Building 1D Lanthanide Chains and non-symmetrical [Ln₂] “Triple-Decker” Clusters Using Salen-type Ligands: Magnetic Cooling and Relaxation Phenomena

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The solvothermal reaction between Ln(NO₃)₃·6H₂O (Ln: Gd, Tb and Dy), 2-hydroxy-1-naphthaldehyde, 2-OH-naphth, and ethylenediamine, en, in MeOH in the presence of base, Na₂CO₃, led to the formation of the 1D coordination polymers [Ln(L)(MeO)(MeOH)]₄·MeOH (Ln = Gd (1·MeOH), Tb(2·MeOH), Dy (3·MeOH); H₂L = the Schiff-base ligand derived from the condensation of 2-OH-naphth and en), while the similar reaction in excess of Na₂O yielded 1D coordination polymers [Ln(L)(N₃)(MeO)(MeOH)]₄·MeOH (Ln = Gd (4), Tb (5), Dy (6)). Finally, upon replacing ethylenediamine with o-phenylenediamine, o-phen, we managed to isolate the discrete dimers [Dy(2L')(MeOH)]·2MeOH (2·MeOH) and [Gd(2L')(MeOH)]·2MeOH (8·2MeOH ) [H₂L' = the Schiff-base ligand from the condensation of 2-OH-naphth and o-phen].

Polymers 1-3 describe one-dimensional chains, containing alternating seven- and eight-coordinate Ln³⁺ metal centers, polymers 4-6 contain eight-coordinate lanthanide ions, while in both 7 and 8 the two Ln³⁺ centers are eight- and seven-coordinate, adopting square antiprismatic and “piano-stool” geometry, respectively. The magnetocaloric properties of the three Gd³⁺ analogues were determined from magnetic measurements, yielding the magnetic entropy change −ΔSₘ = 21.8, 23.0 and 16.0 J K⁻¹ for T = 3.0 K on demagnetization 7 T to 0, for 1, 4 and 8, respectively. The study of the magnetic properties also revealed that the three Dy³⁺ analogues (3, 6 and 7) display out-of-phase signals, therefore suggesting slow magnetic relaxation, while such behaviour was not established in the Tb³⁺ analogues.

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the Schiff-base ligand from the condensation of 2-OH-naphth and en), and we also succeeded in isolating the discrete dinuclear units \([\text{Dy}_2(L)_{\text{MeOH}}]_2\text{MeOH}\) (7·2MeOH) and \([\text{Gd}_2(L)_{\text{MeOH}}]_2\text{MeOH}\) (8·2MeOH) (L’ = the Schiff-base ligand from the condensation of 2-OH-naphth and o-phen, Scheme 1).

Experimental Section

Materials and physical measurements

All manipulations were performed under aerobic conditions, using materials as received. Elemental analyses (C, H, N) were performed by the University of Ioannina microanalysis service. Variable-temperature, solid-state direct (dc) and alternating (ac) current magnetic susceptibility data, as well as isothermal magnetization down to 2.0 K were collected on a Quantum Design MPMS-XL SQUID magnetometer equipped with a 5 T DC magnet at the University of Zaragoza. Diamagnetic corrections were applied to the observed paramagnetic susceptibilities using Pascal’s constants.

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Syntheses

General synthetic strategy applicable to 1-3:

In a typical procedure, Ln(NO₃)₃·6H₂O (Ln = Gd, Tb, Dy) (0.33 mmol), 2-OH-naphth (113 mg, 0.66 mmol), en (0.33 mmol) and NEt₃ (2.0 mmol) were added in MeOH (10 ml total volume) and transferred to a Teflon-lined autoclave and kept at 120 °C for 12 hours. After slow cooling to room temperature, light yellow-brown needle crystals of \([\text{Ln}(\text{L})(\text{MeOH})\text{MeOH}]_2\text{MeOH}\) were obtained in ~25% yield and collected by filtration, washed with Et₂O and dried in air. Elemental Anal. calcd (found) for 4: C 50.97 (51.11), H 3.85 (3.61), N 10.00 (10.15); 5: C 50.83 (50.95), H 3.84 (3.60), N 9.98 (9.85); 6: C 50.53 (50.62), H 3.82 (3.59), N 9.90 (9.75).

