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# A new family of hetero-tri-metallic complexes $[M(\text{CuTb})]_n$ ( $n = 1, 2, \infty$ ; $M = \text{Co}, \text{Cr}, \text{Fe}$ ): synthesis, structure and tailored single-molecule magnet behavior†

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A new family of hetero-tri-metallic complexes  $[M(\text{CuTb})]_n$  ( $M^{\text{III}} = \text{Co}, \text{Cr}, \text{Fe}$ ;  $n = 1, 2, \infty$ ), composed of three series of three compounds (oligo- and poly-nuclear complexes based on  $[\text{Cu}-\text{Tb}]$  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  $[\text{CuTb}]$  moiety can be modulated via the control of intermolecular interactions. Specifically, the combination of the “non-innocent” diamagnetic  $[\text{Co}^{\text{III}}(\text{CN})_6]^{3-}$  center with a  $[\text{Cu}-\text{Tb}]^{3+}$  moiety enabled isolation of the magnetic entities, resulting in an improvement of the SMM behavior (ranging from  $U_{\text{eff}} = 5-7 \text{ cm}^{-1}$  to  $15-17 \text{ cm}^{-1}$ ).

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## Introduction

The design and synthesis of single-molecule magnets (SMMs) have attracted increasing interest over the years<sup>1</sup> due to their potential application in information storage at the molecular scale. Since their discovery in the 90s with  $\text{Mn}_{12}$ -acetate,<sup>2</sup> numerous kinds of SMMs have been obtained by varying the metal ion composition as well as the molecular assembly.<sup>3</sup> At the same time, great attention has been devoted to the understanding of the SMM behavior and the increase of the expected energy barrier.<sup>4</sup> 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 interactions  $J'$ . 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.<sup>5</sup> 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,<sup>6</sup> 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,<sup>7</sup>  $[\text{CuTb}]$  units,<sup>8</sup> by forming hetero-tri-metallic compounds with the use of hexacyanometalate complexes  $\text{K}_3[\text{M}^{\text{III}}(\text{CN})_6]$  (with  $M = \text{Co}, \text{Cr}$  or  $\text{Fe}$ ). Although the synthesis of hetero-tri-metallic<sup>9</sup> and hetero-tetra-metallic<sup>10</sup> compounds remains challenging, the use of  $[\text{CuTbL}]$  moieties (with  $L$  a compartmental Schiff-base ligand) is already known in the literature to form bimetallic and tri-metallic assemblies such as square<sup>11</sup> compounds, or chains<sup>12</sup> and networks.<sup>13</sup> With this idea in mind, the use of two  $[\text{CuTbL}]^{3+}$  building blocks as precursors coupled to hexacyanometalate ions  $[\text{M}(\text{CN})_6]^{3-}$  ( $M = \text{Co}, \text{Cr}, \text{Fe}$ ) enabled the synthesis of nine hetero-tri-metallic compounds of various nuclearities.

All complexes exhibit SMM behavior originating from the  $[\text{Cu}^{\text{II}}-\text{Tb}^{\text{III}}]$  moiety. The compounds described here are divided into three series of three compounds each, showing different molecular organizations of the subunits as depicted in Fig. 1.

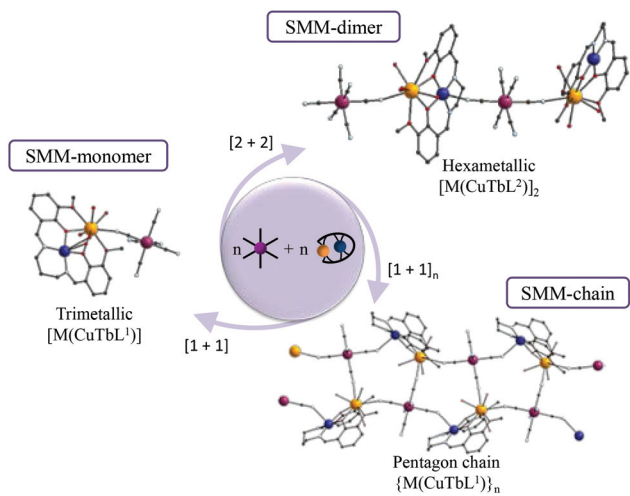
The first series of three trinuclear compounds incorporate one  $[\text{Cu}-\text{Tb}]$  bimetallic subunit and one hexacyanometalate moiety, herein referred to as the “SMM-monomer”  $[\text{M}(\text{CuTbL}^1)]$  ( $M = \text{Co}, \text{Cr}, \text{Fe}$ ). Using different synthetic conditions, a so-called “SMM-dimer”  $[\text{M}(\text{CuTbL}^2)]_2$  was obtained bearing six metal centers. Finally, a “SMM-chain”  $\{\text{M}(\text{CuTbL}^1)\}_n$  was obtained by varying the stoichiometry of precursors.

