Supplementary Material (ESI) for Chemical Communications

SUPPORTING INFORMATION

Coexistence of Ferro- and antiferromagnetic interactions in a metal-organic radical-based (6,3)-helical network with large channels.

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Characterization of MOROF-3

IR (KBr, cm-1): 3422, 1603, 1488, 1446, 1399, 1347, 1321, 1040, 757, 723, 699, 579, 528.

Guest solvent molecules of as-synthesized MOROF-3 are slowly evacuated at room temperature for 12 hours, as confirmed by thermogravimetric and elemental analysis of the resulting solid. The X-ray powder diffraction of evacuated solid only presents four highly broad discernible diffraction lines, in accordance with the loss of crystallinity and degradation at long range. However, the fact that FT-IR of evacuated solid shows identical absorption bands to those of the as-synthesized MOROF-3 and that no other weight loss is observed up to 200 °C suggested the sustenance of the connectivity and framework of each (6,3) network. A comparable magnetic behaviour for the as-synthesized and evacuated/amorphous MOROF-3 also corroborates this hypothesis.

Magnetic measurements of MOROF-3

Due to the fact that MOROF-3 slowly loses crystallinity in contact with the air, an as-synthesized crystalline sample of MOROF-3 had to be kept in pyridine and ethanol during magnetic measurements. So it was placed in a cylindrical Teflon container filled with pure pyridine and drops of ethanol, which was closed hermetically with a screw-on lid to prevent evaporation of the solvent due to the low pressure inside the sample chamber. Then, magnetic properties of an evacuated amorphous sample of MOROF-3 (exposed to the air for 24 hours) were also measured. The temperature dependence of $\chi_m \cdot T$ is almost the same as for the as-synthesized sample; as shown in Figure 2S.

Magnetic behavior of MOROF-3 at high temperatures.

For Co(II) complexes, the decrease of $\chi_m \cdot T$ value at high temperature may be due to the depopulation of the higher energy Kramer's doublets of the Co(II) centers with a $^4T_1$ term as ground state. The $^4T_1$ ground state is split into a sextet, a quartet and a Kramer's doublet by spin-orbit coupling (see B. N. Figgis, M. Gerloch, J. Lewis, F. E, Mabbs, G. A. Webb, *J. Chem. Soc. A* **1968**, 2086). The Hamiltonian describing the spin-orbit coupling is given by Eq. 1,

$$\mathbf{H}_{SO} = -Ak\lambda\mathbf{LS} \qquad (1)$$

where k and λ are the orbital reduction factor and spin-orbit coupling, respectively. The inclusion of the A factor is due to the use of T-P isomorphism. That is, A appears to distinguish between the matrix elements of the orbital angular momentum operator calculated with the wavefunctions of the ground $^4T_1$ term and those calculated with the use of P-basis (|1, -1>, |1, 0> and |1, -1>). So, A can be defined by the symbolic equation: $\mathbf{L}(T_1) = - A\mathbf{L}(P)$. In the weak crystal-field limit, one obtains that $A = 3/2$ (a value used in most of the studies dealing with the magnetism of Co(II) compounds) whereas in the strong crystal-field limit one gets $A = 1$.

In order to analyze the magnetic interactions between the Co(II) ions and radicals in MOROF-3, we studied, firstly, the magnetic behaviour at high temperature assuming that no magnetic interaction between the different spin carriers occurs.

There are seven crystallographic different octahedral Co(II) units in MOROF-3. However, the coordination environments for all the sites are very similar, with two carboxylate groups of two different PTMTC moieties coordinated in axial positions (trans positions). In a first approach, we can consider the six-coordinated Co(II) ions identical and axially distorted. Under an axial distortion, the triplet orbital $^4T_1$ ground state splits into a singlet $^4A_2$ and a doublet ^4E levels with an energy gap of

D ($D > 0$ means that $^4A_2$ is lower in energy). The one-center operator responsible for an axial distortion can be expressed as in Eq. 2,

$$\mathbf{H}_{\mathbf{ax}} = D\left[\mathbf{L}_{\mathbf{Z}}^{\mathbf{2}} - \frac{1}{3}L(L+1)\right] \tag{2}$$

