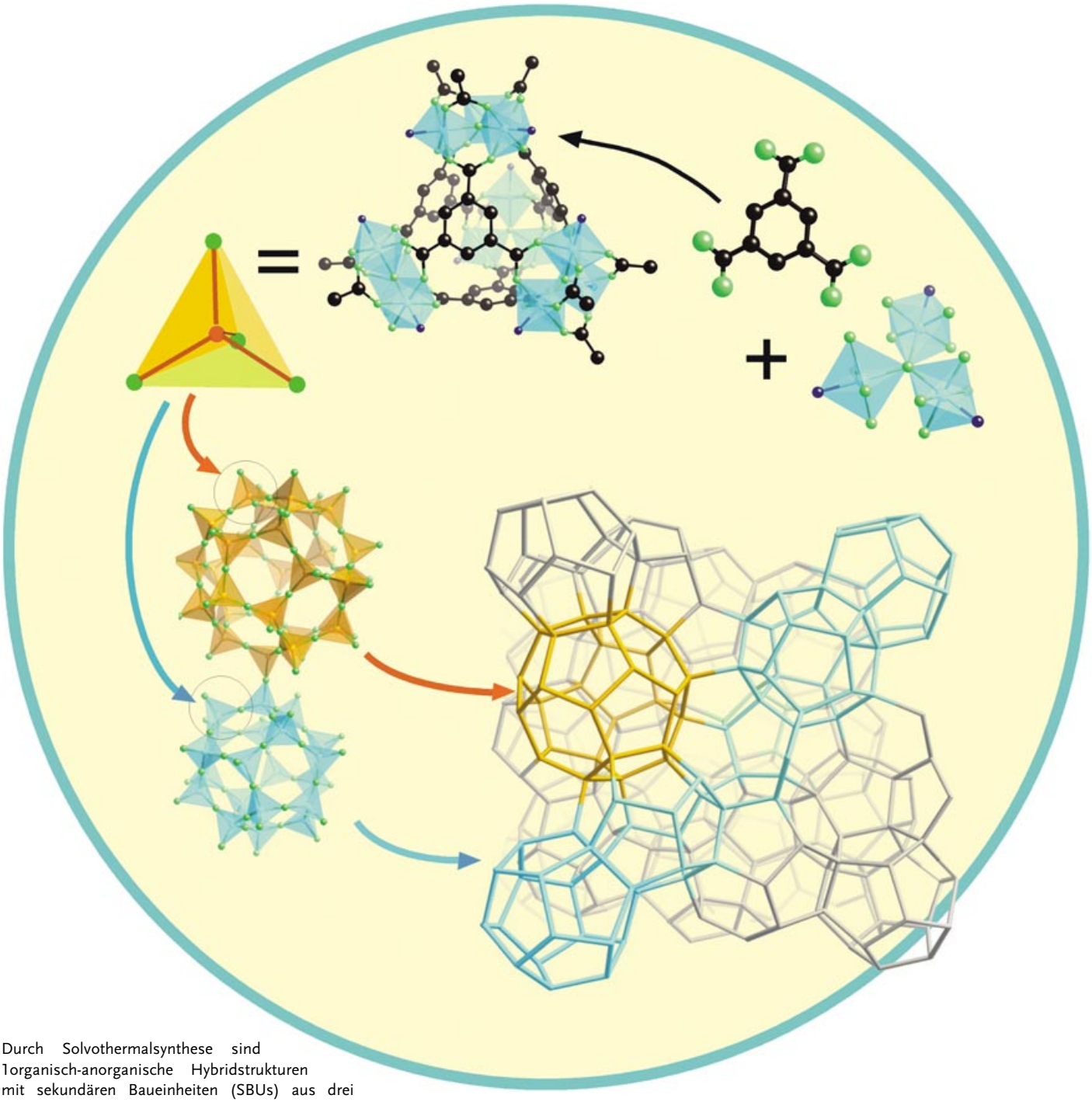
Zuschriften



Durch Solvothermalsynthese sind 1organisch-anorganische Hybridstrukturen mit sekundären Baueinheiten (SBUs) aus drei Metall(III)-Zentren zugänglich, deren Kristallstrukturen vorhergesagt werden können. Für den mikro- und mesoporösen Feststoff aus einer trimeren Chrom(III)-SBU und 1,3,5-Benzoltricarboxylat entspricht die berechnete Kristallstruktur dem experimentellen Beugungsbild. Weiteres erfahren Sie in den Zuschriften von C. Serre, C. Mellot-Draznieks, G. Férey und Mitarbeitern auf den folgenden Seiten.