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**Fig. 1** Family of hetero-tri-metallic complexes (blue =  $\text{Cu}^{\text{II}}$ ; orange =  $\text{Tb}^{\text{III}}$ ; purple  $\text{M} = \text{Co}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$  or  $\text{Fe}^{\text{III}}$ ).

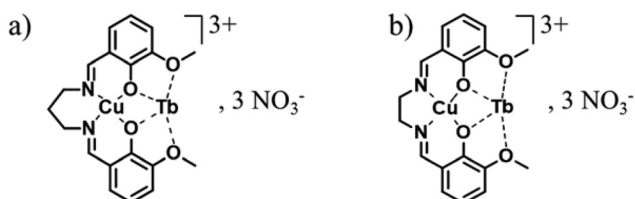
While all compounds incorporate  $[\text{Cu-Tb}]$  units with a similar local environment of the  $\text{Cu}^{\text{II}}$  and  $\text{Tb}^{\text{III}}$  ions, the nine complexes show different magnetic properties when varying the nature of the hexacyanometalate that can be either diamagnetic ( $\text{Co}^{\text{III}}$   $S = 0$ ) or paramagnetic ( $\text{Cr}^{\text{III}}$   $S = 3/2$ ,  $\text{Fe}^{\text{III}}_{\text{LS}}$   $S = 1/2$ ).

## Synthesis and structural description

Bimetallic building blocks  $[\text{Cu}^{\text{II}}\text{Tb}^{\text{III}}\text{L}]$  ( $\text{L} = \text{L}^1, \text{L}^2$ ) were formed from compartmental Schiff-base ligands derived from 3-methoxysalicylaldehyde:  $\text{L}^1 = N,N'$ -bis(3-methoxysalicylidene)propylenediamine and  $\text{L}^2 = N,N'$ -bis(3-methoxysalicylidene)ethylenediamine. The two coordination sites of the ligand are selectively occupied by the copper(II) ion in the  $\text{N}_2\text{O}_2$  site and the terbium(III) ion in the  $\text{O}_2\text{O}_2$  compartment, the average Cu–Tb distance being 3.45 Å. Structures of the bimetallic building blocks are presented in Scheme 1.

### “SMM-monomer” compounds

**Trinuclear complexes  $[\text{M}(\text{CuTbL}^1)]$**  ( $\text{M}^{\text{III}} = \text{Co}$  (1),  $\text{Cr}$  (2),  $\text{Fe}$  (3)). The first family of hetero-tri-metallic complexes was obtained by condensation of the  $(\text{CuTbL}^1)$  and  $\text{K}_3[\text{M}(\text{CN})_6]$  precursors in 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.



**Scheme 1** Bimetallic units (a)  $[\text{CuTbL}^1]$ ; (b)  $[\text{CuTbL}^2]$ .

**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, and  $c = 22.2188(5)$  Å with a cell volume of  $3246.41(13)$  Å<sup>3</sup> ( $Z = 4$ ). Cell parameters slightly vary from 1 to 3 according to the ionic radius of their respective hexacyanometallate ion:  $(a, b, c)_{\text{Co}} < (a, b, c)_{\text{Fe}} < (a, b, c)_{\text{Cr}}$  and  $r_{\text{Co}} < r_{\text{Fe}} < r_{\text{Cr}}$  (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 Fig. 2 (see ESI† for 2 and 3).

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  $\text{Tb-N}\equiv\text{C}$  angle of  $167.9(4)^\circ$ . 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), with the second one situated at half the distance of the copper and terbium sites (O8A, 75% occupation site, at 2.71 and 2.72 Å respectively). This bridging aqua ligand between Cu and Tb in the compartmental ligand is unusual in the literature and has never been reported before. Nevertheless there exist analogous structures that indicate that such arrangement might exist.<sup>8c</sup> In both cases, the copper atom is penta-coordinated to the  $\text{N}_2\text{O}_2$  site of the  $\text{L}^1$  ligand and an oxygen atom from a water molecule. Metal centers from two different molecules are well separated, with a metal–metal average distance of 7.29 Å.

