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A three-dimensional lanthanide-organic radical open-framework†

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The reaction of a 3-connecting PTMTC radical with Tb(III) ions forms a three-dimensional open-framework with the formula [Tb(PTMTC)(DMF)$_3$] (1), which associates a lattice complex *T* topology with large channels, guest-induced reversible crystal to amorphous transformations and ferromagnetic metal-radical interactions.

One of the challenges in the field of metal-organic frameworks (MOFs)[1] is the fabrication of novel materials that display more than one functionality, such as magnetism and conductivity, porosity and magnetism, porosity and optical properties, *etc.*[2] Among them, multifunctional magnetic porous MOFs are rapidly increasing in number because of their potential applications in magnetic molecular sensors or actuators.[3] However, the synthesis of robust MOFs with increasing pore size dimensions and simultaneous long-range magnetic properties still remains a challenge. While the achievement of strong magnetic interactions requires short superexchange pathways between open-shell units, the synthesis of porous MOFs usually requires long polytopic connectors.[4] Therefore, the use of long organic ligands to connect open-shell units is expected to decrease, or in the worst of the cases disrupt, the superexchange magnetic pathways. A promising strategy to overcome such inconvenience is based on the linkage of magnetically active metal ions by persistent polytopic organic radicals. Organic radicals act as a magnetic relay,[5] and therefore, the resulting porous structures exhibit larger magnetic couplings and dimensionalities in comparison with those of systems made up from diamagnetic polytopic coordinating ligands.

Carboxylate-substituted polychlorotriphenylmethyl radicals (PTM) have stood out as very interesting open-shell organic building-blocks to be used in this approach.[6] To date, their use as connectors of transition metal ions has allowed the fabrication of one- and two-dimensional magnetic open-frameworks.[7] Herein, we report the synthesis, X-ray structure and magnetic properties of the first example of a 3-D open-framework built up using an organic radical. This lanthanide-organic radical open-framework with the formula [Tb(PTMTC)(DMF)$_3$] (**1**)‡ is constructed from the linkage of Tb(III) ions and tricarboxylate PTM radicals (PTMTC). The lanthanide metal ions such as Tb(III) were chosen because of the high coordination number and connectivity usually exhibited by these ions and related clusters.[8] Besides its framework, **1** also associates a rare complex *T* topology with very large channels, a guest-induced reversible crystal to amorphous transformation and ferromagnetic metal-radical interactions at low temperatures.

Red diamond-like crystals of **1** (65% yield) were prepared by slow diffusion over 25 days of an excess of pyridine in ethanol onto a solution of PTMTC and Tb(NO$_3$)$_3$·5H$_2$O in DMF. Single-crystal X-ray diffraction analysis shows that the 3-D framework of **1** is created from the linkage of dinuclear Tb(III) subunits by tricarboxylate PTMTC radicals. An ORTEP representation of one of these subunits is shown in Fig. 1. Two crystallographic equivalent octa-coordinated Tb(III) ions connected through two *syn-syn* carboxylate bridges of PTMTC radicals form each dimer, with a Tb···Tb distance of 5.735 Å. The remaining coordinating sites of Tb(III) ions are occupied by three oxygen atoms of two different PTMTC radicals and three DMF molecules.

