A new isoreticular class of metal-organic-frameworks with the MIL-88 topology†

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We report here a new family of isoreticular MOFs, comprising three larger analogues of the nanoporous metallocarboxylate MIL-88; these solids were synthesized using a controlled SBU approach and the three crystal structures were solved using an original simulation-assisted structure determination method in direct space.

The number of possible associations between inorganic moieties and organic linkers (phosphonates, carboxylates, sulfonates...) to form hybrid inorganic–organic porous materials is quasi infinite and explains the tremendous activity in this field.[1–4] Besides the applications they imply in gas separation or storage and in catalysis, an interesting feature of these solids is the possibility to achieve "design" *i.e.* obtain tailor-made solids with the required structures and properties, starting from well identified inorganic and organic species. Using different inorganic clusters, a huge number of hybrid solids with large pore sizes (up to 23 Å) and high surface areas was obtained.[5] Within this challenge, our group recently reported new hybrid solids, *i.e.* the chromium carboxylates MIL-100[6] and MIL-101,[7,8] built up from trimeric building units. Using a new computational approach,[9,10] the structures of both compounds were successfully solved in direct space using synchrotron powder data, revealing an unprecedented zeotype architecture, with a hierarchy of giant pores (25–34 Å) and high surface areas (3,100–5,900 m^2 g^{-1}). We also developed a 'chemically controlled SBU' (SBU for Secondary Building Units) approach.[11] The trimeric building unit, *i.e.* three metallic octahedra shared by μ_3-O, which already exists in the iron(III) acetate precursor, would remain intact during the exchange of the acetate anions by dicarboxylates. This reaction leads to a new structural type,[11] adopted by the open-framework iron(III) carboxylate MIL-88 (Fig. 1) and MIL-89. Using this approach, we report here a series of three isoreticular upper homologues of MIL-88. Their crystal structures were solved using a simulation-assisted structure determination method in direct space while X-ray thermodiffractometry showed that these solids are flexible and belong to the "third generation of porous coordination compounds".[12]

The aim of this study was to explore the possible isoreticularity of solids containing the metallic trimers, by using larger dicarboxylate groups for extending the pore sizes. Terephthalic acid (1,4-BDC), 2,6-naphthalenedicarboxylic (2,6-NDC) and 4,4′-biphenyldicarboxylic (4,4′-BPDC) acids were combined either with the trimers of iron(III) [following the low temperature synthesis of MIL-88 (2,6-NDC)], or with the trimers of chromium(III) in hydro-solvothermal conditions (1,4-BDC and 4,4′-BPDC) (Fig. 1). Whatever the synthetic route, three new compounds are obtained. The indexation of their powder patterns reveals that these solids exhibit the same symmetry (hexagonal) and space group (*P*-62*c*) as the MIL-88 fumarate structure.[11] These solids are labelled MIL-88B (1,4-BDC), MIL-88C (2,6-NDC) and MIL-88D (4,4′-BPDC) while the previously reported MIL-88 is labelled as MIL-88A. When comparing their cell parameters, *a* seems roughly invariant, while *c* consistently evolves as a function of the size of the organic linker (Table 1).

TGA and elemental analyses also indicate that these solids possess the same metal : dicarboxylate ratio (1 : 1) as in MIL-88A (see supplementary information). At this stage, the above features strongly suggest that the new solids might be isoreticular nets of the MIL-88A structure. In the absence of single crystals, a structure determination from powder data was needed. Therefore, a simulation approach was decided for solving their structures rather than re-applying the time-consuming process of *ab initio* structure determination from powder data for each member of the series. If the simulations are successful, the predicted structures might be directly used as initial models for further Rietveld refinements from powder patterns. Starting exclusively from the knowledge of the MIL-88A crystal structure[11] together with experimental values‡ for the cell parameters of the new compounds, an original simulation strategy to possibly anticipate the crystal structures of each isoreticular network, *i.e.* MIL-88B-C-D, was developed as follows (Fig. 2).

