Volume 1 | Number 1 | Jan 2013 | Pages 1–100

Dalton Transactions

An international journal of inorganic chemistry
www.rsc.org/dalton

ROYAL SOCIETY OF CHEMISTRY

This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Please note that technical editing may introduce minor changes to the text and/or graphics, which may alter content. The journal's standard **Terms & Conditions** and the **Ethical guidelines** still apply. In no event shall the Royal Society of Chemistry be held responsible for any errors or omissions in this *Accepted Manuscript* or any consequences arising from the use of any information it contains.

Journal Name

ARTICLE

New family of hetero-tri-metallic complexes [M(CuTb)]ₙ (n = 1, 2, ∞; M=Co, Cr, Fe) : synthesis, structure and tailored single-molecule magnet behavior

N. Bridonneau,[a*] G. Gontard[a] and V. Marvaud[a*]

A new family of hetero-tri-metallic complexes [M(CuTb)]ₙ (M^{III} = Co, Cr, Fe; n = 1, 2, ∞), composed of three series of three compounds (oligo- and poly-nuclear complexes based on [Cu-Tb] subunits), is presented and fully characterized. These nine compounds, viewed as different assemblies of single-molecule magnet (SMM) building blocks, connected to various hexacyanometalate centers, illustrate how the SMM behavior of the [CuTb] moiety can be modulated via the control of intermolecular interactions. Specifically, the combination of the "non-innocent" diamagnetic $[Co^{III}(CN)_6]^{3-}$ center with a $[Cu-Tb]^{3+}$ moiety, enabled to isolate the magnetic entities, results in an improvement of the SMM behavior (ranging from U_{eff} = 5-7 cm^{-1} to 15-17 cm^{-1}).

INTRODUCTION

The design and the synthesis of single-molecule magnets (SMM) have attracted increasing interest over the years,[1] due to their potential application for information storage at the molecular scale. Since their discovery in the 90's with the Mn_{12}-acetate,[2] numerous example of SMM have been obtained, by varying the metal ions composition as well as the molecular assembly.[3] At the same time, great attention has been devoted to the understanding of the SMM behavior and the increase of the expected energy barrier.[4] The identified key parameters are the ground-state spin value, S, the strength of the magnetic exchange interaction, J, the uniaxial (negative) anisotropy, D, and a low value of intermolecular exchange interaction J'. The present article focuses on this last parameter, intended to create a synergy between the magnetism of each constituent through the control of intermolecular interactions.[5] The precise arrangement of SMMs in a crystal is a real challenge in coordination chemistry, while it has a great impact on the observed magnetic properties. Indeed, it is often seen that potentially good SMM candidates (with high values of S and J) exhibit less interesting properties than expected because of the presence of multiple pathways of weak intermolecular interactions. A common way of overcoming these unwanted interactions is to vary the crystallization conditions, or to add bulky counter-ions that can impose a preferential crystallization mode,[6] but these methods do not allow good prediction of structures.

The approach proposed in the present article is to control the assembly of bimetallic SMM building blocks,[7] [CuTb] units,[8] by forming hetero-tri-metallic compounds with the use of hexacyanometallate complexes $K_3[M^{III}(CN)_6]$ (with M= Co, Cr or Fe). Although the synthesis of hetero-tri-metallic[9] and hetero-tetra-metallic[10] compounds remains challenging, the use of [CuTbL] moieties (with L a compartmental Schiff-base ligand) is already known in the literature to form bimetallic and tri-metallic assemblies such as square[11] compounds, or chains[12] and networks.[13] With this idea in mind, the use of two $[CuTbL]^{3+}$ building blocks as precursors coupled to hexacyanometallate ions $[M(CN)_6]^{3-}$ (M = Co, Cr, Fe) enabled to synthesize nine hetero-tri-metallic compounds of various nuclearity.
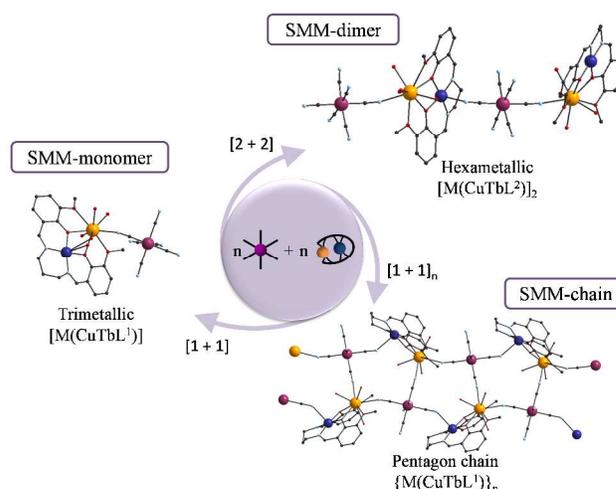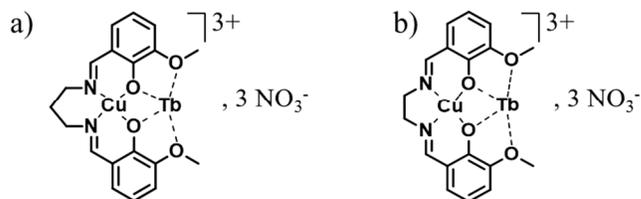

Figure1: Family of hetero-tri-metallic complexes (blue = Cu^{II}; orange = Tb^{III}; purple M = Co^{III}, Cr^{III} or Fe^{III})

All complexes exhibit SMM behavior originating from the $[Cu^{II}\text{-}Tb^{III}]$ moiety. The compounds described here are divided into three series of three compounds each, showing different molecular organization of the subunits as depicted in Figure1.

The first series of three trinuclear compounds incorporate one [Cu-Tb] bimetallic subunit and one hexacyanometalate moiety, herein referenced as "SMM-monomer" $[M(CuTbL^1)]$ (M = Co, Cr, Fe). Using different synthetic conditions, a so-called "SMM-dimer" $[M(CuTbL^2)]_2$ was obtained bearing six metal centers. Finally, a "SMM-chain" $\{M(CuTbL^1)\}_n$ was obtained when varying the stoichiometry of precursors. While all compounds incorporate [Cu-Tb] units with a similar local environment of the Cu^{II} and Tb^{III} ions, the nine complexes show different magnetic properties when varying the nature of the hexacyanometalate that can be either diamagnetic (Co^{III} S = 0) or paramagnetic (Cr^{III} S = 3/2, Fe^{III}_{LS} S = 1/2).

SYNTHESIS AND STRUCTURAL DESCRIPTION

Bimetallic building blocks $[Cu^{II}Tb^{III}L]$ (L = L^1, L^2) were formed from compartmental Schiff-base ligands derived from 3-methoxysalicylaldehyde: L^1 = N,N'-bis(3-methoxy-salicylidene)propylenediamine and L^2 = N,N'-bis(3-methoxysalicylidene)ethylenediamine. The two coordination sites of the ligand are selectively occupied by the copper(II) ion in the N_2O_2 site and the terbium(III) ion in the O_2O_2 compartment, the average Cu-Tb distance being 3.45 Å. Structures of the bimetallic building blocks are presented on scheme 1.

