An EXAFS study of the formation of a nanoporous metal–organic framework: evidence for the retention of secondary building units during synthesis†

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EXAFS data measured from amorphous intermediates and crystallisation solutions provides the first evidence that trimeric iron oxide secondary building units remain intact during crystallisation of the metal–organic framework MIL-89 from starting materials to products.

In the past few years, metal–organic framework materials have established themselves as an important class of nanoporous solids, with properties and applications to rival the well established zeolites.[1–3] The materials have very different structures to the tetrahedral frameworks of zeolitic materials in that they are constructed from metal oxide clusters, chains or layers linked by organic moieties to give three-dimensionally extending nets. These structural characteristics offer hitherto unprecedented implications in the rational design of novel framework materials whose structures (channel size and connectivity) and chemistry (the presence of active sites for catalysis or sorption) are tuned for a particular application. By combining the metal cluster units of choice (secondary building units, SBUs) with organic linkers of prescribed chain length and branching characteristics, it should be feasible to design a new solid. This has now been demonstrated in the MIL-*n* family of solids (MIL = Matériaux Institut Lavoisier).[3,4]

Yaghi and co-workers have also developed a highly versatile route to a diverse family of metal–organic frameworks containing tetrameric, and later dimeric and trimeric, zinc oxide SBUs.[1,5] In this case, however, soluble, monomeric zinc species are used as the starting materials in the synthesis, and these must assemble in solution into polymeric clusters during the formation of the extended structure. The true potential for rational design of new materials is therefore limited. This is not the case for some of the MIL-*n* family, where a 'controlled SBU' approach is taken, using transition metal oxide clusters as chemical reagents, whose connectivity is maintained in the metal–organic framework produced.[3,4,6] The aim of the work described herein was to provide experimental evidence for the first time that such SBUs are present at all stages of crystallisation; verification of this idea will aid the future design of new nanoporous network structures. We used Fe K-edge extended X-ray absorption fine structure (EXAFS) spectroscopy to achieve this objective and studied the formation of MIL-89, an Fe(III) oxycarboxylate, $Fe_3O(CH_3OH)_3[O_2C-(CH)_4-CO_2]_3 \cdot Cl \cdot (CH_3OH)_6$,[6] as illustrated in Fig. 1. EXAFS uniquely enables us to study the local structure of crystalline materials, amorphous materials and solutions found during the course of reactions.

MIL-89 synthesis was performed as described previously[6] from trimeric Fe(III) acetate,[7] *trans–trans*-muconic acid, sodium hydroxide, water and methanol in the ratio 1 : 3 : 1.5 : 50 : 1000 (per trimer). The resulting mixture was sealed in a Teflon-lined autoclave and heated for various periods of time at 100 °C. After the desired heating time, the autoclave was cooled and the solid and filtrate separated by filtration, both of which were retained. All solids isolated were orange in colour, and the supernatant solution was also a pale orange colour. Fig. 2 shows the powder X-ray diffraction data of the solids isolated after various periods of time. Characteristic Bragg peaks for MIL-89 appear at a reaction time around 4 hours, and there is no evidence for the presence of any other crystalline intermediate phases during the crystallisation. At times shorter than 4 hours, the recovered solid is a mixture of amorphous solid and some recrystallised *trans–trans*-muconic acid. Elemental analysis showed that all solids contained typically >10% iron by mass, but the iron content was variable and showed no trend with increasing time. Rationalising the elemental analysis data is complicated by the precipitation of
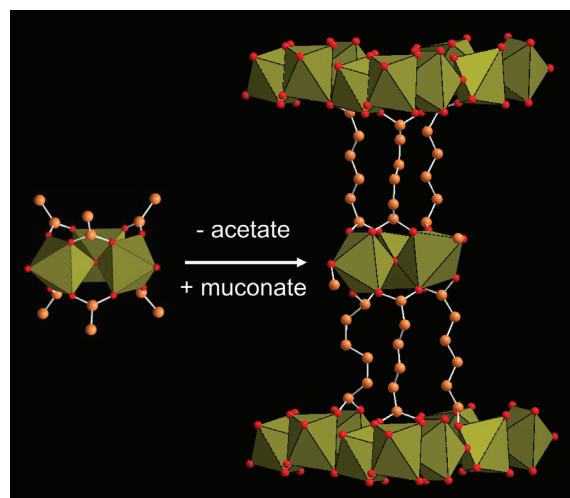
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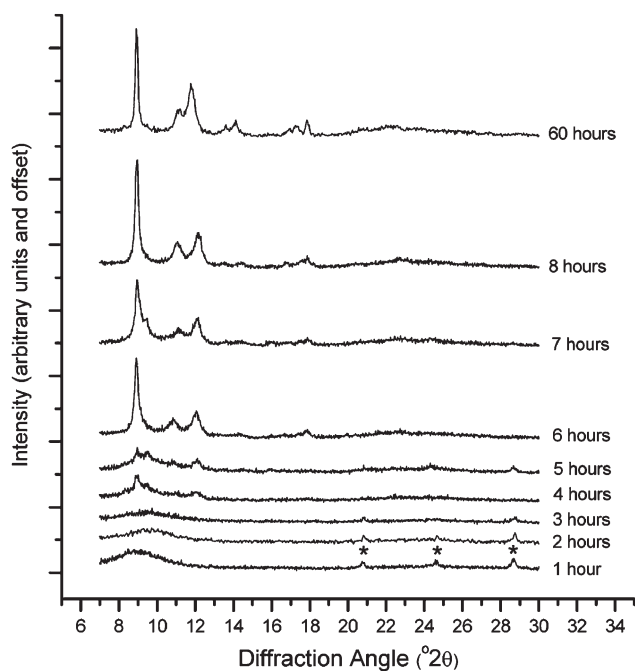

