

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: Localization of the CO ₂ and CH ₄ adsorption sites in a nanoporous lanthanide-based carboxylate	Experiment number: CH-2138
Beamline:	Date of experiment: from: 07.19.2006 to: 07.23.2006	Date of report: 08.28.06
Shifts: 12	Local contact(s): Yaroslav Filinchuk	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): T. Devic,* Institut Lavoisier, UMR CNRS 8180, Versailles, France C. Serre,* Institut Lavoisier, UMR CNRS 8180, Versailles, France S. Bourrelly,* MADIREL, UMR CNRS 6121, Marseille, France P. Llewellyn,* MADIREL, UMR CNRS 6121, Marseille, France		

Report:

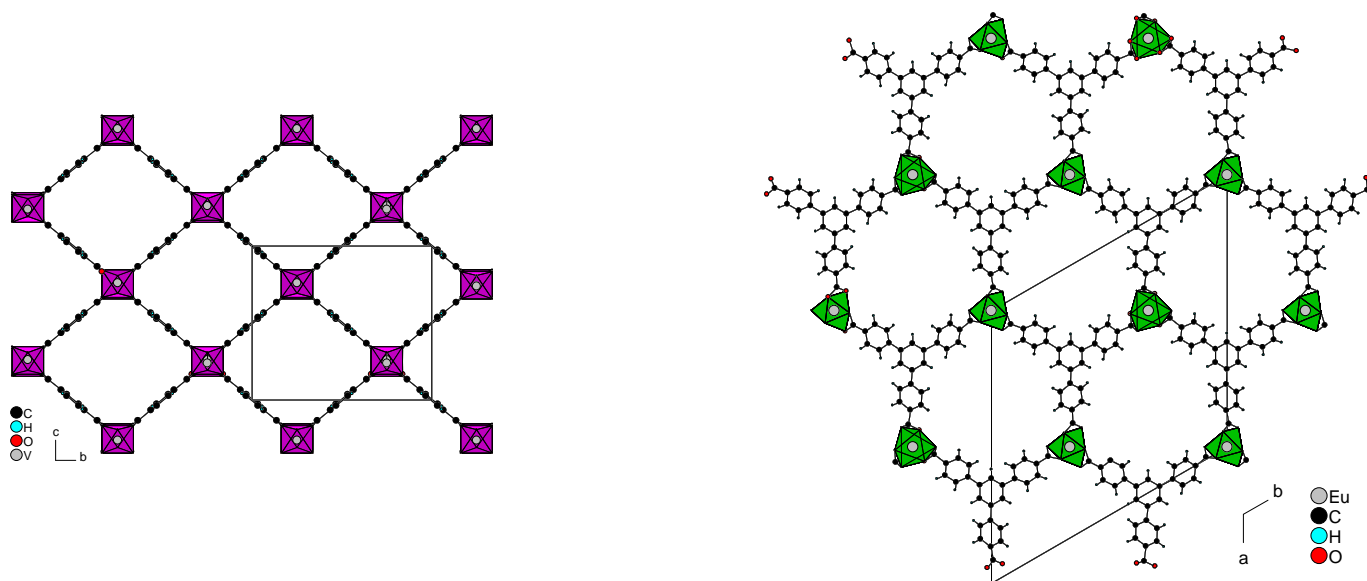
Introduction

The use of porous Metal Organic Frameworks for simple gas (H₂, CH₄, CO₂, CO,...) storage and separation is an area of growing interest, and these compounds have already reached high sorption capacities, comparable or even better than those of other materials (carbon, mesoporous silica...). In order to improve their absorption capacity, a better understanding of the gas/framework interaction is needed, and for that the localization of absorbed gas species is a prerequisite. We thus focus on two polycarboxylate-based MOFs prepared in our laboratory, both produced in a *single crystalline* form and showing a high CO₂ sorption capacity. These solids, formulated V(O)[C₆H₄(CO₂)₂] (MIL47) and Eu[C₆H₃(C₆H₄CO₂)₂] (MIL103-Eu) both exhibit one dimensional pores. The purpose of this experiment was to localize adsorbed CO₂ molecules in the pores at low CO₂ loading, in order to determine the absorption sites of highest affinity.

