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# Experiment Report Form

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- 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:**<br>Localization of gas adsorption sites in porous Metal-Organic-Frameworks | **Experiment number**:<br>CH-2375 |
|---|---|---|
| **Beamline**: | **Date of experiment**:<br>from: 04.06.2007 to: 06.10.2007 | **Date of report**:<br>09.07.07 |
| **Shifts:**<br>12 | **Local contact(s)**:<br>Yaroslav Filinchuk | *Received at ESRF:* |

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## Report:

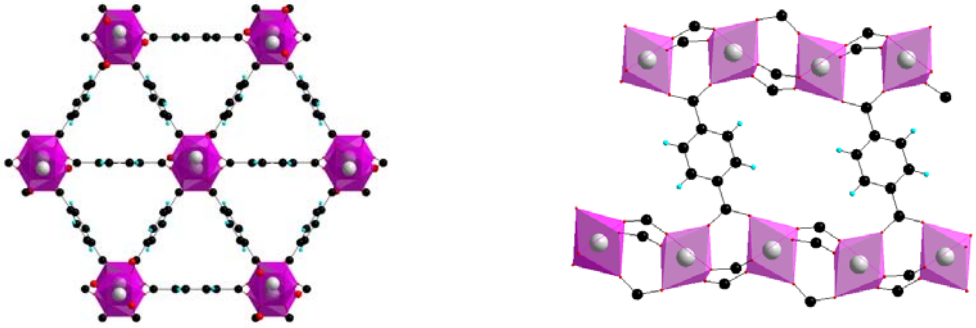
### Introduction

The use of porous Metal Organic Frameworks for simple gas ($H_2$, $CH_4$, $CO_2$, 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, mespoporous 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 prerequiste. During a previous experiment (CH-2138), we were able to localize $CO_2$ sorbed molecule in two polycarboxylate-based MOFs by single crystal X-Ray diffraction. These solids, formulated $V(O)[C_6H_4(CO_2)_2]$ (MIL-47) and $Eu[C_6H_3(C_6H_4CO_2)_2]$ (MIL103-Eu) both exhibit large one dimensional pores, and the structural resolution revealed the absence of any gas-network short contacts and thus the absence of any strong interaction, what is in complete agreement with microcalorimetry experiments and computer simulation.[1] We thus focused our attention on another MOF (a scandium terephthalate),[2] this time exhibiting small one-dimensional pores, which may present a higher affinity toward gases. The purpose of this experiment was to localize adsorbed gaseous molecules (either polar or apolar) in the pores of this small-pore MOF at low gas loading, in order to determine the absorption sites of highest affinity.

### Experimental section

$Sc^{III}$ $[C_6H_4(CO_2)_2]$ (later denoted Sc(BDC)) was provided by S. Miller and P. Wright (University of St Andrews, St Andrews, UK) in the form of 150 µm-sized diamond-shaped single crystals.[2]

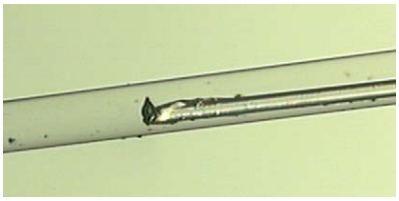
This solid is built of chains of $ScO_6$ octahedra, which are connected through terephtahlate anions, in order to define small 1-D channels running parallel to the chains. The channels are connected to each other through small windows (see the picture below).

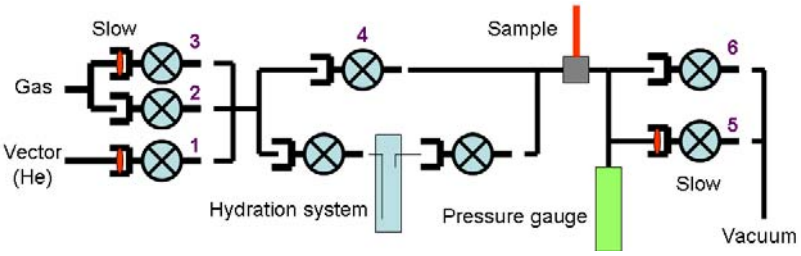


structure of Sc(BDC). Left: view along (left) and perpendicular to (right) the chain axis.

The as-synthesized solid already presents empty pores, and no activation step was thus performed.

One of the crystals was picked up, mounted on a glass fiber, which was then carefully indroduced in a 0.3 mm quartz capillary and glued to it (see picture below). The capillary was then connected to a home-made vacuum/gas pressure controller and put on a goniometer head (see the scheme below).






Experimental setup. Left: picture of a crystal of Sc(BDC) mounted in a capillary; right: pressure controller setup.

The quality of the crystals was checked under vaccum recording 20 frames at room temperature. When a good crystal was found, a small amount of $CO_2$ was introduced (P = 1 bar) and the capillary was cooled down to 235 K. 175 frames were then collected at the BM01-A beamline at $\lambda \cong 0.81$ Å using the MAR-345 image plate detector. The same procedure was used for other gases ($CH_4$: P = 9 bar, T = 230 K, $H_2$: P = 0.25 bar, T = 85 K), each time with a new crystal.

