

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: In situ study of gas-solid reactions involving coordination bond breaking and forming

Experiment number:
CH-2391

Beamline:
ID31

Date of experiment:
from: 08May08 to: 12May08

Date of report:
29/02/09

Shifts:
12

Local contact(s): Dr Michela Brunelli

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

Prof. Lee BRAMMER, University of Sheffield, UK

Dr. Guillermo MINGUEZ, University of Sheffield, UK

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

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

Report: Experiment CH-2391 involved a single visit to station ID31 (12 shifts).

The experimental work continued our work on a family of compounds that we had discovered were able to undergo a reversible reaction involving loss or uptake of HCl (Fig. 1). These reactions are particularly unusual since they occur within *non-porous* microcrystalline materials. 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*-[CuCl₂(3-halopyridine)₂] on loss of two equivalents

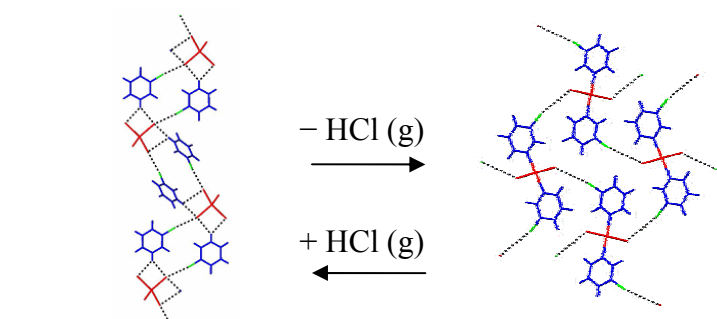


Figure 1. Interconversion of halopyridinium salt (3-XpyH)₂[CuCl₄] (left) and halopyridine complex *trans*-[CuCl₂(3-Xpy)₂] (right).

HCl, 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. The reverse process occurs upon re-uptake of HCl. Prior studies at ESRF enabled us to establish the reactions are not mediated by water through use of an experimental design

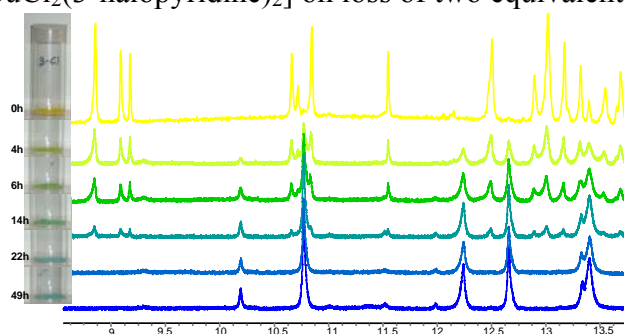


Figure 2. Samples from the *ex situ* reaction study showing the change in colour over time as (3-XpyH)₂[CuCl₄] (yellow) is converted to **2** (blue) through extrusion of gaseous HCl (left) together with the corresponding synchrotron X-ray powder patterns (T = 100 K).

provided by the station scientists which permitted high quality powder patterns to be obtained using a rotating capillary connected to a cylinder supply of dry HCl gas. Studies of the reactions both in situ and ex situ using ID31 enabled us to establish the rate 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 reactions. 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.

In experiment CH-2391 we focussed on studies to understand the mechanism of the reaction. Specifically, we undertook studies of the reaction of $\text{trans-}[\text{CuBr}_2(3\text{-Clpy})_2]$ with HCl in order to form a mixed halide product. The aim was to examine the statistical distribution of halide ligands(X) in the halocuprate anion of the product $(3\text{-ClpyH})_2[\text{CuX}_4]$. Ex situ reactions were conducted using vapour from aqueous HCl and in situ reactions were conducted using dry HCl gas and involving the apparatus described above. The two studies showed consistent results. The flux and narrow line width available at ID31 allowed the Cl/Br ratios to be determined at each site and indicate that the mechanism involves a directing influence of hydrogen bonds between the pyridinium cations and the halocuprate anions that discriminates between chloride and bromide sites. We expect to write an initial publication based upon these results in the near future and aim to follow up with additional experiments of this type, which could be referred to as a chemical labelling approach to exploring the reaction mechanism.

These studies have led to a number of invitations to speak at conferences both for the PI (Brammer) and for the student, Guillermo Mínguez Espallargas whose PhD project contained these studies. Dr. Mínguez gave invited talks at the British Crystallographic Association meeting in April, 2008 (just prior to experiment CH-2391) and subsequently at the IUCr meeting in Osaka in August 2008 at which he was able to present the most recent results. Most significantly, however, he was entered for the EuCheMS European Young Chemist Award, which was awarded based upon his CV and upon a research presentation by shortlisted candidates at the 2nd EuCheMS Congress in Torino, September 2008. He was awarded the gold medal in the PhD student category [2].

[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] See <http://www.euchems.org/News/LAW.asp> and <http://www.euchems.org/News/ECYNA.asp>