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Synthesis, structure determination and properties of MIL-53as and MIL-53ht: the first Cr^{III} hybrid inorganic–organic microporous solids: $Cr^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}\cdot\{HO_2C-C_6H_4-CO_2H\}_x$†

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The first three-dimensional chromium(III) dicarboxylate compounds have been isolated and their structures solved from powder X-ray diffraction data; the flexible framework of these materials delimits large pores.

The search for novel microporous materials continues to be very active because of the wideness of their potential applications in catalysis, shape-selective absorption, non linear optical (NLO) devices or molecular-based magnetism.

The recent interest in the synthesis of hybrid inorganic–organic solids gives a new dimension to the domain of porous compounds.[1–4] They offer significant scientific and technological opportunities by combining attractive features of both moieties within a single material. Most of them are prepared under mild hydrothermal conditions ($T < 200$ °C, autogenous pressure) using functionalized organic ligands (*e.g.* phosphonates, carboxylates). Many elements in the Periodic Table have been incorporated in new framework materials exhibiting structures not seen in zeolite chemistry.[5] The introduction of transition metals within the skeleton provides new electronic properties.[4,6] However, one of the fascinating questions still under investigation is why some metals are difficult to incorporate into the framework. Chromium is one of these metals because of its chemical inertness (slow polymerisation and difficulty of substitution).[7,8] To the best of our knowledge, only a few materials have been reported: partial substitution of Cr into $AlPO_4$-5,[9] and cyano-bridged 3D coordination polymers.[10] Herein we describe the synthesis, structures, magnetic and sorption properties of the first three-dimensional and microporous chromium(III) dicarboxylates.

One of the new solids was isolated as a pure, polycrystalline powder from a reaction mixture of composition $1.0\,Cr(NO_3)_3\cdot xH_2O : 1.0\,$1,4-BDC$: 1.0\,HF : 280\,H_2O$ (1,4-BDC = benzenedicarboxylic acid or terephthalic acid) that was held at 220 °C in a Teflon-lined autoclave for 3 days. The pH remains very acidic (< 1) throughout the synthesis. The light purple solid product was recovered by filtration, washed with deionized water, and dried at room temperature. A laboratory powder X-ray diffraction pattern showed that a novel crystalline phase had been produced, although contaminated with traces of recrystallised terephthalic acid. Elemental analysis indicated that the contents of Cr, C and H are in good agreement with the values based on the structure formula $Cr^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}\cdot\{HO_2C-C_6H_4-CO_2H\}_{0.75}$ (labelled **MIL-53as**). It has not been possible to prepare crystals of suitable size for single-crystal diffraction studies whatever the synthesis conditions. If HF is omitted from the reaction, the resulting materials are poorly crystallised. Thermal analysis (TGA2050 TA apparatus, O_2 flow, heating rate 2 K min^{-1}) has shown two weight losses between 298 and 873 K. The first (*ca.* 28%) at 523 K is attributed to the departure of the free terephthalic acid remaining inside the pores. The removal of the terephthalic guest gave the evacuated high temperature form: $Cr^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}$ (labelled **MIL-53ht**). The second weight loss (*ca.* 50%) at 723 K is related to the combustion of the terephthalic acid of the framework. These two losses are on the whole in agreement with the theoretical values (calc. 75%). The residual solid has been identified as poorly crystallised chromium oxide Cr_2O_3. The high temperature calcined form **MIL-53ht** can be isolated as a pure, polycrystalline powder by calcination (for 200 mg of **MIL-53as**) for 30 h under air at 573 K in a tubular furnace. At room temperature, **MIL-53ht** reabsorbs atmospheric water immediately to give finally the low temperature form: $Cr^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}\cdot H_2O$ (labelled **MIL-53lt**). Thermal analysis (TGA) measurements performed on **MIL-53lt** show two different weight losses. After a slight continuous weight loss at low temperature (< 353 K: obs. 7.3%; calc. 7.2%), which is due to absorbed water, the removal of the terephthalic acid of the framework is observed at 723 K (obs. 58%; calc. 62%).

