First Heterotrimetallic {3d-4d-4f} Single Chain Magnet, Constructed from Anisotropic High-Spin Heterometallic Nodes and Paramagnetic Spacers

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Dedicated to Dr. Jean-Pierre Costes as a tribute to his contributions to the development of the chemistry and magnetism of 3d–4f complexes

Polymetallic complexes are more and more involved in materials science. The metal ions exert a functional role, carrying magnetic, optical, or redox properties, and a structural one, directing and sustaining the overall architecture of the polymetallic systems. The use of different metal ions in con-

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structing coordination compounds brings novel properties that are not exhibited by the homometallic complexes.[1] Since the first report on the Cu^{II}–Gd^{III} ferromagnetic interaction,[2] the 3d-4f combined chemistry attracted much attention, aiming, in a first stage, to obtain "classical" (3D) molecule-based magnets.[3] The results were rather disappointing: the critical temperatures for the molecular magnets constructed from Cu^{II} and Gd^{III} ions were found to be very low.[4] More recently, the interest of chemists moved towards lanthanides exhibiting a high anisotropy, which is a prerequisite for designing single molecule magnets (SMMs) and single chain magnets (SCMs). The best candidates for this purpose are terbium(III), dysprosium(III) and holmium-(III). Indeed, several SMMs,[5] and SCMs,[6] based upon 3d and 4f (Tb^{III}, Dy^{III}, Ho^{III}) ions, were reported recently. Moreover, it has been shown that even mononuclear Tb^{III} and Dy^{III} complexes fulfil the necessary conditions to exhibit slow relaxation of the magnetization.[7]

A plethora of polynuclear complexes with interesting magnetic properties are constructed from two different paramagnetic metal ions (3d-3d′, 3d-4d, 3d-5d, 3d-4f, 4d-4f, 5d-4f), while the number of heterotrimetallics is much more limited. Only few 3d-3d′-4f complexes are reported to date.[8] The main problem the chemist is faced with is to obtain pure products in high yield, by avoiding the scrambling of the three different metal ions. A successful synthetic approach consists of self-assembly processes involving preformed 3d-4f oligonuclear cationic complexes and stable metal-containing anions with potentially bridging ligands, for example hexacyanometallates, $[M(CN)_6]^{3-}$. We have recently shown that bi- and trinuclear 3d-4f species $\{(CuL)_nLn\}$ ($n=1$, 2; $L^{2-}=$ a dissymetric compartmental Schiff-base ligand) can efficiently act as tectons in designing both high-nuclearity clusters and coordination polymers with various dimensionalities and network topologies.[9] Fol-

lowing this strategy, we were able to obtain the first 2p/3p-3d-4f heterospin complexes,[10] and a novel 3d-3d′-4f family of coordination polymers.[8b,9a] The 3d-3d′-4f polynuclear complexes result by connecting {(CuL)Ln} nodes with [M(CN)$_6$]$^{3-}$ linkers (H$_2$L is the Schiff-base resulted from the 2:1 condensation of 3-methoxysalycilaldehyde with 1,3-di-amino-propane). Following this approach heteronuclear {3d-4f-5d} compounds have been obtained by assembling [W(CN)$_8$]$^{3-}$ and [L^{Me2}NiLn]$^{3+}$ building units [L^{Me2}=$N,N′$-2,2-dimethylpropylenedi(3-methoxysalicylideneiminato)], some of which exhibiting SMM-type behaviour.[11]

The versatility of the [(CuL)Ln]$^{3+}$ and [(CuL)$_2$Ln]$^{3+}$ tectons prompted us to enlarge the family of heterotrimetallics with new 3d-4(5)d-4f complexes. Moreover, high-spin {Cu^{II}–Ln^{III}} oligonuclear complexes, where Ln^{III} is a strongly anisotropic lanthanide cation, are very appealing in designing SCMs, connecting them through paramagnetic linkers.

Herein we report on the first 1D coordination polymers containing 3d (Cu^{II}), 4d (Mo^{V}) and 4f ions (Gd^{III}, Dy^{III}): [{(CuL)$_2$Gd}{Mo(CN)$_8$}]·2CH$_3$CN, **1**, and [{(CuL)$_2$Dy}{Mo(CN)$_8$}]·CH$_3$CN·H$_2$O, **2**, in which L^{2-} is $N,N′$-propylene-bis(3-methoxysalicylideneiminato). The dysprosium derivative is shown to exhibit the characteristic features of a SCM.