General synthetic strategy applicable to 7-8:

Ln(NO₃)₃·6H₂O (0.33 mmol), 2-OH-naphth (113 mg, 0.66 mmol), o-phen (0.036 mg, 0.33 mmol) and NEt₃ (2.0 mmol) were added in MeOH (10 ml total volume) and transferred to a Teflon-lined autoclave and kept at 120 °C for 12 hours. After slow cooling to room temperature, orange needle crystals of \([\text{Ln}_2(L)(\text{MeOH})]_2\text{MeOH}\) were obtained in ~20% yield and collected by filtration, washed with Et₂O and dried in air. Elemental Anal. calcd (found) for 7: C 63.31 (63.18), H 3.77 (4.01), N 5.15 (5.29); Anal. calcd (found) for 8: CMeOH: C 63.72 (63.59), H 3.79 (4.03), N 5.18 (5.33).

X-Ray Crystallography

Diffraction data for 1MeOH, 6 and 72MeOH were collected at 100 K on an Xcalibur RUBY and KUMA diffractometer. All structures were solved by direct methods and refined by full-matrix least-squares technique on F2 with SHELXL.[10] In 1MeOH all non-hydrogen were found directly form the solution of the structure. In further stages of refinement occupancy of coordinated methanol molecule was refined freely and finally fixed at 0.5. Therefore Gd atom is alternately seven- (MeOH not coordinated) or eight-coordinate (MeOH coordinated). In 62MeOH, from E-map position of Dy and all non-H atoms from L’ ligand were found. After refinement additional maxima appeared. These peaks were interpreted as statistical disordered azide and methoxy groups which are in the same position. In the final refinement, disorder was modelled with the occupancy of 0.75 for N-atoms from azide and 0.25 for methoxy group. Atoms N1 and O2 and also N2 and C2 were modelled using EADP instruction. Hydrogen atoms were placed in calculated positions and refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model.[10] Data collection parameters and structures solution and refinement details are listed in Table S1. Full details can be found in the CIF files: 1494777-1494779.

Results and Discussion

Syntheses

The reaction between Ln(NO₃)₃·6H₂O (Ln = Gd, Tb, Dy), 2-hydroxy-1-naphthaldehyde, 2-OH-naphth, and ethylenediamine, en, in MeOH under solvothermal conditions, in the presence of base, NEt₃, led to the formation and isolation of three new 1D coordination polymers of the general formulae \([\text{Ln}_2(L)(\text{MeOH})\text{MeOH}]_2\text{MeOH}\). In further stages of refinement occupancy of coordinated methanol molecule was refined freely and finally fixed at 0.5. Therefore Gd atom is alternately seven- (MeOH not coordinated) or eight-coordinate (MeOH coordinated). In 62MeOH, from E-map position of Dy and all non-H atoms from L’ ligand were found. After refinement additional maxima appeared. These peaks were interpreted as statistical disordered azide and methoxy groups which are in the same position. In the final refinement, disorder was modelled with the occupancy of 0.75 for N-atoms from azide and 0.25 for methoxy group. Atoms N1 and O2 and also N2 and C2 were modelled using EADP instruction. The non-hydrogen atoms, except disordered atoms from azide (N1, N2) and methoxy (O2, C2), were refined anisotropically. Hydrogen atoms were placed in calculated positions and refined using a riding model.[10] Data collection parameters and structures solution and refinement details are listed in Table S1. Full details can be found in the CIF files: 1494777-1494779.
\[ \text{[Ln(L)(MeO)(MeOH)_{0.5}]_n \cdot MeOH + 3n HNO_3 + 6n H_2O} \quad (1) \]
\[ \text{(Ln = Gd (1-MeOH), Tb (2-MeOH), Dy (3-MeOH))} \]

