A polymeric, layered bimetallic Mn(II)Fe(III) imidazolate network; crystal structure and magnetic properties

François Lambert,*[a] Jean-Philippe Renault,[a] Clotilde Policar,[a] Irène Morgenstern-Badarau[a] and Michèle Cesario[b]

[a] Laboratoire de Chimie Bioorganique et Bioinorganique, Institut de Chimie Moléculaire d'Orsay, Université Paris-Sud, F-91405 Orsay, France. E-mail: flambert @icmo.u-psud.fr
[b] Institut de Chimie des Substances Naturelles, CNRS, F-91198 Gif-s/-Yvette, France.

The use of a C_3 complex bearing three imidazolate groups as a 'building block' allowed us to synthesize an infinite corrugated two-dimensional (2D) low-spin Fe(III)–high-spin Mn(II) polymer exhibiting weak ferromagnetic intralayer interaction through imidazolate bridge.

Imidazolate is a highly studied bridge in dimetallic compounds,[1a] as models of (Cu–Zn)SOD[1b,c] and cytochrome c oxidase.[1d] Imidazolate has been previously used in building two- or three-dimensional homo or poly-metallic polymers[2a,b] and is known to induce moderate magnetic coupling.[3]

In order to construct bidimensional structures, we used a pseudo-octahedral iron complex from a N-tripodal ligand (LH$_3$ = tris{[2-(2-imidazol-2-yl)methyl]iminoethyl}amine) bearing an imidazolate group at the end of each chain as a building block. A dimer based on an analogous iron complex with imidazole substituted in the 4-position has been previously prepared.[2c] We chose a 2-substituted imidazole group to design a more planar M1–imidazolate-M0–imidazolate–M1 geometry.† The iron monomer used is a stable neutral triimidazolate Fe(III) low-spin complex.[4]

Here, we report the X-ray structure of [Mn(hfac)$_2$]$_3$[Fe(L)]$_2$ (hfac = 1,1,1,5,5,5-hexafluoroacetylacetonate), an infinite 2D polymer and a preliminary magnetic study of this compound.

Small dark-blue crystals suitable for X-ray diffraction‡ were obtained readily by slow evaporation of a mixture of methanolic solutions of the iron and manganese complexes [Fe(L)] and [Mn(hfac)$_2$].§ X-Ray crystallography shows an infinite honeycomb-like layered structure in the product. Each Fe(III)(L) entity is linked by imidazolate bridges with three Mn(II), whereas each Mn(hfac)$_2$ is bound in *cis* position to two Fe(III) complexes. The
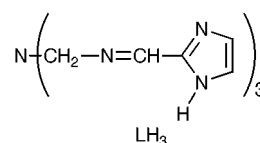

iron atoms are alternately capped above and below by the tripodal ligand L [Fig. 1(a)]. Within each layer the iron complexes display the same helicity, however, the crystal is non-chiral as revealed by the space group. The iron atoms of a given layer are located at the vertices of a chair-like structure (see Fig. 2) leading to a corrugated 2D-network similar to the Cr–Ni cyanide-bridged compound described by Ferlay et al.[5a] A remarkable feature is the *cis* substitution of imidazolate bridges around the manganese. This probably favours overall compactness and therefore the formation of a very stable hexagonal structure.[5a,b] Also, the small imidazolate–Mn– imidazolate angles) compensate for the large Mn–imidazolate– Fe–imidazolate–Mn distance.