The structures of two of the new materials were solved from laboratory powder X-ray diffraction data.‡ It appeared that **MIL-53as** and **MIL-53ht** have X-ray diffraction patterns and cell parameters close to those of the vanadium analogues MIL-47 recently isolated by our group: $V^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}\cdot\{HO_2C-C_6H_4-CO_2H\}_{0.75}$ and $V^{IV}O\cdot\{O_2C-C_6H_4-CO_2\}$.[6] The crystal structure of MIL-47as was then used as the starting model for **MIL-53as**. In the case of **MIL-53ht**, however, a different space group was found and an *ab initio* approach was undertaken for the structure solution; the final Rietveld plot is shown in Fig. 1.

Both solids **MIL-53as** and **MIL-53ht** present the same topology with a three-dimensional structure, built up from chromium(III) octahedra and terephthalate anions, that exhibits large pores. The Cr polyhedra share the axial μ_2 hydroxy groups to produce an almost linear chain and all of the (equatorial) oxygens are shared with the dicarboxylate molecules. Bond

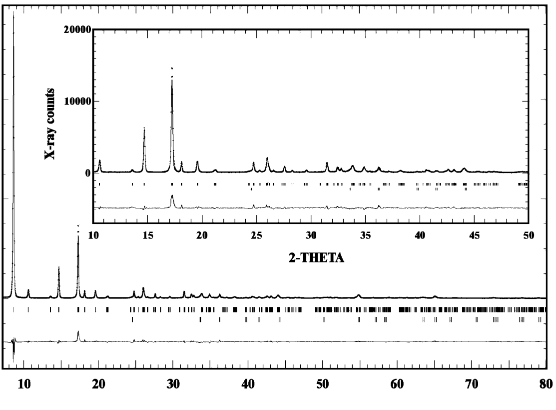

Fig. 1 Final Rietveld refinement plot for $Cr^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}$ (**MIL-53ht**) in the space group *Imma*. Observed, calculated and difference profiles are plotted on the same scale. Bragg peaks are indicated by tick marks for the main phase $Cr^{III}(OH)\cdot\{O_2C-C_6H_4-CO_2\}$ and a small impurity (Eskolaïte, Cr_2O_3). Inset is an expanded region of a small part of the data.

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† Electronic supplementary information (ESI) available: crystal data, atomic coordinates and metrical parameters for **MIL-53as** and **MIL-53ht**. See http://www.rsc.org/suppdata/cc/b2/b201381a/

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valence calculations and infra-red spectroscopy gave further evidence for the presence of this bonding: a narrow band at 3500 cm^{-1} is assigned to the vibrations of OH groups. The chains are then linked together with dicarboxylates to create the three-dimensional microporous structure. Each tunnel is delimited by four walls of benzyl units and four chains of corner-shared chromium octahedra (Fig. 2). Such a topology is close to that of $[\{CuSiF_6(4,4'\text{-bipyridine})_2\}_n]$ in which the chains are formed by alternation of CuN_2F_4 and SiF_6 octahedra linked by corners, leading to a 2D compound.[11] In **MIL-53as**, the terephthalic acid guest is highly disordered. Chemical analysis, density measurement, and the recrystallisation of terephthalic acid in the cold parts of the apparatus during the degassing phase for BET measurements confirm this hypothesis. The third compound, $Cr^{III}(OH)\cdot\{O_2C\text{–}C_6H_4\text{–}CO_2\}\cdot H_2O$ (**MIL-53lt**), which, in analogy to its parent (**MIL-53ht**) compound, should also contain infinite chains separated by dicarboxylates, exhibits a totally different X-Ray diffraction pattern. No cell indexing or its structure have been determined from powder diffraction data due to an anisotropic enlargement, which is reversible upon heating, of some Bragg reflections.

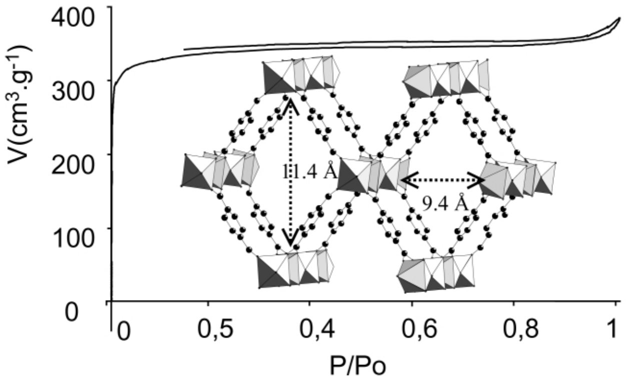

Fig. 2 N_2 sorption and desorption isotherms measured at 77 K for $Cr^{III}(OH)\cdot\{O_2C\text{–}C_6H_4\text{–}CO_2\}$ (**MIL-53ht**). Inset is a perspective view of the structure.