The reaction was carried out in a 1:2:1 Ln:2-OH-naphth:en ratio, as a means of favoring the formation of the salen-type ligand H₂L. Furthermore, increasing the metal:ligands’ ratio did not lead to different crystalline products, as verified by means of pXRD and IR spectra comparison; on the contrary it led to a decrease of the reactions’ yield. In addition, repeating the reaction under normal “bench” laboratory conditions did not lead to the formation of any material, crystalline or powder, thus proving the need for heat/pressure.

Given the presence of the bridging methoxide in the structures of 1-3 (vide infra) the next step for us was to replace it with an azide anion, N₃⁻, as a means of potentially propagating ferromagnetic interactions between the metallic centres (vide infra).[11] Therefore, we repeated the reaction in the presence of excess NaN₃, and we managed to isolate the three “azide” analogues of the general formulae
\[ \text{[Ln(L)(N_3)_{0.75}(MeO)_{0.25}(MeOH)]_n} \quad (\text{Ln = Gd (4), Tb (5), Dy (6)}) \], according to eqn. (2):
\[ \text{n Ln(NO}_3)_3 \cdot 6H_2O + 2n \text{ 2-OH-naphth} + n \text{ en} + n \text{ NaN}_3 \rightarrow \text{MeOH, base} \]
\[ \text{[Ln(L)(N_3)_{0.75}(MeO)_{0.25}(MeOH)]_n} + 2n \text{ HNO}_3 + 1n \text{ NaN}_3 + 6n \text{ H}_2\text{O} \quad (2) \]
\[ \text{(Ln = Gd (4), Tb (5), Dy (6))} \]

Finally, the last goal was to block the polymerization process, and for that reason we used o-phenylenediamine, o-phen, which carries a rigid aromatic “linker” between the two amine groups, rather than a “flexible” ethylene group as in the case of ethylenediamine. Indeed, we managed to stop the polymerization process, and we were able to isolate the Dy and Gd dimers [Dy₂(L’₃)(MeOH)]·2MeOH (7) and [Gd₂(L’₃)(MeOH)]·2MeOH (8), according to eqn. (3):
\[ 2\text{Ln(NO}_3)_3 \cdot 6\text{H}_2\text{O} + 3 \text{ 2-OH-naphth} + 3 \text{ o-phen} \rightarrow \text{MeOH, base} \]
\[ \text{[Ln₂(L’₃)(MeO)(MeOH)] + 6 HNO}_3 + 12 \text{ H}_2\text{O} \quad (3) \]
\[ \text{(Ln = Dy (7), Gd (8))} \]

We were able to obtain large single crystals suitable for X-ray single-crystal crystallography for all eight complexes. Yet, since all complexes displayed both similar pXRD diagrams (Figs. S1, S2) and IR spectra (Fig. S3), we chose to solve only the representative crystal structures of 1-MeOH, 6 and 7 2MeOH. Despite our attempts to isolate the Tb dimeric analogue, all our efforts proved fruitless.