The magnetic properties of [Mn(hfac)$_2$]$_3$[Fe(L)]$_2$ (Fig. 3) were recorded using a SQUID magnetometer with an applied field $H = 1$ kOe in the temperature range 50–300 K and with an
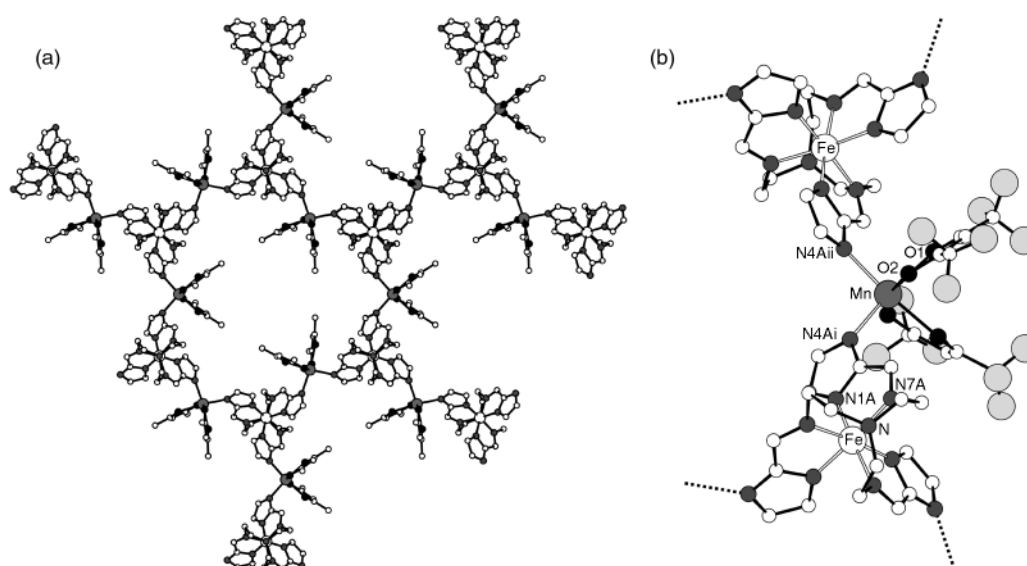
Fig. 1 (a) View of a sheet down the c axis. H atoms and F atoms have been omitted for clarity. Shortest Fe···Mn, Fe···Fe and Mn···Mn separations are 5.889(3), 11.26(1) and 9.62(1) Å, respectively. The Mn–Fe–Mn angle is 109.5°; (b) Molecular structure of two iron units bonded to one manganese unit. H atoms have been omitted for clarity. Each F atom has two partially occupied positions with those shown being in the major sites. Selected bond lengths (Å): Fe–N 3.130(10), Fe–N(1A) 1.924(5), Fe–N(7A) 1.983(5), Mn–N(4A) 2.176(5), Mn–O(1) 2.209(6), Mn–O(2) 2.164(5). Symmetry operations: i = x, y, z; ii = x − y + 1/3, − y + 2/3, −z + 1/6).
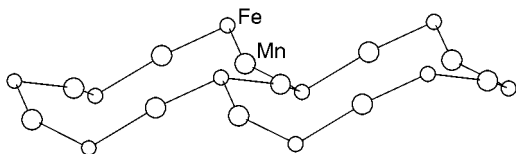
Fig. 2 View of the iron–manganese network showing the corrugated structure of a layer. Only two adjacent chair-like arrangements are represented.
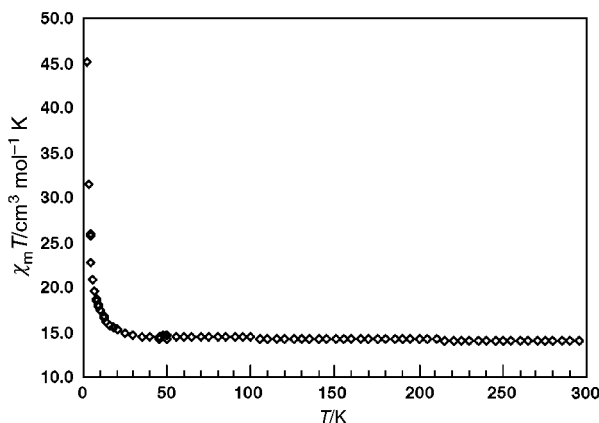
Fig. 3 Experimental temperature dependence of $\chi_M T$ (χ_M susceptibility). From 300 to 50 K, the magnetization was recorded with an applied field of 10 kOe, and from 50 to 2 K with an applied field of 100 Oe. The diamagnetic contribution of the ligands has been subtracted as usual.