The simulation method consists of gradually replacing the ligand of a MIL-88A type "mother" structure by another of larger size, and then minimizing the energy of the resulting model. This entails two main steps, exemplified here through the simulation of MIL-88B from MIL-88A. The model for MIL-88A was computationally built from its experimental structure (a = 11.18 Å, c = 14.68 Å, *P*-62*c*). First, proper addition and deletion of carbon and hydrogen atoms are performed in MIL-88A in the region of the fumaric acid molecule in order to build a 1,4-BDC molecule. The required bonds are created in order to match the sequence of the 1,4-BDC skeleton. At this stage, the constructed "pre-model" of MIL88-B still possesses the symmetry and the cell-parameters of the "mother" structure, *i.e.* MIL-88A, while being unrealistic. The next step consists of energy minimizing the MIL-88B "pre-model" in *P*-62*c*, relaxing all atomic coordinates and cell parameters. This

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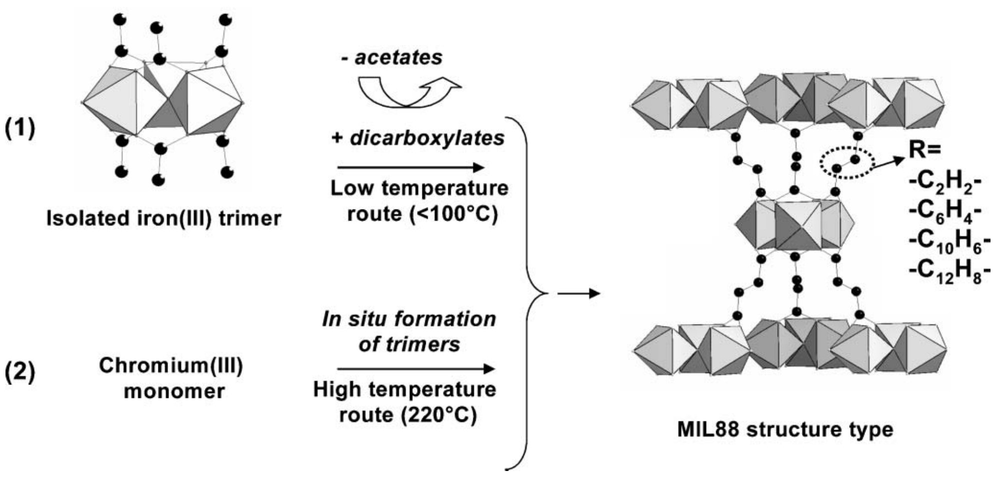

Fig. 1 Schematic synthetic schemes involved for the open-framework metallocarboxylates based on trimeric Secondary Building Units. (1) Low temperature route used for the iron(III) carboxylates MIL-88A (R = $-C_2H_2-$ (fumarate)), MIL-88C (R = $-C_{10}H_6$ (2,6-naphthalene)). (2) High temperature route used for the chromium(III) carboxylates MIL-88B (R = $-C_6H_4$ (terephthalate)) and MIL-88D (R = $-C_{12}H_8$ (4,4′-biphenyl)).

Table 1 Cell parameters of the MIL-88 type isoreticular nets

	MIL-88A	MIL-88B	MIL-88C	MIL-88D
a (Å)	11.18	11.05	10.22	12.05
c (Å)	14.68	18.99	23.60	27.50
V (Å^3)	1500	1980	2020	3500

allows the organic ligand to adopt its correct geometry while the inorganic units adjust consequently. A key feature of this step is the use of appropriate external constraints along the cell axes (*i.e.* pressure) during energy minimizations using the experimental cell parameters of MIL-88B ($a \sim 11$ Å, $c \sim 19.0$ Å) as targeted values. Typically, a negative hydrostatic pressure was applied along c when minimizing the MIL-88B pre-model in order to converge towards the expected larger cell, obviously required to accommodate the larger 1,4-BDC ligand. Indeed, the calculated powder pattern of the simulated MIL-88B crystal structure matched remarkably well the experimental pattern, the differences in intensies being interpreted in terms of the absence of extra-framework species in the simulations. Finally, the simulated MIL-88B crystal structure was directly used to perform the Rietveld refinement against the experimental powder pattern of MIL-88B.

