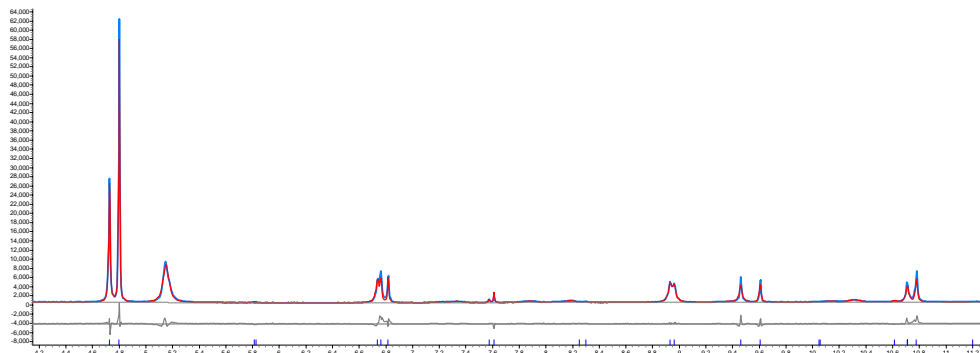


Fig. 2. Rietveld fit for solid-state MOF reaction product.

[1] “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.

[2] “Understanding the mechanism of gas uptake by a non-porous crystalline solid: hydrogen bonding directs the uptake of HCl,” G. Mínguez Espallargas, J. van de Streek, P. Fernandes, A. J. Florence, M. Brunelli, K. Shankland and L. Brammer*, *Angewandte Chemie International Edition*, **2010**, in preparation.

[3] See <http://www.rsc.org/ConferencesAndEvents/RSCEvents/PrizeAwardEvents/Minguez/index.asp> and <http://www.rsc.org/ScienceAndTechnology/Awards/DaltonYoungResearchersAward/2009winner.asp>

[4] “Ligand substitution within non-porous crystals of a coordination polymer involving extrusion from or insertion into Ag–O bonds by alcohol molecules,” S. Libri, M. Mahler, G. Mínguez Espallargas, D. C. N. G. Singh, J. Soleimannejad, H. Adams, M. D. Burgard, N. P. Rath, M. Brunelli and L. Brammer*, *Angewandte Chemie International Edition*, **2008**, *47*, 1693-1697.