The reaction of [LCu], Ln(NO$_3$)$_3$, and (NHBu$_3$)$_3$[Mo(CN)$_8$] with ratio 2:1:1 in MeCN, affords dark green crystal of **1** (Gd) and **2** (Dy) in almost quantitative yields.

Crystal structure investigations revealed that compounds **1** and **2** are isomorphous (see the Experimental Section). We will describe here the structure details for the Gd derivative, **1**, those for **2** are very similar (Supporting Information). A 1D coordination polymer is constructed from almost linear trinuclear [(CuL)$_2$Gd] nodes connected by [Mo(CN)$_8$]$^{3-}$ spacers (Figure 1).

The octacyanomolybdate exhibits a unique bridging mode with two cyano-ligands linked to the Cu and Gd ions of one trimetallic node, and a third connected to the Cu of a second node, hence developing a chain where each Cu^{II} and Gd^{III} centres are cyano-bridged to Mo^{V}. Each copper(II) ion is hosted within the inner compartment (the N$_2$O$_2$ site) of the organic ligand. Two [CuL] mononuclear complexes are coordinated through their outer O$_2$O$_2′$ cavities to the Gd^{III} ion (two oxygen atoms arise from the phenoxo groups, the two others from the methoxy ones) thus forming an almost linear trimetallic unit [170.48(2)°]. The coordination number of gadolinium is nine, with eight oxygen atoms from two [CuL] units, and one nitrogen atom from the cyano bridge. The copper ions display a square pyramidal geometry, with the apical positions occupied by the nitrogen atoms arising from the cyano bridges. The intra-node Cu⋯Gd distances are 3.5833(5) and 3.5655(5) Å. The Mo-CN-Gd and the two Mo-CN-Cu linkages are bent, with angles of 148.7(4) (Gd1-N1-C1), 140.9(4) (Cu1-N2-C2), and 143.1(4)° (Cu2-N3-C3) [in **2** the last two angles are 138.4(5) and 143.5(5)°, respectively]. The distances between the cyano-bridged metal ions are 5.222(1) (Cu1⋯Mo1), 5.348(1) (Cu2⋯Mo1^b; ^{b}=x, −1+y, z), and 5.5302(5) Å (Gd1⋯Mo1). The geometry of octacya-
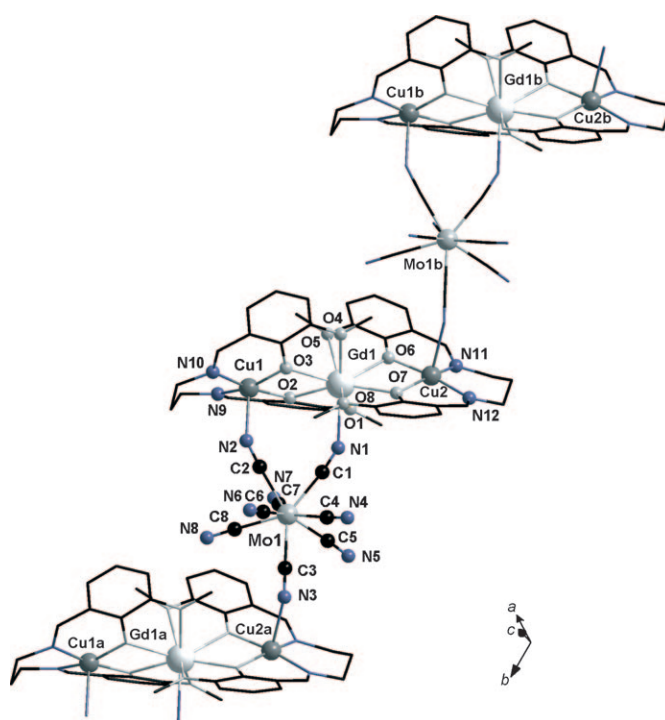

