

$V^{III}(OH)\{O_2C-C_6H_4-CO_2\} \cdot (HO_2C-C_6H_4-CO_2H)_x(DMF)_y(H_2O)_z$ (or MIL-68), a new vanadocarboxylate with a large pore hybrid topology : reticular synthesis with infinite inorganic building blocks?†

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$V^{III}(OH)\{O_2C-C_6H_4-CO_2\} \cdot (HO_2C-C_6H_4-O_2H)_x(DMF)_y(H_2O)_z$ or MIL-68 was solvothermally synthesised in a non-aqueous medium. Its structure, built up from octahedral chains connected by terephthalate linkers, exhibits large hexagonal channels containing different occluded moieties. Their irreversible removal releases a specific surface area of 603(22) $m^2 \cdot g^{-1}$ (BET).

First devoted to the aluminosilicate zeolite compounds, then extended to the organically templated metallophosphates, the microporous solids field is characterised to date by a large range of compounds differing both in their chemical composition and their topology.^{1–2} Derived from coordination chemistry, the use of the hybrid microporous compounds leads to structures built up from the association of inorganic and organic moieties inside the same framework. That requires organic reactants functionalized by complexing groups (carboxylates, sulfonates, phosphonates ...) or hetero-atoms (nitrogen, sulfur ...) available to integrate the coordination of the metallic ions. The pioneering works of Robl³ have been so largely reinvestigated under hydrothermal conditions by many research groups that it would be difficult to give an exhaustive list of references. However, the papers of Yaghi are of the first importance because they attempt to rationalise this type of synthesis^{4–5} and remarkably illustrate with the IRMOF-n series the possibility to modulate the porosity of the structures by controlling the steric hindrance of the organic molecules.⁶ Indeed, the association of one zinc tetrameric cluster with different carboxylates allows the control of the pore size in the range 3.8–19.1 Å. Transposed to vanadium, we have recently described new vanado(m)carboxylates whose inorganic building blocks are not discrete species but infinite octahedral chains.^{7–8} This particular feature opens the way toward hybrid compounds with extended physical properties; for the vanadocarboxylates, magnetic ordering is observed inside the chains (at a temperature close to 100 K for MIL-47_{as}⁷). We report here on the solvothermal synthesis and the structure of a new vanadocarboxylate strongly related to the previous ones.

In contrast to the previously reported hybrid vanadocarboxylates,^{7–10} MIL-68 is synthesised under solvothermal conditions using a non-aqueous medium.†), the water is totally substituted by *N,N*-dimethylformamide. Nevertheless, the resulting structure is built up from the same inorganic building blocks as those already encountered in MIL-47_{as},⁷ MIL-60 and MIL-61.⁸ They are constituted of tilted chains running along [001] of $V^{III}(OH)_2O_4$ octahedra (Fig. 1) sharing their *trans* apices occupied by hydroxy functions. The almost regular octahedral geometry around the vanadium atoms as well as the valence bond calculations¹¹ give the evidence of vanadium in the +3 oxidation state. The tilting is induced by the linkage of two consecutive octahedra by two carboxylate functions. The connection of these octahedral chains by the terephthalate linkers deals with the formation of two kinds of one-directional channels (Fig. 2): small triangular channels delimited by three inorganic files and large channels delimited by six files. The first ones are empty whereas the second whose diameter

is equal to 18.6 Å (O(2)–O(2) distances) are filled by disordered molecules of water, DMF and terephthalic acid not located from X-ray diffraction experiments. The chemical formula of the title compound was then deduced from different chemical analyses (elemental analyses, IR spectroscopy and TG measurements).

The calcination of these occluded species (typically 12 h at 250 °C) does not destroy the MIL-68 framework which conserves a

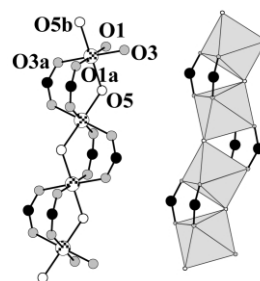


Fig. 1 “Ball & stick” and polyhedral representations of one octahedral chain; just the carbon atoms ensuring the anchorage of the terephthalate linkers are drawn (circles : hatched for V(2), black for carbon, grey for oxygen, hollow for oxygen of hydroxy groups). [V2–O3 1.984(2) Å, V2–O1 1.987(2) Å, V2–O5 1.933(2) Å, V2–O5–V2 125.1(2)°; symmetry operators (a) for $\frac{1}{2}-x \frac{1}{2}-y 1-z$ and (b) for $\frac{1}{2}-x \frac{1}{2}-y \frac{1}{2}+z$.]