The simulations of MIL-88C and MIL-88D were readily realized in a similar fashion. The energy minimized MIL-88B was used as the "mother" structure for building a pre-model of MIL-88C by substituting the 1,4-BDC with 2,6-NDC. Then, the energy minimized MIL-88C was used as the "mother" structure for the MIL-88D pre-model by substituting 2,6-NDC with 4,4′-BPDC. Both structures were finally refined using the predicted simulated structures (see ESI†). All simulations were performed using the Cerius2 suite of software,[13] using the UFF forcefield.[14] Here, the forcefield is used as a means of enforcing the structure to a realistic model, rather than for estimating lattice energies. Hence, electrostatic interactions were not computed in this work. It has to be mentioned also that our approach is on the whole not dissimilar to the least squares arguments method developed by Baerlocher and co-workers and used in zeolite work.[15]

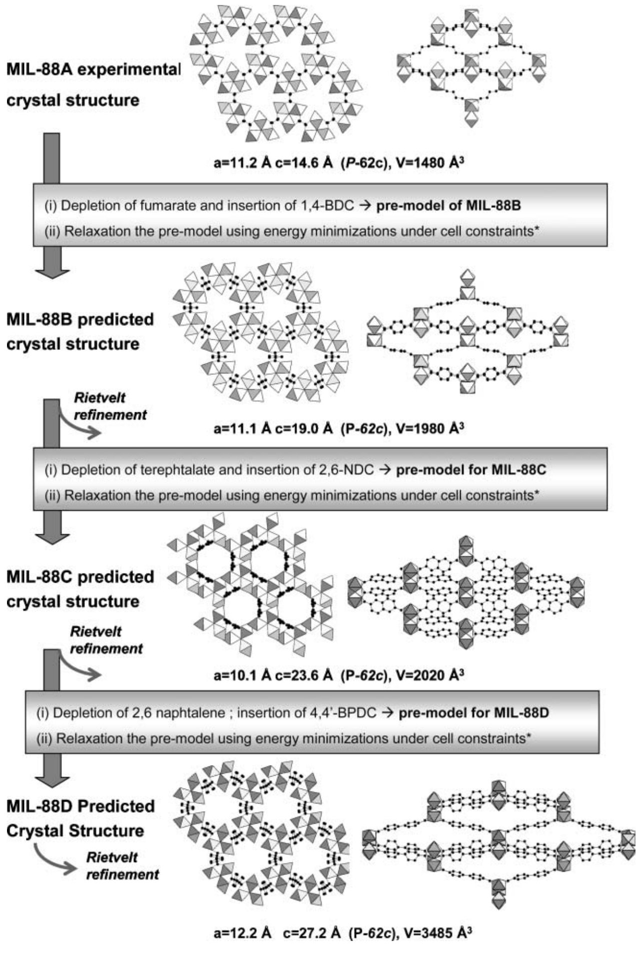

Fig. 2 Synthetic scheme of the combined simulation–refinement structure determination of the MIL-88 isoreticular MOFs. Inserts showing two different views of the structures of the MIL-88A, -88B, -88C and -88D are shown (right: along the c axis; left: along the a axis). For a better understanding, free solvent molecules and anions have been omitted. Metal octahedra and carbon atoms are represented in gray and black, respectively.

