

A new versatile class of hetero-tetra-metallic assemblies: highlighting single-molecule magnet behaviour†

Cite this: *Chem. Commun.*, 2013, **49**, 9476

Received 5th July 2013,
Accepted 16th August 2013

DOI: 10.1039/c3cc45037f

www.rsc.org/chemcomm

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Hetero-tetra-metallic species based on hexanuclear assemblies $[(\text{valen})\text{M1Ln}(\text{OH}_2)_2(\mu\text{M2}(\text{CN})_8)]_2^{2-}$ ($\text{Ln} = \text{Gd}^{\text{III}}$, Tb^{III} ; $\text{M1} = \text{Cu}^{\text{II}}$, Ni^{II} and $\text{M2} = \text{Mo}^{\text{IV}}$, W^{IV}) and co-crystallized mononuclear complexes $[\text{M3}(\text{tpy})_2]^{2+}$ ($\text{M3} = \text{Ni}^{\text{II}}$, Ru^{II} , Os^{II}) were identified, fully characterized, and shown to constitute a new class of single-molecule magnets.

Inorganic molecular magnetism can be regarded as a natural subfield of co-ordination chemistry because of its basic reliance on paramagnetic building blocks (*viz.* cations of d and f elements as spin carriers). The design and synthesis of high-spin molecules (HSMs) and single-molecule magnets (SMMs) have both attracted the interest of the molecular magnetism community since the discovery of Mn12, in the 1990s.¹ Following this breakthrough, most of the hitherto reported candidate compounds were based on metal-oxide cores with capping ligands, such as clusters referred to as Fe4,² Fe8,³ Mn6,⁴ Fe19,⁵ Mn25 ($S = 51/2$),⁶ Mn19 ($S = 83/2$),⁷ showing up to 84 metal centres, as in the case of giant single-molecule magnet Mn84.⁸ Parallel to increasing nuclearity, increasing elemental diversity within purposely elaborated assemblies of controlled shape (Supramolecular Chemistry approach) has progressively emerged as an alternative strategy to improve the two key features of SMMs, which are namely their (high) ground-state spin value (S) and their uniaxial anisotropy (D).

This strategy of stepwise assembling essentially relies on cyanide-based co-ordination chemistry⁹ that can be viewed as the supramolecular counterpart of oxo- and hydroxo-based co-ordination chemistry of the above-mentioned compact oligonuclear compounds.^{1–8} Given that symmetry/anisotropy-related

requirements at both electronic and structural levels are different for HSMs and SMMs, different types of molecular topologies are targeted: radial geometries (globular with core-shell structure) for the former *versus* (axially-) distorted geometries for the latter. The key building blocks are polycyanometallates that most often function as cores for HSMs¹⁰ and as bridging units in SMMs. In this context, following the concept of “heterometallic complexes as ligands”, several hetero-tri-metallic^{11,12} complexes have been isolated and fully characterized, but they remain rather scarce. The challenge was however to go further,¹³ by adding a fourth metallic element, in order to combine several properties.

Herein, we report the first example of a series of multi-functional and modular hetero-tetra-metallic compounds of general formula $\{[(\text{valen})\text{M1Ln}(\text{OH}_2)_2(\mu\text{M2}(\text{CN})_8)]_2 \cdot 2[\text{M3}(\text{tpy})_2](\text{X})_2\}$, of which two representatives are described in details, with $\text{M1} = \text{Cu}^{\text{II}}$, $\text{Ln} = \text{Tb}^{\text{III}}$, $\text{M2} = \text{Mo}^{\text{IV}}$, W^{IV} and $\text{M3} = \text{Ni}^{\text{II}}$ (see ESI† for some other members of the family and reaction conditions).

