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$[V^{III}(H_2O)]_3O(O_2CC_6H_4CO_2)_3\cdot(Cl, 9H_2O)$ (MIL-59): a rare example of vanadocarboxylate with a magnetically frustrated three-dimensional hybrid framework

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$[V^{III}(H_2O)]_3O(O_2CC_6H_4CO_2)_3\cdot(Cl, 9H_2O)$ (denoted MIL-59) presents a three-dimensional framework built up from octahedral vanadium trimers joined *via* the isophthalate anionic linkers to delimit cages where water molecules and chlorine anions are occluded; the frustrated magnetic behaviour of MIL-59 is discussed.

Among the numerous research devoted to microporous compounds,[1] the use of the hybrid compounds[2] was recently investigated to circumvent the difficult step of deintercalation of the organic template. This crucial stage is eliminated for hybrid compounds since their open framework is directly built up from the iono–covalent association of organic and inorganic moieties and allows direct accessible porosity. Suitable organic moieties are very often functionalised by at least two complexing groups which ensure the anchorage of the organic molecules on the inorganic building units by complexing the metals, and preferentially give rise to frameworks, whereas monofunctionalised moieties tend to lead to layered structures. Three series: metaloalkyldicarboxylates,[3,4] metaloalkyldiphosphonates[5–8] and mixed metaloalkylcarboxyphosphonates[8–11] are now sufficiently documented to demonstrate the strong correlation between the rigidity of the alkyl chain and the porosity of the resultant solid. The vanadoalkyldiphosphonate series[12] particularly exemplified this role: the alkyldiphosphonic acid with the shortest chain provides a 3D framework characterised by 14-membered tunnels whereas longer chains lead to pillared structures. However, the more exciting example was first provided by Yaghi and coworkers[13] with MOF-5 whose structure is constituted from zinc tetramers joined by rigid terephthalate anions presents very large pores. More recently, they increased the porosity in this family by substituting the terephthalate anions by longer organic linkers (MOF 9-16).[14] In all these solids, the 3D character is ensured by the linkage of inorganic clusters and organic moieties.

One of our recent contributions to the hybrid family concerned MIL-47, the first vanadocarboxylate with porous structure.[15] This is built up from *trans*-chains of vanadium octahedra (instead of clusters) linked by 1,4-benzenedicarboxylate anions. Besides its large porosity (BET specific surface close to 1000 $m^2 g^{-1}$), MIL-47 presents the particular feature of becoming antiferromagnetic below the exceptionnally high T_N temperature of 95(5) K. With a view to study the importance of the π electron delocalized system on the magnetic properties, we have undertaken a similar study replacing the terephthalic acid by one of its isomers 1,3-benzenedicarboxylic acid (isophthalic acid). This paper deals with the synthesis, structure determination and the magnetic behaviour of MIL-59: a vanadocarboxylate with an original three-dimensional structure.

$[V^{III}(H_2O)]_3O(O_2CC_6H_4CO_2)_3\cdot(Cl, 9H_2O)$ (denoted MIL-59) was synthesized by the reaction of VCl_3, 1,3-benzenedicarboxylic acid and deionized water under hydrothermal conditions to give dark green cubic crystals (Fig. 1). Its chemical formula was first deduced from the structure resolution and confirmed by elemental analysis.†‡ The cubic structure of MIL-59 (Fig. 2) is built up from octahedral trimers joined by the organic isophthalate linkers. The trimers (Fig. 3) contain three $V^{III}O_5(H_2O)$ octahedra sharing one central μ_3 oxo-anion located on a three-fold axis leading to three V–O(μ_3)–V angles all equal to 120°. In each octahedron, the apex *trans* located to the μ_3 oxo-anion is terminal, and valence bond calculations[16] show that it corresponds to a water molecule. TG measurements confirm this assessment. The four remaining oxygen atoms belong to four carboxylate functions of four different isophthalate anions. Each trimer is connected *via* six isophthalate anions to six other similar trimers (Fig. 3), this particular orientation of the organic linkers building up the three-dimensionality of the whole framework. Therefore, MIL-59 exhibits cuboidal cages (Fig. 2) delimited by eight trimeric

