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[$Fe_2(C_{10}O_8H_2)$]: An antiferromagnetic 3D iron(II) carboxylate built from ferromagnetic edge-sharing octahedral chains (MIL-62)

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The first three-dimensional iron(II) tetracarboxylate is built from the connection of chains of edge-sharing Fe(II) octahedra by 1,2,4,5-benzenetetracarboxylates; magnetic measurements show an antiferromagnetic coupling of ferromagnetic chains below T_N = 25(1) K.

The search for functionalized hybrid organic–inorganic solids with interesting physical properties is an emerging field.[1] As far as magnetism is concerned, most of the best known families of metal–organic frameworks are not good candidates since they are based on the linkage of metallic clusters (monomers,[2] dimers,[3] trimers,[4] or tetramers[5]) by rigid aromatic carboxylate ligands, which does not favour strong long range magnetic interactions at low temperatures owing to the low-dimensionality of the cluster.

However, there are few recent examples of 3D hybrid compounds built up from inorganic chains instead of clusters, which are connected by such carboxylate linkers;[6] these solids (ferromagnetic Fe/Co trimesate MIL-45[6a] and the porous antiferromagnetic V/Cr terephthalate MIL-47[6b,c]) present long-range magnetic interactions with interesting ordering temperatures (50–100 K). Herein, we describe the synthesis, structure and magnetic properties of the Fe(II) pyromellitate [$Fe_2(C_{10}O_8H_2)$], denoted MIL-62, which displays chains of edge-sharing Fe(II) octahedra covalently bonded by 1,2,4,5-benzenetetracarboxylate (or pyromellitate) anions, hereafter denoted BT4C.

MIL-62 was synthesized hydrothermally (200 °C, for 3 days, autogenous pressure) from a mixture of composition: Fe, 1,2,4,5-benzenetetracarboxylic acid, HF, H_2O (molar ratios 1 : 1 : 0.5 : 100 (5 mL)). Hydrofluoric acid acts as a mineralizer and few drops of a KOH solution (10 M) were added to increase the pH to *ca.* 3. The resulting product was filtered off and washed with deionized water; MIL-62 was identified as red platelets.

Semi-quantitative EDX analysis revealed that neither fluorine nor potassium were present in the sample. Elemental analysis† of Fe and C is in agreement with the proposed formula of MIL-62. Thermal analysis (TGA 2050 TA apparatus, O_2 flow, heating rate 5 K.min^{-1}) showed a single weight loss from *ca.* 450 °C (exptl. 56.1%, calc. 55.8%) related to the combustion of the organic part of the structure. The residue is iron oxide α-Fe_2O_3 (JCDPF file no. 84–0307). The experimental density (Micromeritics Accupyc 1330 Pycnometer): 2.66(1) g cm^{-3} is close to the calculated value (2.64 g cm^{-3}).

The three-dimensional structure of MIL-62 was solved by single crystal X-ray diffraction.‡ Chains of edge-sharing distorted FeO_6 octahedra which propagate along [100] are linked by BT4C anions (Fig. 1). Within the chain, Fe–O bond lengths, in the range 2.054(2)–2.234(2) Å, correspond to iron(II), as verified by valence bond calculations[7] (2.062 v.u.). Each BT4C moiety connects six chains, two *via* O(1) and four *via* O(2) atoms. This involves a quite dense hybrid structure displaying short distances (*ca.* 3.6 Å) between staggered aromatic BT4C ions. The phenyl rings are close to the (10−1) plane, and the four carboxylate groups of BT4C strongly deviate from this plane (*ca.* 30°).

The magnetization measurements (between 4.5 and 290 K) used a SQUID magnetometer with applied fields in the range 0–5.5 T. The $\chi^{-1}(T)$ curve at low fields (Fig. 2(a)) is typical of antiferromagnetism below T_N = 25(1) K; moreover the ZFC–FC and $M(H)$ curves at 4.5 K under 0.01 T (Fig. 2(b)) indicate a non-canted behaviour. Above 150 K, the Curie–Weiss law is verified, with a Curie constant of 7.874 emu Oe^{-1} K mol^{-1} and an experimental magnetic moment of 7.94 μ_B mol^{-1}, in fair agreement with the expected theoretical value of 7.64 μ_B mol^{-1}when some L–S coupling for Fe^{2+} in high spin octahedral coordination is taken into account. Finally, in this chain-like compound, the weak positive value of θ_p (+7 K) is difficult to rationalize in terms of low-dimensional magnetism since $|\theta_p|$ should be much higher than T_N.

Mössbauer experiments carried out at 300, 77 and 4.2 K§ are in agreement with the structural results, the spectra at 300 and 77 K exhibit one doublet, the hyperfine parameters of which are characteristic of high spin Fe^{2+} (isomer shift 1.35 mm s^{-1}; linewidth at half height 0.36 mm s^{-1}; quadrupolar splitting 1.50 mm s^{-1} at 77 K). At 4.2 K (Fig. 3), the spectrum exhibits four broad and resolved lines consistent with a magnetic hyperfine structure where quadrupolar interactions (giving rise to the crystalline field) compete with dipolar magnetic interactions.

