Heptanuclear disk-like MII3LnIII4 (M=Ni, Co) coordination clusters: synthesis, structures and magnetic properties

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**Abstract:** The synthesis, characterization, crystal structures and magnetic properties of isoskeletal heptanuclear disk-like MII3LnIII4 coordination clusters with the general formula [CoII3LnIII4(µ3-OH)6L6(CF3SO3)](CF3SO3)5] where Ln= Gd (**2**), Y (**3**) and [NiII3LnIII4(µ3-OH)6L6(CF3SO3)](CF3SO3)5] where Ln= Dy (**4**), Gd (**5**), Y (**6**) are presented. All the compounds are stable in solution as confirmed by ESI-MS. Magnetic studies were performed for compounds **2**, **4**, **5** and **6** and indicate ferromagnetic coupling while the magnetocaloric properties of **5** are characterized by Δ*S*m = -15.4 Jkg-1K-1 at *T* = 5.0 K and Δ*T*ad = 5.9 K at *T* = 2.3 K, for *µ*0Δ*H* = 7 T.

Introduction

3d and/or 4f coordination clusters (CCs) have been of considerable interest in the past few years due to their aesthetically pleasant structures[1–4] and applications.[5–9] These can be synthesized via self-assembly of organic or inorganic ligands, with metal ions, following the hard soft base acid principle.[10] Serendipitous assembly has been the traditional route of synthesis for these types of molecules, not just relying upon the metal ions and coordination modes of ligands, but on a multitude of other factors including concentration, steric effects, solvent, pH and counter anions.[11] These factors can dramatically affect the shape and topology of the final product. More recently, various approaches have been applied to synthesize these molecules in a more predictable manner.[12–14]

The importance of controlling the shape and topology of CCs is highlighted by their extended study as molecular magnetic materials.[15–18] There are many examples of polynuclear CCs displaying interesting magnetic phenomena such as high spin value,[19–22] single-molecule magnet (SMM)[23–28] or magnetocaloric effect (MCE)[29–33] behavior. The combination of 3d and 4f ions has been proposed to be an efficient strategy to reach heterometallic CCs with improved magnetic properties.[34–36] This combination has resulted in a plethora of examples with various 3d metals; FeII2DyIII,[37] CoII2DyIII2,[38] MnIIDyIII2,[39] NiII3Ln3,[40] CrIII2LnIII2,[41] and CuII4DyIII4.[42] In addition 3d/Gd(III) CCs have been recognized as excellent examples displaying magnetocaloric effect (MCE) behavior.[43] The first of these was a Mn4Gd4 CC supported by calix[4]arene.[44] Notable examples experiencing a large MCE effect have been reported including Mn4Gd4,[44,45] M8Gd4,[46] Cu36Ln24[47] and Cu5Gd4.[48]

Schiff base ligands are an ideal host to accommodate both 3d and 4f elements and allow them to interact due to their compartmental nature.[49–56] Recently, we reported a number of 3d and 3d/4f CCs synthesized by the employment of the Schiff base ligand (E)-4-(2-hydroxy-3-methoxy-benzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (H**L1**, Scheme 1).[57–59] The use of H**L1** in Co/Ln cluster chemistry has afforded a series of CoII/DyIII CCs with various nuclearities (4-8).[57,59] Among these compounds the heptanuclear disk-like CC formulated [CoII3DyIII4(μ3-OH)6(**L1**)6(CF3SO3)] (ClO4)5 (**1**) displays behavior indicative of an SMM below 4K.[57]



**Scheme 1.** (E)-4-(2-hydroxy-3-methoxy-benzylideneamino)-2,3-dimethyl-1-phenyl-1,2-dihydropyrazol-5-one (HL1)

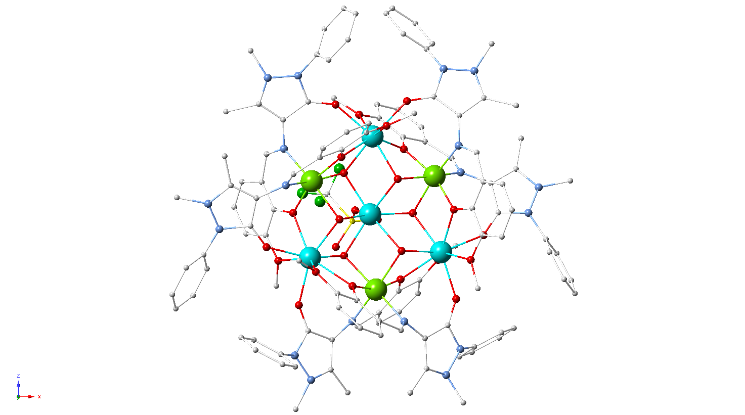
The alternating fashion of CoII/DyIII ions in **1**, prompted us to synthesize other Ln analogues of this motif and study their magnetic properties. In addition, the use of anisotropic CoII 3d ion restrains the construction of magnetic coolers,[29] thus an attempt was made to replace these with the more isotropic NiII ions, which have previously led to NiII/ GdIII CCs with large MCE, i.e. the 48-member metallocycle Ni12Gd36[60] and the cage like Ni6Gd6.[61] Thus, we herein report a series of five isoskeletal MII3LnIII4 disk – like CCs formulated as [CoII3GdIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5](**2**), [CoII3YIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5](**3**), [NiII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5](**4**), [NiII3GdIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5)] (**5**), [NiII3YIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5] (**6**). Synthetic and topological insights as well the magnetic properties of **2**-**6** are discussed, together with an evaluation of the MCE for **5**.