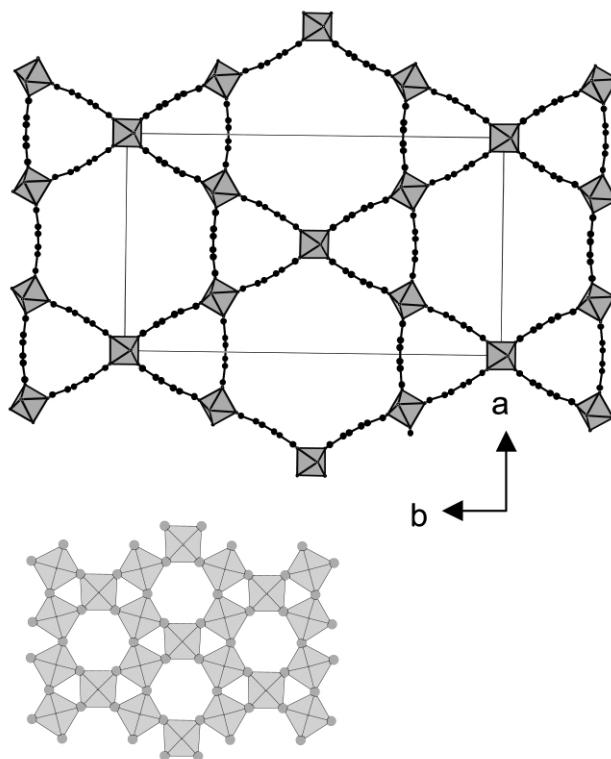


Fig. 2 Projections of the structure of MIL-68 along [001] (the disordered species inside the channels are not represented) and its related hexagonal bronze topology.

† Electronic supplementary information (ESI) available: Schemes S1–3 and Tables S1–4. See <http://www.rsc.org/suppdata/cc/b3/b312589k/>

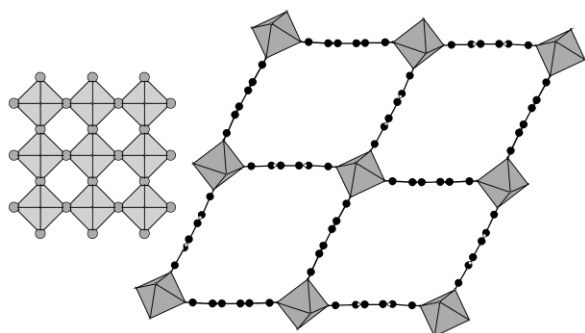


Fig. 3 Projections of the structure of MIL-47 and its related ReO_3 topology.

permanent porosity measured by gas sorption isotherm experiments in liquid nitrogen. MIL-68 reveals a type I isotherm without hysteresis upon desorption. The measured BET surface area is $603(22) \text{ m}^2\text{g}^{-1}$ and, assuming monolayer coverage by N_2 , the Langmuir surface area is $847(1) \text{ m}^2\text{g}^{-1}$.

Structurally, MIL-68 exhibits strong relationships with MIL-47 since their two structures are built up from identical octahedral chains linked *via* the same organic linkers (Fig. 3) in such a way that their 3D frameworks correspond to the same stoichiometry. However, using the Schläfli notation, MIL-47 and MIL-68 correspond to 4^4 and $6.3.6.3$ networks of vanadium atoms respectively and no structural transition between the two phases can be expected without a reconstructive mechanism. The inorganic sub-network of MIL-68 could be described as a lacunar variety of MIL-47 with one octahedral chain missing over four. Since the octahedral chains appear as invariant building blocks of the vanado(III)carboxylate series, the comparison between MIL-47 and MIL-68 may be revisited using the reticular synthesis concept recently introduced by Yaghi⁵ for hybrid compounds containing discrete inorganic moieties. This one is defined as 'the process of assembling judiciously designed rigid molecular building blocks into predetermined ordered structures' (extract from ref. 5). Transposed to infinite octahedral files (rigid building blocks), this requires that the targeted structures result from the condensation of such polymeric moieties. That is encountered with the ReO_3 and hexagonal bronze structural types whose frameworks (inserts of Figs. 2 and 3) consist of parallel octahedral chains fused by anions (grey circles on the figures). The replacement of these anions by linear organic linkers (terephthalate anions) leads to the 'augmented' structures (as described in ref. 4) MIL-47 and MIL-68. This concept provides two ways to imagine new microporous compounds not yet discovered: (i) by increasing the length of similar bidentate carboxylates, the ReO_3 or hexagonal bronze topologies could be conserved, (ii) by synthesising new structures related to other parent structural types built up from octahedral chains as for example the tetragonal bronze topology.