### “SMM-dimer” compounds

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

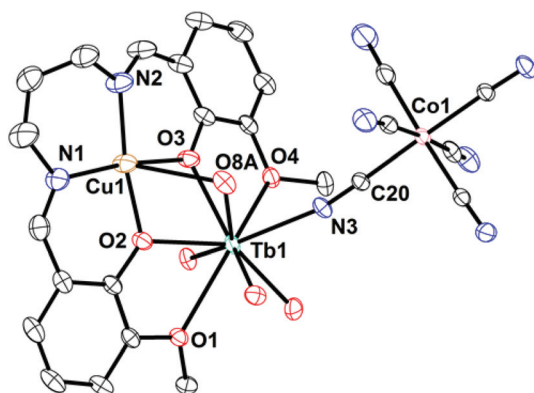
**Crystallography.** Hexanuclear complexes 4, 5 and 6 have been characterized by X-ray crystallography. All three compounds are iso-structural and crystallize in a monoclinic system ( $P2_1/c$  space group). Unit cell parameters for 4 are  $a = 25.5005(6)$  Å,  $b = 11.9284(3)$  Å, and  $c = 22.7251(6)$  Å with a cell volume of  $6546.61(29)$  Å<sup>3</sup> ( $Z = 4$ ). As for the previous series of compounds, cell parameters vary slightly 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 Fig. 3 (see ESI† for 5 and 6). Complexes crystallize in a linear array formed by two hexacyanometallate atoms and two  $[\text{CuTbL}^2]$  units alternatively linked with cyanide bonds.

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

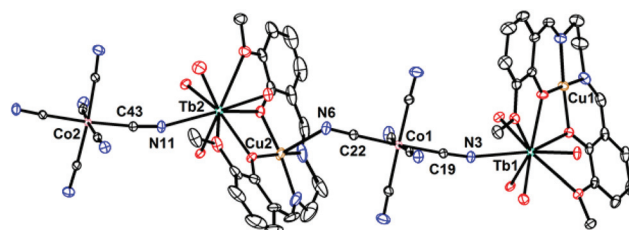
	1	2	3	4
Formula	C <sub>25</sub> H <sub>20</sub> CoCuN <sub>8</sub> O <sub>11</sub> Tb	C <sub>25</sub> H <sub>20</sub> CrCuN <sub>8</sub> O <sub>11</sub> Tb	C <sub>25</sub> H <sub>20</sub> CuFeN <sub>8</sub> O <sub>11</sub> Tb	C <sub>48</sub> H <sub>66</sub> Co <sub>2</sub> Cu <sub>2</sub> N <sub>16</sub> O <sub>23</sub> Tb <sub>2</sub>
<i>M</i> /g mol <sup>-1</sup>	889.88	882.95	886.80	1797.95
Cryst. syst.	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>
<i>a</i> /Å	12.7684(3)	13.0818(3)	12.8562(3)	25.5005(6)
<i>b</i> /Å	11.8653(3)	12.1299(2)	11.9304(3)	11.9284(3)
<i>c</i> /Å	22.2188(5)	22.1408(5)	22.1909(5)	22.7251(6)
$\beta$ /°	105.3290(10)	105.4790(10)	105.4930(10)	108.7260(10)
<i>V</i> /Å <sup>3</sup>	3246.41(13)	3385.89(12)	3279.95(13)	6546.6(3)
<i>Z</i>	4	4	4	4
<i>d</i> <sub>calc.</sub> /g cm <sup>-3</sup>	1.821	1.732	1.796	1.824
$\theta$ range	4.13–66.52°	1.64–30.55°	1.67–30.59°	0.84–30.6°
Reflns coll'd	19 513	56 207	56 260	195 962
Indep. reflns/ <i>R</i> <sub>int</sub>	5670/0.0429	10 377/0.0214	10 028/0.0225	20 102/0.0265
GOF	1.027	1.041	1.061	1.062
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0397, 0.1113	0.0358, 0.0964	0.0295, 0.0826	0.0282, 0.0620

	5	6	7	8
Formula	C <sub>48</sub> H <sub>66</sub> Cr <sub>2</sub> Cu <sub>2</sub> N <sub>16</sub> O <sub>23</sub> Tb <sub>2</sub>	C <sub>48</sub> H <sub>66</sub> Cu <sub>2</sub> Fe <sub>2</sub> N <sub>16</sub> O <sub>23</sub> Tb <sub>2</sub>	C <sub>25</sub> H <sub>34</sub> CoCuN <sub>8</sub> O <sub>11</sub> Tb	C <sub>25</sub> H <sub>34</sub> CrCuN <sub>8</sub> O <sub>11</sub> Tb
<i>M</i> /g mol <sup>-1</sup>	1784.09	1791.79	903.99	897.06
Cryst. syst.	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>	<i>P</i> 2 <sub>1</sub> 2 <sub>1</sub> 2 <sub>1</sub>
<i>a</i> /Å	26.0774(5)	25.6467(6)	12.9082(3)	13.2421(3)
<i>b</i> /Å	12.0578(2)	11.9352(3)	14.9710(4)	15.1115(4)
<i>c</i> /Å	22.9454(4)	22.8151(6)	16.9463(4)	17.0360(4)
$\beta$ /°	108.6210(10)	108.6690(10)	90	90
<i>V</i> /Å <sup>3</sup>	6837.2(2)	6616.2(3)	3274.85(14)	3409.04
<i>Z</i>	4	4	4	4
<i>d</i> <sub>calc.</sub> /g cm <sup>-3</sup>	1.733	1.799	1.834	1.748
$\theta$ range	0.82–30.64°	0.84–30.55°	2.40–30.57°	2.369–30.559°
Reflns coll'd	106 004	202 359	49 038	73 633
Indep. reflns/ <i>R</i> <sub>int</sub>	20 979/0.0298	20 323/0.0293	10 033/0.0216	10 451/0.0590
GOF	1.099	1.079	1.046	0.943
<i>R</i> <sub>1</sub> , <i>wR</i> <sub>2</sub> [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0282, 0.0696	0.0289, 0.0634	0.0146, 0.0333	0.0267, 0.0526

Fig. 2 Crystal structure of the [Co(CuTbL<sup>1</sup>)] (1) representative of the subclass.

