

## 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:** Reversible extrusion and uptake of gas-phase small molecules by crystalline solids involving metal-ligand bond cleavage and formation

**Experiment number:**  
CH-2257

<b>Beamline:</b> ID31	<b>Date of experiment:</b> from: 30Nov06 to: 02Dec06 from: 16Apr07 to: 20Apr07	<b>Date of report:</b> 29/02/08  <i>Received at ESRF:</i>
	<b>Shifts:</b> 6 + 9	

**Local contact(s):** Dr Michela Brunelli

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

Dr. Lee BRAMMER, University of Sheffield, UK

Prof. William I.F. DAVID, ISIS, Rutherford Appleton Laboratory, UK

Mr. Guillermo MINGUEZ, University of Sheffield, UK

Dr. Kenneth SHANKLAND, ISIS, Rutherford Appleton Laboratory, UK

Dr Jacco VAN DE STREEK, Cambridge Crystallographic Data Centre, UK

**Report:** Experiment CH-2257 was a great success, indeed well beyond what we had anticipated. The experimental work conducted over two visits to ESRF for six and then nine shifts focussed a family of compounds that we had discovered were able to undergo a reversible reaction involving loss or uptake of HCl (Fig. 1). Remarkably these reactions occur within *non-porous* microcrystalline materials. Thus, there is not only an unexpected capacity for migration of HCl through the crystals but dramatic changes in the molecular moieties and crystal structure results from the chemical reaction leading to release or incorporation of HCl. Specifically salts such 3-halopyridinium tetrachlorocuprate containing two planar cations and a distorted tetrahedral anion and converted to a square planar coordination complex *trans*-[CuCl<sub>2</sub>(3-halopyridine)<sub>2</sub>] on loss of two equivalents HCl, requiring cleavage of Cu–Cl and N–H bonds, as well as N–H...Cl(Cu) hydrogen bonds, and formation of

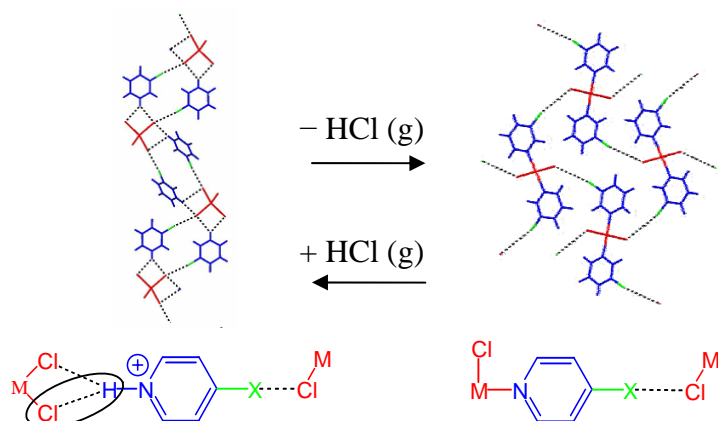


Figure 1. Interconversion of halopyridinium salt (3-XpyH)<sub>2</sub>[CuCl<sub>4</sub>] (left) and halopyridine complex *trans*-[CuCl<sub>2</sub>(3-Xpy)<sub>2</sub>] (right).

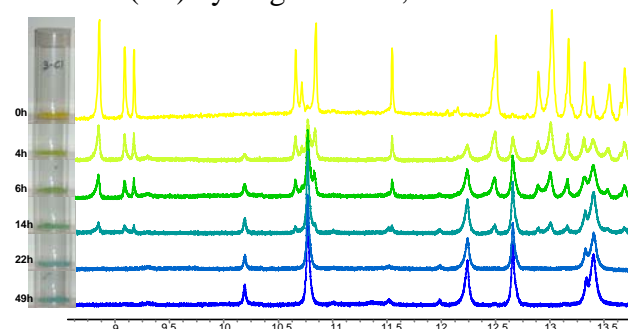


Figure 2. Samples from the *ex situ* reaction study showing the change in colour over time as (3-XpyH)<sub>2</sub>[CuCl<sub>4</sub>] (yellow) is converted to **2** (blue) through extrusion of gaseous HCl (left) together with the corresponding synchrotron X-ray powder patterns (T = 100 K).

new Cu–N coordination bonds. The reverse process occurs upon re-uptake of HCl. Prior to the work at ESRF we had been done some preliminary work at SRS and using a laboratory diffractometer to establish that HCl could be removed or added as an aqueous vapour. However, we knew nothing of the reaction rate, the possible involvement of intermediate species or if the uptake reaction could occur in the absence of water.