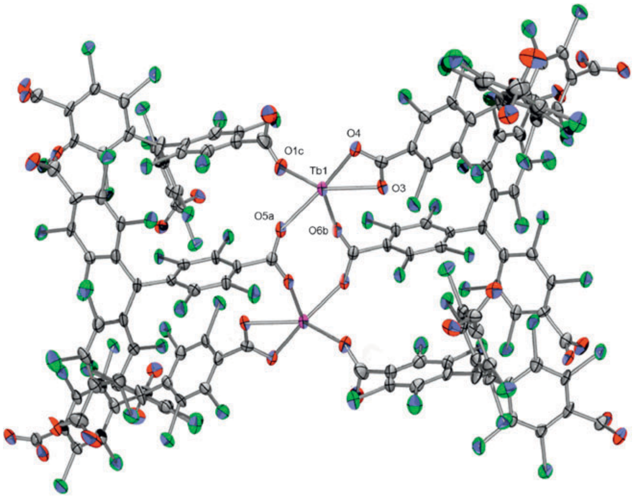

Fig. 1 ORTEP representation of the dinuclear Tb(III) subunit of **1** at the 30% probability level. DMF auxiliary ligands are omitted for clarity. Only oxygen atoms bonded directly to Tb1 are numerated for clarity. O5a, O1c and O6b atoms are generated by following symmetry operations (O5a) $3/4 - y, -3/4 + x, 1/4 + z$; (O1c) $-1/2 + x, y, 1/2 - z$; (O6b) $3/4 + y, 5/4 - x, 1/4 - z$, respectively.

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† Electronic supplementary information (ESI) available: Crystallographic data and elemental analyses for **1** and **2**, XRPD diffractograms for desolvated and refilled **1**, TGA curve for **1**; crystallographic data in cif format [CCDC reference numbers 676448 (**1**) and 676449 (**2**)]. See DOI: 10.1039/b802196a

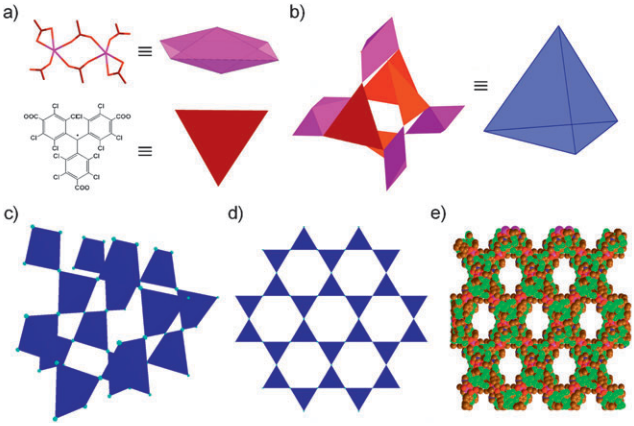

Fig. 2 Crystal structure of [Tb(PTMTC)(DMF)$_3$] (**1**). (a) Representation of the structural motifs of the dinuclear Tb(II) subunits (six-connecting distorted octahedral units) and PTMTC radicals (three-connecting trigonal units). (b) Tetrahedral secondary building unit for **1** created from the linkage of Tb(III) dimers (vertices) by PTMTC radicals (faces). (c) View of the connectivity of framework **1**, showing the typical lattice complex *T* network. (d) View of the framework along the *b* axis. (e) Space-filling representation showing the large channels in **1**.

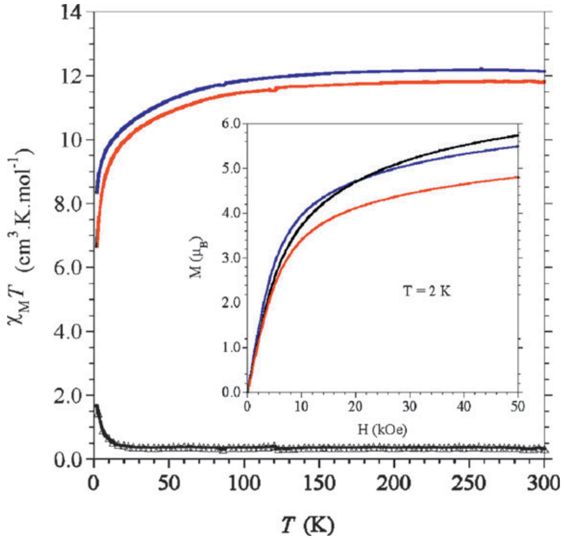

Fig. 3 Temperature dependence of χT for **1** (blue) and **2** (red) and $\Delta(\chi T)$ (black triangles). Inset: Field dependence of the magnetization at 2 K for **1** (blue), **2** (red) and for the calculated non-correlated spin system (black).