The full Hamiltonian involving the spin-orbit coupling, axial distortion and Zeeman interaction is given in Eq. 3.

$$\mathbf{H} = -Ak\lambda\mathbf{LS} + D\left[\mathbf{L}_{\mathbf{Z}}^{\mathbf{2}} - \frac{1}{3}L(L+1)\right] + \beta(-Ak\mathbf{L} + g_e\mathbf{S})H \tag{3}$$

From this Hamiltonian, the magnetic susceptibility for a six-coordinated Co(II) axially distorted, χ_{Co}, can be calculated. No analytical expression for the magnetic susceptibility, which depends on A, k, λ and D, can be derived from Eq. 3 and we must use matrix diagonalisation techniques to obtain it.

Because of MOROF-3 contains six Co(II) ions and four radicals, in absence of any magnetic interaction between the different spin carriers, the magnetic susceptibility (χ_m) can be calculated as with Eq. 4,

$$\chi_m = 6\chi_{Co} + 4\chi_R \tag{4}$$

where χ_R corresponds to the magnetic susceptibility per radical is given by Eq. 5.

$$\chi_R = \frac{N\beta^2 g_R^2}{4k_B T} \tag{5}$$

Matrix diagonalization techniques allowed us to determine the values of the different parameters implied in Eq. 4. The best-fit parameters using the experimental data for T > 30 K are: A = 1.47(1), λ = -110(5) cm^{-1}, k = 0.96(2), and $D < |100|$ cm^{-1}. The value of g_R was fixed to 2.0 to avoid over-parametrization. The calculated curve matches well the experimental data in the temperature range $30 \leq T \leq 300$ K. The values of the parameters obtained are within the range of those reported for high-spin octahedral Co(II) complexes. The energy gap between the orbital singlet, $^4A_2$, and the orbital triplet, ^4E, must be very small ($D < |100|$ cm^{-1}), indicating a low distortion, in agreement with the high magnetic moment at room temperature. Both the sign and magnitude of *D* are not unambiguous and similar fits are obtained for values of *D* in the range $-100 < D < +100$ cm^{-1}. For our calculation, the theoretical curve corresponds to $D = 0$.

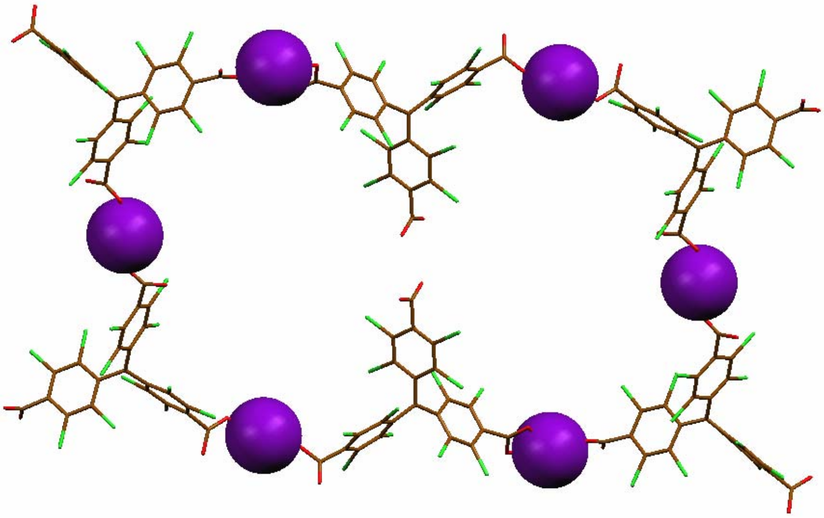

Figure 1S. Shortest circuit composed of six PTMTC moieties and six Co(II) ions. The latter are represented by filled balls.