Fig. 1 A schematic of the formation, under solvothermal conditions, of open framework MIL-89 from trimeric clusters as starting materials.

Fig. 2 Powder X-ray diffraction patterns of the solids isolated from solvothermal reactions used to prepare MIL-89. Asterisks indicate Bragg peaks due to unreacted *trans–trans*-muconic acid.

Fig. 3 Fe K-edge EXAFS spectra (left) and their Fourier transforms (right) of (a) trimeric Fe(III) acetate, (b) MIL-89 and (c) the amorphous solid isolated after 2 hours of solvothermal reaction. Points are the experimental data and the line is the best fit obtained by modelling.

variable amounts of unreacted *trans–trans*-muconic acid (also seen by IR spectroscopy) along with the amorphous Fe-containing materials. To avoid degrading the structure of the amorphous material, washing out of the unreacted carboxylic acid was not attempted. This does not affect the EXAFS experiments, which are element specific. Fe K-edge EXAFS studies were performed on Station 7.1 of the Daresbury SRS.[8]‡

Fig. 3 shows the Fe K-edge EXAFS data for the crystalline trimeric iron acetate, the final product MIL-89 and one of the amorphous solids isolated. Table 1 contains some results of the analysis of these data (see the ESI for details of the EXAFS refinements and all structural parameters obtained†). For the crystalline materials, shell occupation numbers were fixed at their expected values for five atomic shells, and the radial distances and Debye–Waller factors refined with the Fermi energy. This approach allowed determination of typical values for the Debye–Waller factors when interpreting the parameters obtained from the amorphous solids. Table 1 shows the agreement between the expected and refined parameters, which yielded very respectable goodness-of-fit parameters. It is important to note that the EXAFS signals from the trimeric precursor and final product can be distinguished. In the case of MIL-89, the Fourier transform (Fig. 3b) shows evidence of further atomic shells beyond 3.5 Å. The crystal structure of the material shows a range of Fe–C and Fe–O correlations between 3.8 and 4.8 Å, but no way of modelling this spread of backscattering atoms was found without increasing the number of refined parameters to a statistically invalid value.[9]