Scheme1: Bimetallic units a)[CuTbL^1]; b) [CuTbL^2]

	1	2	3	4
Formula	C25 H20 Co Cu N8 O11 Tb	C25 H20 Cr Cu N8 O11 Tb	C25 H20 Cu Fe N8 O11 Tb	C48 H66 Co2 Cu2 N16 O23 Tb2
M / (g/mol)	889.88	882.95	886.80	1797.95
cryst syst	monoclinic	monoclinic	monoclinic	monoclinic
space group	$P2_1/n$	$P2_1/n$	$P2_1/n$	$P2_1/c$
a / Å	12.7684(3)	13.0818(3)	12.8562(3)	25.5005(6)
b / Å	11.8653(3)	12.1299(2)	11.9304(3)	11.9284(3)
c / Å	22.2188(5)	22.1408(5)	22.1909(5)	22.7251(6)
β / °	105.3290(10)	105.4790(10)	105.4930(10)	108.7260(10)
V / Å^3	3246.41(13)	3385.89(12)	3279.95(13)	6546.6(3)
Z	4	4	4	4
d_{calc} / (g/cm^3)	1.821	1.732	1.796	1.824
θ range	4.13 to 66.52°	1.64 to 30.55°	1.67 to 30.59°	0.84 to 30.6°
reflns colld	19513	56207	56260	195962
indep reflns / R_{int}	5670 / 0.0429	10377 / 0.0214	10028 / 0.0225	20102 / 0.0265
GOF	1.027	1.041	1.061	1.062
R1, wR2 [I>2σ(I)]	0.0397, 0.1113	0.0358, 0.0964	0.0295, 0.0826	0.0282, 0.0620

	5	6	7	8
Formula	C48 H66 Cr2 Cu2 N16 O23 Tb2	C48 H66 Cu2 Fe2 N16 O23 Tb2	C25 H34 Co Cu N8 O11 Tb	C25 H34 Cr Cu N8 O11 Tb
M / (g/mol)	1784.09	1791.79	903.99	897.06
cryst syst	monoclinic	monoclinic	orthorhombic	orthorhombic
space group	$P2_1/c$	$P2_1/c$	$P2_1 2_1 2_1$	$P2_1 2_1 2_1$
a / Å	26.0774(5)	25.6467(6)	12.9082(3)	13.2421(3)
b / Å	12.0578(2)	11.9352(3)	14.9710(4)	15.1115(4)
c / Å	22.9454(4)	22.8151(6)	16.9463(4)	17.0360(4)
β / °	108.6210(10)	108.6690(10)	90	90
V / Å^3	6837.2(2)	6616.2(3)	3274.85(14)	3409.04
Z	4	4	4	4
d_{calc} / (g/cm^3)	1.733	1.799	1.834	1.748
θ range	0.82 to 30.64°	0.84 to 30.55°	2.40 to 30.57°	2.369 to 30.559°
reflns colld	106004	202359	49038	73633
indep reflns / R_{int}	20979 / 0.0298	20323 / 0.0293	10033 / 0.0216	10451 / 0.0590
GOF	1.099	1.079	1.046	0.943
R1, wR2 [I>2σ(I)]	0.0282, 0.0696	0.0289, 0.0634	0.0146, 0.0333	0.0267, 0.0526

Table 1: Crystallographic data and structure refinement for series of hetero-tri-metallic assemblies (**1 – 8**)

"SMM-monomer" compounds

Trinuclear complexes [M(CuTbL^1)] (M^{III} = Co (1), Cr (2), Fe (3)). The first family of hetero-tri-metallic complexes was obtained by condensation of the (CuTbL^1) and K$_3$[M(CN)$_6$] precursors in a 2:1 ratio in a water/acetonitrile mixture. Slow evaporation of the reaction mixture allowed in a few days the crystallization of square shaped green crystals.

Crystallography. Compounds **1**, **2** and **3** have been characterized by single crystal X-ray crystallography. All compounds are iso-structural and crystallize in a monoclinic system (P2$_1$/n space group). Unit cell parameters for **1** are a = 12.7684(3) Å, b = 11.8653(3) Å, c = 22.2188(5) Å with a cell volume of 3246.41(13) Å^3 (Z = 4). Cell parameters slightly vary from **1** to **3** according to the ionic radius of their respective hexacyano-metallate ion: $(a, b, c)_{Co} < (a, b, c)_{Fe} < (a, b, c)_{Cr}$ and $r_{Co} < r_{Fe} < r_{Cr}$ (Table 1). All compounds are neutral and show the complexation of the hexacyanometallate moiety and the lanthanide ion through a cyanide bond. The structure of complex **1** is shown in Figure 2. See ESI for **2** and **3**.
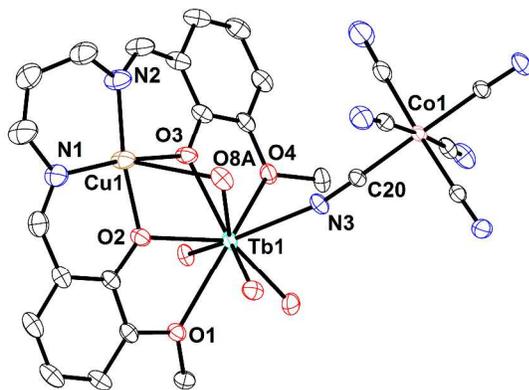

Figure 2: Crystal structure of [Co(CuTbL^1)] (**1**) representative of the subclass

The cobalt atom (Co1) adopts an almost perfect octahedral geometry. The cyanide bond between Co1 and the terbium(III) ion is linear on the cobalt side but bent on the terbium side, with a Tb-N≡C angle of 167.9(4)°. The lanthanide ion has a coordination number of 8 or 9: four oxygen sites of the ligand (methoxy and phenoxo groups), three or four aqua ligands and the nitrogen atom from the bridging cyano group. The coordination to the fourth aqua ligand is shared with two crystallographic positions: one located on the apical position of the copper ion (O8B, 25% occupation site, at 2.67 Å of the copper), while the second one situated at half distance of the copper and the terbium site (O8A, 75% occupation site, at 2.71 and 2.72 Å respectively). This bridging aqua ligand between Cu and Tb in compartmental ligand is unusual in the literature and has never been reported before. Nevertheless it exists analogous structures that indicate that such arrangement might exist.[8c] In both cases, the copper atom is penta-coordinated with the N$_2$O$_2$ site of L^1 ligand and an oxygen atom from a water molecule. Metal centers from two different molecules are well separated, with metal-metal average distances of 7.29 Å.

"SMM-dimer" compounds

Hexanuclear complexes [M(CuTbL^2)]$_2$ (M = Co (4), Cr (5), Fe (6)). When changing the ligand to L^2 the same reacting conditions enabled to obtain a second family of compounds having six metal centers. These hexanuclear-tri-metallic complexes were obtained as the first series by condensation of the (CuTbL^2) and K$_3$[M(CN)$_6$] precursors in a 2:1 ratio in a water/acetonitrile mixture. Slow evaporation of the reaction medium allowed crystallization of red needles crystals within a few days.

