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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.

ESRF	**Experiment title:** Understanding gas-solid reactions involving nonporous crystals: a continuation	**Experiment number**: CH-2894
Beamline: ID31	**Date of experiment**: from: 09Jul09 to: 14Jul09	**Date of report**: 29/03/10
Shifts: 16	**Local contact(s)**: Dr Catherine Curfs	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

*Prof. Lee BRAMMER, University of Sheffield, UK

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Report: Experiment CH-2894

The main focus of the this experiment was the *in situ* monitoring of reactions of two related metal-organic coordination compounds with HCl gas. The studies represent a continuation and extension of previous work[1,2]
and complements ongoing spectroscopic studies in Sheffield. A gas-handling apparatus designed and built at ESRF was used to connect a lecture bottle of HCl 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. Although we were able to collect data satisfactorily, it was concluded following these experiments that a significant redesign was needed and that this would be undertaken prior to our next visit (CH-3025), which was indeed carried out.

The first uptake experiment in CH-2894 resulted in a two-stage solid-state transformation, the first step being the direct result of reaction with HCl gas (Fig. 1) and the second being an unexpected change of structure from one polymorphic form to another (Fig. 2). Although we have observed some polymorphism within this family of coordination compounds this is the first observation of such a polymorphic transition taking place under exposure to HCl gas.

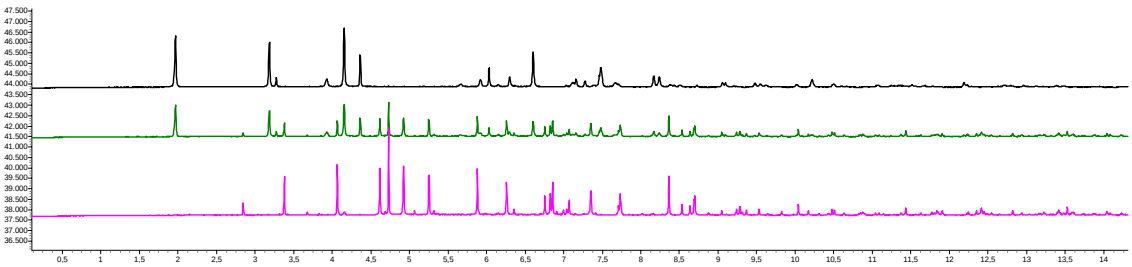

Fig. 1. Sequential scans monitoring reaction of HCl gas with coordination compound.

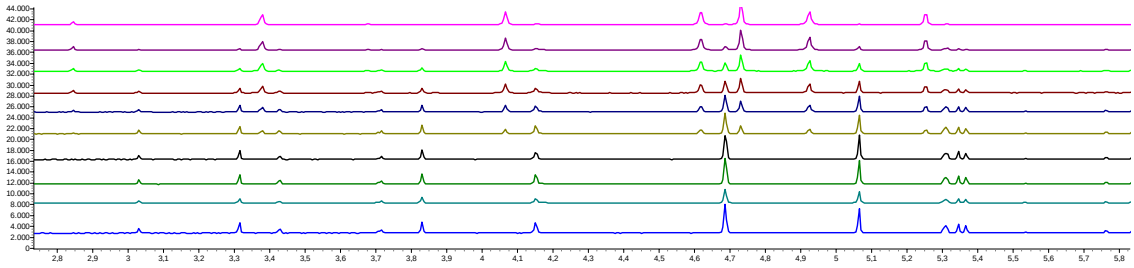

Fig. 2. Sequential scans monitoring a polymorphic phase transition that follows reaction of HCl gas shown in Fig. 1.

Following HCl uptake/reaction the sample was heated to reverse the reaction. Although we have successfully achieved this reversal with related compounds, the reaction in this case was too slow to monitor within the available beam time and efforts to speed up the reaction by increasing the temperature ultimately led to sample degradation. However, the study provided valuable information on how we might best study the HCl loss in the products in future. Analogous experiments were also conducted on a very similar related compound. We have found that by studying closely a number of related compounds, here changing a chloro substituent for a bromo substituent, has subtle effects on reaction rates and where significant differences in structure arise the outcome of the recation can also differ.

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. Indeed a small part of the beam time was used to examine the products of some *ex situ* reactions with HCl gas of other classes of materials. 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.

[1] "Reversible extrusion and uptake of HCl moelcules 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.