The permanent porosity of the three new solids was measured by gas sorption isotherm experiments performed in liquid nitrogen. While **MIL-53as** evidently did not present any capacity for N_2 sorption, both **MIL-53ht** and **MIL-53lt** revealed a type I adsorption–desorption isotherm characteristic of microporous solids (Fig. 2). The corresponding Langmuir surface area was estimated to be over 1500 $m^2\ g^{-1}$ and 1150 $m^2\ g^{-1}$ for **MIL-53ht** degassed at 473 K overnight and for **MIL-53lt** degassed at room temperature overnight, respectively. This confirms that the pores of **MIL-53lt** are almost empty despite the presence of water molecules. The evolution of the X-ray powder pattern between the filled and evacuated phases allows us to illustrate the flexibility of the framework with or without guest (terephthalic acid) (Fig. 3).

This is in agreement with the evolution of the free aperture of the pores estimated, taking into account the van der Waals radius of oxygen, *ca.* 8.3 × 12 Å and 9.4 × 11.4 Å for **MIL-53as** and **MIL-53ht**, respectively (inset of Fig. 2). This breathing phenomenon is, however, slightly less pronounced than with the vanadium analogue MIL-47.

Magnetic measurements performed on **MIL-53as** and **MIL-53lt** revealed an antiferromagnetic behaviour with Néel temperatures T_N of 65 and 55 K, respectively. The fit of the paramagnetic part of the two $1/\chi$ curves with a Curie–Weiss law provided a negative paramagnetic temperature θ_p (of approximatively −75 K in both cases), indicative of antiferromagnetic interactions. The Curie constants of 1.70 and 1.80, respectively, are in good agreement with the values found in the literature (between 1.6 and 2.1).

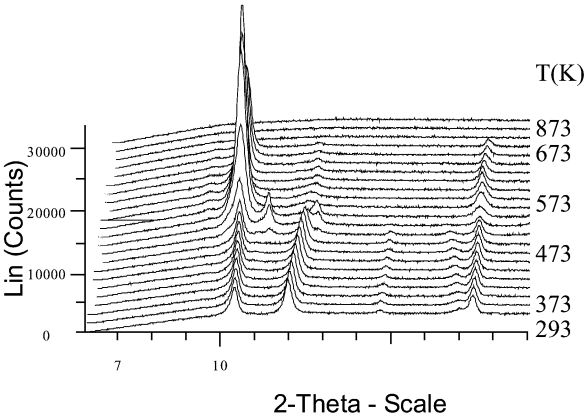

Fig. 3 X-Ray thermodiffractogram under air, showing the evolution from **MIL-53as** to **MIL-53ht** upon heating.

We have now synthesised chromium(III) dicarboxylates with a 3D structure under hydrothermal conditions. What is particularly noteworthy is that the use of chromium for synthesis offers the way for the discovery of new open-framework materials with potential applications. This result is also another example of a non-interpenetrating porous framework with infinite SBUs (secondary building units).[6,12] We are currently surveying phases produced from other chromium dicarboxylate systems.

Notes and references

‡ Powder X-ray diffraction data were collected from **MIL-53as** at room temperature on a Siemens D5000 diffractometer using CuKα radiation (λ = 1.5418 Å) and from **MIL-53ht** at 523 K using a Siemens D5005 equipped with an Anton Paar HTK1200 high temperature device. Structure determination of **MIL-53ht** was performed using the EXPO[13] package, which combines a full pattern decomposition program (EXTRA) and a direct method program (SIR97) optimised for powder diffraction data. Refinement was realised using Fullprof2k and Winplotr.[14,15] Crystal data for **MIL-53as**: orthorhombic, space group *Pnma*, a = 17.340(1), b = 6.822(1), c = 12.178(1) Å, Z = 4. For **MIL-53ht**: orthorhombic, space group *Imma*, a = 6.812(1), b = 16.733(1), c = 13.038(1) Å, Z = 4.
CCDC reference numbers 181153 and 181154.

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