Crystallography. Hexanuclear complexes **4**, **5** and **6** have been characterized by X-Ray crystallography. All three compounds are iso-structural and crystallize in a monoclinic system (P2$_1$/c space group). Unit cell parameters are for **4** : a = 25.5005(6) Å, b = 11.9284(3) Å, c = 22.7251(6) Å with a cell volume of 6546.61(29) Å^3 (Z = 4). As for the previous series of compounds, cell parameters slightly vary from **4** to **6** according to the ionic radius of the metal ion. All complexes are discrete and neutral, and the structure of **4** is given in Figure 3 (see ESI for **5** and **6**). Complexes crystallize in a linear array formed by two hexacyanometalate atoms and two [CuTbL^2] units alternatively linked with cyanide bonds. One cobalt atom (Co1) links both [CuTbL^2] units in a *trans* manner: one cyanide ligand connected to Tb1 and the other linked to the copper atom of the second [CuTbL^2] unit (Cu2) on its apical position. The second cobalt atom (Co2) is connected, through a cyanide ligand, to the other Terbium site (Tb2). Even though the distance between the two subunits is slightly too long to be considered as a true coordination bond (2.59, 2.69 and 2.60 Å for **4**, **5** and **6** respectively), there exists however a non negligible interaction between the two moieties. Consequently, the hexanuclear complex is viewed as a dimer of trinuclear species and noted [M(CuTbL^2)]$_2$.
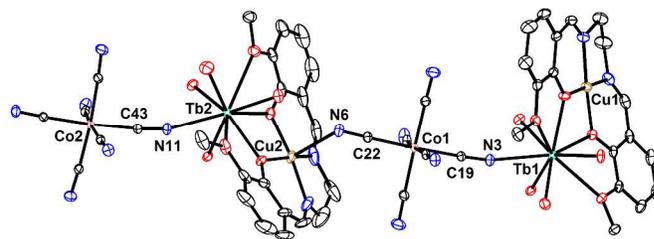

Figure 3: Crystal structure of [Co(CuTbL^2)]$_2$ (**4**) representative of the subclass

Metal-metal average distances for two adjacent centers are 5.542 Å for Co-Tb and 3.336 Å for Tb-Cu. Cyanide ligands are linear on the cobalt side but very bent on the other metal side: C≡N-Tb angles are comprised between 164.639(24)° and 167.630(24)°. The link formed with the Copper atom is even more bent with a value of 119.273(23)° for C≡N-Cu2, that can be explained by the long distance between the copper and nitrogen atoms (2.5877(27) Å).

"SMM-chain" compounds

{M(CuTbL^1)}$_n$ complexes (M = Co (7), Cr (8), Fe (9)). This third family of compounds was synthesized from the same building blocks as **1 – 3** heterotrimetallic complexes but with different stoichiometry of subunits composition. Condensation of the (CuTbL^1) and K$_3$[M(CN)$_6$] precursors was realized in a 6:1 ratio in a water/acetonitrile mixture. Slow evaporation of the reacting mixture allowed crystallization of green needle shaped crystals. Complex **9** has already been published in the literature[14] using a slightly different synthetic method, and complexes **7** and **8** are isostructural to their gadolinium equivalent that were also previously published by M. Andruh's group.[15] New complexes **7** and **8** are described here in addition to the two previous families of trinuclear and hexanuclear complexes, as comparison purpose.

Crystallography. The compounds crystallize in an orthorhombic system (P2$_1$2$_1$2$_1$ space group). Unit cells parameters for **7** are a = 12.9082(3) Å, b = 14.9710(4) Å and c = 16.9463(4) Å with a cell volume of 3274.85(14) Å^3 (Z = 4). The structure is once again neutral and composed of an array of alternated hexacyanometalate atoms and [CuTbL^1] units linked together by cyanide bonds, as depicted in figure 4. Each cobalt center Co1 connects meridionally three [CuTbL^1] moieties through cyano groups: two cyanide bonds are formed with the Terbium(III) ion, with C≡N-Tb angles of 162.92(14)° and 169.94(15)°. The third cyano group connects the copper atom, with a C≡N-Cu angle of 142.62(12)°. This strongly bent angle can be justified (just as for the hexanuclear structure) by the long distance between the copper and nitrogen atoms, Cu-N = 2.5198(16) Å. In order to accommodate the complexation of the two building blocks in this particular configuration, the [CuTbL^1] unit shows strong distortion of the L^1 ligand, as illustrated in figS5 (SI). The compound is regarded as a 1D pentagon chain and noted [M(CuTbL^1)]$_n$

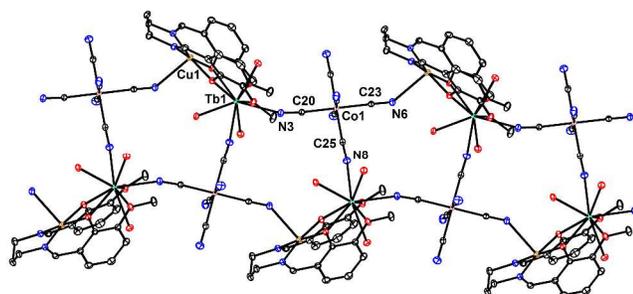**Figure 4:** Crystal structure of {Co(CuTbL^1)}$_n$ (**7**) representative of the subclass

MAGNETIC PROPERTIES AND DISCUSSION

Magnetic properties were investigated for all nine compounds. From one type of compound to the other, χ_mT plots show similar shapes when the same hexacyanometallate building blocks is involved (see ESI). Within the same family of compounds (trinuclear, hexanuclear or chain), magnetic

properties differ in relation with the nature of the hexacyanometallate precursor used: Co^{III} (d^6, S = 0); Cr^{III} (d^3, S = 3/2), or Fe$^{III}_{LS}$ (d^5, S = 1/2). As an example, Figure 5 shows the temperature dependence of magnetic susceptibility for compounds **1 - 3** of the trinuclear family.

For the three compounds, the temperature dependence of the magnetic susceptibility was recorded under a 1000 Oe field within the 300 K – 2 K range. At room temperature χ_mT values amount to 11.08 cm^3.mol^{-1}K for **1**, 13.92 cm^3.mol^{-1}K for **2** and 14.06 cm^3.mol^{-1}K for **3**, in good agreement with the expected theoretical values for independent Cu^{II}, Tb^{III}, Cr^{III} and Fe^{III} ions (Co^{III} being diamagnetic): $\chi_mT = (N\beta^2/3k)[g^2_{Cu}S_{Cu}(S_{Cu}+1) + g^2_{Tb}J_{Tb}(J_{Tb}+1) + g^2_{M}S_{M}(S_{M}+1)]$, (M = Cr for **2** and Fe for **3**).

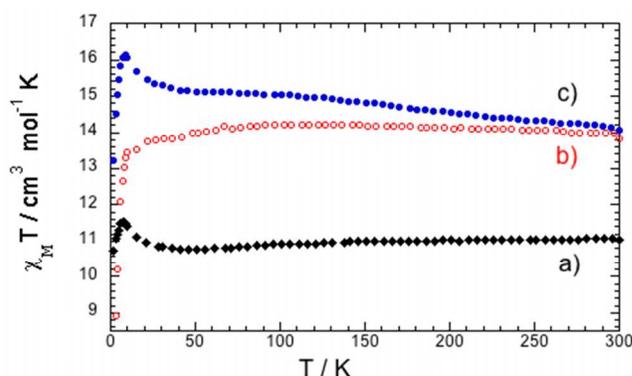**Figure 5:** χ_mT versus T plots for **1** (a, ◆), **2** (b, ⬤) and **3** (c, •)

Since compound **1** bears a diamagnetic Co^{III} ion, the χ_mT plot shows typical behavior of an isolated [Cu-TbL] unit,[16] L being a Schiff-base ligand: the χ_mT curve first decreases to a minimum of 10.77 cm^3.mol^{-1}K at 40.8 K, then increases abruptly to reach a maximum value of 11.54 cm^3.mol^{-1}K at 7.1 K. Finally, a second decrease of the χ_mT plot is recorded at very low temperature and can be interpreted as weak intermolecular interactions or zero field splitting. The thermal depopulation of Stark sublevels of the Tb^{III} ion makes it difficult to quantitatively analyze the Cu-Tb coupling[17] but numerous examples generally attribute the decrease in temperature to the depopulation of Stark sublevels whereas the rise at low temperature is due to the ferromagnetic coupling between the Cu^{II} and Tb^{III} ions. In order to confirm this assumption the [Co(NiTbL^2)]$_2$ structural analogue of **4** was synthesized (where Cu^{II} is replaced by Ni^{II} which is diamagnetic in the same square planar environment). The difference $\Delta(\chi_mT) = (\chi_mT)_{(CoCuTb)2} - (\chi_mT)_{(CoNiTb)2}$ shows a positive deviation below 100 K (figS35, SI) that is attributed to ferromagnetic interaction between Cu^{II} and Tb^{III}.