Figure 1. View of chain in crystal **1** along with atom numbering scheme. Hydrogen atoms are omitted. Selected bond distances (Å): Cu1−N2=2.270(5); Cu1−N9=1.978(4); Cu1−N10=1.980(4); Cu1−O2=1.953(4); Cu1−O3=1.985(3); Cu2^a−N3=2.340(4); Cu2−N11=1.961(5); Cu2−N12=1.977(4); Cu2−O6=1.950(3); Cu2−O7=1.963(4); Gd1−N1=2.491(4); Gd1−O1=2.487(3); Gd1−O2=2.419(3); Gd1−O3=2.393(3); Gd1−O4=2.509(4); Gd1−O5=2.527(3); Gd1−O6=2.383(4); Gd1−O7=2.386(3); Gd1−O8=2.540(4). (^{a}=x, 1+y, z).

nomolybdate ion deserves a particular attention. It has been shown that the geometry of the {M(CN)$_8$} polyhedron has a significant incidence on to the strengths of the exchange interaction mediated by the CN bridges.[12] The geometry of the {Mo(CN)$_8$} fragment has been analyzed with the SHAPE program[13] revealing a slightly distorted square antiprismatic shape,[14] the results being tabulated in the Supporting Information (Table S1). The packing diagrams for both compounds reveal that the chains are well isolated in the crystal and only very weak slipped-off inter-ring contacts are established between phenolic rings of the organic ligands from neighbouring chains: the centroid-centroid distance is 4.376 Å for **1** and 4.205 Å for **2** (Figure S1, S2).

The most intriguing properties of compounds **1** and **2** are the magnetic ones, which arise from the presence of three different spin carriers and from the original spin topology. Let us discuss first the magnetic behaviour of the gadolinium derivative, **1**. The temperature dependence of $\chi_M T$ is represented in Figure 2 (top). At room temperature the value of the $\chi_M T$ product is 9.17 cm^{3}mol^{-1}K, that corresponds to the spin-only value calculated for uncoupled Cu^{II}, Gd^{III} and Mo^{V} ions (9.00 cm^{3}mol^{-1}, assuming $g_{Cu}=g_{Gd}=g_{Mo}=2$). The characteristic Cu^{II}–Gd^{III} ferromagnetic interaction is immediately detected by the increase of the $\chi_M T$ product upon lowering the temperature. The maximum
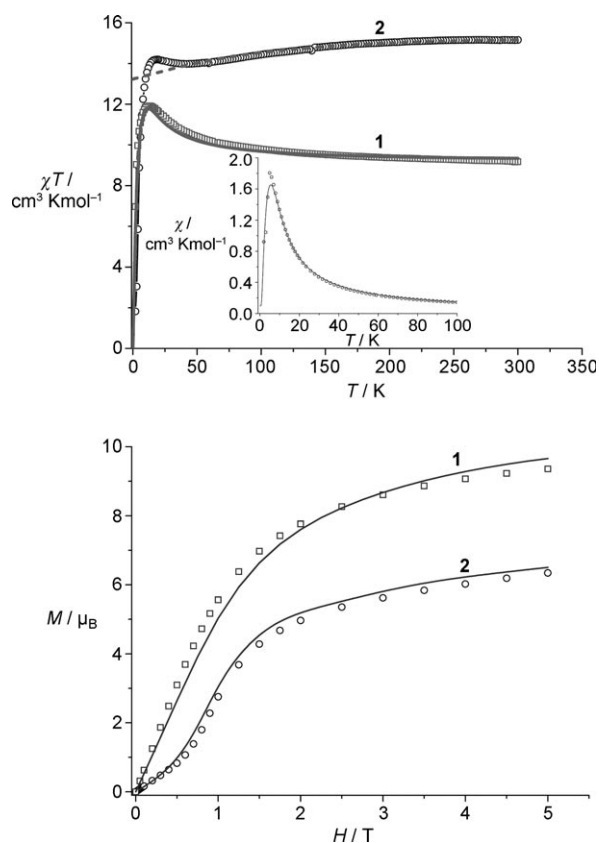
Figure 2. Top: Temperature dependence of $\chi_M T$ for compounds **1** and **2** (experimental in squares (**1**) and circles (**2**), and simulated in solid line), the dashed curve corresponds to ab initio calculation of $\chi_M T$ for non-interacting magnetic centres in **2**; the inset shows the experimental (circles) and simulated (line) susceptibility χ_M of **2** taking into account the exchange interaction between metal centres (see the text for the details). Bottom: Field dependence of the magnetization recorded at 2 K for **1** (squares) and **2** (dots), the continuous curves are the ab initio based simulations for **1** and **2** when the exchange interaction between magnetic ions, with parameters specified in the text, is taken into account.