**Description of structures**

The molecular structure of [Gd(L)(MeO)(MeOH)_{0.5}]₃-MeOH (1-MeOH) is presented in Figure 1, while selected bond distances and angles are given in Table S2. The compound crystallizes in the orthorhombic Pccn space group. Its structure consists of alternating [Gd(L)(MeO)(MeOH)] and [Gd(L)(MeO)] units forming 1D chains running perpendicular to the ab plane. Each unit is connected to its neighboring units via two bridging μ-CH₃⁻ and two μ-OR⁻ groups, with the latter belonging to two salen-type ligands, H₂L. Each ligand, is found in its dianionic form, L²⁻, adopting a 2.2111 coordination mode (Harris notation[12]), forming three chelate rings around the central lanthanide ion, and further bridging via one alkoxide group to a neighboring lanthanide center. The gadolinium centers are seven and eight-coordinate, with the latter ones adopting triangular dodecahedral geometry, as found by a SHAPE[11] analysis (Figure 2). The distance between neighboring Gd centers within the same chain is ~3.95 Å. In the crystal, the chains run parallel to each other, with the closest Gd···Gd distance for metals belonging to neighboring chains being ~8.21 Å, while finally there are no inter-chain H-bonds present (Figure 3). The molecular structure of compound 6 is shown in Figure 4, while selected bond distances and angles are given in Table S3. The molecule crystallizes in the orthorhombic Pbcn space group, and its structure resembles the structure of 1 with the major difference being the presence of an μ-end-on N₃⁻ group vs. the μ-CH₃⁻ group present in 1. Again, each ligand is found in its dianionic form, L²⁻, adopting a 2.2111 coordination mode, while as in the case of 1, each lanthanide center is eight-coordinate adopting triangular dodecahedral geometry.
The similarity of compounds 1 and 6 is presented in Figure 5; the overlay of the two structures clearly demonstrates that the main difference is indeed the replacement of the methoxide, μ-OCH₃, groups in 1 with azide, μ-1,1-N₃ ligands. In 1 the Ln-O₇methoxide-Ln angle is ~116.8°, while in 6 the Ln-N₇azide-Ln angle is slightly decreased to ~110.0°.

The crystal structure of complex 7 is shown in Figure 6, while bond distances and angles are given in Table S4. The complex crystallizes in the triclinic P-1 space group. It consists of the dimeric metallic unit [Dy₂(μ-OR)₂] which is held in position by two alkoxide groups belonging to one doubly deprotonated L²⁻ ligand, with bridging Dy-OR-Dy angles of 111.45(13)° and 110.83(12)°, and the dysprosium centers separated by 3.872(2) Å. All three ligands, fully deprotonated, adopt two coordination modes: two are found in a strictly chelate 1.1111 fashion, forming three chelates rings around the lanthanide center, while the remaining central ligand is found in a 2.2211 binding fashion. Furthermore, the metal ions are not located in the same plane with the L²⁻ ligands, but are located between neighboring ligands, thus forming a “triple-decker” cluster. The two Dy³⁺ centres are seven- and eight-coordinate, with the latter one adopting square antiprismonic geometry, and the former one a distorted “piano-stool” geometry, in which the triangular upper {O₃} plane and the lower {O₂N₂} plane are converging, deviating from parallel by ~11° (Figure 7). Furthermore, Dy² is displaced ~1.1 Å out of the mean {O₂N₂} plane, and ~1.6 Å from the {O₃} plane. Respectively, Dy¹ is displaced ~1.3 Å from the upper {O₂N₂} face of the square antiprism, and ~1.5 Å from the lower {O₂N₂} one.
In the crystal structure there are three intermolecular H-bonds, between the coordinated MeOH ligand, the two solvate MeOH molecules and one deprotonated alkoxide group bound on Dy1 (Figure 8). Finally, there are no intermolecular H-bonds linking neighboring dimeric units.

From a quick look at the susceptibility in Fig. 9, we observe two main trends present: i) compounds 1, 2, 4, 5, 6, 7 and 8 display decreasing $\chi_M T$ product upon cooling, and ii) compound 3 displays a decreasing $\chi_M T$ product upon cooling, followed by a sudden increase at low temperatures. Another noteworthy observation, is the fact that the substitution of the bridging hydroxide groups by end-on azide ligands, does not seem to have a clear impact on the magnetic behaviour of the compounds, besides the case of the DyIII analogue 3 which surprisingly enough switches from “ferromagnetic” (for the hydroxide analogue) to “antiferromagnetic” (for the azide version); obviously, the small geometric changes between the two kinds of bridges of 3 and 6 switch the sign of the magnetic exchange interaction.