When the Co^{III} ion in **1** is replaced with the Cr^{III} (**2**) or Fe^{III} (**3**) ions, χ_mT vs T plots show different shapes, indicating a coupling between lanthanide(III) ion and the hexacyanometallate atom. This behavior has already been reported in similar systems, especially in the gadolinium equivalents of the pentagon chain: for the two compounds

[CuGdFe]$_n$ and [CuGdCr]$_n$[15] authors have shown that the interaction corresponds to weak antiferromagnetic coupling between the paramagnetic linker Fe^{III} ($S = 1/2$) or Cr^{III} ($S = 3/2$) and the ferromagnetically coupled[18] [Cu-Gd] subunit ($S = 4$). For the three chain compounds of the present study, (**7, 8** and **9**) the magnetization versus field data (see ESI) show a saturation value at 70 kOe in agreement with the ones reported in literature[19] for similar compounds.

The dynamic magnetic behavior of the series of compounds was investigated in the 10 Hz – 1.5 kHz frequency (v) range and down to 2.2 K. As for DC experiments, AC curves were similar when the same hexacyanometallate precursor was used. Compounds incorporating iron(III) or chromium(III) atoms (**2**, **3**, **5**, **6**, **8** and **9**) showed distinct frequency dependence of AC susceptibility in temperature only upon the application of a small supplementary static field, which is known to remove zero-field fast tunneling.[20] For these compounds, the slowest relaxation was observed at 1.6 kOe and enabled to bring out the field-induced single-molecule magnet behavior (see ESI).

Cobalt derivatives (compounds **1**, **4** and **7**) behave differently and showed distinct SMM behavior without the application of a DC field. Figure 6 shows the result of the experiment for compound **4** (see ESI for the other compounds).
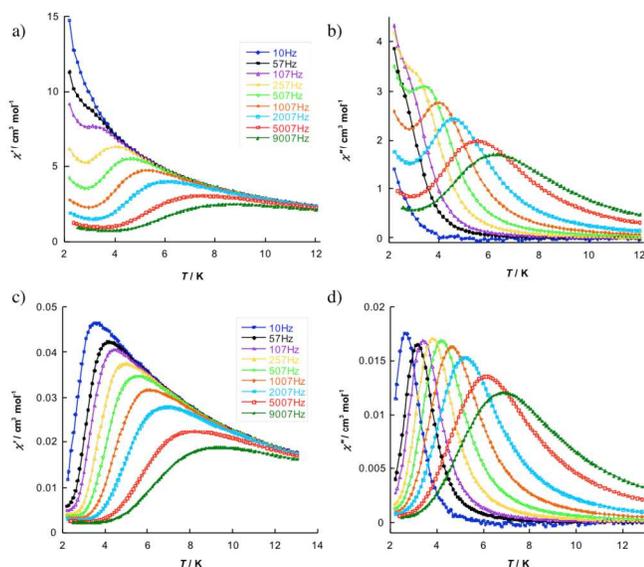

Figure 6: AC measurements for 4 at zero field (a (χ') and b (χ'')) and under a 1.6 kOe applied field (c (χ') and d (χ''))

As depicted in Figure 6, **4** shows distinct maxima of χ'' curves in temperature for each frequencies applied. For each compound (**1** – **9**) the data were fitted to a distribution of single relaxation processes following the extended Debye model:[21]

$$\chi''(\omega) = (\chi_T - \chi_S) \frac{(\omega\tau)^{1-\alpha}\cos(\pi\alpha/2)}{1 + 2(\omega\tau)^{1-\alpha}\sin(\pi\alpha/2) + (\omega\tau)^{2-2\alpha}}$$

In the above equation $\omega = 2\pi v$ and χ_T and χ_S are the isothermal and adiabatic susceptibility respectively. In each case, the α parameter was found to be close to zero and varying from 0.03 to 0.20, which indicates a narrow distribution of relaxation times. The use of this model enabled to extracted the relaxation times τ of each compound despite the fact that iron(III) and chromium(III) compounds did not show a maximum value in χ'' curves. Results follow a thermally activated relaxation mechanism that allowed to extract the energy barrier U_{eff} and the relaxation time τ_0 of compounds using the Arrhenius law $\tau = \tau_0 \exp(U_{eff}/kT)$, assuming that above 2 K thermal relaxation prevails over tunneling relaxation process. As an example, Figure 7 shows the Arrhenius plot obtained for **4**, giving $\tau_0 = 6.25\ 10^{-6}$ s and $U_{eff} = 14.76$ cm^{-1} (21.24 K).
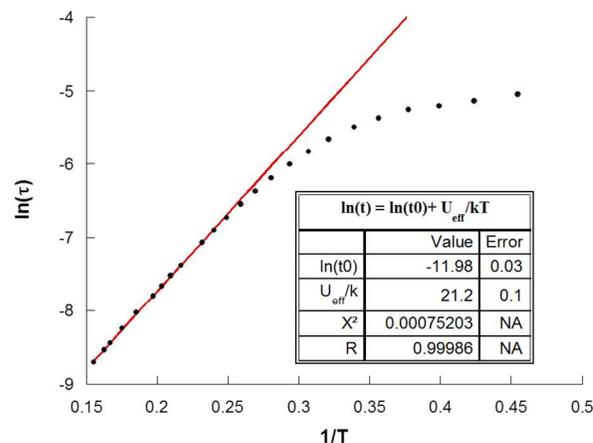

Figure 7: Arrhénius plot obtained for **4**

The energy barrier and the relaxation time of all the described compounds (**1** – **9**) are summarized on Table 2 as well as the values obtained for their precursors [CuTbL^1] and [CuTbL^2].

Compound	Precursor		"SMM-Monomer"			"SMM-Dimer"			"SMM-Chain"		
	[CuTbL^1]	[CuTbL^2]	[Co(CuTbL^1)] **(1)**	[Cr(CuTbL^1)] **(2)**	[Fe(CuTbL^1)] **(3)**	[Co(CuTbL^2)]$_2$ **(4)**	[Cr(CuTbL^2)]$_2$ **(5)**	[Fe(CuTbL^2)]$_2$ **(6)**	{Co(CuTbL^1)}$_n$ **(7)**	{Cr(CuTbL^1)}$_n$ **(8)**	{Fe(CuTbL^1)}$_n$ **(9)**
U_{eff}	15.36 cm^{-1} (22.10 K)	21.02 cm^{-1} (30.25 K)	18.27 cm^{-1} (26.29 K)	4.49 cm^{-1} (6.47 K)	5.52 cm^{-1} (7.94 K)	14.76 cm^{-1} (21.24 K)	7.49 cm^{-1} (10.78 K)	7.67 cm^{-1} (11.03 K)	14.56 cm^{-1} (20.95 K)	7.07 cm^{-1} (10.18 K)	5.39 cm^{-1} (7.75 K)
τ_0	5.33 10^{-9} s	1.44 10^{-9} s	1.50 10^{-5} s	1.25 10^{-5} s	1.37 10^{-7} s	6.25 10^{-6} s	1.89 10^{-5} s	5.48 10^{-8} s	6.70 10^{-6} s	7.10 10^{-6} s	1.40 10^{-7} s
α			0.03 - 0.10	0.17 - 0.23	0.14 - 0.20	0.20 - 0.27	0.15 - 0.27	0.20 - 0.35	0.05 - 0.20	0.11 - 0.25	0.11 - 0.19