value of the $\chi_M T$ product is 11.91 cm³ mol⁻¹ K at $T = 13$ K. Below this temperature, $\chi_M T$ decreases, reaching 6.96 cm³ mol⁻¹ K at $T = 2$ K. The shape of the $\chi_M T$ vs. T curve is characteristic for a dominant ferromagnetic interaction followed by antiferromagnetic interactions at low temperatures. Literature information concerning the nature of the Gd^{III}–Mo^V exchange interaction are very scarce[15] but suggests weak antiferromagnetic coupling, in agreement with the related Gd^{III}–W^V interaction.[11c,16] According to recent experimental and theoretical results,[12] we can anticipate that the Gd^{III}–Mo^V interaction is similar to the Gd^{III}–W^V one but slightly weaker. The field dependence of the magnetization for **1** recorded at 2 K (Figure 2, bottom) exhibits a continuous increase with field reaching 9.36 μ_B for 5 T, a value slightly below the saturation value anticipated for three $S = 1/2$ and one $S = 7/2$ spins in ferromagnetic interaction.

The $\chi_M T$ versus T curve for compound **2** is also depicted in Figure 2 (top). At room temperature, the $\chi_M T$ product is

15.15 cm³ mol⁻¹ K, a value that corresponds to the four uncoupled metal ions: one Dy^{III} ion ($4f^9$, $J = 15/2$, $S = 5/2$, $L = 5$, $^6H_{15/2}$; $g_{15/2} = 1.33$), two Cu^{II} ions ($S = 1/2$), and one Mo^V ion ($S = 1/2$), the expected $\chi_M T$ value being 15.27 cm³ mol⁻¹ K. Upon cooling, $\chi_M T$ decreases slowly down to a minimum value of 13.97 cm³ mol⁻¹ K at 41.8 K, then it increases up to 14.19 cm³ mol⁻¹ K at 18.9 K. Below this temperature, $\chi_M T$ drops abruptly. The slight decrease of the $\chi_M T$ product between 300 and 41.8 K is owed to the depopulation of the Stark levels of the dysprosium(III).[17] The increase of $\chi_M T$ below 40 K is associated with an intranode ferromagnetic interaction between Cu^{II} and Dy^{III}, as observed with other compounds containing these two ions.[5r,18] The field dependence of the magnetization recorded at 2 K for **2** (Figure 2, bottom) exhibits a sigmoid shape and remains below the anticipated saturation value. Such behaviour can be attributed either to the occurrence of an antiferromagnetic interaction or to significant anisotropy.

To get insight into the origin of the observed behaviours we performed fragment CASSCF calculations within MOLCAS 7.2 ab initio package[19] and investigated local magnetic anisotropy on individual metal fragments using a recently developed calculation methodology (see the Supporting Information).[20] On the dysprosium sites of the compound **2** we obtain the ligand-field splitting of the ground atomic term $^6H_{15/2}$ into eight Kramers doublets of ≈ 560 cm⁻¹, the first excited Kramers doublet being separated from the ground one by 141 cm⁻¹. The ground Kramers doublet shows strong axial anisotropy with $g = 19.6$ along the main anisotropy axis, which lies close to the Dy–Cu direction (Figure 3). The ab initio calculation of $\chi_M T$ for non-
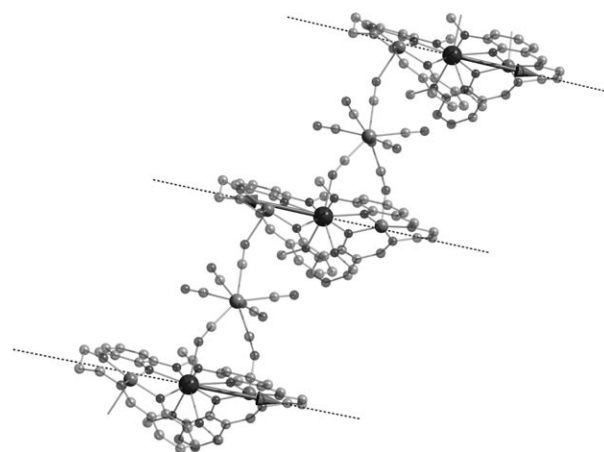

Figure 3. Direction of local anisotropy axes (dashed lines) and the low-temperature alignment of magnetic moments (grey arrows) on dysprosium ions along a chain in crystal **2**.

interacting magnetic centres is shown in Figure 2 (top) by dashed line. By contrast the overall zero-field splitting of the ground term $^8S_{7/2}$ of gadolinium ions in crystal **1** amounts to only ≈ 1 cm⁻¹, which means that the effect of spin-orbit coupling is negligible.