More specifically, for the Gd analogues 1 and 4, the room temperature $\chi_M T$ values of 7.92 cm$^3$mol$^{-1}$K and 7.64 cm$^3$mol$^{-1}$K, respectively, are very close to the theoretical value of 7.87 cm$^3$mol$^{-1}$K expected for a GdIII ion ($g = 2.00$). Upon cooling the $\chi_M T$ values remain constant until ~40 K, before they decrease to their minimum value of 4.00 cm$^3$mol$^{-1}$K and 5.49 cm$^3$mol$^{-1}$K, for 1 and 4, respectively. For 2 and 5 (Tb analogues), the room-temperature $\chi_M T$ values are 11.84 cm$^3$mol$^{-1}$K and 10.76 cm$^3$mol$^{-1}$K, respectively, very close to the theoretical $\chi_M T$ value of 11.80 cm$^3$mol$^{-1}$K expected for a TbIII ion ($g = 1.5$). Upon cooling, the $\chi_M T$ values remain practically unchanged until ~100 K, below which they gradually decrease to reach the minimum value of 7.99 cm$^3$mol$^{-1}$K and 8.68 cm$^3$mol$^{-1}$K for 2 and 5. Concerning the two DyIII polymers, 3 and 6, the room-temperature values of 14.57 cm$^3$mol$^{-1}$K and 14.35 cm$^3$mol$^{-1}$K, respectively, are very close to the theoretical value corresponding to one DyIII ion ($g = 1.33$) of 14.16 cm$^3$mol$^{-1}$K. Upon cooling the $\chi_M T$ product for 3 slightly decreases until ~10 K to the value of 12.68 cm$^3$mol$^{-1}$K, before...
rapidly increasing to its maximum value of 19.41 cm\(^3\)mol\(^{-1}\)K at 2.0 K. On the other hand, the \(\chi_M T\) product for 6 slightly decrease to the value of 12.74 cm\(^3\)mol\(^{-1}\)K at ~30 K, before it further decreases to its minimum value of 9.30 cm\(^3\)mol\(^{-1}\)K at 2.0 K. Finally, regarding the two dimer complexes: i) for complex 7 ([Dy\(_2\)]) the room-temperature \(\chi_M T\) value of 27.13 cm\(^3\)mol\(^{-1}\)K, very close to the theoretical value of 28.33 cm\(^3\)mol\(^{-1}\)K expected for two non-interacting Dy\(^{III}\) ions, slightly decreases to 26.19 cm\(^3\)mol\(^{-1}\)K at ~100 K, before reaching the minimum value of 20.45 cm\(^3\)mol\(^{-1}\)K at 2.0 K; ii) for the Gd analogue 8, the room-temperature value of 15.59 cm\(^3\)mol\(^{-1}\)K very close to the theoretical value of 15.74 cm\(^3\)mol\(^{-1}\)K for two non-interacting Gd\(^{III}\) centers, remains constant until ~40 K, before it reaches the minimum value of 9.77 cm\(^3\)mol\(^{-1}\)K at 2.0 K.

For 1, 4 and 8 the shape of the \(\chi_M T\) product vs. \(T\) plot allows us to safely assume antiferromagnetic interactions between neighboring Gd pairs, while for 2, 3, 5, 6 and 7 the curvature of the \(\chi_M T\) product vs. \(T\) plot is not a good indicator of either ferro- or anti-ferromagnetic interactions, due to the depopulation of the m\(_J\) sublevels of the lanthanide centers (usually termed as Stark sublevels). In order to confirm the dominant interactions within 1, 4 and 8, we performed a Curie-Weiss analysis of the magnetic susceptibility data yielding \(\theta\) values of -2.23 K, -0.71 K and -0.890 K, for 1, 4 and 8, respectively. Given that in the Gd analogues 1 and 4, all Gd···Gd intrachain distances are the same (3.955(1) Å in 1 and 3.974(1) Å in 4) we managed to fit the magnetic susceptibility data, assuming a wheel-like structure\(^{[35]}\) containing six Gd\(^{III}\) centers with one magnetic interaction between neighboring centers, \(J\) (Figure 10). Using the program PHI\(^{[16]}\) and employing the Hamiltonian in eqn. (4)