Experimental section

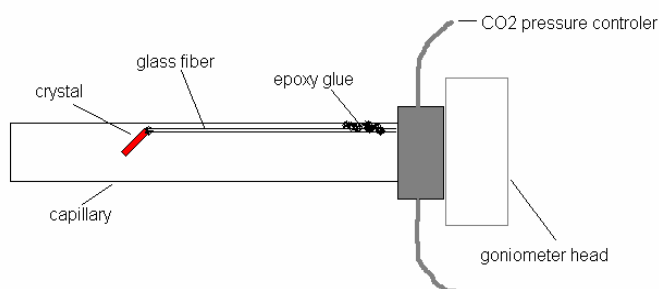
V^{III}(OH)[C₆H₄(CO₂)₂] \cdot x C₆H₄(CO₂H)₂ was prepared as about 80 μ m-sized single crystals using the published procedure.¹ The free carboxylic acid remaining in the pores was removed by exchange in DMF, which was then evacuated under heating in order to afford the emptied material V^{IV}(O)[C₆H₄(CO₂)₂] (MIL47) (see picture). Eu[C₆H₃(C₆H₄CO₂)₂](H₂O) \cdot x C₆H₁₁OH was prepared using a procedure similar to the one already

published.² The 300 μm -sized needle-like crystals were then dried at 150°C to afford the emptied material $\text{Eu}[\text{C}_6\text{H}_3(\text{C}_6\text{H}_4\text{CO}_2)_2]$ (MIL103-Eu) (see picture).



MIL47(left) and MIL103-Eu (right), views along the pore axes. $S_{\text{Langmuir}} = 1300 \text{ m}^2\cdot\text{g}^{-1}$ (MIL47) and $1000 \text{ m}^2\cdot\text{g}^{-1}$ (MIL103-Eu).

One of the crystals was picked up, mounted on a glass fiber, which was then carefully introduced in a 0.5 mm quartz capillary and glued to it. The capillary was then connected to a home-made vacuum/ CO_2 pressure controller and put on a goniometer head (see scheme).



The quality of the crystals was checked under vacuum recording 20 frames at room temperature. When a good crystal was found, small amount of CO_2 was introduced ($P = 0.5 \text{ bar}$ (MIL47) or 1 bar (MIL-103)) and the whole system was then cooled at 200 K. About 150/200 frames were then collected at the BM01-A beamline at $\lambda \approx 0.71 \text{ \AA}$ using the MAR-345 image plate detector.

Results and discussion

For each compound, reasonably good datasets were obtained under CO_2 atmosphere, even if some crystallinity loss due to the heating/cooling-outgassing/regassing procedures were observed. Data were processed using the CrysAlis software, and the structures were solved using the Shelx softwares. Cell parameters of the precursors and the CO_2 -loaded compounds are summarized in the following table.

	<i>empty</i>	<i>under CO₂ atmosphere</i>	<i>as synthesized</i>	<i>under CO₂ atmosphere</i>
<i>formula</i>	V ^{IV} (O)(L)	V ^{IV} (O)(L)·(CO ₂) _y , y~2.5-3	Eu ^{III} (L)(H ₂ O)·(C ₆ H ₁₁ OH) _x	Eu ^{III} (L)·(CO ₂) _y , y ~1
<i>unit cell</i>	orthorhombic	orthorhombic	trigonal	trigonal
	a = 6.818(1) Å	a = 6.819(3) Å	a = 28.6264(8) Å	a = 28.212(4) Å
	b = 16.143(3) Å	b = 16.23(2) Å	c = 12.2435(5) Å	c = 3.7756(6) Å
	c = 13.939(2) Å	c = 13.80(2) Å		
<i>space group</i>	Pnma	Pnma	R32	P3