The exchange interactions in the Mo−Cu1 and Mo−Cu2 pairs are isotropic for both compounds and have been estimated from broken-symmetry DFT calculations[21] of the corresponding binuclear fragments of **2** (see the Supporting Information). Both couplings are obtained ferromagnetic with $J(\text{Mo−Cu1}) = 1.5 \text{ cm}^{-1}$ and $J(\text{Mo−Cu2}) = 5.2 \text{ cm}^{-1}$.[22] This reflects a general tendency of d^1 octacyanometallates to have ferromagnetic interaction with metal ions containing unpaired electrons in d orbitals of σ type,[23a] which is enhanced by increasing the angle C-N-M(d_σ).[24] This tendency has been confirmed for several compounds of this type.[12,23b] The magnetic molecular orbitals of these fragments (Figure 4 for Mo−Cu2; see the Supporting Information for
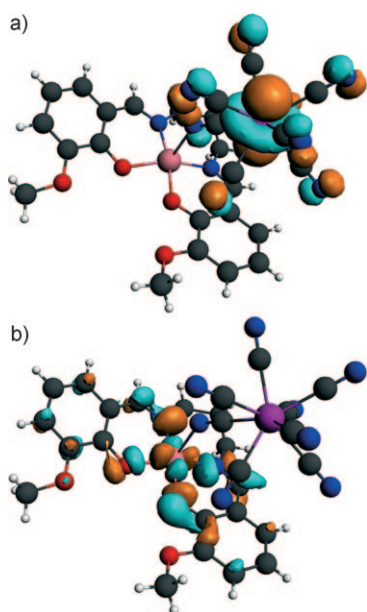
Figure 4. Molecular magnetic orbitals (molecular orbitals containing unpaired electrons) in the Mo-Cu2 fragment of **2**.

Mo−Cu1), containing unpaired electrons, show indeed lack of hybridization of atomic orbitals surrounding the opposite metal centres. Figure 4 shows that this hybridization is absent even on the bridging cyanide group, which contributes with a π orbital to the molybdenum magnetic orbital, that is, d_{z^2} for the square antiprism geometry (Figure 4a), and gives no contribution to the copper magnetic orbital (Figure 4b). This means that the antiferromagnetic contribution, always related to electron delocalization between magnetic orbitals, is effectively blocked. A smaller J obtained for the Mo−Cu1 pair correlates with its smaller Cu-N-C angle compared to the Mo−Cu2 fragment resulting in increased antiferromagnetic contribution.[24]

In principle, the interpretation of the magnetic properties of heterometal complexes containing gadolinium(III) is much easier than for the other rare earths cations. The absence of the orbital contribution to the magnetic moment of gadolinium(III) ion allows the straightforward determination of the exchange coupling constants by using the isotropic HDVV spin Hamiltonian, provided that the other metal

ion is isotropic too. However, the simulation of the magnetic properties of compound **1** is a very difficult theoretical task: it is an infinite chain with a quite complicated topology of the interacting spin carriers, that involves four exchange pathways (Figure S3 in the Supporting Information).