\[
\hat{\mathcal{H}} = -2J(\hat{S}_1 \cdot \hat{S}_2 + \hat{S}_2 \cdot \hat{S}_3 + \hat{S}_3 \cdot \hat{S}_4 + \hat{S}_4 \cdot \hat{S}_5 + \hat{S}_5 \cdot \hat{S}_6 + \hat{S}_6 \cdot \hat{S}_1)
\] (4)

afforded the parameters \(J = -0.05\) cm\(^{-1}\) and \(g = 2.00\) for 1, and \(J = -0.02\) cm\(^{-1}\) and \(g = 2.00\) for 4. Such weak interactions are well expected for Gd pairs due to the inner nature of the 4f electrons, and are in excellent agreement with previously reported values.\(^{[17]}\)

For the dimer cluster 8, we were able to successfully fit the magnetic susceptibility data assuming one magnetic interaction, \(J\), between the two centers. Using the Hamiltonian eqn. (5) and the mathematical formula in eqn. (6):\(^{[18]}\)

\[
\hat{\mathcal{H}} = J(\hat{S}_1 \cdot \hat{S}_2)
\] (5)

\[
\chi_M = \frac{(2N_A\beta^2g^2)}{(kT)} F(J)
\] (6)

where

\[
F(J) = (e^{2x} + 5e^{6x} + 14e^{12x} + 30e^{20x} + 55e^{30x} + 91e^{42x} + 140e^{56x})/(1 + 3e^{2x} + 5e^{6x} + 7e^{12x} + 9e^{20x} + 11e^{30x} + 13e^{42x} + 15e^{56x})
\]

with \(x = J/kT\), where \(N_A\) is the Avogadro constant, \(\beta\) the Bohr magneton, \(g\) the Landé factor, \(k\) the Boltzmann constant and \(T\) the absolute temperature. The best parameters obtained were \(J = -0.04\) cm\(^{-1}\) and \(g = 1.99\), in very good agreement with previously reported systems.\(^{[18]}\)

For compound 3, [Dy/OH/polymer], we used the non-critical scaling theory in order to study the ferromagnetic-like behaviour, using the sum of the two exponential functions in eqn. (7):\(^{[19]}\)

\[
\chi T = C_1\exp(E_1/T) + C_2\exp(E_2/T)
\] (7)

in which the sum of \(C_1 + C_2\) is the high-temperature extrapolated Curie constant, \(E_1\) represents a ferromagnetic contribution dominant at low temperatures and \(E_2\) denotes a high temperature crystal-field effect. Fitting of the magnetic susceptibility data in the 2-300 K temperature range (Figure 11) yields \(C_1 = 11.44\) cm\(^3\)mol\(^{-1}\)K, \(C_2 = 3.16\) cm\(^3\)mol\(^{-1}\)K, \(E_1 = 1.08\) K and \(E_2 = -44.32\) K, thus indicating ferromagnetic intra-chain interactions.\(^{[20]}\) That was further supported upon subtraction of the second term from the magnetic susceptibility data, resulting in a net ferromagnetic contribution, \(\chi T = C_1\exp(E_1/T)\).\(^{[19, 20]}\)

Despite the fact that many 1D Dy\(^{III}\) containing coordination...
polymers have been reported to date,[21] only a handful have been found to display ferromagnetic intra-chain interactions.[20,22]

Figure 11 Fit of the magnetic susceptibility data for 3 (black squares) using the scaling theory (red line). The blue dashed line represents the resulting net ferromagnetic contribution, $\chi_T = \chi T - C_2 \exp(E_2/T)$.