Table 2: Energy barrier and relaxation time for the described compounds (**1** – **9**) and their precursors [CuTbL^1] and [CuTbL^2]

Discussion. Results presented above show unambiguously the SMM behavior of the whole family of compounds, with presence of slow magnetic relaxation. It should be mentioned that most of the isolated Cu–Tb derivatives described in the literature behave as SMMs with relatively low energy barriers (about 13 K).[22] In our case, the effective anisotropic barriers are found to be similar or even higher, with U_{eff} in the range of 8-30 K. Compared to the precursors, [CuTbL^1] and [CuTbL^2], the hetero-trimetallic compounds show a relaxation time significantly slower (by a factor 10 to 100). More interestingly, the hetero-tri-metallic samples show different magnetic behavior according to the nature of the hexa-cyanometallate precursor. From one family of hetero-tri-metallic complex to the other, the single-molecule magnet behavior is relatively similar. But within the same family of compounds a clear increase of the energy barrier U_{eff} is observed when the diamagnetic cobalt center is used (compounds **1**, **3** and **7**). [CuTb] compounds based on Schiff base ligands are widely described in the literature, which enabled to make magneto-structural correlations. Until now, factors influencing the SMM behavior in [CuTb] compounds were generally attributed to either slight changes in the ligand field of the Tb^{III} ion[23] (in particular nitrate coordination), or as the influence brought by the ligand itself. Indeed, as the Cu^{II} magnetic orbital ($d_{x^2-y^2}$) lies in the N_2O_2 plane of the ligand, any variation of the dihedral angle formed between the two cavities (O-Cu-O and O-Tb-O) will induce a modification of the magnetic coupling between the two spin carriers.[18,24] As already described in the literature the coordination of the lanthanide(III) ion to a supplementary radical[25] or transition metal ion[26] can also enhance the overall SMM behavior. This is usually a consequence of the exchange interaction between the spin carriers, resulting in the barrier of multi-exchange type with significantly reduced quantum tunneling mechanism. In our system, when the coordinated hexacyanometallate is paramagnetic (M = Cr^{III}, Fe^{III}), dynamic magnetic characterizations reveal that the effective energy barriers depreciate the overall magnetic behavior, probably due to antiferromagnetic interactions between the spin carriers. But, the use of a Co^{III} diamagnetic building block can improve the [CuTb] magnetic properties, on the contrary to the common belief that such a combination should involve high spin and highly anisotropic building blocks. Our approach might be viewed as an additional strategy in the building block modular synthesis for the design of tailored single molecule or single chain magnets. [27]

Conclusions

In our continuous effort to engineering SMM metallic assemblies, this work describes the synthesis of nine hetero-tri-metallic compounds formed with [Cu-Tb] units and hexacyanometallate (M = Co, Cr, Fe) precursors (trinuclear, hexanuclear and chain). All compounds exhibit SMM behavior

originating from the [Cu-Tb] moiety. These new assemblies put forward the benefit of using a supplementary diamagnetic metal ion in order to control SMM layout in the crystal. When chromium and iron centers are used, weak antiferromagnetic interactions are responsible for the decrease of the SMM efficiency. However, the diamagnetic cobalt equivalents show an increase of SMM properties compare to the reference [Cu-Tb] unit, with significantly longer relaxation time. This work shows that the addition of a diamagnetic $[Co^{III}(CN)_6]^{3-}$ (d^6) entity to the SMM [Cu-Tb] unit enables to isolate them in order to minimize the number of possible intermolecular interactions pathways (J') that would decrease the SMM efficiency.

EXPERIMENTAL SECTION

Physical Measurements.

IR spectra were obtained between 4000 and 250 cm^{-1} on a Bio-Rad FTS 165 FT-IR spectrometer on KBr pellets. DC magnetic susceptibility measurements were carried out on a Quantum Design MPMS SQUID susceptometer equipped with a 7 T magnet and operating in the range of temperature from 1.8 to 400 K. The powdered samples (10±50 mg) were placed in a diamagnetic sample holder and the measurements realised in a 1000 Oe applied field using the extraction technique. Before analysis, the experimental susceptibility was corrected from diamagnetism using Pascal constants and from temperature independent paramagnetism (TIP) of the transition metals. AC susceptibility measurements were performed using an oscillating field of 1 Oe or 1600 Oe and AC frequencies ranging from 10 to 9007 Hz.

X-ray diffraction data on the ground state were collected at 100 K on a Supernova diffractometer equipped with an ATLAS CCD detector, MoKα radiation and a Helijet open flow cryosystem. The structures were solved by direct methods using SHELXS-97 and refined against F^2 by full-matrix least-squares techniques using SHELXL-97 All calculations were performed using the Crystal Structure crystallographic software package WINGX. See the supporting information for further details on the structural analysis. CCDC 1000393 for **1**, 1000394 for **2**, 1000395 for **3**, 1000396 for **4**, 1000397 for **5**, 1000398 for **6**, 1000399 for **7**, 1000400 for **8** contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from the Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Synthesis of precursors

Ligands L^1 (N,N'-bis(3-methoxysalicylidene)propylene-diamine), and L^2 (N,N'-bis(3-methoxysalicyli-dene)ethylenediamine), were synthesized as previously described by reacting one equivalent of the appropriate amine (propylenediamine for L^1 and ethylenediamine for L^2) with two equivalents of o-vanillin in ethanol. The bimetallic building blocks [CuLTb](NO$_3$)$_3$ (L=L^1 or L^2) were synthesized

according to a protocol also described in the literature.[28] Hexacyanometallate precursors were synthesized as described elsewhere $(K_3[Cr(CN)_6])$[29] or purchased from AlfaAesar $(K_3[Co(CN)_6], K_3[Fe(CN)_6])$.

Caution! Cyanides are very toxic and must be handled with care.

1. [Co(Cu-valpn-Tb)].7H$_2$O

$[Co(CN)_5\{(\mu-CN)CuTbC_{19}H_{20}N_2O_4(H_2O)_x\}].7H_2O$

$[Co(CN)_6]K_3$ (0.0075 g, 0.0228 mmol, 1eq.) in 5 mL of water/acetonitrile (1: 2) was carefully added to a solution of [Cu-valpn-Tb](NO$_3$)$_3$; 0.037 g, 0.045 mmol, 2eq.) in 20 mL of the same solvent and the mixture was stirred for 2 minutes. Slow evaporation of the green solution afforded green crystals (squares) after two days.

Yield = 40 %; IR (KBr): 3140, 2164, 2142, 2128, 1620, 1470, 1300, 1240, 1070, 730 cm^{-1}. Anal Calc for CoTbCuC25H33N2O11: C 33.22, H 3.79, N 12.39, Co 6.52, Cu 7.03, Tb 17.58. Found: C 26.35, H 2.69, N 13.79, Co 6.27, Cu 7.04, Tb 17.06.

2. [Cr(Cu-valpn-Tb)].7H$_2$O

$[Cr(CN)_5\{(\mu-CN)CuTbC_{19}H_{20}N_2O_4(H_2O)_x\}].7H_2O$

Complex **2** was obtained using the same experimental procedure, with $[Cr(CN)_6]K_3$ (0.0074 g, 0.0228 mmol). Slow evaporation of the green solution afforded green crystals after a few days.