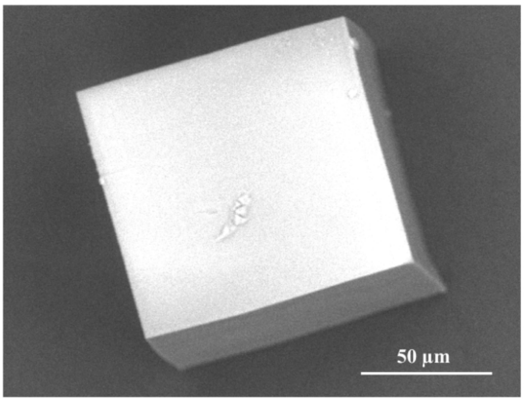

Fig. 1 Electron scanning micrograph (performed with a JEOL 5800 LV) of the cubic crystals of MIL-59.

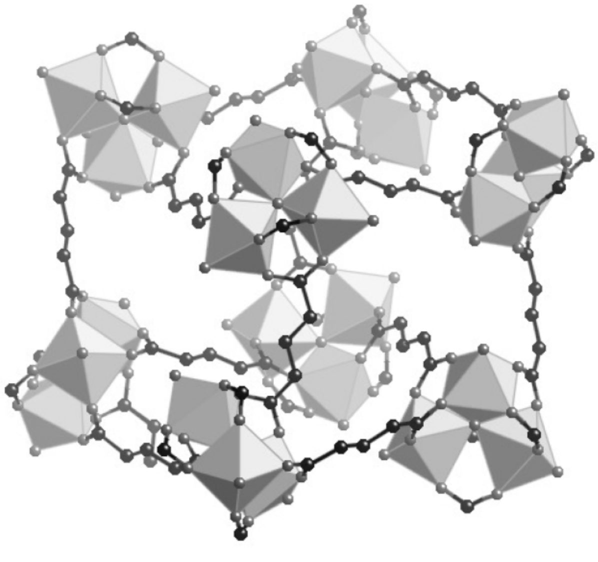

Fig. 2 Cuboidal cage of MIL-59 delimited by eight trimers (water molecules and chlorine anions are omitted for clarity, only the ‘active carbons’ of isophthalate anions in the linkage are represented; the active carbons are defined as the atoms constituting the shorter pathway between the two carboxylate functions of one isophthalate anion).

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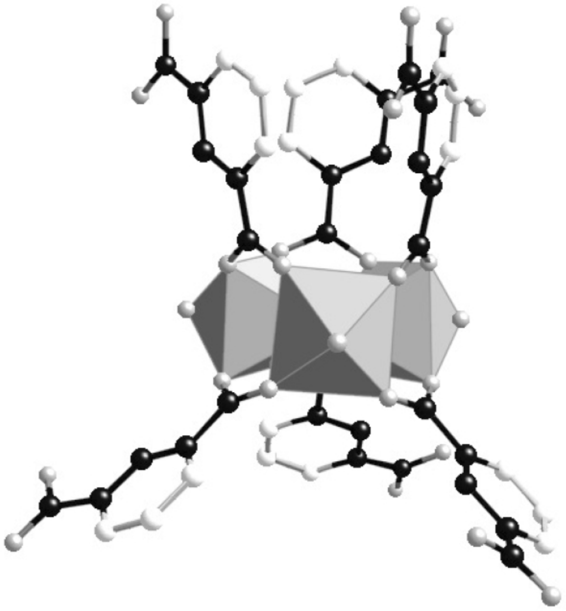

Fig. 3 Polyhedral representation of one octahedral trimeric unit of MIL-59 connected *via* six isophtalate anions to six other trimers. Black spheres represent 'active carbons' which are involved in the linkage. Pale grey spheres represent the other carbons of the isophtalic moieties.

building blocks with organic linkers on the walls. Water molecules and chlorine anions are trapped inside these cages.

Magnetically, MIL-59 is paramagnetic at all measured temperatures with an experimental Curie constant of 1.05, very close to the theoretical spin only value of 1 expected for V^{3+} cations. θ_P (≈ 1.5 K) is slightly positive indicating very weak ferromagnetic interactions. The difference between antiferromagnetic MIL-47 ($T_N \approx 95$ K) and paramagnetic MIL-59 arises since (i) 1D chains in MIL-47 favour long range magnetic interactions instead of clusters in MIL-59, (ii) the triangular geometry of the cluster in MIL-59 cannot satisfy simultaneously all the magnetic interactions. It is expected that the three spins are arranged at 120° one from each other. The resulting frustration character is well known[17] to drastically lower the temperature for magnetic ordering. This is observed once more here and the π electron system is not sufficient to ensure the propagation of long range interactions.