One cobalt atom (Co1) links both [CuTbL<sup>2</sup>] units in a *trans* manner: one cyanide ligand connected to Tb1 and the other linked to the copper atom of the second [CuTbL<sup>2</sup>] 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

Fig. 3 Crystal structure of the [Co(CuTbL<sup>2</sup>)]<sub>2</sub> (4) representative of the subclass.

(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 denoted as [M(CuTbL<sup>2</sup>)]<sub>2</sub>.

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 formed are 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–Cu<sub>2</sub>, which can be explained by the large distance between the copper and nitrogen atoms (2.5877(27) Å).

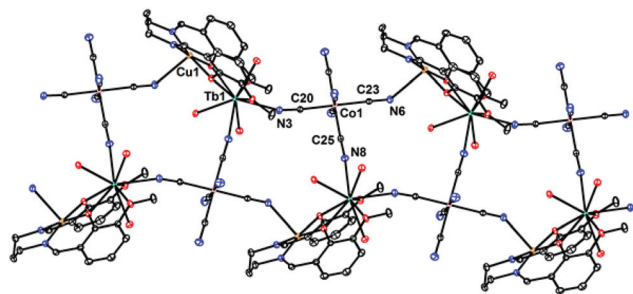


Fig. 4 Crystal structure of the  $\{\text{Co}(\text{CuTbL}^1)\}_n$  (7) representative of the subclass.

### “SMM-chain” compounds

$\{\text{M}(\text{CuTbL}^1)\}_n$  complexes ( $\text{M} = \text{Co}$  (7),  $\text{Cr}$  (8),  $\text{Fe}$  (9)). This third family of compounds was synthesized from the same building blocks as 1–3 heterotrimetallic complexes but with a different stoichiometry of the subunit composition. Condensation of the  $(\text{CuTbL}^1)$  and  $\text{K}_3[\text{M}(\text{CN})_6]$  precursors was realized in 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<sup>14</sup> using a slightly different synthetic method, and complexes 7 and 8 are isostructural to their gadolinium equivalents that were also previously published by M. Andruh’s group.<sup>15</sup> New complexes 7 and 8 are described here in addition to the two previous families of trinuclear and hexanuclear complexes, for comparison purposes.

**Crystallography.** The compounds crystallize in an orthorhombic system ( $P2_12_12_1$  space group). Unit cell 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<sup>3</sup> ( $Z = 4$ ). The structure is once again neutral and composed of an array of alternate hexacyanometallate atoms and  $[\text{CuTbL}^1]$  units linked together by cyanide bonds, as depicted in Fig. 4. Each cobalt center Co1 connects meridionally three  $[\text{CuTbL}^1]$  moieties through cyano groups: two cyanide bonds are formed with the terbium(III) ion, with  $\text{C}\equiv\text{N}-\text{Tb}$  angles of  $162.92(14)^\circ$  and  $169.94(15)^\circ$ . The third cyano group connects the copper atom, with a  $\text{C}\equiv\text{N}-\text{Cu}$  angle of  $142.62(12)^\circ$ . This strongly bent angle can be justified (just as for the hexanuclear structure) by the large distance between the copper and nitrogen atoms,  $\text{Cu}-\text{N} = 2.5198(16)$  Å. In order to accommodate the complexation of the two building blocks in this particular configuration, the  $[\text{CuTbL}^1]$  unit shows strong distortion of the  $\text{L}^1$  ligand, as illustrated in Fig. S5 (ESI†). The compound is regarded as a 1D pentagon chain and denoted as  $[\text{M}(\text{CuTbL}^1)]_n$ .