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Nanoporous Materials

A Route to the Synthesis of Trivalent Transition-Metal Porous Carboxylates with Trimeric Secondary Building Units**

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Porous solids with either purely inorganic[1] or organic–inorganic hybrid skeletons[2] are currently very topical,[3–7] owing to their applications in ion exchange, gas separation, catalysis, and more recently in hydrogen storage.[8–10] The recent introduction of transition metals in the framework has increased the range of possible applications by exploiting their electronic and magnetic properties.[11–13] However, most hydrothermal or solvothermal syntheses are based on "trial and error" but with some successes with divalent (e.g., Co, Ni, Cu) or trivalent cations (V, Cr),[11,13,14] The most important goal in the field is always to reach a real "design" of hybrid porous solids, that is, the way to obtain tailor-made solids with the required structures and properties starting from well-characterized inorganic and organic species. From this point of view, the number of synthetic routes that use a controlled approach based on secondary building units (SBUs) is still scarce. If some relative successes have been achieved in the past decade with the use of porphyrin building blocks[15] or by the combination of zinc, bypiridine, and SiF_6^{2-} ions,[16,17] then the most efficient synthetic route was developed by Yaghi and co-workers with the use of tetrameric Zn_4O zinc clusters.[18] A few solids were also obtained recently with dimeric[19] or trimeric zinc SBUs.[20–22] Thus, a large number of hybrid solids with pore sizes up to 27 Å and very high surface areas ($\approx 4500\ m^2 g^{-1}$) have been prepared. However, in the cases mentioned above their synthesis conditions are not a complete SBU approach. Soluble monomeric zinc precursors and defined synthesis conditions are used either to allow the formation, with reasonable stability, of these building units in solution prior to the reaction with carboxylate moieties, or to allow the cooperative formation of the building unit in the presence of the carboxylates moieties.

We report herein a new and "controlled SBU" approach for trimeric inorganic species (three metallic octahedra shared by μ_3-O), which keeps the integrity of the inorganic precursor during the formation of the solid. The approach involves acetates of trivalent transition metals (e.g., Fe, Cr, V, Ru, Mn, Co),[23,24] as precursors, which are trimeric. The trimeric acetate building unit is first prepared, then introduced into the reaction media in the presence of the dicarboxylic acid and finally, by increasing the temperature and in the presence of base, a direct exchange between the monocarboxylate (acetate) and the dicarboxylate moieties occurs to produce a 3D solid in which the trimeric SBU remains intact. We also report the successful use of these SBUs in the rational synthesis of two new open-framework iron(III) dicarboxylates. This paper deals with the synthesis, characterization and the structure determination from X-ray powder data of two new 3D open-framework iron(III) dicarboxylates: $Fe^{III}_3O(CH_3OH)_3\{^-O_2C\text{-}(CH)_n\text{-}CO_2^-\}_3 \cdot X^- \cdot (CH_3OH)_m$; $X^- = CH_3CO_2^-$, $n = 2$, $m \approx 4.5$ (**MIL-88**; see Figure 1) or $X = Cl^-$ $n = 4$, $m \approx 6$ (**MIL-89**).

MIL-88 exhibits a 3D structure built up from trimers of iron(III) octahedra linked to fumarate dianions to create a 3D framework (Figure 2). This structure delimits both a 1D pore-channel system along the *c* axis (Figure 2a), which is filled with solvent molecules, and cages, which are filled with acetate groups (Figure 2b). The free methanol molecules that are present within the pores interact both through hydrogen bonds with oxygen atoms of the inorganic trimers and through Van der Waals interactions with the $-CH_3$ groups of both the free and bound methanol molecules. It should be noticed that during the determination of the structure, a partial-site occupancy was applied (see Supporting Information) for the disordered free methanol (C(4)-O(6) and C(7)-O(5)) and acetate groups (C(5), C(6) and O(7)).