applied field $H = 100$ Oe in the temperature range 2–50 K to avoid saturation.¶ At 300 K $\chi_M T = 14.1$ cm³ K mol⁻¹, in good agreement with the expected value for two non-coupled low-spin iron(III) ($g = 2.28$) and three high-spin manganese(II) ($g = 2$) ions.‖ Upon cooling, $\chi_M T$ increases and reaches a value of 45 cm³ K mol⁻¹ at 2 K. This behavior indicates the occurrence of a short range ferromagnetic exchange coupling between low-spin Fe(III) and high-spin Mn(II) through the imidazolato bridge. The variation of magnetization as a function of field has also been measured at 2 K. At saturation, expected values would be 17 μ_B ($S = 17/2$) and 13 μ_B ($S = 13/2$) for ferromagnetic and antiferromagnetic coupling, respectively (assuming an average g-value of 2). The observed magnetization reaches a value of 16.27 μ_B per Fe₂Mn₃ unit at 5.5 kOe which clearly indicates a ferromagnetic coupling. The overall shape of the $M = f(H)$ curve and the low value (45 cm³ K mol⁻¹) observed at 2 K for $\chi_M T$ shows only weak magnetic correlation within a layer,** restricted approximately to one Fe₂Mn₃ unit. Moreover, no interaction between the layers is observed down to 2 K. The compound can be considered at most as two dimensional from the magnetic point of view.

This compound is a good example of the ability for C_3 complexes, derived from a tripodal ligand bearing three bridging groups, to be a building block for 2D polymers. As far as we know, it is the first example of a 2D-bimetallic compound containing imidazolate bridges.[6]

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Notes and references

† The Mn–Fe–Mn angle for the present compound is 109°. For a 4-imidazolate iron complex this angle is estimated to be 80°.

‡ *Crystal data*: [C₆₆N₂₀O₁₂H₄₈F₃₆Mn₃Fe₂]ₙ, $M = 2273.76$, trigonal, space group $R\bar{3}c$, $a = b = 18.328(9)$, $c = 48.80(2)$ Å, $\gamma = 120°$, $V = 14196(11)$ Å³, $Z = 6$, $D_c = 1.596$ g cm⁻³. The asymmetric unit is 1/6 of the molecular entity as defined above with Fe, the tripodal N atom and Mn, located in special positions (symmetry 3, 3 and 2). A blue dark prism single crystal ($0.2 \times 0.3 \times 0.5$ mm) was mounted on an Enraf-Nonius CAD4 diffractometer with graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The unit cell dimensions were refined from setting angles of 25 reflections ($6 < \theta < 9°$). The data collection was *via* the θ–2θ scan technique mode (range 2–25.8°). Three standard reflections were measured every hour and showed no significant decay. A total of 7674 reflections was collected ($-22 \leqslant h \leqslant 19, 0 \leqslant k \leqslant 22, 0 \leqslant l \leqslant 54$). From 2294 independent reflections, 1279 were considered with [$I > 2\sigma(I)$]. Lorentz-polarisation and absorption corrections were applied. The structure was solved by direct methods (program SHELXS86) and refined on F^2 for all reflections by the least-squares method using SHELXL-93. Hydrogen atoms were included in the refinement at their ideal positions with an isotropic thermal parameter 1.2 times that of the bonded atoms. The crystal structure is affected by disorder. Two different sites of each CF₃ group were found from difference Fourier syntheses. Best convergence was obtained with occupancy factors of 60 and 40%. Refinement was performed with constraints. The final conventional residuals are $R1 = 0.054$ and $wR2 = 0.14$ for [$I > 2\sigma(I)$] and $R1 = 0.11$ and $wR2 = 0.19$ (all data). CCDC 182/1490. See http://www.rsc.org/suppdata/cc/a9/a907068k/ for crystallographic files in .cif format.

§ Sample elemental analysis is in agreement with the proposed formula while the IR spectrum of the polymer is the superimposition of the spectra of iron and manganese building blocks. This is consistent with the geometric similarity of the Fe unit in the monomer and in the polymer (X-ray structure).

¶ Magnetic properties have been recorded for ground crystals from the same batch used for X-ray diffraction and elemental analysis.

‖ At 300 K, $\chi_M T = \{[0.125 g_{Fe}^2 S(S+1)] \times 2\} + \{[0.125 g_{Mn}^2 S(S+1)] \times 3\}$. A g_{Fe}-value of 2.28 is consistent with the g_{Fe} value obtained for the iron monomer (2.35).[4]

** This is entirely consistent with imidazolate bridges which are known to induce only very weak magnetic interactions.[1]

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6 We thank one of the referees for having suggested this.

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