## Magnetic properties and discussion

Magnetic properties were investigated for all nine compounds. From one type of compound to the other,  $\chi_m T$  plots show similar shapes when the same hexacyanometallate building blocks are involved (see ESI†). Within the same family of com-

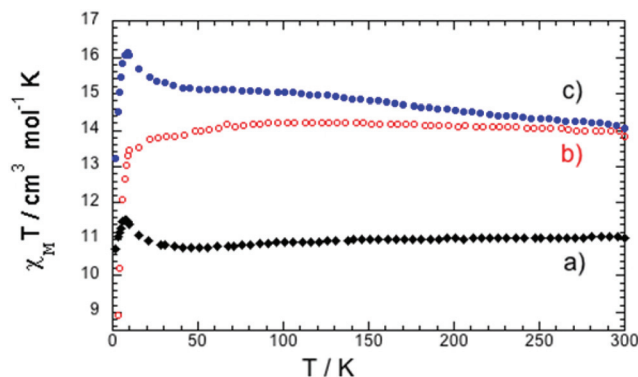


Fig. 5  $\chi_m T$  versus  $T$  plots for 1 (a,  $\blacklozenge$ ), 2 (b,  $\circ$ ) and 3 (c,  $\bullet$ ).

pounds (trinuclear, hexanuclear or chains), magnetic properties differ in relation to the nature of the hexacyanometallate precursor used:  $\text{Co}^{\text{III}}$  ( $d^6$ ,  $S = 0$ );  $\text{Cr}^{\text{III}}$  ( $d^3$ ,  $S = 3/2$ ), or  $\text{Fe}^{\text{III}}_{\text{LS}}$  ( $d^5$ ,  $S = 1/2$ ). As an example, Fig. 5 shows the temperature dependence of the 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  $\chi_m T$  values amount to  $11.08 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for 1,  $13.92 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for 2 and  $14.06 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  for 3, in good agreement with the expected theoretical values for independent  $\text{Cu}^{\text{II}}$ ,  $\text{Tb}^{\text{III}}$ ,  $\text{Cr}^{\text{III}}$  and  $\text{Fe}^{\text{III}}$  ions ( $\text{Co}^{\text{III}}$  being diamagnetic):  $\chi_m T = (N\beta^2/3k) [g_{\text{Cu}}^2 S_{\text{Cu}}(S_{\text{Cu}} + 1) + g_{\text{Tb}}^2 J_{\text{Tb}}(J_{\text{Tb}} + 1) + g_{\text{M}}^2 S_{\text{M}}(S_{\text{M}} + 1)]$  ( $\text{M} = \text{Cr}$  for 2 and  $\text{Fe}$  for 3).

Since compound 1 bears a diamagnetic  $\text{Co}^{\text{III}}$  ion, the  $\chi_m T$  plot shows typical behavior of an isolated  $[\text{Cu}-\text{TbL}]$  unit,<sup>16</sup>  $\text{L}$  being a Schiff-base ligand: the  $\chi_m T$  curve first decreases to a minimum of  $10.77 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 40.8 K, then increases abruptly to reach a maximum value of  $11.54 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$  at 7.1 K. Finally, a second decrease in the  $\chi_m T$  plot is recorded at very low temperatures and can be interpreted as weak intermolecular interactions or zero field splitting. The thermal depopulation of Stark sublevels of the  $\text{Tb}^{\text{III}}$  ion makes it difficult to quantitatively analyze the Cu–Tb coupling<sup>17</sup> but numerous examples generally attribute the decrease in temperature to the depopulation of Stark sublevels whereas the rise at low temperatures is due to the ferromagnetic coupling between the  $\text{Cu}^{\text{II}}$  and  $\text{Tb}^{\text{III}}$  ions. In order to confirm this assumption the  $[\text{Co}(\text{NiTbL}^2)]_2$  structural analogue of 4 was synthesized (where  $\text{Cu}^{\text{II}}$  is replaced by  $\text{Ni}^{\text{II}}$  which is diamagnetic in the same square planar environment). The difference  $\Delta(\chi_m T) = (\chi_m T)_{(\text{CoCuTb})_2} - (\chi_m T)_{(\text{CoNiTb})_2}$  shows a positive deviation below 100 K (Fig. S35, ESI†) that is attributed to the ferromagnetic interaction between  $\text{Cu}^{\text{II}}$  and  $\text{Tb}^{\text{III}}$ .

When the  $\text{Co}^{\text{III}}$  ion in 1 is replaced with the  $\text{Cr}^{\text{III}}$  (2) or  $\text{Fe}^{\text{III}}$  (3) ions,  $\chi_m T$  vs.  $T$  plots show different shapes, indicating a coupling between the 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  $[\text{CuGdFe}]_n$  and

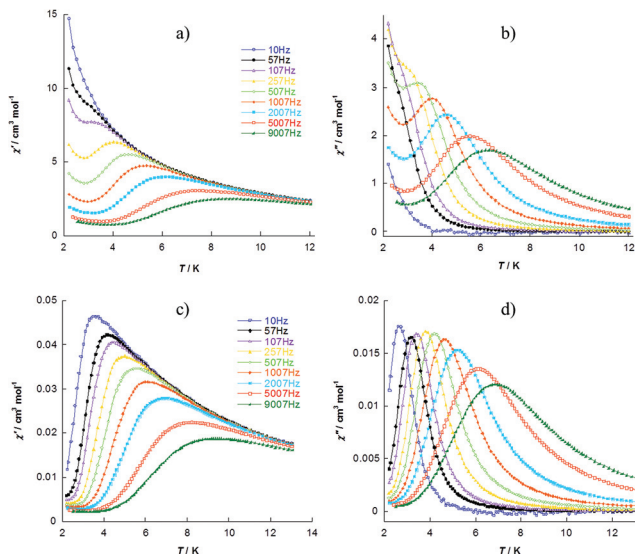


Fig. 6 AC measurements for **4** at zero field (a ( $\chi''$ ) and b ( $\chi'$ )) and under a 1.6 kOe applied field (c ( $\chi''$ ) and d ( $\chi'$ )).