Studies of the reactions both in situ and ex situ using ID31 enabled us to establish the reate of reaction and helped establish that the reaction is an equilibrium process. The in situ experiments at modest elevated temperatures (370 K) were possible only because of the high flux and resolution provided by ID31. These characteristics also enabled us to suggest that no crystalline intermediate was formed during the recations. Highly significantly we were able to establish that the uptake reaction can take place in the absence of water since an experimental design provided by the station scientists permitted high quality powder pattenrens to be obtained using a rotating capillary connected to a cylider supply of dry HCl gas. These studies were published as a full paper in *Journal of the American Chemical Society* [1] for the system  $(3\text{-ClpyH})_2[\text{CuCl}_4] / \text{trans-}[\text{CuCl}_2(3\text{-Clpy})_2]$  (3-Clpy = 3-chloropyridine) together with gas phase infra-red spectroscopy studies. Similar diffraction studies were also conducted on the 4-chloropyridine derivative and following completion of spectroscopic studies we expect to publishe this work also. Some preliminary studies were then conducted during the second visit on related compounds that require loss or uptake of HBr gas. Initial results show similar behaviour, but some marked differences, wherein isostructural bromo and chloro-substituted compounds are converted into non-isostructural compounds following the previously described reactions. The relationship to water may also be different form the bromo derivatives. We also obtained some preliminary results on mixed halide systems that we are using to exlore mechanistic aspects of the reactions since such reactions are not only rare but poorly understood. Some of this work can be published but other results will await further studies before inclusion in publications. These experiments on the bromo derivatives stringly indicate that further study and choice of the right experiments could lead to a significantly greater understanding of these unusual reactions. A proposal will be submitted to develop these projects further will be submitted and could lead to major breakthroughs in the understanding of these reactions, which have implications in understanding recation processes in a wider range of crsytalline materials.

During the second period of the experiment (April 2007) an opportunity arose to study a new reaction that also involved coordination bond formation and cleavage in the solid state. Again loss and/or uptake of a vapour, in this case ethanol, involving a non-porous crystalline solid was studied. The compound that exhibited the behaviour is a 1D coordination polymer in which silver perfluorocarboxylate units are linked via tetramethylpyrazine ligands. We had been able to show that ethanol is deinserted leading to formation of a new Ag–O(carboxylate) bond and that this process can occur in a single crystal to single crystal transformation. Reinsertioin of ethanol and reformation of the original structure was clearly demonstrated by the powdr diffraction study conducted at ID31. This work has recently been published again in *Angewandte Chemie*. [2]

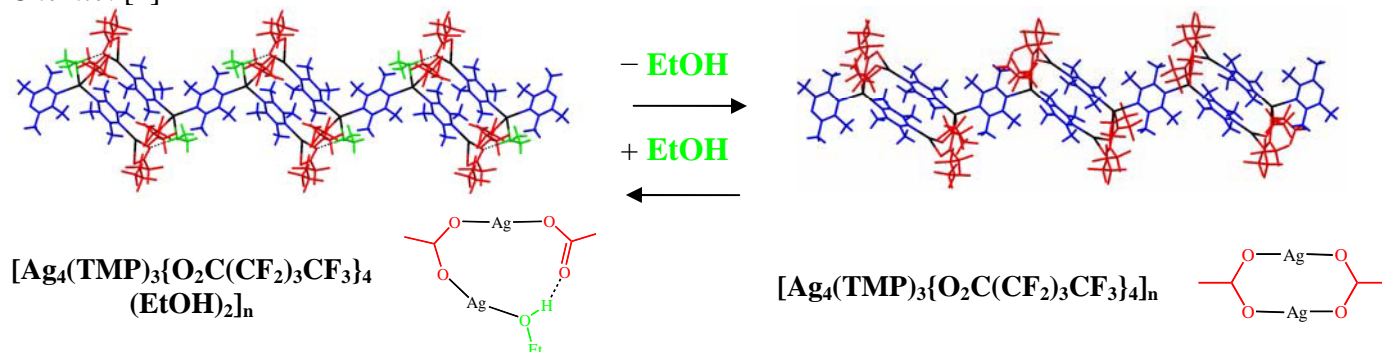


Figure 2. Reversible insertion/deinsertion of ethanol into/from the Ag–O bond of a non-porous crystalline coordination polymer.

[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] “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.