Yield = 40 %; IR (KBr): 2158, 2142, 2128, 1627, 1477, 1300, 1227, 1066, 744 cm^{-1}. Anal Calc for CrTbCuC25H33N2O11: C 33.47, H 3.80, N 12.49, Cr 5.78, Cu 7.08, Tb 17.72. Found: C 33.33, H 3.75, N 12.26, Cr 5.72, Cu 7.21, Tb 17.49.

3. [Fe(Cu-valpn-Tb)].7H$_2$O

$[Fe(CN)_5\{(\mu-CN)CuTbC_{19}H_{20}N_2O_4(H_2O)_x\}].7H_2O$

Complex **3** was obtained using the same experimental procedure, with $[Fe(CN)_6]K_3$ (0.0075 g, 0.0228 mmol). Slow evaporation of the green solution afforded green crystals after a few days.

Yield = 71 %; IR (KBr): 3200, 2149, 2130, 2117, 1618, 1472, 1299, 1236, 1069, 736 cm^{-1}. Anal Calc for FeTbCuC25H33N2O11: C 33.33, H 3.80, N 12.44, Fe 6.20, Cu 7.05, Tb 17.64. Found: C 33.27, H 3.76, N 12.45, Fe 6.32, Cu 7.04, Tb 17.65.

4. [Co(Cu-valen-Tb)]$_2$.14H$_2$O

$[Co(CN)_5\{(\mu-CN)CuTbC_{18}H_{18}N_2O_4(H_2O)x\}].14H_2O$

$[Co(CN)_6]K_3$ (0.0075 g, 0.0228 mmol, 1eq.) in 5 mL of water/acetonitrile (1: 2) was carefully added to a solution of [Cu-valen-Tb](NO$_3$)$_3$; 0.036 g, 0.045 mmol, 2eq.) in 20 mL of the same solvent and the mixture was stirred for 2 minutes. Slow evaporation of the red solution afforded red crystals (needles) after two days.

Yield = 50 %; IR (KBr): 3400, 2169, 2142, 1630, 1616, 1472, 1455, 1289, 1072, 733 cm^{-1}. Anal Calc for Co2Tb2Cu2C48H76N4O22: C 32.40, H 3.62, N 12.60, Co 6.60, Cu 7.14, Tb 17.86. Found: C 31.94, H 3.71, N 12.26, Co 5.92, Cu 6.79, Tb 17.42.

5. [Cr(Cu-valen-Tb)]$_2$.14H$_2$O

$[Cr(CN)_5\{(\mu-CN)CuTbC_{18}H_{18}N_2O_4(H_2O)_x\}].14H_2O$

Complex **5** was obtained using the same experimental procedure, with $[Cr(CN)_6]K_3$ (0.0074 g, 0.0228 mmol). Slow evaporation of the red solution afforded red crystals after a few days.

Yield = 44 %; IR (KBr): 2160, 2142, 2126, 1639, 1561, 1477, 1455, 1383, 1283, 1083, 739 cm^{-1}. Anal Calc for Cr2Tb2Cu2C48H76N4O22: C 32.60, H 3.65, N 12.70, Cr 5.89, Cu 7.20, Tb 18.00. Found: C 37.92, H 3.97, N 10.75, Cr 5.75, Cu 7.12, Tb 17.60.

6. [Fe(Cu-valen-Tb)]$_2$.14H$_2$O

$[Fe(CN)_5\{(\mu-CN)CuTbC_{18}H_{18}N_2O_4(H_2O)_x\}].14H_2O$

Complex **6** was obtained using the same experimental procedure, with $[Fe(CN)_6]K_3$ (0.0075 g, 0.0228 mmol). Slow evaporation of the red solution afforded red crystals after a few days.

Yield = 52 %; IR (KBr): 3180, 2152, 2130, 2114, 1632, 1479, 1292, 1222, 1076, 736 cm^{-1}. Anal Calc for Fe2Tb2Cu2C48H76N4O22: C 32.50, H 3.64, N 12.64, Fe 6.30, Cu 7.17, Tb 17.92. Found: C 31.83, H 3.65, N 12.44, Fe 6.15, Cu 7.33, Tb 17.69.

7. {Co(Cu-valpn-Tb)}$_n$.7H$_2$O

$[Co(CN)_3\{(\mu-CN)CuTbC_{19}H_{20}N_2O_4(H_2O)_x\}].7H_2O$

$[Co(CN)_6]K_3$ (0.0075 g, 0.0228 mmol, 1eq.) in 5 mL of water/acetonitrile (1: 2) was carefully added to a solution of [Cu-valpn-Tb](NO$_3$)$_3$; 0.110 g, 0.136 mmol, 6eq.) in 20 mL of the same solvent and the mixture was stirred for 2 minutes. Slow evaporation of the green solution afforded crystals (green needles) after two days.

Yield = 25 %; IR (KBr): 3400, 2150, 2130, 1625, 1471, 1450, 1325, 1241, 1225; 1075, 741 cm^{-1}. Anal Calc for CoTbCuC25H33N2O11: C 33.22, H 3.79, N 12.39, Co 6.52, Cu 7.03, Tb 17.58. Found: C 28.32, H 3.07, N 9.92, Co 1.27, Cu 7.46, Tb 18.12.

8. {[Cr(Cu-valpn-Tb)]}$_n$.7H$_2$O

$[Cr(CN)_5\{(\mu-CN)CuTbC_{19}H_{20}N_2O_4(H_2O)_x\}].7H_2O$

Complex **8** was obtained using the same experimental procedure, with $[Cr(CN)_6]K_3$ (0.0074 g, 0.0228 mmol). Slow evaporation of the green solution afforded green crystals after a few days.

Yield = 10 %; IR (KBr): 2157, 2152, 2129, 1621, 1473, 1298, 1228, 1069, 738 cm^{-1}. Anal Calc for CrTbCuC25H33N2O11: C 33.47, H 3.80, N 12.49, Cr 5.78, Cu 7.08, Tb 17.72. Found: C 33.33, H 3.75, N 12.26, Cr 5.72, Cu 7.21, Tb 17.49.

9. {[Fe(Cu-valpn-Tb)]}$_n$.7H$_2$O

$[Fe(CN)_5\{(\mu-CN)CuTbC_{19}H_{20}N_2O_4(H_2O)_x\}].7H_2O$

Complex **9** was obtained using the same experimental procedure, with $[Fe(CN)_6]K_3$ (0.0075 g, 0.0228 mmol). Slow evaporation of the green solution afforded green crystals after a few days.