Similar trimers containing trivalent cations are already known, formulated as $[\mathrm{M^{III}}_3\mathrm{O(O_2CR)_6L_3}]^+$.[18] However, they lead to structures built up from molecular species interacting by hydrogen bonding or van der Waals contacts. Furthermore, relatively few structural data[19–21] are known for these species. The title compound provides the first example of a three-dimensional framework built up from the connection of such $[\mathrm{M^{III}}_3\mathrm{O(O_2CR)_6L_3}]^+$ molecular units by organic linkers. The MOF-38, -39 structures described by Yaghi and coworkers[22] exhibit zinc trimers built up around a central μ_3 oxygen atom, however, the disposition of the six carboxylate functions around the central core differs. The connection of molecular species by appropriate linkers to obtain open-frameworks was realized by Khan[23] using purely inorganic linkers. Here, the molecular species are linked *via* organic connectors, and it seems that this method could be extended at least to all the trivalent cations giving rise to the trimeric precursors.

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Notes and references

† The title compound was hydrothermally synthesized from a mixture of VCl_3 (Merck, 99%), 1,3-benzenedicarboxylic acid (Aldrich, 99%) and deionized water (molar ratio 1:0.25:100) heated for 72 h at 473 K in a Teflon-lined stainless steel Parr autoclave (filling level ~25%). The pH remains close to 1 throughout the synthesis. The solid phases were separated from the solution by filtration, washed with water and then dried in air at room temperature. MIL-59 crystallizes in the form of dark green cubic crystals mixed with white recrystallized isophtalic acid. TG experiments were performed under O_2 with a heating rate of 5 K min^{-1} using a TA Instrument TG2050 apparatus. The density was measured with a Micromeritics multipycnometer working under He flow. Elemental analysis (%): found (calc.): C, 31.6 (31.56); V, 16.2 (16.77); Cl, 3.8 (3.89). The magnetization (M) of a MIL-59 sample was measured in the range 4.2–290 K for different applied magnetic fields (H) with a Quantum Design SQUID Device. The magnetic susceptibility $\chi = H/M$ could thus be deduced.

‡ *Crystal data* for $[\mathrm{V^{III}(H_2O)}]_3\mathrm{O(O_2CC_6\underline{H}_4CO_2)_3}\cdot(\mathrm{Cl}, 9\mathrm{H_2O})$ (MIL-59): $M = 912.5$ g mol^{-1}, cubic, space group $Pa3$ (no. 205), $a = 19.2907(1)$, $V = 7178.67(6)$ Å^3, $Z = 8$, $D_c = 1.689$ g cm^{-3}, $D_m = 1.670(4)$ g cm^{-3}, $\mu = 9.33$ cm^{-1}, $T = 293$ K. 47867 collected reflections, 3345 independent reflections $I \geqslant 2\sigma(I)$ ($R_{\mathrm{int.}} = 0.0567$), 170 refined parameters, $R1(F_o) = 0.0513$, $wF2(F_o{}^2) = 0.1238$. Single crystal (0.160 × 0.160 × 0.160 mm). X-Ray diffraction data were recorded on a three-circle Siemens SMART diffractometer equipped with a bidimensional CCD detector (monochromatized Mo-Kα radiation, $\lambda = 0.71073$ Å). Lattice parameters were determined from a first set of frames then refined during the data collection with all the intensities $I \geqslant 10\sigma(I)$. Reduction data and Lorentz-polarization corrections were performed using the SAINT program then a semi-empirical absorption correction was applied using SADABS program.[24] The structure was solved applying direct methods (TREF option) of SHELX-TL,[25] V and O atoms were first located then the remaining atoms were deduced from Fourier difference syntheses. The H atoms were found using geometrical constraints. All the atoms (except H) were anisotropically refined. CCDC reference number 182284. See http://www.rsc.org/suppdata/cc/b2/b202749f/ for crystallographic data in CIF or other electronic format

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