[CuGdCr]<sub>n</sub><sup>15</sup> the authors have shown that the interaction corresponds to weak antiferromagnetic coupling between the paramagnetic linker Fe<sup>III</sup> ( $S = 1/2$ ) or Cr<sup>III</sup> ( $S = 3/2$ ) and the ferromagnetically coupled<sup>18</sup> [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<sup>†</sup>) show a saturation value at 70 kOe in agreement with those reported in the literature<sup>19</sup> for similar compounds.

The dynamic magnetic behavior of the series of compounds was investigated in the 10 Hz–1.5 kHz frequency ( $\nu$ ) 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 the distinct frequency dependence of the AC susceptibility in temperature only upon the application of a small supplementary static field, which is known to remove zero-field fast tunneling.<sup>20</sup> For these compounds, the slowest relaxation was observed at 1.6 kOe and this enabled bringing out the field-induced single-molecule magnet behavior (see ESI<sup>†</sup>).

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

As depicted in Fig. 6, **4** shows distinct maxima of  $\chi''$  curves for the temperature for each frequency applied. For each compound (**1**–**9**) the data were fitted to a distribution of single relaxation processes following the extended Debye model:<sup>21</sup>

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

In the above equation  $\omega = 2\pi\nu$  and  $\chi_T$  and  $\chi_S$  are the isothermal and adiabatic susceptibility respectively. In each case, the  $\alpha$  parameter was found to be close to zero and varying from 0.03 to 0.20, which indicates a narrow distribution

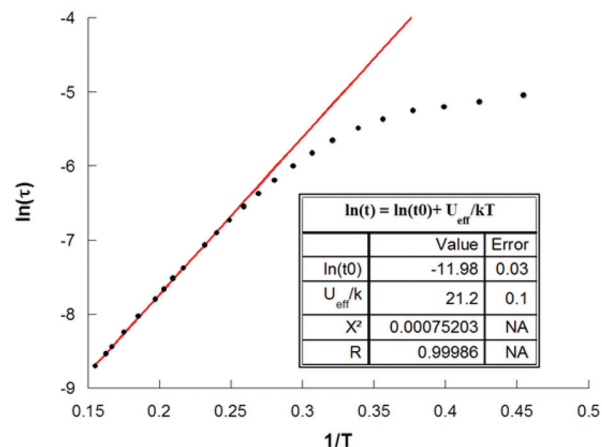


Fig. 7 Arrhenius plot obtained for **4**.

of relaxation times. The use of this model enabled the extraction of the relaxation times  $\tau$  of each compound despite the fact that iron(III) and chromium(III) compounds did not show a maximum value in  $\chi''$  curves. Results follow a thermally activated relaxation mechanism that allowed the extraction of the energy barrier  $U_{\text{eff}}$  and the relaxation time  $\tau_0$  of compounds using the Arrhenius law  $\tau = \tau_0 \exp(U_{\text{eff}}/kT)$ , assuming that above 2 K thermal relaxation prevails over the tunneling relaxation process. As an example, Fig. 7 shows the Arrhenius plot obtained for **4**, giving  $\tau_0 = 6.25 \times 10^{-6}$  s and  $U_{\text{eff}} = 14.76 \text{ cm}^{-1}$  (21.24 K).

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

## Discussion

The results presented above show unambiguously the SMM behavior of the whole family of compounds in the 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).<sup>22</sup> In our case, the effective anisotropic barriers are found to be similar or even higher, with  $U_{\text{eff}}$  in the range of 8–30 K. Compared to the precursors, [CuTbL<sup>1</sup>] and [CuTbL<sup>2</sup>], the heterotrimetallic compounds show a significantly slower relaxation time (by a factor of 10–100). More interestingly, the hetero-tri-metallic samples show different magnetic behaviors according to the nature of the hexacyanometallate precursor. From one family of a 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  $U_{\text{eff}}$  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 making magneto-structural correlations. Until now, factors influencing the SMM behavior in [CuTb] compounds were generally attributed to either slight changes

**Table 2** Energy barrier and relaxation time for the described compounds (1–9) and their precursors [CuTbL<sup>1</sup>] and [CuTbL<sup>2</sup>]