Thus, tricationic (M1 , Ln)-hetero-dinuclear complexes,¹⁴ denoted as $[\text{M1Ln}]^{3+}$, that are based on the valen binucleating and blocking ligand (valen = *N,N'*-bis(3-methoxy-salicylidene)-ethylenediamine),¹⁵ were found to react in a water-acetonitrile mixture with octacyanometallate units $[\text{M2}(\text{CN})_8]\text{K}_4$ to form square assemblies $[(\text{valen})\text{M1Ln}(\text{OH}_2)_2(\mu\text{M2}(\text{CN})_8)]_2^{2-}$ (hereafter denoted $[\text{M1LnM2}]_2$). *In situ* metathesis of their cationic counterions (K^+) with different dications of type $[\text{M3}(\text{tpy})_2]^{2+}$ ($\text{M3} = \text{Ni}$, Ru or Os ; tpy = 2,2':6',2''-terpyridine) allowed crystallization of the abovementioned hetero-tetrametallic assemblies as double salts, electroneutrality being ensured by available monovalent anions X^- (*i.e.* ClO_4^- or NO_3^-).¹⁶ Hetero-tetra-metallic compounds were obtained within a few days as red ($\text{M3} = \text{Ni}$, Ru) or reddish brown ($\text{M3} = \text{Os}$) crystals. These compounds are referred to as **1** (Fig. 1), **2** and **3** for $[\text{CuTbM2}]_2 \cdot [\text{M3}]$ (with $\text{M2} = \text{Mo}$ and $\text{M3} = \text{Ni}$, Ru , Os respectively), and as **4**, **5** and **6** for related assemblies with $\text{M2} = \text{W}$ (see ESI†). Elemental analyses confirmed the presence of the three different transition metals plus one lanthanide in the expected 1:1:1:1 stoichiometry. Infrared spectroscopy provided clear evidence for the presence of terminal (end-on) and bridging cyanide ligands: 2153, 2147, 2118, 2108 cm^{-1} for (**1**), 2152, 2146, 2118, 2107 for (**2**) and 2152,

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† Electronic supplementary information (ESI) available: Experimental details for compounds **1–6**, X-ray data and magnetic studies. CCDC 904312 (**1**), 904313 (**4**), 904314 (**2**) and 931580 (**6**) For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3cc45037f

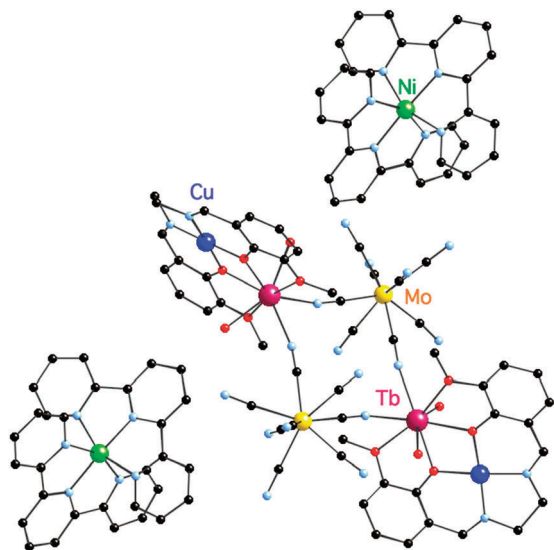


Fig. 1 X-ray structure of compound (**1**) $\{[(\text{valen})\text{Cu}]\text{Tb}(\text{OH}_2)_2(\mu\text{Mo}(\text{CN})_8)\}_2 \cdot 2[\text{Ni}(\text{tpy})_2]\}(\text{ClO}_4)_2$ (hydrogen atoms and perchlorates have been omitted for clarity).

2145, 2118, 2107 for (**3**), similar to the stretching frequencies observed for a related decanuclear square.¹⁴

Compounds **1–6** have been characterized by X-ray crystallography: all the complexes are iso-structural and crystallize in an orthorhombic system (*Fddd* space group). In the typical case of **1**, the unit cell parameters are $a = 23.0051(4)$ Å, $b = 29.8285(6)$ Å, $c = 42.2334(8)$ Å, with a volume of $28980.88(95)$ Å³ ($Z = 8$). The structure of this compound is shown in Fig. 1 and selected bond distances and angles are listed in Table S1 (ESI†). For compounds **2**, **4** and **6**, see ESI†. This complex, like others, crystallizes as a discrete cyanide-bridged square molecular motif composed of alternated $[\text{Mo}(\text{CN})_8]^{4-}$ and $[\text{CuTb}]^{3+}$ subunits, the octacyanomethylate and lanthanide ions being directly linked *via* cyanide ligands. The structure of $[\text{Ln-M2}]_2$ core assembly approaches a perfect square, with angles of 88.8° for Tb–Mo–Tb and 91.1° for Mo–Tb–Mo, and with the cyanide edges slightly bent towards the middle of the square. Metal–metal distances are 5.626 Å for two adjacent centres and about 7.95 Å for two opposite centres. The coordination bond lengths around the Tb, Cu and Mo atoms are in the range 2.306–2.527, 1.909–1.917 and 2.125–2.169 Å, respectively.