The simulations of $\chi_M T$ and $M(H)$ (Figure 2) have been done within our ab initio based approach.[20] For **1** we took two translational units with periodic boundary conditions. In **2** the whole chain was treated exactly by applying the transfer matrix method.[25] In these simulations we took $J(\text{Mo−Cu1}) = -3 \text{ cm}^{-1}$, $J(\text{Mo−Cu2}) = 7 \text{ cm}^{-1}$ for **1** and $J(\text{Mo−Cu1}) = -8 \text{ cm}^{-1}$, $J(\text{Mo−Cu2}) = 11.8 \text{ cm}^{-1}$ for **2**. The smaller values of exchange parameters for Cu1 compared to Cu2 agree with DFT calculations, while the larger difference between the two exchange parameters in **2** reflects a larger difference between Cu1−NC and Cu2−NC angles in this compound. The isotropic exchange parameters involving gadolinium ion ($S = 7/2$) in the compound **1** are $J(\text{Gd−Cu1}) = J(\text{Gd−Cu2}) = 5 \text{ cm}^{-1}$ and $J(\text{Gd−Mo}) = -1 \text{ cm}^{-1}$. Note that the last value is in a good agreement with known exchange parameters for Gd−Mo/W pairs.[11c,15,16] On the contrary, given a very anisotropic character of the Dy^III ground state ($g_\parallel = 19.6$, $g_\perp \approx 0$), its interaction with the neighbour metal ions in **2** will be mostly of the Ising type, involving spin projections along the anisotropy axis of dysprosium (Figure 3). The fitting of magnetic data for the crystal **2** required the following parameters of Ising exchange interaction between the ground Kramers doublet of dysprosium ion ($S = 1/2$) and the surrounding metal spins: $J(\text{Dy−Cu1}) = J(\text{Dy−Cu2}) = 15.3 \text{ cm}^{-1}$ and $J(\text{Dy−Mo}) = -8.3 \text{ cm}^{-1}$. The simulations reproduce the main difference in the magnetization of **1** and **2**, the S-shaped $M(H)$ for the dysprosium and the absence of inflection on the magnetization curve for the gadolinium compound (Figure 2, bottom). This difference arises from a strong axial anisotropy on the Dy^III sites in **2**, which induces an effective Ising exchange interaction between dysprosium ions and determines the S-shaped behaviour of magnetization in this compound.

Owing to the exchange anisotropy of Ising type brought by the dysprosium ion, compound **2** could be a single chain magnet. Another important condition, that is, the occurrence of only very weak interactions between the chains in the crystal, is fulfilled as well. In zero dc field, frequency-dependent signals, both in-phase and out-of-phase, were clearly observed below 3 K (Figure 5). This behaviour is indicative of slow relaxation effects that are typical for single chain magnets.[26] The energy barrier and the characteristic relaxation time for this system have been obtained by fitting the peak temperatures with the Arrhenius law, $\tau = \tau_0 \exp(U_{\text{eff}}/k_B T)$, giving $\tau_0 = 1.28 \times 10^{-7} \text{ s}$ and $U_{\text{eff}}/k_B T = 19.1 \text{ K}$ (Figure 6 top).

The analysis of the maxima at T_{peak} in χ'' that shift toward higher temperatures with increasing frequencies was made by using Mydosh's formula in Equation (1):[27]

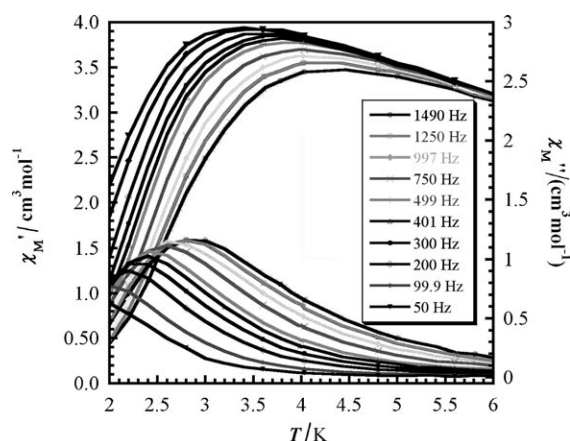$$F = (\Delta T_{\text{max}}/T_{\text{max}})/(\Delta \log \nu) \qquad (1)$$

Figure 5. Temperature dependence of the in-phase (top), and out-of-phase (bottom) signals for **2**, at different frequencies of the oscillating field.

For compound **2**, *F* takes a value of 0.3 which corresponds to a superparamagnet.[27] The Argand plots (χ_M'' against χ_M') at several temperatures (Figure 6, bottom) were simulated using the conventional generalized Debye model in Equation (2), taking into account the width of the τ distribution using α parameters ($0 \leq \alpha \leq 1$, the simple Debye model corresponding to $\alpha = 0$):

$$\chi_M'' = (\chi_S - \chi_T)\tanh(\alpha\pi/2)/2$$
$$+ \{(\chi_M' - \chi_S)(\chi_T - \chi_M') \quad (2)$$
$$+ (\chi_T - \chi_S)^2 \tan h^2(\alpha\pi/2)/4\}^{1/2}$$

In which χ_T is the isothermal susceptibility and χ_S is the adiabatic susceptibility.[28] The fit to the data gives α values ranging from 0.3 (at 2 K) to 0.12 (at 3.6 K), suggesting multiple relaxation processes.