To fully appreciate the structure and its topology, it is necessary to consider that the dinuclear Tb(III) subunit provides a six-connecting slightly distorted octahedron-like structural motif, and the tricarboxylate PTMTC radical provides a threefold symmetry element, as seen in Fig. 2a. The direct combination of both elements creates larger secondary building units (SBUs). The key SBU in **1** is a tetrahedral unit (Fig. 2b) with the dinuclear Tb(III) units at its vertices and four PTMTC radicals that occupy its four faces. The framework can then be analyzed by connecting those SBUs through the corner sharing of tetrahedrons. The resulting 6-coordinated net corresponds to the lattice complex *T* (Fig. 2c and d).[9]

Similar to some zeolite structures such as sodalite, the connectivity of such large SBUs in **1** creates large pore sizes. The framework of **1** generates a 2-D channel-like system with pores along the *a* and *b* axes. The identical cavities along the two directions have minimum dimensions of 22.2 Å × 11.3 Å when van der Waals radii are considered, and they are large enough to endow this material with a total potential void volume of 61.7% of the cell volume (Fig. 2e).[10] In absolute terms, it represents a volume of 22 589.7 Å^3 per 36 591.0 Å^3 of the unit cell. Such a volume is occupied by solvent molecules. Because of disorder, guest molecules in the pore channels could not be directly identified and located in the crystal structure analysis.

Single crystals of **1** removed from the mother liquor lose solvent molecules very rapidly at room temperature, becoming an amorphous material, but they recover their crystallinity when re-immersed in liquid DMF, as confirmed by XRPD patterns (see ESI†). A similar behavior was not evidenced when amorphous material was immersed in ethanol or pyridine. Thus, the open-framework of **1** exhibits reversible DMF sorption and **1** can be considered a type 1 compound of the third generation of solvated solids,[11] *i.e.* the material experiences guest-induced and fully reversible crystal-to-amorphous transformations. Upon heating desolvated **1**, the complex loses coordinated solvent molecules up to 230 °C, and shows signs of decomposition from 300 °C to 495 °C to yield Tb_2O_3.

The magnetic properties of **1** both in the presence of DMF and desolvated were investigated in the 2-300 K temperature range with an applied field of 1000 Oe. Interestingly, the magnetic behavior of both phases was identical. The temperature dependence of the product χT (χ stands for the molar magnetic susceptibility) for **1** is shown in Fig. 3. At room temperature, the value of χT is 12.12 cm^3 K mol^{-1}, which is in good agreement with the expected 12.20 cm^3 K mol^{-1} for a non-interacting PTMTC radical ($S = \frac{1}{2}$) and one Tb(III) ion ($J = 6$). As the temperature is lowered, the χT value slightly decreases up to 50 K, whereupon it decreases more rapidly to reach 8.29 cm^3 K mol^{-1} for 2 K. No evidence for magnetic ordering is found for **1** above 2 K.

To investigate the nature of the metal-radical interactions in **1**, we prepared a second coordination polymer with the formula [Tb(αH-PTMTC)(DMF)$_2$H$_2$O] (**2**) by using a non-magnetic counterpart of the PTMTC radical, the substituted triphenylmethane hydrocarbon αH-PTMTC.[12c] As previously seen in other PTM-based complexes, **2** is isostructural to **1**. Overall, the temperature dependence of the product χT for **2** is very similar to **1**, with a χT value at room temperature and 2 K of 11.82 and 6.64 cm^3 K mol^{-1}, respectively (Fig. 3). The diamagnetic organic ligands in **2** provide us an excellent situation to study the magnetic exchange interactions between Tb(III) ions and PTMTC radicals.[12] Fig. 3 shows the temperature dependence of $\Delta(\chi T)$, where $\Delta(\chi T)$ refers to $\chi T(\mathbf{1})-\chi T(\mathbf{2})$. At room temperature, the value for $\Delta(\chi T)$ is 0.30 cm^3 K mol^{-1} is in good agreement with the value expected for the $S = \frac{1}{2}$ radical. This value remains constant down to 20 K, whereupon it starts to increase to reach a value of 1.65 cm^3 K mol^{-1} at 2 K. This low temperature behavior clearly demonstrates the presence of Tb(III)-radical interactions. However, at this stage, the structural complexity of **1** does not allow us to differentiate whether this increase is realted to ferromagnetic metal-radical interactions or to the occurrence of short range ferrimagnetic correlations. This question was addressed by measuring the field dependence of the magnetization at 2 K. The inset of Fig. 3 presents the experimental data for **1** and **2**, and the calculated magnetization for a non-correlated {Tb-Rad} spin system. For the lower fields, the experimental curve of **1** is above the calculated curve for the non-correlated system, and the value reached by the two curves at 50 kOe are very close. This suggests that ferromagnetic interactions are operative between the Tb and the radical units.