Compound	Precursor		
	[CuTbL <sup>1</sup> ]	[CuTbL <sup>2</sup> ]	
$U_{\text{eff}}$	15.36 cm <sup>-1</sup> (22.10 K)	21.02 cm <sup>-1</sup> (30.25 K)	
$\tau_0$	$5.33 \times 10^{-9}$ s	$1.44 \times 10^{-9}$ s	
$\alpha$			
Compound	“SMM-Monomer”		
	[Co(CuTbL <sup>1</sup> )] (1)	[Cr(CuTbL <sup>1</sup> )] (2)	[Fe(CuTbL <sup>1</sup> )] (3)
$U_{\text{eff}}$	18.27 cm <sup>-1</sup> (26.29 K)	4.49 cm <sup>-1</sup> (6.47 K)	5.52 cm <sup>-1</sup> (7.94 K)
$\tau_0$	$1.50 \times 10^{-5}$ s	$1.25 \times 10^{-5}$ s	$1.37 \times 10^{-7}$ s
$\alpha$	0.03–0.10	0.17–0.23	0.14–0.20
Compound	“SMM-Dimer”		
	[Co(CuTbL <sup>2</sup> )] <sub>2</sub> (4)	[Cr(CuTbL <sup>2</sup> )] <sub>2</sub> (5)	[Fe(CuTbL <sup>2</sup> )] <sub>2</sub> (6)
$U_{\text{eff}}$	14.76 cm <sup>-1</sup> (21.24 K)	7.49 cm <sup>-1</sup> (10.78 K)	7.67 cm <sup>-1</sup> (11.03 K)
$\tau_0$	$6.25 \times 10^{-6}$ s	$1.89 \times 10^{-5}$ s	$5.48 \times 10^{-8}$ s
$\alpha$	0.20–0.27	0.15–0.27	0.20–0.35
Compound	“SMM-Chain”		
	{Co(CuTbL <sup>1</sup> )} <sub>n</sub> (7)	{Cr(CuTbL <sup>1</sup> )} <sub>n</sub> (8)	{Fe(CuTbL <sup>1</sup> )} <sub>n</sub> (9)
$U_{\text{eff}}$	14.56 cm <sup>-1</sup> (20.95 K)	7.07 cm <sup>-1</sup> (10.18 K)	5.39 cm <sup>-1</sup> (7.75 K)
$\tau_0$	$6.70 \times 10^{-6}$ s	$7.10 \times 10^{-6}$ s	$1.40 \times 10^{-7}$ s
$\alpha$	0.05–0.20	0.11–0.25	0.11–0.19

in the ligand field of the Tb<sup>III</sup> ion<sup>23</sup> (in particular the nitrate coordination), or the influence brought by the ligand itself. Indeed, as the Cu<sup>II</sup> magnetic orbital ( $d_{x^2-y^2}$ ) lies in the N<sub>2</sub>O<sub>2</sub> plane of the ligand, any variation of the dihedral angle formed between the two cavities (O–Cu–O and O–Tb–O) will induce modification of the magnetic coupling between the two spin carriers.<sup>18,24</sup> As already described in the literature the coordination of the lanthanide(III) ion to a supplementary radical<sup>25</sup> or transition metal ion<sup>26</sup> can also enhance the overall SMM behavior. This is usually a consequence of the exchange interaction between the spin carriers, resulting in a barrier of multi-exchange type with a significantly reduced quantum tunneling mechanism. In our system, when the coordinated hexacyanometallate is paramagnetic (M = Cr<sup>III</sup>, Fe<sup>III</sup>), dynamic magnetic characterization reveals 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<sup>III</sup> diamagnetic building block can improve the [CuTb] magnetic properties, in contrast 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.<sup>27</sup>

## Conclusions

In our continuous effort to engineer 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 chains). 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 the 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 compared to the reference [Cu–Tb] unit, with a significantly longer relaxation time. This work shows that the addition of a diamagnetic [Co<sup>III</sup>(CN)<sub>6</sub>]<sup>3-</sup> ( $d^6$ ) entity to the SMM [Cu–Tb] unit enables their isolation in order to minimize the number of possible intermolecular interaction pathways ( $J'$ ) that would decrease the SMM efficiency.

## Experimental section

### Physical measurements

IR spectra were obtained between 4000 and 250 cm<sup>-1</sup> on a Bio-Rad FTS 165 FT-IR spectrometer using 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 temperatures from 1.8 to 400 K. The powdered samples (10 ± 50 mg) were placed in a diamagnetic sample holder and the measurements were realised in a 1000 Oe applied field using the extraction technique. Before analysis, the experimental susceptibility was cor-

rected for diamagnetism using Pascal constants and for the 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 in the ground state were collected at 100 K on a Supernova diffractometer equipped with an ATLAS CCD detector, MoK $\alpha$  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 ESI† 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** contain the supplementary crystallographic data for this paper.