In conclusion, the first 3d-4d-4f heterospin 1D coordination polymers, have been constructed in a rational way by assembling heteronuclear 3d-4f cationic species and an anionic 4d complex acting as a spacer. The [Mo(CN)$_8$]$^{3-}$ moiety exhibits an unprecedented bridging mode. Moreover, compounds **1** and **2** are rare examples of complexes containing cyano-bridged Ln^{III} and Mo^V ions. This synthetic procedure opens new routes in coordination chemistry since it can be further extended by using many other cationic complexes as nodes. The combination of three different spin carriers could lead to a new generation of molecule-based magnetic materials. The dysprosium derivative, **2**, represents the first heterotrimetallic single chain magnet.

Following the same synthetic procedure, but with [W(CN)$_8$]$^{3-}$ as a metalloligand, we obtained the homologue compounds [{(CuL)$_2$La}{W(CN)$_8$}]·2H$_2$O **3**, [{(CuL)$_2$Gd}{W(CN)$_8$}]·2CH$_3$CN **4**, and [{(CuL)$_2$Dy}{W(CN)$_8$}]·4CH$_3$CN **5**. The crystal structures of compounds **3** and **5** have been solved, the two compounds showing the same chain organisations as compounds **1** and **2** (Table S19). The magnetic properties of **4** and **5** (Figures S14 and S16) are quite similar
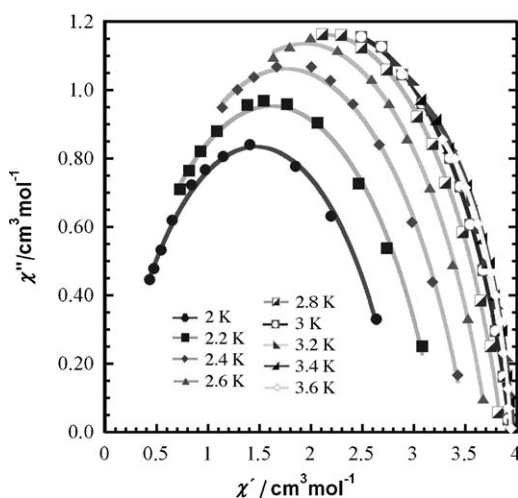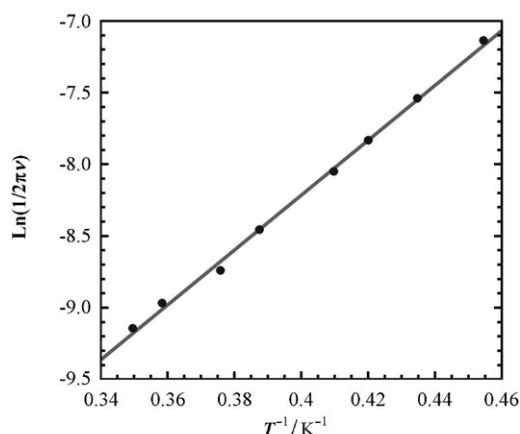

Figure 6. Top: Arrhenius plot for **2**. Bottom: Cole–Cole plot of χ'' versus χ' in the 2–3.6 K temperature range, in zero applied dc field, for compound **2**. The solid lines represent a least-squares fitting of the data to a distribution of multiple relaxation processes.

to those discussed here for compounds **1** and **2**. The lanthanum derivative, **3**, is particularly useful, since it gives additional information on the Cu^{II}–W^V exchange interaction, La^{III} being diamagnetic. The $\chi_M T$ vs. *T* curve for **3** is given in the Supporting information (Figure S15), and indicates a weak antiferromagnetic interaction between the metal ions along the chain. The fit of the χ_M^{-1} vs. *T* data (inset Figure S15) with a Curie–Weiss law gives: $C = 1.261$ emuK-mol^{-1}; $\theta = -1.5$ K. Further work on these families of heterotrimetallic complexes is in progress.

Experimental Section

Acknowledgements

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