In summary, a 3-D metal-organic open-framework built up from open-shell organic connectors has been constructed from the linkage of lanthanide Tb(III) ions by tricarboxylate PTMTC radicals. Such material exhibits a rare lattice complex *T* structure with large channels, a fully reversible guest-induced crystal to amorphous transformation and lanthanide-PTMTC ferromagnetic interactions. Both the ability of lanthanide ions to provide 3-D structures and the presence of ferromagnetic interactions between lanthanide ions and PTMTC radicals open exciting perspectives towards the design of novel magnetic porous MOFs.

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Notes and references

‡ *Experimental data for* **1** *and* **2**: Red crystals of **1** form in 65% yield within twenty five days of layering a 10 mL ethanolic solution of pyridine (40 mg, 0.5 mmol) through a 10 mL ethanol buffer layer onto a 10 mL DMF solution containing the PTMTC ligand (100 mg, 0.13 mmol) and $Tb(NO_3)_3 \cdot 5H_2O$ (55 mg, 0.13 mmol). **2** was obtained as colourless crystals in 61% yield following the same methodology, only replacing the PTMTC ligand by its hydrogenated precursor, αH-PTMTC. See ESI for elemental analysis‡.

Crystallographic data: X-ray single-crystal diffraction data for **1** and **2** were collected on the BM16 Spanish line of ESRF synchrotron in Grenoble. In both structures, the H atoms have been included in theoretical positions but not refined. The low θ_{max} value is due to the data collections having been performed in the BM16 line with only a φ scan. For both compounds the structures were solved by direct methods using the program SHELXS-97; the refinement and all further calculations were carried out using SHELXL-97.[13] Empirical absorption corrections were applied in both cases with SCALEPACK.[14]

Crystal data for **1**: $C_{31}H_{19}Cl_{12}N_3O_9Tb$, M_r = 1161.84 g mol^{-1}, crystal dimensions 0.32 × 0.16 × 0.14 mm^3, tetragonal, space group $I41/a$, a = 27.920(5) Å, b = 27.920(5) Å, c = 46.940(5) Å, V = 36 591(10) Å^3, Z = 16, ρ_{calcd} = 0.843 g cm^{-3}, $F(000)$ = 9072, $\mu(\lambda_{sync.}$ = 0.987 Å) = 3.290 mm^{-1}, T = 150 K, $2\theta_{max}$ = 39.8°. Final results (for 510 parameters) were $R1$ = 0.045, $wR2$ = 0.137 and S = 1.05 for 3083 reflections with $I > 2\sigma(I)$.

Crystal data for **2**: $C_{28}H_{15}Cl_{12}N_2O_9Tb$, M_r = 1109.74 g mol^{-1}, crystal dimensions 0.10 × 0.12 × 0.22 mm^3, tetragonal, space group $I41/a$, a = 28.486(5) Å, b = 28.486(5) Å, c = 46.678(5) Å, V = 37 877(10) Å^3, Z = 16, ρ_{calcd} = 0.776 g cm^{-3}, $F(000)$ = 8640, $\mu(\lambda_{sync.}$ = 0.987 Å) = 3.170 mm^{-1}, T = 150 K, $2\theta_{max}$ = 41.2°. Final results (for 465 parameters) were $R1$ = 0.078, $wR2$ = 0.265 and S = 1.10 for 3389 reflections with $I > 2\sigma(I)$.

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