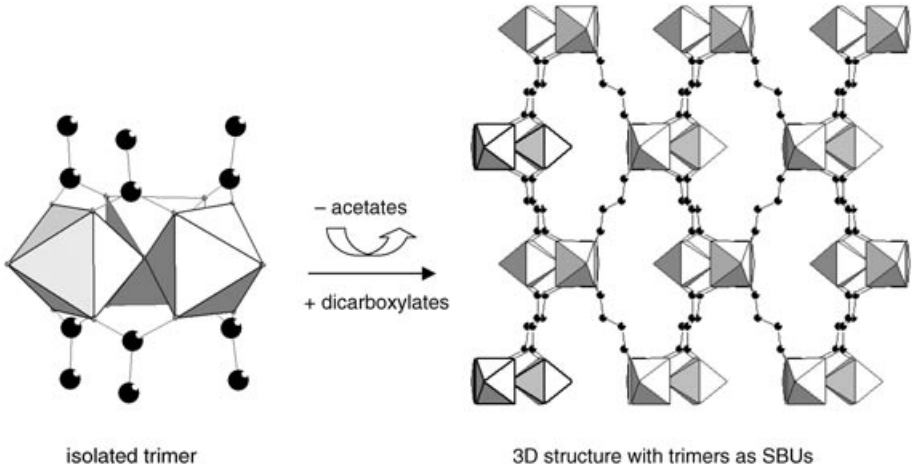

Figure 1. Schematic representation of the synthetic route involving trimeric SBUs with **MIL-88** given as an example.

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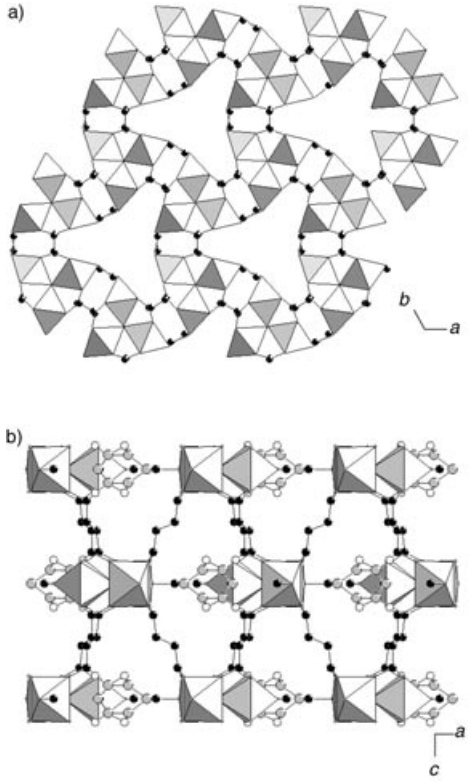

Figure 2. View of the structure of **MIL-88**: a) along the *c* axis; b) along the *b* axis. Iron octahedra, oxygen and carbon atoms are represented in white, white and black respectively. For a better understanding, free methanol molecules and acetate groups have been removed from (a) whereas carbon atoms from the acetate are in gray in (b).

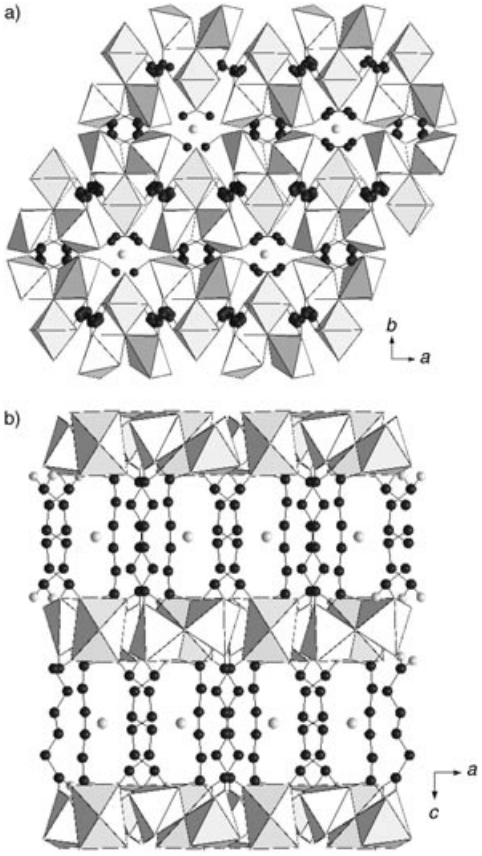

Figure 3. View of the structure of **MIL-89ht**: a) along the *c* axis; b) along the *b* axis. Key: Fe octahedra white; O atoms white; C atoms black; Cl atoms gray.