For all of the amorphous materials studied, the EXAFS data were very similar, and were best modelled as having local structure about iron similar to that seen in MIL-89; note the comparable Fe–Fe distance of 3.36 Å, slightly longer than in the acetate precursor. A model based on the acetate cluster always gave a
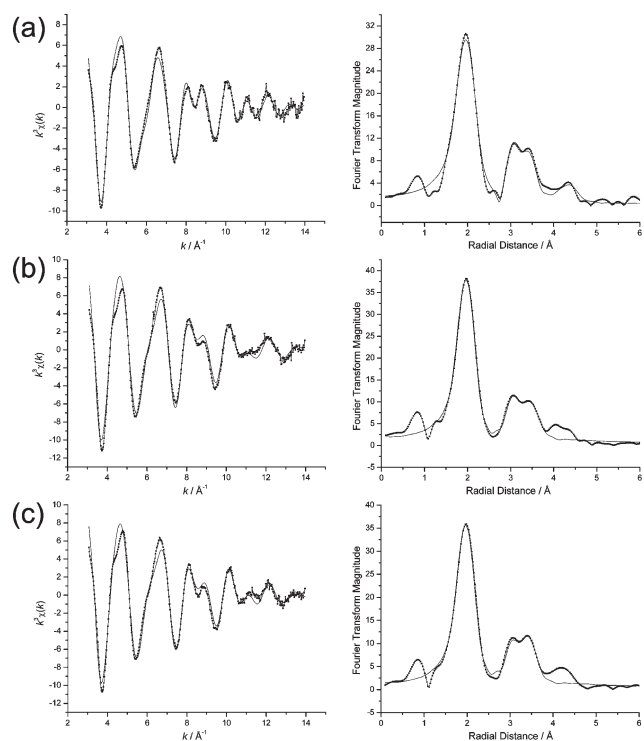
Table 1 Refined EXAFS structural parameters for the crystalline materials Fe(III) acetate and MIL-89, with crystallographic interatomic distances (R_{cryst}) for comparison, and the amorphous material isolated after 2 hours. Note that the errors quoted are purely statistical; the true errors on distances are $\pm$ 0.02 Å and on Debye–Waller factors are $\pm$ 10% (see the ESI for further details)

Material	Shell	N	R_{EXAFS}/Å	R_{cryst}/Å	$2\sigma^2$/Å^2
Fe acetate	O	6	2.007(3)	1.911	0.022(1)
	C	4	3.010(10)	2.996	0.009(2)
	Fe	2	3.232(21)	3.279	0.029(10)
	O	4	3.308(16)	3.340	0.008(18)
	C/O	8	4.487(14)	4.409	0.023(4)
MIL-89	O	6	2.002(3)	1.949	0.016(1)
	C	5	3.001(20)	2.952	0.033(9)
	O	2	3.219(19)	3.182	0.001(4)
	Fe	2	3.358(25)	3.340	0.013(5)
	O	2	3.549(67)	3.468	0.010(14)
Amorphous	O	6	2.006(4)	—	0.012(1)
	C	5	3.010(23)	—	0.035(9)
	O	2	3.202(20)	—	0.000(4)
	Fe	2	3.356(21)	—	0.010(5)
	O	2	3.527(41)	—	0.003(6)

statistically poorer fit. The Debye–Waller factor of the Fe–Fe shell is also very similar to the same shell in MIL-89, showing the consistency of this interpretation and also that the shell occupation number of two, characteristic of trimeric units, is most reasonable. The alternative approach to data analysis is to refine shell occupation numbers and Debye–Waller factors. This was performed using a model with fewer shells to reduce the total number of refined parameters (ESI†), and in all cases a Fe–Fe coordination number of 2 $\pm$ 1 was found, consistent with the
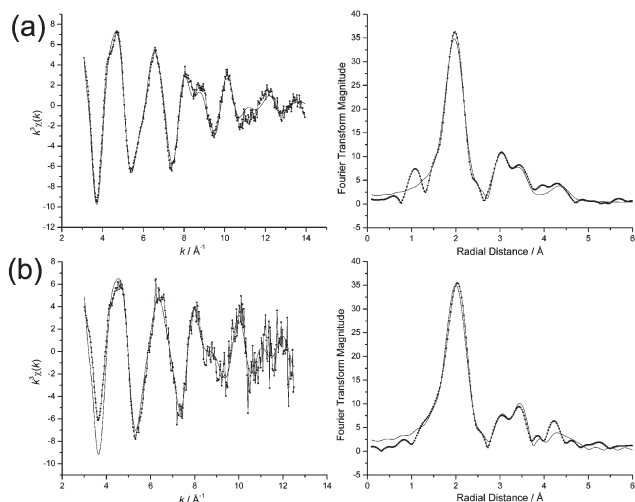
Fig. 4 Fe K-edge EXAFS spectra (left) and their Fourier transforms (right) of (a) a ∼0.1 M solution of trimeric Fe(III) acetate in methanol and (b) the synthesis solution isolated after 5 hours of hydrothermal reaction.

presence of the trimeric unit. It is also important to note that the Fe^{III}–Fe^{III} distance of between 3.2 and 3.4 Å, and the pattern of other interatomic correlations we model is characteristic of the trimeric cluster. If monomeric units were present then clearly no such distance would be observed. For complexes containing dimeric Fe^{III} clusters, a wide range of Fe–Fe distances have been reported, depending on the nature of the bridging ligands,[10] but for the most common mode of bridging seen, *via* a single oxo anion, the Fe–Fe distance is longer than we have observed: 3.4–3.5 Å.[10]