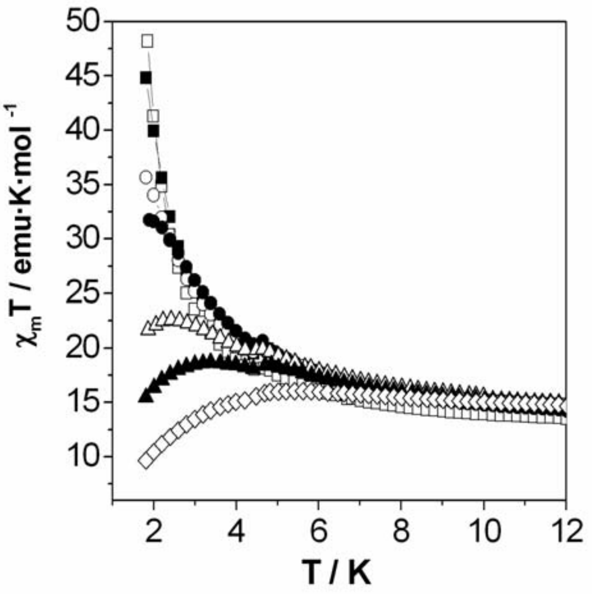

Figure 2S. Magnetic properties of as-synthesized MOROF-3. χT value as a function of the temperature for MOROF-3 at different applied magnetic fields: (□)100 G, (•) 500 G, (o)1000 G, (•)1500 G, (Δ)3000 G (•)5000 G and (◊)10000 G.

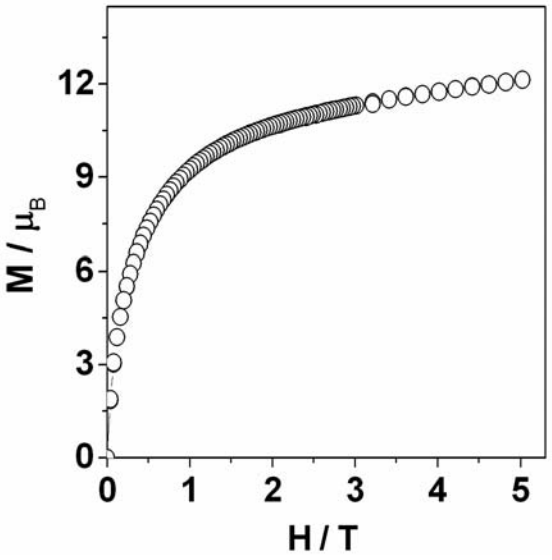

Figure 3S. Magnetic field dependence of the magnetization at 1.8K.

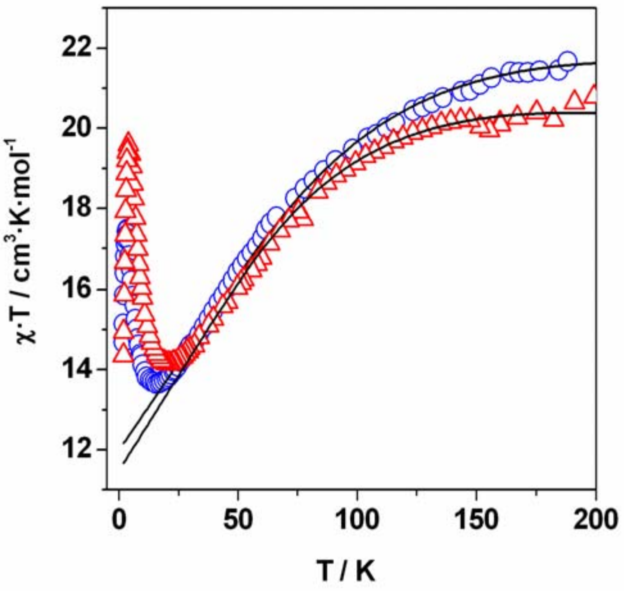

Figure 4S. Comparison of the magnetic properties of an as-synthesized (o) and evacuated/amorphous (Δ) samples of MOROF-3. χT value as a function of the temperature for MOROF-3 at 5000 G. Theoretical curves are calculated with the parameters given in the text for the case of D = 0 cm^{-1}.