In the case of **MIL-89**, only the structure of the high-temperature form of **MIL-89** labeled **MIL-89ht** (ht signifies high temperature) or $Fe^{III}_3O(CH_3OH)_3\{^-O_2C\text{-}C_4H_4\text{-}CO_2^-\}_3\cdot Cl^-$ has been determined (see Experimental Section). **MIL-89ht** also exhibits a 3D structure built up from trimers of iron(III) octahedra. The trimers are related together by *trans*, *trans* muconate moieties, which ensures the three-dimensionality of the framework (Figure 3); small channels are also present along the *c* axis and are filled with terminal methanol groups and chloride ions. As previously observed for **MIL-88**, a partial occupancy was found for a carbon atom (C(11)) of one terminal methanol molecule (C(11)-O(7)).

In both structures, iron atoms are situated within an octahedral environment of four oxygen atoms from the bidendate dicarboxylates, one μ_3O atom, and one oxygen atom from the terminal methanol group. Octahedra are related through the μ_3O oxygen atom to form the trimeric building units. Interatomic distanes and angles are generally well defined with Fe–O, C–O, and C–C bond lengths within 1.83–2.04, 1.26–1.50, and 1.37–1.40 Å, respectively, for **MIL-88** and 1.88–2.23, 1.27–1.50 A, 1.37–1.48 Å, respectively, for **MIL-89ht**. Bond-valence calculations indicate that iron atoms in both structures are in a trivalent state. Mössbauer experiments indicate that both solids have only octahedral iron(III) centers in a high-spin state; these results will be reported soon in a full paper with a detailed study of the thermal behavior and the sorption capacities of these solids.[25]

Despite the presence of the same SBUs in both **MIL-88** and **MIL-89ht**, their structures have significant differences. First, the position of the counteranion (Figure 4): in **MIL-88**, the counterions are disordered acetate groups located at the centre of cages and surrounded by five trimers and six organic chains. **MIL-88** can thus be considered as being built up from successive layers of trimers alternating with acetate groups in the (010) plane; the three-dimensionality is ensured by the fumarate moieties along the *c* axis. In **MIL-89ht**, the packing of trimers in the (010) plane is much denser and thus the chloride counterion is now located between the layers within the small channels along the *c* axis, delimited by six different alkenes chains and six iron trimers. These differences could come from the presence of free solvent in **MIL-88**, whereas solvent from **MIL-89ht** has been removed; it is likely that **MIL-89** increases its cell volume when filled with methanol as this phenomenon occurs with **MIL-88** (cell volume increase $>50\,\%$) when filled with methanol. This "breathing" is probably accompanied by a displacement of the anions in both cases; these results will be reported soon.[25]

As described above, two new open-framework iron(III) dicarboxylates have been obtained through the "controlled SBU" approach with retention of the initial trimeric SBU. However, it cannot be proven experimentally whether the trimeric SBU precursor remains intact throughout the synthesis or whether it breaks up and reforms. In the presence of

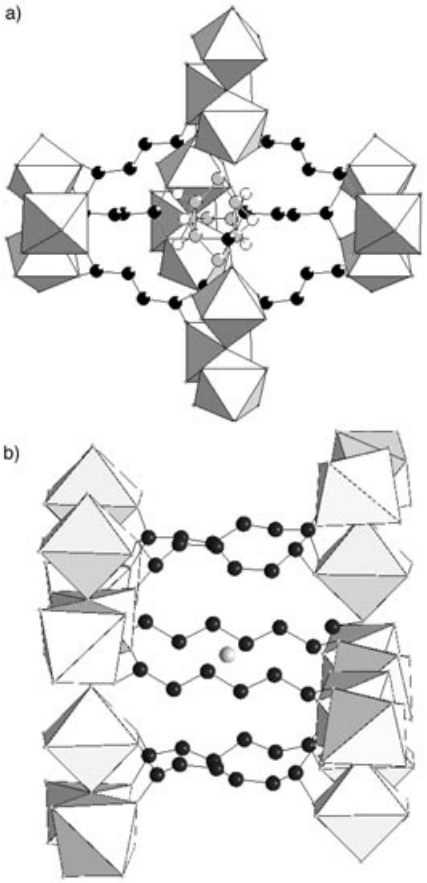

Figure 4. View of the cages delimiting the anionic moieties in **MIL-88** (a) and **MIL-89ht** (b). Key: same as that Figure 3 except C atoms from the acetate and Cl atoms are in gray.

terephthalic acid and with the same trimeric SBU precursor under similar solvothermal conditions, a partial destruction of the SBU occurred during the synthesis. The resulting solid, **MIL-85**, was built up from both trimeric SBUs and monomers and even some of the acetate ligands present in the initial precursor were retained.[26] The presence of both trimers and acetate moieties within **MIL-85** indicates that part of the trimeric precursor is probably kept during the synthesis.