Next, we study the magnetocaloric properties of the Gd analogues, namely 1, 4 and 8. We derive the change of the magnetic entropy, $\Delta S_m$, which follows from the change of the applied magnetic field, $\Delta B$, by applying the Maxwell equation:

$$\Delta S_m(T, \Delta B) = \int \left[ \frac{\partial M(T, B)}{\partial T} \right] dB,$$

(8)

to the magnetization data, $M$, (Figures S4, S7 and S11). To facilitate the comparison between the results inferred from each compound, the $\Delta S_m(T, \Delta B)$ data are reported per molar unit (right axis in Figure 12), in addition to per mass unit (left axis). For the dimer cluster 8, the molar data are normalized also per Gd atom to further expedite the comparison. For any investigated $\Delta B$ and experimentally accessed $T$ range, $-\Delta S_m(T, \Delta B)$ of each compound increases on lowering the temperature. Note that $-\Delta S_m(T, \Delta B)$ cannot exceed the maximum entropy value per mole Gd involved, which corresponds to $R \ln(2S_{Gd}+1) = 2.08 \ R$, where $S_{Gd} = 7/2$. For the maximum applied field change ($\Delta B = 5 \ T$) and $T = 3 \ K$, $-\Delta S_m$ reaches 21.8 Jkg$^{-1}$K$^{-1} = 1.4 \ R$ for 1, 23.0 Jkg$^{-1}$K$^{-1} = 1.6 \ R$ for 4, 16.0 Jkg$^{-1}$K$^{-1} = 1.6 \ R$ (per mole Gd) for 8. These values are somewhat smaller than the ones found for the same $\Delta B$ and $T$ in other Gd-based compounds exhibiting 1D polymeric or dimeric structures.[6d,23] In terms of molar Gd units, 4 and 8 provide almost identical $-\Delta S_m(T, \Delta B)$ curves (Figure 12). For 1, we observe a smaller MCE, which has to be ascribed to the presence of relatively stronger antiferromagnetic interactions, as already evidenced from magnetic measurements.

As well known, antiferromagnetic interactions are the least favorable for observing a large MCE.[7] In terms of mass units, the two polymers 1 and 4 show a much larger MCE than the dimer cluster 8. This is chiefly due to the difference in the Gd density, i.e., the metal:non-metal mass ratio.[6d,6e,23] Despite 8 having two Gd atoms per formula unit that contribute to the MCE and 1 and 4 only one, both polymers have a nearly three-times lighter molecular mass than the dimer. In terms of applications, this means that to obtain the same cooling power ($= -\int \Delta S_m dT$) we should use ca. 40-50% more material for 8 than 1 or 4.
Alternating current magnetic susceptibility studies were performed on samples of 2, 3, 5, 6 and 7, in the 1.8 – 20 K range under zero applied dc field and 4.0 G ac field oscillating at 7 – 1285 Hz range, as a means of investigating possible magnetic relaxation phenomena. The two terbium analogues, 2 and 5, showed no frequency in-phase magnetic susceptibility dependence, as well as no out-phase-signals, suggesting the absence of magnetic relaxation in these species. On the contrary, all dysprosium compounds display interesting ac magnetic behaviour; for 3, the temperature dependence of the in-phase, $\chi_M'$, and out-of-phase, $\chi_M''$, magnetic susceptibility signals present temperature dependence below ~10 K, and in combination with the frequency dependence of the out-of-phase signals slow magnetic relaxation in these species is suggested. Unfortunately, no fully formed out-of-phase signals (peaks) are observed, and thus no further analysis was possible. Similarly, this is the case for 6, since temperature dependence of both the in-phase and out-of-phase signals is observed at temperatures < 15 K (Figure 14), but again no characteristic maxima in the out-of-phase signals are observed. Yet, one significant observation is that this dependence now occurs at elevated temperature than the corresponding one for compound 3 (15 K for 6 vs. 10 K for 3), thus indicating the impact of substituting the bridging methoxide groups in 3 with azide groups in 6, since it is well established that both the coordination sphere and the environment of the 4f center plays an important role in magnetic relaxation phenomena.[24]