From the viewpoint of co-ordination chemistry, it is interesting to note that the formation of the square motif $[\text{M1LnM2}]_2$ was observed for a wide range of stoichiometries of $[\text{M1Ln}]:[\text{M2}]$ building blocks, at least from 1:2 (see ref. 14) to 1:1 (present work) and 1:0.5. Together with the possibility of carrying out metathesis, this finding is a clear indication of the kinetic inertia (solution stability) of $[\text{M1LnM2}]_2$, the robustness of which is reminiscent of the renowned stability of bis- μ -hydroxo-based analogous motifs (Fig. 2). Besides identifying the related species, single-crystal X-ray crystallography was a method of choice for establishing the series as a genuine class of six isostructural compounds. Thus, on the basis of this analysis (rationalized serendipity), we can derive a strategy to enhance elemental diversity within defined assemblies. It consists of taking the basic functional ingredients of a charged co-ordination complex, that is,

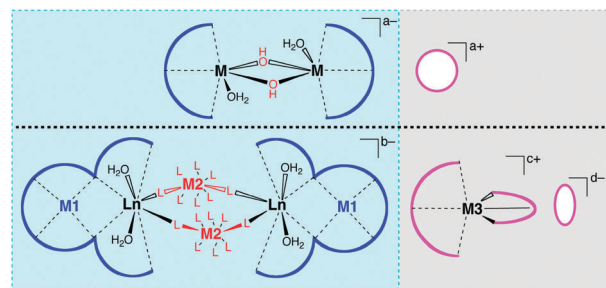


Fig. 2 Pictorial representation of a homo-dinuclear complex (top) and its expanded hetero-oligonuclear and metal-enriched counterpart (bottom); blue: blocking ligands, red: bridging ligands and pink: counterions.

its core metal cation, its (organic) ligand(s) of various types (capping, bridging, ...) and its counter-ion(s) and replacing them by composite metal-containing functional counterparts, according to a “boxes within boxes” strategy, a little like nesting dolls. In other words, the whole idea here is to build supramolecular co-ordination compounds (*i.e.* assemblies) using selected co-ordination compounds as *ligands* and *counterions* (Fig. 2).

From the viewpoint of molecular magnetism, properties of various complexes in the series are comparable, owing to their similarity at both structural and elemental levels. The typical behaviour of compound **1** is fully described (refer to ESI† for the other compounds). For all the complexes, the temperature dependence of the magnetic susceptibility was measured under a 1000 Oe field in the 300–2 K range. At room temperature, $X_m T$ value amounts to $26.34 \text{ cm}^3 \text{ K mol}^{-1}$ for **1**, which is in good agreement with the expected theoretical value of $26.37 \text{ cm}^3 \text{ K mol}^{-1}$ for independent Cu^{II} , Tb^{III} and Ni^{II} ions, given that $\text{Mo}^{\text{IV}}(\text{CN})_8$ is a closed shell – diamagnetic – ion ($\chi T = 2(N\beta^2/3k)[g_{\text{Cu}}^2 S_{\text{Cu}}(S_{\text{Cu}} + 1) + g_{\text{Tb}}^2 J_{\text{Tb}}(J_{\text{Tb}} + 1) + g_{\text{Ni}}^2 S_{\text{Ni}}(S_{\text{Ni}} + 1)]$). Upon decreasing the temperature, the $X_m T$ plot shows a positive deviation from Curie’s law, showing a maximum value of $46.17 \text{ cm}^3 \text{ K mol}^{-1}$ at 7.2 K. Despite thermal depopulation of Stark sublevels, the nature of the interaction between metallic centres could be established by using the $[\text{NiTbMo}]_2$ structural analogue (Cu^{II} is replaced by a diamagnetic Ni^{II} ion in the same square planar geometry). The difference $\Delta(\chi T) = (\chi T)_{\text{CuTbMo}} - (\chi T)_{\text{NiTbMo}}$ shows a positive deviation below 50 K, which can be ascribed to ferromagnetic interactions between Cu^{II} and Tb^{III} . The M versus H plot for **1** is shown in Fig. S5 (ESI†); the magnetization value M_s at 7.0 T amounts to $15.8 \mu_B$ for **1**, which is in agreement with prediction ($M_s = 16.0 \mu_B$). For all compounds, the frequency dependence of ac susceptibility, measured under a 1.6 kOe dc field, shows a slow relaxation of the magnetization that unambiguously discloses a field-induced SMM behaviour.¹⁷ For tungsten derivatives (Fig. 3), the energy barrier can be extracted using a thermally activated relaxation model, assuming that above 2 K the thermal relaxation prevails over the tunnelling relaxation process. The plot of the relaxation time τ as a function of $1/T$ (between 2 and 6 K) shows that the systems follow the Arrhenius law $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$, with derived τ_0 and U_{eff} (anisotropy barrier) values of $3.93 \times 10^{-8} \text{ s}$ and 11.7 cm^{-1} (16.83 K), respectively. These values are consistent with those previously reported for Cu–Tb systems, and more generally for 3d–4f-based SMMs.¹⁸