Indeed, the four solids are part of a new class of isoreticular MOFs. They are all built up from oxo-centered trinuclear iron(III) or chromium(III) SBUs and dicarboxylate linkers. The trimers of octahedra are related together by *trans, trans* dicarboxylate moieties ensuring the three-dimensionality of the framework (Fig. 2). In both structures, iron or chromium atoms exhibit an octahedral environment with four oxygen atoms of the bidentate dicarboxylates, one μ_3O atom and one oxygen atom from either a terminal water (or methanol) molecule or a F/OH group. Octahedra are related through the μ_3O oxygen atom to form the trimeric building units. Distances and angles are on the whole well defined (see supplementary information). Bond valence calculations[16] indicate that chromium or iron atoms are in a trivalent state in all structures. Two types of pores are present. First, narrow hexagonal channels run along the *c* axis filled with either water/pyridine (MIL-88B and -D) or terminal methanol groups (MIL-88C). These hexagonal channels are delimited by six trimers whose vertexes are the central μ_3O atoms; the free aperture of the channels is rather small ($\sim$2–4 Å). The second pore system consists of bipyramidal cages, the equatorial plane of which is (001) and the axis the *c* parameter. They are delimited by five trimers and six dicarboxylate groups. The size of these windows is related to the *c* parameter which increases directly with the length of the linker ($c \sim 14.5$, 19, 23.5 and 27.5 Å for MIL-88A, -B, -C and -D, respectively). This gives a maximum free aperture of $\sim$3*14 Å^2 for MIL-88D. The pore dimensions involved within the MIL-88 class of solids are however relatively small but swelling capacities are expected in the presence of solvents such as in the case of the chromium carboxylates MIL-53.[17]

As previously observed for MIL-89, a partial occupancy is attributed to the carbon atom of the terminal methanol group in MIL-88C. The counteranions are disordered acetate in the case of MIL-88C while one fluorine counteranion per chromium atom is present for MIL-88B and -D. Since these latter solids are made under similar hydrothermal conditions to those for the chromium carboxylate MIL-100, it is assumed that the fluorine counteranions are bound to the chromium atoms.

TGA and X-ray thermodiffractometry show they are thermally stable up to $\sim$300 °C under air (see Figs. S1 and S2). A significant pore contraction is observed in both cases for the MIL-88B and MIL-88D solids. The MIL-88C X-ray pattern shows however a much smaller cell contraction. Based on the Bragg peak positions, the estimated cell parameters of the anhydrous forms are $a \sim$ 9.6 Å, $c \sim$ 19.1 Å, $V \sim$ 1500 Å^3 for MIL-88B and $a \sim$ 10.1 Å, $c \sim$ 27.8 Å, $V \sim$ 2480 Å^3 for MIL-88D. This represents cell volume contractions close to 25% and 29% for these two solids. Besides, a precedent study has shown that the smallest compound of this isoreticular class of solid, *i.e.* MIL-88A, exhibits almost a doubling of its cell volume between the anhydrous and the open forms while fully retaining its open-framework topology.[18] Atomic displacements larger than 4 Å without any bond breaking are observed when water or various alcohols are adsorbed in the porous structure, revealing an unprecedented flexible crystallized framework. Such behavior, currently under investigation, is expected within the three larger analogues and results will soon be published elsewhere.

We have now synthesized and solved the crystal structures of a new isoreticular class of MOFs built up from trimeric SBUs with the MIL-88 topology, which is a new example of 'scale chemistry'. Preliminary experiments show that these solids breathe with respiration capacities. Since it was previously reported that flexible hybrid solids might exhibit original gas sorption properties, *i.e.* the "gate-opening" phenomenon,[19] this could enlarge the field of applications in gas storage for hybrid solids. To our knowledge, this is also the first computational contribution in the field. Indeed, the prediction using energy minimisation methods of a complete series of homologous three-dimensional crystal structures resulting from the substitution of an organic linker by another, keeping the inorganic subnetwork identical, is performed for the first time. With our approach, it is now possible to anticipate the structures of whole families of new compounds, starting only with the data of the parent structure, and to minimize the time-consuming process of crystal structure determination from powder patterns. Finally, the study of the properties of this new class of solids is currently in progress and will soon be reported.

Notes and references

‡ Powder X-ray diffraction data were collected at room temperature on a Siemens D5000 diffractometer using CuKα radiation (λ = 1.5418 Å). Structure refinements were done using Fullprof2k and Winplotr.[20,21] Successive Fourier differences were performed using Shelxtl to locate the approximate position of the guest species.[22] CCDC 285810–285812. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b512169h

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