Yield = 51 %; IR (KBr): 2150, 2131, 2117, 1622, 1473, 1296, 1233 cm^{-1}. Anal Calc for FeTbCuC25H33N2O11: C 33.33, H 3.80, N 12.44, Fe 6.20, Cu 7.05, Tb 17.64. Found: C 33.27, H 3.76, N 12.45, Fe 6.32, Cu 7.04, Tb 17.65.
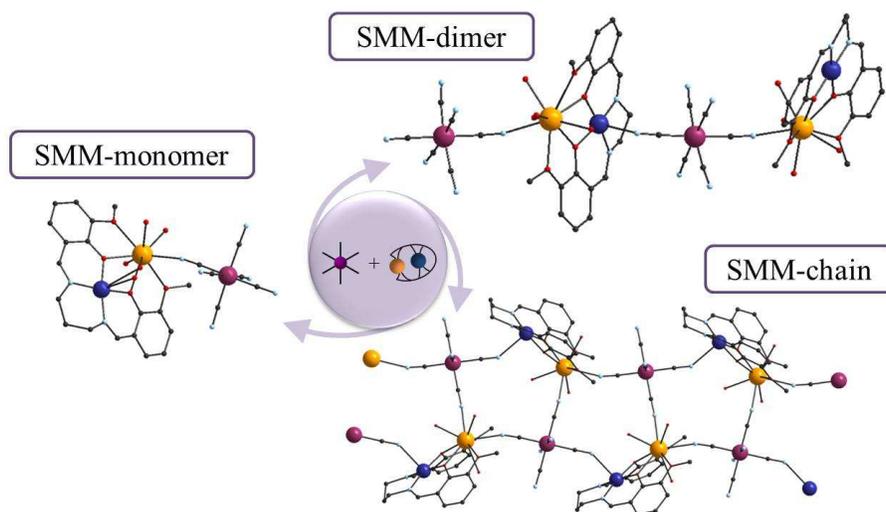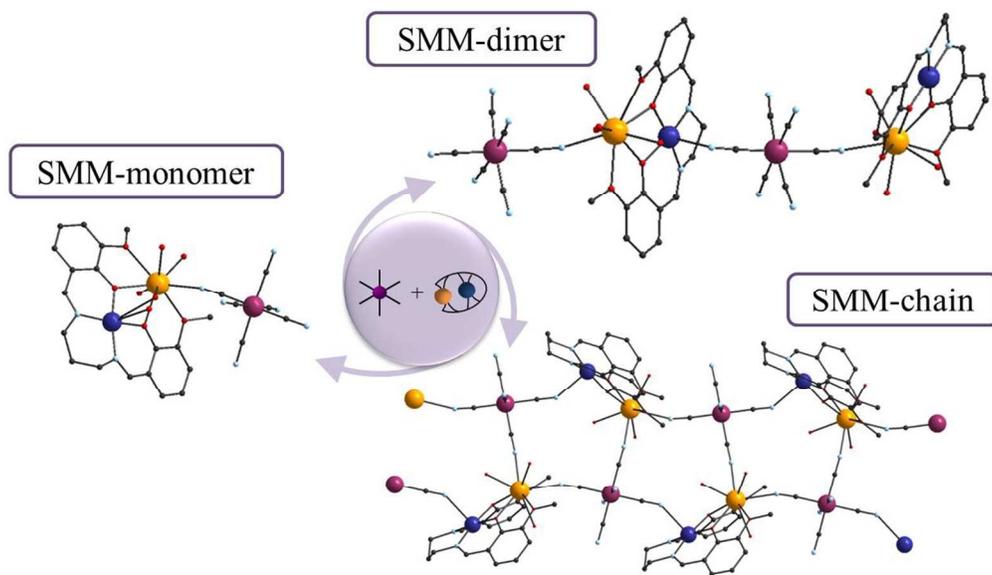
Acknowledgements

Notes and references

* Dr. Valérie Marvaud, IPCM-CNRS-7201, UPMC-Univ Paris 6, cc 42, 4 place Jussieu, 75252 Paris Cedex 05, FRANCE. Fax: +33 (0)1 44 27 38 41, Tel: +33 (0)1 44 27 32 77; * E-mail : valerie.marvaud@upmc.fr

a IPCM-CNRS-7201, UPMC-Univ Paris 6, cc 42, 4 place Jussieu, 75252.

[1] a) G. Christou, D. Gatteschi, D. Hendrickson, R. Sessoli, single molecule magnets, *MRS bulletin*, 2000, **25** (11), 66-71; b) D.N. Woodruff, R.E.P. Winpenny, R.A. Layfield, *Chem. Rev.*, 2013, **113** (7), pp 5110–5148; D. Gatteschi, R. Sessoli, J. Villain, *Molecular Nanomagnets*; Oxford University Press: Oxford, 2006.

[2] a) A. Caneschi, D. Gatteschi, R. Sessoli, *J. Am. Chem. Soc.*, 1991, **113**, 5873-5874; b) R. Sessoli, H.-L. Tsai, A. R. Schake, S. Wang, J. B. Vincent, K. Folting, D. Gatteschi, G. Christou, D.N. Hendrickson, *J. Am. Chem. Soc.*, 1993, **115**, 1804-1816; c) R. Sessoli, D. Gatteschi, A. Caneschi, M. A. Novak, *Nature*, 1993, **365**, 141.

[3] a) D. Gatteschi, R. Sessoli, A. Cornia, *Chem Commun.* 2000, 725-732; b) C. J. Milios, S. Piligkos, E.K. Brechin, *Dalton Trans.* 2008, **14**,1809-1817 c) E. Yang, N. Harden, W. Wernsdorfer, L. Zakharov, E.K. Brechin, A.L. Rheingold, G. Christou, D.N. Hendrickson, 2003, *Polyhedron* **22** (14–17), 1857-1863; d) F. Habib, J. Long, P.H. Lin, I. Korobkov, L. Ungur, W. Wernsdorfer, L.F. Chibotaru, M. Murugesue, *Chem. Sci.*, 2012, **3** (6), 2158-2164.

[4] a) Y.-Y. Zhu, C. Cui, K. Qian, J. Yin, B.-W. Wang, Z.-M. Wang, S. Gao, *Dalton Trans.*, 2014, **43**, 11897-11907; b) A. L. Barra, A. Caneschi, A. Cornia, F. Fabrizi de Biani, D. Gatteschi, C. Sangregorio, R. Sessoli and L. Sorace, *J. Am. Chem. Soc.*, 1999, **121**, 5302-5310; c) T. Glasser, *Chem Commun.*, 2011, **47**, 116-130; d) F. Tuyeras, A. Scuiller, C. Duhayon, M. Hernandez Molina, F. Fabrizi de Biani, M. Verdaguer, Mallah Talal, W. Wernsdorfer, V. Marvaud *Inorg. Chim. Acta*, 2008, **361**, 3505-3518.

[5] K.J. Heroux, H.M. Quddusi, J. Liu, J.R. O'Brien, M. Nakano, E. del Barco, S. Hill, D.N. Hendrickson, *Inorg. Chem.* 2011, **50**, 7367-7369.

[6] a) V. Hoeke, M. Heidemeier, E. Krickemeyer, A. Stammler, H. Bogge, J. Schnack, A. Postnikov, and T. Glaser, *Inorg. Chem.,* 2012 **51** (20), 10929-54.

[7] a) W. Wernsdorfer, N. Aliaga-Alcalde, D. N. Hendrickson, G. Christou, *Nature,* 2002, **416**, 406-409. b) L. Lecren, O. Roubeau, Y.-G. Li, X. F. Le Goff, H. Miyasaka, F. Richard, W. Wernsdorfer, C. Coulon and R. Clérac, *Dalton Trans.*, 2008, 755-766; c) O. Roubeau and R. Clérac, *Eur. J. Inorg. Chem.*, 2008, 4315-4342; d) L. Lecren, W. Wernsdorfer, Y.-G. Li, A. Vindigni, H. Miyasaka, R. Clérac, *J. Am. Chem. Soc.* 2007, **129**, 5045-5051 e) M. Ferbinteanu, H. Miyasaka, W. Wernsdorfer, K. Nakata, K. Sugiura, M. Yamashita, C. Coulon, R. Clérac *J. Am. Chem. Soc.* 2005, **127**, 3090-3099.

[8] a) J.-P. Costes, F. Dahan, et al, *Inorg. Chem.*, 2006, **45(1)**, 5. b) M. Andruh, *Chem. Commun*., 2011, **47**, 3025-3042; c) M. Andruh, D. G. Branzea, R. Gheorghe and A. M. Madalan, *CrystEngComm.*, 2009, **11**, 2571-2584; c) G. Novitchi, W. Wernsdorfer, L. F. Chibotaru, J.-P. Costes, C. E. Anson, and A K. Powell, *Angew. Chem. Int. Ed.,* 2009, **48**, 1614-1619.