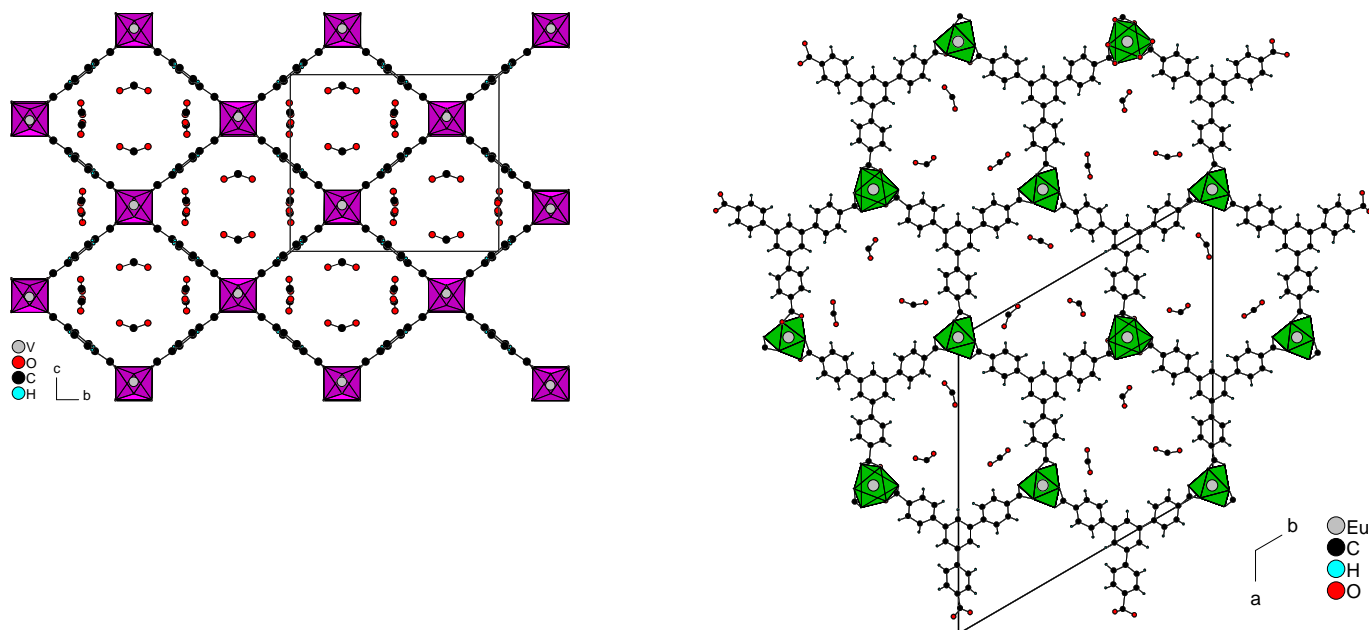
In both cases, the atoms of the framework were first localized. In the case of MIL103, the dataset obtained using synchrotron radiation allowed us to clearly determine a change in the *c* parameter (which is divided by 3 upon outgassing) and thus in the space group. This transformation is associated with the departure of a coordinated water molecule (see picture). In-situ IR spectroscopy already gave us an indication of the water departure, but the structure solved using the ESRF radiation is the first direct evidence of this phenomenon on this compound.



Change in the Eu coordination in MIL103-Eu: before (left) and after (right) outgassing.

In both compounds, the residual electronic density (not taking into account the ghosts related to the framework) lies in the pores, close to the oxygen atoms of the carboxylate groups. Using intramolecular geometrical constraints (C=O and O=C=O distances close to 1.25 and 2.5 Å respectively), CO₂ molecules were introduced at these positions and their occupancies refined. Preliminary results are as followed:

In MIL47, two sites of absorption are observed : one seems fully occupied, and the other only half occupied. Both sites are close to the inorganic [VO₆] chain (see picture). The same procedure applied to MIL103-Eu afforded three sites of absorption, with a comparable 0.3 occupancy (see picture).



CO₂-loaded MIL47(left) and MIL103-Eu (right), views along the pore axes.

These experiments clearly demonstrate that the CO₂ molecules are preferentially localized close to the inorganic subunits (the [VO₆] or [EuO₉] chains), i.e. to the most polar part of the network. This is in accordance with the properties of the gas sorbate: although the CO₂ molecule itself does not exhibit any dipolar moment, the C=O bonds are polar.

Conclusion

This work represents, to our knowledge, the first example of localization of CO₂ molecules in one dimensional porous MOFs using single crystal X-Ray diffraction.³ The results are in accordance with the one obtained on other porous MOFs using powder diffraction (experiment CH-2141 on BM01-A),⁴ and will be submitted for publication soon. As a concluding remark, the technical difficulties encountered during the experiment (mainly related to the sample preparation) have been solved during the allocated beamtime: the same equipment and methodology can now be easily used for the localization of other gas (H₂, CH₄) or vapor.

Eventually, the synthesis of new MOFs exhibiting more polar groups (purely organic) is under way, in order to obtain new adsorbates exhibiting a high affinity for carbon dioxide.

References

- [1] K. Barthelet, J. Marrot, D. Riou, G. Férey, *Angew. Chem. Int. Ed.* **2002**, *41*, 281.
- [2] T. Devic, C. Serre, N. Audebrand, J. Marrot, G. Férey, *J. Am Chem. Soc.* **2005**, *127*, 12788.
- [3] One example of CO₂ localization in small zero dimensional pores using single crystals has been reported: S. Takamizawa, E. Nakata, H. Yokoyama, K. Mochizuki, W. Mori, *Angew. Chem. Int. Ed.* **2003**, *42*, 4331-4334.
- [4] P. Llewellyn S. Bourrelly, C. Serre, Y. Filinchuk, G. Férey, *Angew. Chem., Int. Ed.* **2006**, *in press*.