Trivalent metal dicarboxylate (**MIL-59**) built up from trimers of octahedra has been reported recently by our group by using a vanadium(III) complex and isophtalic acid under hydrothermal conditions following the "trial and error" method. In this case, a cubic structure with cuboidal cages filled with solvent and chloride ions was observed.[14] This is the only case of trimeric transition-metal carboxylate obtained to date under hydrothermal conditions that exhibit trimeric SBU.

Finally, our method is a new synthetic route that favors the synthesis of open framework transition-metal carboxylates with the trimeric SBUs.

These results show also that despite the presence of identical trimeric SBUs, the structural type in the final solids strongly depends on the nature of the organic linker, thus demonstrating the structural richness of this synthetic route. This successful use of predetermined SBUs in the synthesis of metal carboxylates also opens the way for the "design" of hybrid solids by using the simulation tool.[27–29] This is also the first SBU route that involves trivalent cations; the number of hybrid solids based on trivalent transition or p-block metals is still scarce.[11–14,30–32]

In addition, as clusters of trimeric metal acetates with various physical properties can be obtained with a large number of transition metals, such as chromium, iron, vanadium, ruthenium, manganese, or cobalt,[23,24] there is a the potential to synthesize open-framework trivalent metal polycarboxylates with different pore shapes and sizes as well as unique physical properties. Several other porous hybrid solids based on these trimeric SBUs with various trivalent cations have been synthesized and will be soon reported, thus enlarging the field of hybrid phases based on trimeric transition-metals SBU.

Experimental Section

Synthesis: The trimeric iron(III) acetate SBU was first prepared according to Dziobkowski et al.[33] Subsequently, iron(III) acetate, fumaric acid (HO_2C-C_2H_2-CO_2H; Acros, 99%) or *trans*,*trans*-muconic acid (HO_2C-C_4H_4-CO_2H; Aldrich, 98%), sodium hydroxide (Aldrich, 97%), deionized water, and methanol (Prolabo, 99%) were mixed in the following ratios: 1:3:1.5:50:1000 (based on one trimer). The resulting orange gels were aged at 100°C for 3 days in a teflon-lined Parr bomb and cooled down to room temperature. The light-orange solids are filtered, washed with methanol and acetone, and dried at room temperature.

General analysis: Structure determination of **MIL-89** was carried out only on the high-temperature form **MIL-89ht**; general analysis was carried out on the room-temperature form that contains free solvent molecules.

Thermal gravimetric analysis (TGA): TGA were performed in air on both solids (**MIL-88** and **MIL-89**) by using a TA-Instrument type 2050 analyzer. The results from both samples showed several weight losses in the range from 273 to 873 K (see the Supporting Information). The residual solid was identified as Fe_2O_3. **MIL-88** exhibits two weight losses of $\approx$19.5 and 49%, the first within the range of 373–423 K, which corresponds to the departure of the free methanol groups followed by the departure of bound methanol; the second within the range of 673–773 K, which corresponds to the loss of the dicarboxylate and the anionic group. The same behavior is observed for **MIL-89** with two losses of $\approx$20% and 56%. In the analysis of both samples, Fe_2O_3 crystallizes at higher temperatures. The losses generally agree with the theoretical values (**MIL-88**: free solvent: 17.3%, bound solvent plus organic fraction plus anion: 53.8%; **MIL-89**: free solvent: 20.7%, bound solvent plus organic fraction plus anion: 53.7%). In the case of **MIL-89**, the best matching between observed and calculated TGA losses has been reached for a content of six free methanol groups per trimer of iron octahedra.