[9] a) C.P. Berlinguette, K.R. Dunbar, *Chem. Commun.*, 2005, **19**, 2451-2453 b) D. Visinescu, J.-P. Sutter, C. Ruiz-Perez, M. Andruh*, Inorg. Chim. Acta,* 2006, **359** (2), 433–440. c) H.-Z. Kou, B. C. Zhou, S. Gao, R.-J. Wang, *Angew. Chem., Int. Ed.* 2003, **42** (28), 3288–3291. d) J. Long, L.-M. Chamoreau, C. Mathonière, V. Marvaud, *Inorg.*

Chem., 2009, **48** (1) 22-24 ; e) J. Long, L.-M. Chamoreau, V. Marvaud, *Eur. J. Inorg. Chem.*, 2011, **22**, 3478-3483.

[10] a) N. Bridonneau, L.-M. Chamoreau, P. P. Lainé, W. Wernsdorfer, V. Marvaud, *Chem. Commun.,* 2013, **49**, 9476-9478; b) G.F.S. Whitehead, F. Moro, G.A. Timco, W. Wernsdorfer, S.J. Teat, R. E. P. Winpenny, Richard E. P.; *Angew. Chem. Int. Ed.*, 2013, **52**, 38, 9932-9935.

[11] a)) J. Long, L.-M. Chamoreau, V. Marvaud, *Dalton Trans.*, 2010, **39**, 2188-2190; b) W.-B. Sun, P. F. Yan, G.-M. Li, J.-W. Zhang, T. Gao, M. i. Suda and Y. Einaga, *Inorg. Chem. Commun.*, 2010, **13**, 171-174; c) G. S. Papaefstathiou, Z. Zhong, L. Geng and L. R. MacGillivray, *J. Am. Chem. Soc.*, 2004, **126**, 9158-9159; d) G. Marinescu, G. Marin, A. M. Madalan, A. Vezeanu, C. Tiseanu and M. Andruh, *Cryst. Growth Des.*, 2010, **10**, 2096-2103.

[12] a) D. Branzea, A. Guerri, et al, *Cryst. Growth Des.*, 2008, **8** (3), 941-949. b) D. Visinescu, A. M. Madalan, M. Andruh, C. Duhayon, J.-P. Sutter, L. Ungur, W. Van den Heuvel and L. Chibotaru, *Chem. Eur. J.*, 2009, **15**, 11808-11814. c) H. Wang, L.-F. Zhang, Z.-H. Ni, W.-F. Zhong, L.-J. Tian, J. Jiang, *Cryst. Growth Des.*, 2010, **10**, 4231-4234. d) M. L. Kahn, P. Lecante, M. Verelst, C. Mathonière, O. Kahn, *Chem. Mater.*, 2000, **12**, 3073-3079; e) T. Sanada, T. Suzuki and S. Kaizaki, *J. Chem. Soc., Dalton Trans.*, 1998, 959-966; f) T. Yamaguchi, Y. Sunatsuki, H. Ishida, M. Kojima, H. Akashi, N. Re, N. Matsumoto, A. Pochaba and J. Mrozinski, *Inorg. Chem.*, 2008, **47**, 5736-5745 ; g) G. Novitchi, J.-P. Costes and B. Donnadieu, *Eur. J. Inorg. Chem.*, 2004, **9**, 1808-1812.

[13] T. D. Pasatoiu, M. Etienne, A. M. Madalan, M. Andruh, R. Sessoli, *Dalton Trans.,* 2010, **39**, 4802-4808.

[14] R. Gheorghe, A. Madalan, J.-P. Costes, W. Wernsdorfer, M. Andruh, *Dalton Trans.*, 2010, **39** (20), 4734-4736.

[15] a) R. Gheorghe, M. Andruh, J.-P. Costes, B. Donnadieu, *Chem. Commun.*, 2003, **22**, 2778-2779. b) R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadieu, S. Shova, *Chem. Eur. J.*, 2006, **12** (1), 187-203.

[16] J.-P. Costes, F. Dahan, W. Wernsdorfer, *Inorg. Chem.*, 2006, **45** (1), 5-7.

[17] M. Kahn, C. Mathonière, O. Kahn, *Inorg. Chem.*, 1999, **38** (16), 3692-3697.

[18] J.-P. Costes, F. Dahan, A. Dupuis, *Inorg. Chem.*, 2000, **39** (2), 165-168.

[19] T. Ishida, R. Watanabe, K. Fujiwara, A. Okazawa, N. Kojima, G. Tanaka, S. Yoshii, H. Nojiri, *Dalton Trans.*, 2012, **41** (44), 13609-13619.

[20] G. Poneti, K. Bernot, L. Bogani, A. Caneschi, R. Sessoli, W. Wernsdorfer, D. Gatteschi, *Chem. Commun.*, 2007, **18**, 1807-1809.

[21] a) D. Gatteschi, R. Sessoli, J. Villain, Molecular Nanomagnets, Oxford University Press, Oxford, 2006; b) Dekker, C.; Arts, A. F. M.; Wijn, H. W.; van Duyneveldt, A. J.; Mydosh, J. A. *Phys Rev. B* 1989, **40**, 1243; c) Cole, K. S.; Cole, R. H. *J. Chem. Phys.* 1941, **9**, 341-351.

[22] D. Visinescu, I.-R. Jeon, A. M. Madalan, M.-G. Alexandru, B. Jurca, C. Mathoniere, R. Clerac, M. Andruh, *Dalton Trans.* 2012, **41**, 13578–13581.

[23] T. Kajiwara, M. Nakano, S. Takaishi, M. Yamashita, *Inorg. Chem.* 2008, **47**, 8604-8606.

[24] a) J.-P. Costes, L. Vendier, *Comptes Rendus Chimie*, 2010, **13** (6-7), 661. b) J.-P. Costes, L. Vendier, *Eur. J. Inorg. Chem.*, 2010, **18**, 2768-2773.

[25] Z.-X Wang, X. Zhang, Y.-Z. Zhang, M.X. Li, H. Zhao, M. Andruh, K. Dunbar, *Angew. Chem. Int. ed.* 2014, **53**, 11567-11570.

[26] a) S.K. Langley, D.P. Wielechowski, V. Vieru, N.F. Chilton, B. Moubaraki, L.F. Chibotaru, K.S. Murray, *Chem. Sci.*, 2014, **5**, 3246-3256. b) S.K. Langley, D.P. Wielechowski, V. Vieru, N.F. Chilton, B. Moubaraki, B. Abraham, L.F. Chibotaru, K.S. Murray, *Angew. Chem. Int. ed.*, 2013, **52**, 1214-1219.

[27] K.S. Pedersen, J. Bendix, R. Clerac, *Chem. Commun.*, 2014, **50**, 4396-4415.

[28] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, *Inorg. Chem.*, 1996, **35**, 2400-2402.

[29] V. Marvaud, T. Mallah, M. Verdaguer, *Inorg. Synth.* 2004, **34**, 144-146.

Table of Contents

SMM-dimer

SMM-monomer

SMM-chain

Synthesis, structural characterizations and magnetic properties of a new family of hetero-tri-metallic complexes [M(CuTb)]$_n$ (n = 1, 2, ∞; M=Co, Cr, Fe), exhibiting single molecule magnet behaviour.

210x123mm (150 x 150 DPI)