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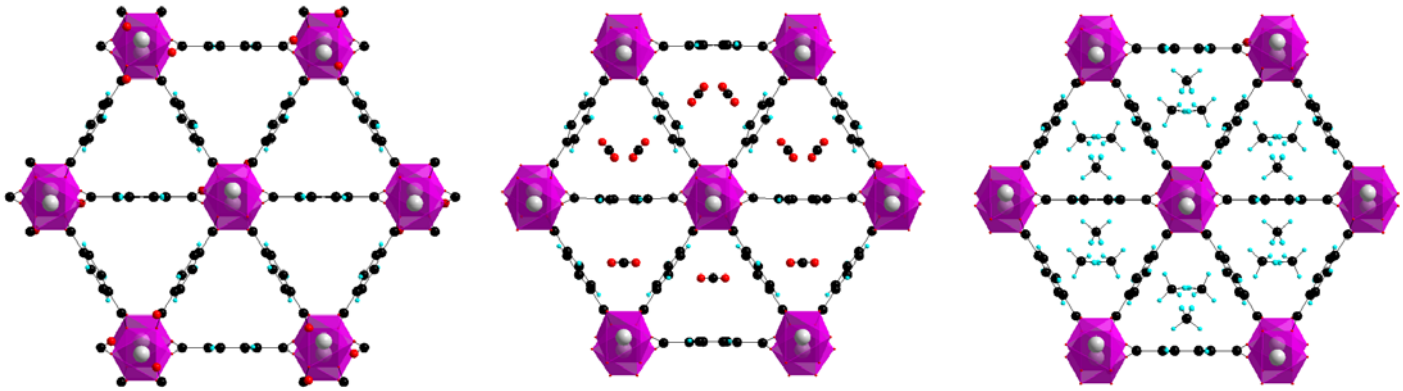
**Results and discussion**

In each case, good datasets were obtained. Data were processed using the CrysAlis software, and the structures were solved using the Shelx software. Cell parameters of the precusor and the gas-loaded compounds are summarized in the following table.

| | *empty* | *$CO_2$* | *$CH_4$* | *$H_2$* |
|---|---|---|---|---|
| ***formula*** | Sc(BDC) | Sc(BDC)·$(CO_2)_x$ x~1 | Sc(BDC)·$(CH_4)_x$ x~3 | Sc(BDC)·$(H_2)_x$ |
| ***temperature*** | 293 K | 235 K | 230 K | 85 K |
| ***unit cell*** | orthorhombic | monoclinic | orthorhombic | monoclinic |
| | a = 8.75 Å | a = 8.75 Å | a = 8.80Å | a = 8.77 Å |
| | b = 20.79Å | b = 34.46 Å | b = 20.79Å | b = 34.45 Å |
| | c = 34.40 Å | c = 11.09 Å | c = 34.40Å | c = 11.14 Å |
| | | $\beta$ = 110.9° | | $\beta$ = 111.1° |
| | V = 6259 $Å^3$ | V = 3122 $Å^3$ | V = 6294 $Å^3$ | V = 3138 $Å^3$ |
| ***space group*** | Fddd | C2/c | Fddd | C2/c |

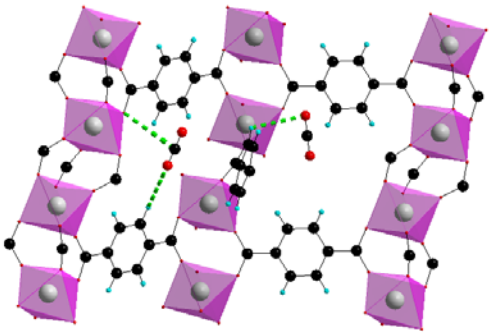
In two cases (loading with $H_2$ and $CO_2$), a change of symmetry was observed, accompagnied by a twinning of the crystals, which was taken into account during the data reduction. The lowering of symmetry seems to be related to the nature of the loaded gas and not to the cooling, as the symmetry of the as-synthesized Sc(BDC) remains unchanged between room temperature and 150K.[2]

In all cases, the atoms of the framework were first localized and refined. Residual electronic densities were then located in the pores, and $CO_2$ and $CH_4$ molecules were easily defined and refined (occupancy and position). In the case of $H_2$, few plausible final structures were obtained, with similar reliabilty factors. Computer simulations (T. Düren, University of Edinburgh, UK) aiming to identify the the true stucture among the availabe models are under way.



View of the crystal structure of Sc(BDC) along the pore axis. Left: as-synthesized solid; middle: loaded with $CO_2$, right: loaded with $CH_4$.

As shown above, the structure of the network remains unchanged. Analysis of the structures of the $CO_2$ loaded sample revealed the presence of few short contacts between the network and the guests, either corresponding to weak C-H...$O_{CO2}$ hydrogen bonds, or to $O_{carbox}$...$C_{CO2}$ donor-acceptor interactions (see the picture below). In the case of methane (apolar), no short contacts were evidenced, and the structure appeared to correspond to a close packing of the $CH_4$ molecules inside the channels.



mol. 1: $C_{CO2}\ldots O_{carbox}$ = 3.171 Å

mol. 2: $O_{CO2}\ldots H_{phenyl}$ = 2.785 Å

Short contacts between the $CO_2$ molecules (two crystallographically independent) and the framework.

**Conclusion**

This work represents one of the rare examples of localization of $CO_2$ and $CH_4$ molecules in one dimensional porous MOFs using single crystal X-Ray diffraction.[3] These results are currently confronted with isotherm and microcalmorimetry adsorption measurment, and should rapidly lead to a publication. This work will further be extended to other guest, either gas or vapors, polar or apolar.

**References**


[1] N. A. Ramsahye, G. Festa, S. Bourrelly, T. Devic, T. Düren, P. L. Llewellyn, Y. Filinchuk, C. Serre, G. Férey, G. Maurin, *submitted*.

[2] S. R. Miller, P. A. Wright, C. Serre, T. Loiseau, J. Marrot, G. Férey, *Chem. Commun.* **2005**, 3850.

[3] One example of $CO_2$ 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.