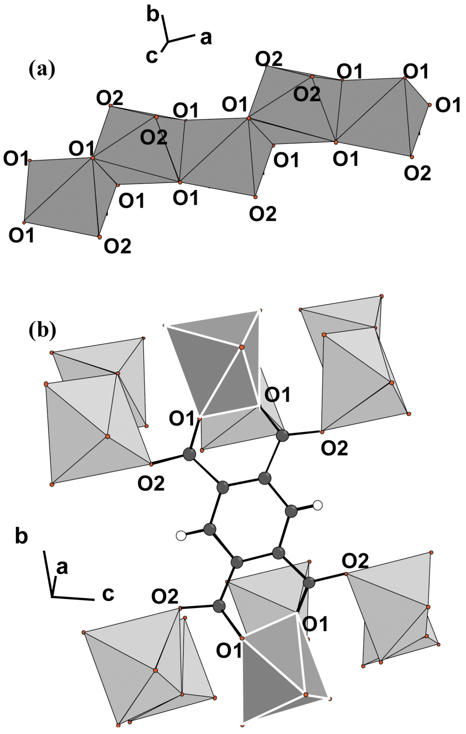

Fig. 1 (a) A chain of edge-sharing FeO_6 octahedral units; (b) connection of these chains by BT4C anions.

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The refinement requires two magnetic components which are equiprobable, with similar values of isomer shifts (1.34–1.35 mm s^{-1}), electric field gradients (1.72–1.73) and hyperfine fields (14.8–13.4 T). The electric field gradient $\Delta = 1/2eQV_{zz}(1 + \eta^2/3)$ is positive, in agreement with an extensive distortion of octahedra. The iron moments are therefore perpendicular to the V_{zz} axis, the main component of the EFG tensor. The existence of these two close contributions could be related with a structural phase transition occuring between 77 and 4.2 K, from a centrosymmetric to a non-centrosymmetric space group.

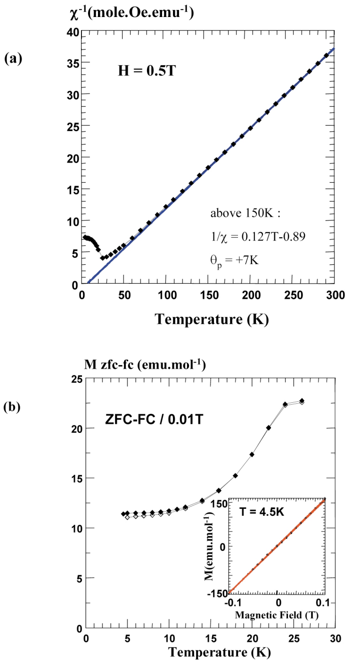

Fig. 2 (a) The $\chi^{-1}(T)$ curve at $H = 0.5\ T$; (b) superposition of ZFC and FC curves at $H = 0.01$ T and the absence of any hysteresis at 4.5 K between -0.1 and 0.1 T (insert).

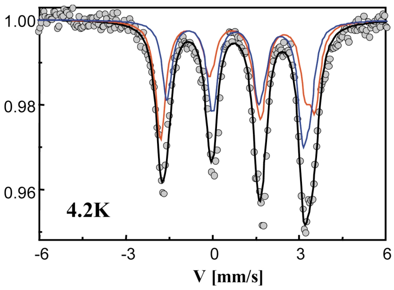

Fig. 3 Mössbauer spectra of MIL-62 at 4.2 K.

Keeping in mind the positive value of θ_p, all the results are consistent with an antiferromagnetic coupling of ferromagnetic chains. Indeed, within the latter, only 90° superexchange couplings occur. They can lead, according to Goodenough's theory[9] to ferromagnetic interactions as far as the e_g–p_σ–$p_{\sigma'}$–e_g correlation mechanism is concerned. The π-delocalized electrons ensure the 3D transmission of magnetic information.

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Notes and references

† Analysis for MIL-62 (wt%, Found (Calc.)): Fe, 29.67 (30.87); C, 32.34 (33.16).

‡ *Crystal data* for $[Fe_2(C_{10}O_8H_2)]$: $M = 361.84$ g mol^{-1}, monoclinic, space group $C2/m$ (no. 12), $a = 6.2378(7)$, $b = 17.589(2)$, $c = 4.6039(5)$ Å, $\beta = 115.863(2)°$, $V = 454.54(9)$ Å^3, $Z = 2$, $\mu = 32.37$ cm^{-1}, 1585 measured reflections, 612 unique reflections, $R_{int} = 0.0244$. The final R values are: $R_1(F) = 0.0291$ and $wR_2(F^2) = 0.0804$ for 560 reflections with $I > 2\sigma(I)$ and 48 refined parameters. CCDC reference number 188871. See http://www.rsc.org/suppdata/cc/b2/b206141d/ for crystallographic files in CIF or other electronic format.

§ Mössbauer spectra are recorded by means of a bath cryostat, using a constant acceleration spectrometer and a Co source diffused into a Rh matrix. The values of the isomer shift are quoted relative to that of α-Fe foil at 300 K. The hyperfine parameters were refined using a least-square fitting procedure in the MOSFIT program.[8]

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