Elemental analysis: Iron, carbon, and chlorine contents were determined at the C.N.R.S. Central Laboratory of Analysis of Vernaison (France). Elemental analysis (%) calcd for **MIL-88**: C 31.04, Fe 20.2; found: C 24.0, Fe 21.8, Cl trace. Elemental analysis (%) calcd for **MIL-89**: C 34.9, Fe 18.1, Cl 3.83; found: C 28.12, Fe 20.22, Cl 3.92. The deficit in observed carbon content comes in both cases from the rapid loss of free methanol at room temperature (**MIL-88**: $\approx$3–4 days; **MIL-89**: $<$1 day), which automatically decreases the carbon content observed by quantitative analysis.

Density measurements: To avoid problems of free methanol desorption at room temperature, an experiment performed on a fresh sample of **MIL-88** by using a Micromeretics apparatus, Accupyc 1330.

A volumic density of 1.55 $g\,cm^{-3}$ corresponds reasonably well with the calculated one (1.73 $g\,cm^{-3}$).

Infrared spectroscopy: The infrared spectra of the title compounds clearly shows in both cases the presence of the vibrational bands characteristic of the -(O-C-O)- groups around 1550 and 1430 cm^{-1}, thus confirming the presence of the dicarboxylate within the solids. Large bands around 3500 cm^{-1} also confirmed the presence of OH groups in both solids.

Structure determination: All attempts at obtaining single crystals failed in both cases. The powder X-ray diffraction pattern of **MIL-88** was collected on a D5000 (θ-2θ mode) Siemens diffractometer with $\lambda(Cu_{K\alpha1,K\alpha2}) = 1.54059$, 1.54439 Å. In the case of **MIL-89**, due to the rapid evolution of the pattern at room temperature as well as a decrease in the crystallinity (see Supporting Information), a temperature in situ data collection was performed at 373 K by using a D5000 (θ-2θ mode) Siemens diffractometer equipped with an Anton Paar HTK1200 oven. The pattern of **MIL-88** was indexed in the hexagonal space group $P\bar{6}2c$ (no. 196) by using the Dicvol program,[34] with the following cell parameters $a = 11.04(1)$ Å, $c = 14.80(1)$ Å. The pattern of **MIL-89ht** was indexed in the orthorhombic space group *Pbnn* (no. 52) with $a = 9.135(1)$ Å, $b = 16.137(1)$ Å, $c = 19.968(1)$ Å. Then, direct methods were realized by using the Expo program to localize the iron atoms and some of the oxygen atoms.[35] Due to poor quality of the data in the case of **MIL-89ht**, a combination of the Expo and the Cerius programs was used,[36] which allows the manipulation of the whole trimeric building block and based on the position of the iron atoms found by Expo, Cerius allowed us to place the whole inorganic SBU and the first carbon atoms of the muconate moieties at a position compatible with the direct-method findings and the experimental X-Ray diffraction pattern. Finally, free and bound methanol molecules and the anionic counterions were located by successive Fourier difference by using Shelxtl.[37] In the case of **MIL-88**, disorder was present for the methanol groups and for the acetate anion and half occupancies were applied during the refinement. For **MIL-89ht**, the carbon atom of one of the terminal methanol groups was also placed with a half occupancy. Finally, both structures were refined by using Fullprof[38] and its Winplotr program.[39] Full details of the structure determination are reported in the Supporting Information.

The formula deduced from the structure determinations for **MIL-88** and **MIL-89ht** are: $Fe^{III}_3O(CH_3OH)_3\{O_2C\text{-}C_2H_2\text{-}CO_2\}_3\cdot(CH_3\text{-}CO_2)\cdot n\,CH_3OH$ ($n = 4.5$) and $Fe^{III}_3O(CH_3OH)_3\{O_2C\text{-}C_4H_4\text{-}CO_2\}_3\cdot Cl$. The final agreement factors[40] were satisfactory for **MIL-88**: $R_p = 11.9\,\%$, $R_{Bragg} = 8.3\,\%$ and $R_F = 7.7\,\%$. In the case of **MIL-89ht**, factors are higher because of the poor quality of the X-ray data ($R_p = 13.7\,\%$; $R_{Bragg} = 15.6\,\%$, $R_F = 9.7\,\%$) and only an approached structure of **MIL-89ht** is proposed for the moment; better X-ray data will be collected soon on the wet phase by using capillaries to determine more precisely the structure of **MIL-89**. Final Rietveld plots, atomic coordinates, and principal interatomic distances are given in the Supporting Information.

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