The solutions isolated from the hydrothermal crystallisations were very dilute, and the only solution that was concentrated enough to allow the measuring of data over a reasonable period of time (even then, only in fluorescence mode and in seven individual scans, later summed to improve the signal to noise ratio) was that isolated at 5 hours, *i.e.* after crystallisation had commenced. We have compared the data measured from this solution with those measured from a ∼0.1 M solution of the trimer precursor in methanol (Fig. 4) (see the ESI for refined parameters†). For the Fe trimer solution, the Debye–Waller factors for the shells of higher radial distance are comparable to those seen in the solid-state, suggesting that the cluster is a robust and relatively rigid unit. In contrast to the amorphous solids, the data from the reaction solutions are clearly best modelled using the iron acetate cluster model; attempts to fit the MIL-89 model gave physically meaningless, negative Debye–Waller factors. The Debye–Waller factor for the Fe–Fe shell, coupled with the distance of ∼3.2 Å, leads us to conclude that the trimeric units are present in solution, but coordinated by acetate rather than the *trans–trans*-muconate, as found in the final product.

In summary, we have presented the first, direct experimental evidence that secondary building units are always present during the crystallisation of an open metal–organic framework. Although this was not an *in situ* study, the particular phase we have studied, MIL-89, does actually crystallise at room temperature over extended periods of time from the same reagents, and so we are

probing close to the real crystallisation conditions. It is apparent from our work that the crystallisation of MIL-89 takes place *via* the initial formation of an amorphous phase, which then dissolves (explaining the increased Fe^{III} concentration in solution just as the crystalline material is detected) before being consumed completely to yield solely the crystalline product. This process is analogous to that found for the hydrothermal crystallisation of classical aluminosilicate zeolites, where an amorphous intermediate phase is commonly found prior to the formation of the zeolite.[11] Future studies of these crystallisation processes, particularly those that occur only under non-ambient conditions, require the design and construction of special reaction cells, from which data are recorded rapidly from both solution and solid phases during crystallisation.[12]

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Notes and references

1 O. M. Yaghi, M. O. Keefe, H. K. Ockwig, M. Chae and M. Eddaoudi, *Nature*, 2003, **423**, 705.
2 X. Zhao, B. Xiao, A. J. Fletcher, K. M. Thomas, D. Bradshaw and M. J. Rosseinsky, *Science*, 2004, **306**, 1012; J. L. C. Rowsell, E. C. Spencer, J. Eckert, J. A. K. Howard and O. M. Yaghi, *Science*, 2005, **309**, 1350.
3 G. Férey, C. Mellot-Draznieks, C. Serre, F. Millange, J. Dutour, S. Surblé and I. Margiolaki, *Science*, 2005, **309**, 2040.
4 G. Férey, C. Serre, C. Mellot-Draznieks, F. Millange, S. Surblé, J. Dutour and I. Margiolaki, *Angew. Chem., Int. Ed.*, 2004, **43**, 6296.
5 M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. Reineke, M. O'Keefe and O. M. Yaghi, *Acc. Chem. Res.*, 2001, **34**, 319.
6 C. Serre, F. Millange, S. Surblé and G. Férey, *Angew. Chem., Int. Ed.*, 2004, **43**, 6286.
7 C. T. Dziobkowski, T. J. Wrobleski and D. B. Brown, *Inorg. Chem.*, 1981, **20**, 671.
8 K.-C. Cheung, R. Strange, I. Harvey, B. Dobson, G. Derbyshire, J. Kay, N. Binsted, R. Linford and S. Hasnain, *J. Synchrotron Radiat.*, 1999, **6**, 161.
9 R. W. Joyner, K. J. Martin and P. Meehan, *J. Phys. C: Solid State Phys.*, 1987, **20**, 4005.
10 D. M. Kurtz, *Chem. Rev.*, 1990, **90**, 585.
11 C. S. Cundy and P. A. Cox, *Microporous Mesoporous Mater.*, 2005, **82**, 1.
12 J. D. Grunwaldt, M. Ramin, M. Rohr, A. Michailovski, G. R. Patzke and A. Baiker, *Rev. Sci. Instrum.*, 2005, **76**, 054104.
13 G. Derbyshire, K.-C. Cheung, P. Sanssingkeow and S. S. Hasnain, *J. Synchrotron Radiat.*, 1999, **6**, 62.
14 N. Binsted, J. W. Campbell, S. J. Gurman and P. C. Stephenson, *EXAFS data analysis program*, Daresbury Laboratory, 1991.