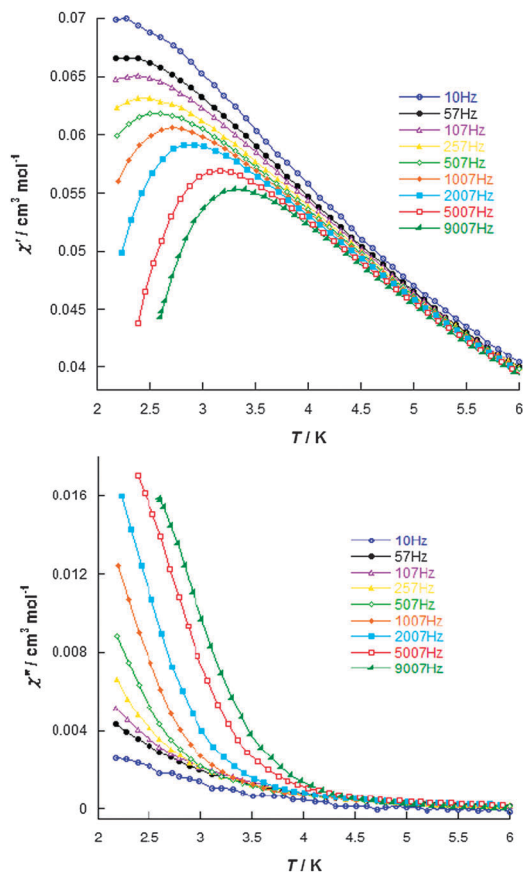


Fig. 3 Temperature dependence of the in-phase (χ' ; top) and the out-of-phase (χ'' ; bottom) ac susceptibility for **4** under a 1600 Oe field.

For molybdenum compounds, we used the micro-SQUID technique to measure magnetization hysteresis loops at different temperatures (below 2 K) and field sweep rates. The corresponding magnetization *versus* applied field curve, presented in Fig. S6 (ESI[†]), confirmed the SMM behaviour, despite the small anisotropy barrier.

In summary, we have demonstrated herein that not only hetero-tetra-metallic compounds can be obtained by taking advantage of the flexibility of cyanide-based co-ordination chemistry, but also that these oligonuclear assemblies constitute a novel and defined class of supramolecular co-ordination compounds. Of particular interest are their unique elemental diversity and their versatility (represented by Ln, M1, M2 and M3) that also includes the variability related to the choice of organic binucleating ligands and the presence of singly ligated (end-on) cyanides as potential further coordination sites. Besides the relevance of these multicomponent systems in the field of molecular magnetism (single-molecule magnet behaviour), their modular nature makes it possible to integrate various properties including photochemical activity

(given by polypyridyl complexes),¹⁹ thereby opening the way to the design of light-responsive magnetic clusters.²⁰

This work was financially supported by CNRS, UPMC and ANR (project SWITCH: 2010-BLAN-712). The authors thank Dr B. Malézieux for fruitful discussions.

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- Caution:** Although no problem was encountered in this work, perchlorate salts are potentially explosive and cyanides are toxic. These starting materials should be handled in small quantities and with care.
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