At least, the more exciting challenge could be the adaptation of both MIL-47 and MIL-68 frameworks as the two constitutive elements of intergrowth hybrid compounds related to the oxide phases ITB developed in the 1970's by Kihlberg *et al.*¹²

Notes and references

‡ The title compound was solvothermally synthesised from a mixture of $\text{VOSO}_4 \cdot 5\text{H}_2\text{O}$ (Prolabo), 1,4-benzenedicarboxylic acid (Aldrich, 98%) and *N,N*-dimethylformamide (Aldrich, 99.8%) in the molar ratio 1 : 2 : 117 heated 72 hours at 473K in a teflon-lined stainless steel autoclave from Parr

(filling level ~25%). The pH remains close to 1 throughout the synthesis. The solid phases were separated from the liquid by filtration, washed with water then dried in air at room temperature. MIL-68 grows in the form of yellow acicular crystals with a yield greater than 80%. TG experiments were performed under O_2 with a heating rate of 5° min^{-1} using a TA Instrument TG2050 apparatus. The thermogram shows four distinct weight losses assigned first to a dehydration phenomenon below 100° C (12.1% obs. vs 11.4 th.) and the departure of the molecules occluded in the channels (DMF at 200° C then free terephthalic acid at 300° C , 7.7% and 9.1% obs. vs 7.6% and 7.9% th. respectively), the last one occurs at 400° C and corresponds to the combustion of the organic species of the framework (40.5% obs. vs 44.5% th.). At higher temperatures, one observes the recrystallization of vanadium pentaoxide V_2O_5 . Density was measured with a Micromeritics multipycnometer working under He flow ($1.625(8) \text{ g}\cdot\text{cm}^{-3}$ meas. vs $1.577 \text{ g}\cdot\text{cm}^{-3}$ th.). Elemental analysis was achieved : C, 37.7% found (38.6% calc.) ; V, 18.4% found (16.1% calc.) ; N, 1.7% found (1.5% calc.). These experiments are in good agreement with the following formula for MIL-68 : $\text{V}^{\text{III}}(\text{OH})\{\text{O}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\}_x(\text{HO}_2\text{C}-\text{C}_6\text{H}_4-\text{CO}_2\text{H})_y(\text{DMF})_z(\text{H}_2\text{O})_z$ with $x = 0.15$, $y = 0.33$, $z = 2$.

IR data (KBr pellets, cm^{-1}) : 3460br, 3020vw, 2670w, 2550w, 1690s, 1660m, 1540s, 1520m, 1420m, 1390s, 1320w, 1290m, 902s, 740s, 575s. Crystal data for MIL-68 : $M = 317 \text{ g}\cdot\text{mol}^{-1}$, orthorhombic system, space group $Cmcm$ ($n^\circ 63$), $a = 21.211(2)$, $b = 36.721(4)$, $c = 6.8606(6) \text{ \AA}$, $V = 5343.5(9) \text{ \AA}^3$, $Z = 16$, $T = 293 \text{ K}$. 7810 collected reflections, 969 independent reflections $I \geq 2\sigma(I)$ ($R_{\text{int}} = 0.1131$), 111 refined parameters, $R1(F_o) = 0.0975$, $wR2(F_o^2) = 0.2635$. CCDC 222072. See <http://www.rsc.org/suppdata/cc/b3/b312589k/> for crystallographic data in .cif or other electronic format.

Single crystal ($0.04 \times 0.02 \times 0.01 \text{ mm}^3$) X-ray diffraction data were recorded on a three-circles Siemens SMART diffractometer equipped with a bidimensional CCD detector (monochromatized $\text{MoK}\alpha$ radiation, $\lambda = 0.71073 \text{ \AA}$). Lattice parameters were determined from a first set of frames then refined during the data collection with all the intensities $I \geq 10\sigma(I)$. Reduction data and Lorentz-polarization corrections were performed using the SAINT program then a semi-empirical absorption correction was applied using SADABS program.¹³ The structure was solved applying the direct methods (TREF option) of SHELX-TL,¹⁴ V (V1 and V2 atoms on (4a) and (8d) special positions respectively) and O atoms were first located then the remaining atoms were deduced from Fourier difference syntheses. The contribution to the intensities of the disordered species located in the channels was corrected using the PLATON/SQUEEZE¹⁵ program to improve the quality of the framework model. The H atoms of the terephthalate linkers were found using geometrical constraints. All the atoms (except H) were anisotropically refined.

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