### Synthesis of precursors

Ligands  $L^1$  ( $N,N'$ -bis(3-methoxysalicylidene)propylenediamine) and  $L^2$  ( $N,N'$ -bis(3-methoxysalicylidene)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.<sup>28</sup> Hexacyanometallate precursors were synthesized as described elsewhere (K $_3$ [Cr(CN) $_6$ ])<sup>29</sup> 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.

**[Co(Cu-valpn-Tb)] $\cdot$ 7H $_2$ O.** [Co(CN) $_5$ ]{( $\mu$ -CN)CuTbC $_{19}$ H $_{20}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 7H $_2$ O

[Co(CN) $_6$ ]K $_3$  (0.0075 g, 0.0228 mmol, 1 eq.) 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, 2 eq.) 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 CoTbCuC $_{25}$ H $_{33}$ N $_2$ O $_{11}$ : 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.

**[Cr(Cu-valpn-Tb)] $\cdot$ 7H $_2$ O.** [Cr(CN) $_5$ ]{( $\mu$ -CN)CuTbC $_{19}$ H $_{20}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 7H $_2$ O

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 CrTbCuC $_{25}$ H $_{33}$ N $_2$ O $_{11}$ : 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.

**[Fe(Cu-valpn-Tb)] $\cdot$ 7H $_2$ O.** [Fe(CN) $_5$ ]{( $\mu$ -CN)CuTbC $_{19}$ H $_{20}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 7H $_2$ O

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 FeTbCuC $_{25}$ H $_{33}$ N $_2$ O $_{11}$ : 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.

**[Co(Cu-valen-Tb)] $_2$  $\cdot$ 14H $_2$ O.** [Co(CN) $_5$ ]{( $\mu$ -CN)CuTbC $_{18}$ H $_{18}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 14H $_2$ O

[Co(CN) $_6$ ]K $_3$  (0.0075 g, 0.0228 mmol, 1 eq.) 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, 2 eq.) 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 Co $_2$ Tb $_2$ -Cu $_2$ C $_{48}$ H $_76$ N $_4$ O $_{22}$ : 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.

**[Cr(Cu-valen-Tb)] $_2$  $\cdot$ 14H $_2$ O.** [Cr(CN) $_5$ ]{( $\mu$ -CN)CuTbC $_{18}$ H $_{18}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 14H $_2$ O

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 Cr $_2$ Tb $_2$ Cu $_2$ C $_{48}$ H $_76$ N $_4$ O $_{22}$ : 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.

**[Fe(Cu-valen-Tb)] $_2$  $\cdot$ 14H $_2$ O.** [Fe(CN) $_5$ ]{( $\mu$ -CN)CuTbC $_{18}$ H $_{18}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 14H $_2$ O

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 Fe $_2$ Tb $_2$ -Cu $_2$ C $_{48}$ H $_76$ N $_4$ O $_{22}$ : 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.

**{Co(Cu-valpn-Tb)} $_n$  $\cdot$ 7H $_2$ O.** [Co(CN) $_3$ ]{( $\mu$ -CN)CuTbC $_{19}$ H $_{20}$ N $_2$ O $_4$ -(H $_2$ O) $_x$ }] $\cdot$ 7H $_2$ O

[Co(CN) $_6$ ]K $_3$  (0.0075 g, 0.0228 mmol, 1 eq.) 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, 6 eq.) 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 CoTbCuC $_{25}$ H $_{33}$ N $_2$ O $_{11}$ : 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.

$\{[\text{Cr}(\text{Cu-valpn-Tb})]\}_n \cdot 7\text{H}_2\text{O}$ .  $[\text{Cr}(\text{CN})_5\{(\mu\text{-CN})\text{CuTbC}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{-}(\text{H}_2\text{O})_x\}] \cdot 7\text{H}_2\text{O}$

Complex **8** was obtained using the same experimental procedure, with  $[\text{Cr}(\text{CN})_6]\text{K}_3$  (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  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{CrTbCuC}_{25}\text{H}_{33}\text{N}_2\text{O}_{11}$ : 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.

$\{[\text{Fe}(\text{Cu-valpn-Tb})]\}_n \cdot 7\text{H}_2\text{O}$ .  $[\text{Fe}(\text{CN})_5\{(\mu\text{-CN})\text{CuTbC}_{19}\text{H}_{20}\text{N}_2\text{O}_4\text{-}(\text{H}_2\text{O})_x\}] \cdot 7\text{H}_2\text{O}$

Complex **9** was obtained using the same experimental procedure, with  $[\text{Fe}(\text{CN})_6]\text{K}_3$  (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  $\text{cm}^{-1}$ . Anal. Calc. for  $\text{FeTbCuC}_{25}\text{H}_{33}\text{N}_2\text{O}_{11}$ : 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.

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