![Figure 13](image13.png) Plot of the in-phase $\chi_M'$ (top) and out-of-phase $\chi_M''$ signals (center) for 3 in ac susceptibility studies vs. $T$ in a 4.0 G oscillating field at the indicated frequencies. Plot of the out-of-phase $\chi_M''$ signals vs. ln($v$) at the indicated temperatures (bottom). Lines are guides for the eyes.

![Figure 14](image14.png) Plot of the in-phase $\chi_M'$ (top) and out-of-phase $\chi_M''$ signals (center) for 6 in ac susceptibility studies vs. $T$ in a 4.0 G oscillating field at the indicated frequencies. Plot of the out-of-phase $\chi_M''$ signals vs. ln($v$) at the indicated temperatures (bottom). Lines are guides for the eyes.
Given the absence of high symmetry for the dysprosium centres in 6, we were able to utilize the electrostatic model recently reported by Chilton et al., which performs electrostatic energy minimization for the prediction of the ground-state magnetic anisotropy axis. Following this approach and program MAGELLAN, the ground state magnetic anisotropy axes for the Dy center in 6 was found to be tilted towards the O2 atoms (O2A and O2B) belonging to the alkoxide groups of the salen-type ligand connected on the lanthanide center (Fig. 15). Despite the fact that there is only one type of Dy centers present in 6, there are two orientations of the magnetic anisotropy axes due to the zig-zag conformation of the chain, with the two “kinds” of axis tilted by ~110° with respect to each other.

Figure 15 (Top) Ground state magnetic anisotropy axes (blue and red bold lines) for the Dy centers present in 6 looking down c axis; (bottom) the relative orientation of the magnetic anisotropy axes of the DyIII ions in 6 looking down the polymer propagation direction, axis b. Lines are guides for the eyes.

For the dimer complex [Dy2(L')3(MeOH)]·2MeOH (7·2MeOH), a similar behaviour is observed; temperature dependent in-phase and out-of-phase signals are observed at temperatures < 10 K (Figure 16), but again no fully-formed out-of-phase peaks are observed. Given the asymmetric nature of the dimeric complex, two magnetic anisotropy axes were found (Fig. 17); for Dy1 the axes are tilted towards O21 (terminal alkoxide), while for Dy2 is tilted towards O2F (bridging alkoxide) and O2A (terminal alkoxide).

A thorough CCDC search revealed over one hundred examples of dimeric, [Dy2] complexes reported to date, with the vast majority being symmetrical while only few are non-symmetrical regarding the coordination sphere/environment of the metallic centres.

Figure 16 Plot of the in-phase \(\chi''\) (top) and out-of-phase \(\chi''\) signals (center) for 7, [Dy2], in ac susceptibility studies vs. \(T\) in a 4.0 G oscillating field at the indicated frequencies. Plot of the out-of-phase \(\chi''\) signals vs. \(\ln(v)\) at the indicated temperatures (bottom).
Conclusions

In conclusion, we have reported our results towards the synthesis of related lanthanide species; we were able to isolate and characterize two families of related 1-D coordination polymers, and their "analogous" discrete dinuclear building units upon employment of suitable “simple” chelate and bridging ligands. For all Dy analogues, the study of their magnetic properties revealed magnetic relaxation phenomena, while the magnetocaloric properties of all three Gd analogues were investigated.

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Notes and references

† Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

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Figure 17 Ground state magnetic anisotropy axes (blue and red bold lines) for the Dy centers present in the dimeric complex 7.