Results and Discussion

**Synthetic issues.** The previously reported CoII3DyIII4 CCs **1** was prepared from the room temperature reaction of Dy(OTf)3 and Co(ClO4)2.6H2O with H**L1** in a molar ratio of 2:1:2.5:2.5 (Dy:Co:HL:Et3N) using MeOH as solvent, yielding crystals after 3 weeks in low yield.[57] When a similar reaction was performed in EtOH, under reflux, an isoskeletal compound formulated [CoII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](ClO4)3(CF3SO3)2 (**1’**) was isolated in only 3 days with moderate yield (Table 1).[57] The latter indicates that the temperature and the solvent of the reaction had a profound effect on the crystallization time and yield of the product. When these two methods were applied to synthesize the CoII/LnIII (Ln= Gd, Y) analogues the yield greatly decreased and when applied to NiII/LnIII analogues either produced the expected product in very low yield (5%, Table 1, entry 6) or hexagonal shaped crystals were obtained in very low yields after almost 6 weeks (compound **4’**, ESI, Table 1, entry 7). An adaption of the synthetic procedure lead (Table 1, entries 3, 4, 5, 8 and 9) to the formation of expected disk-like CCs with all MII3/LnIII4 combinations in very good yields (63-85%), whereas less crystallization time was required. Compounds **2**, **3**, **4**, **5** and **6** were synthesized using the following recipe; EtOH reflux, increased amount of Et3N and a replacement of M(ClO4)2.6H2O with M(NO3)2.6H2O in a molar ratio 2:1:2.5:12. The change in synthetic protocol resulted in the replacement of counter ion ClO4 molecules with CF3SO3 and caused no change to the central [MII3LnIII4(µ3-OH)6L6(CF3SO3)] ion.

**Crystal Structure Description.** Unit cell determinations, IR spectra, elemental analyses and TGA show **2**, **3**, **4**, **5** and **6** to be isoskeletal, therefore only a detailed crystallographic description of **4** will be described here. Crystallographic studies show that **2-4**, crystallize in the orthorhombic space group *Pbca*. The heptanuclear disk like compound, composes of a hexanuclear wheel, three NiII and three DyIII centers in an alternating fashion, and a central DyIII center. The peripheral six centers form a plane and the central DyIII lies 0.671Å out of it. Six, altering above and below the plane, triply bridging hydroxyl groups support the formation of the disk, whereas a CF3SO3 moiety caps the central Dy center ion. The coordination number of the three peripheral and one central DyIII ions is 8 and 7, respectively. The geometry of the central DyIII can be described as a capped octahedron whereas the DyIII ions lying within the wheel is that of a bicapped trigonal prism. The NiII centers adopt what can be best described as a distorted octahedral geometry. The six ligands coordinate in a similar manner (Scheme S1). All six ligands chelate to a NiII ion, through the phenoxido oxygen and the imino nitrogen atoms, to a DyIII ion, through the phenoxido and methoxido oxygen atoms, and bond to another DyIII ion through a carbonyl oxygen atom. The angles of the µ3-OH bridges are within the range 97.2(3) – 106.7(3)°. There are three Dy---Dy distances,3.6470(9) Å, 3.6561(9) Å and 3.6619(12) Å, and nine Ni---Dy distances within the range 3.3715(19) - 3.4806(16) Å. The diameter of the disk is 18.799 Å.

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| **Table 1.** Synthetic conditions for reported disc like CCs. Yield % based on LnIII. | | | | | | |
| **Entry** | **Compound** | **Synthetic Ratio**  **(Ln:M:HL:Et3N)** | **Formula** | **Solvent** | **Yield/ %** | **Crystallisation time/ days** |
| 1 | **1** | 2:1:2.5:2.5 | [CoII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](ClO4)5 | MeOH | 22 | 21 |
| 2 | **1**’ | 2:1:2.5:2.5 | [CoII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](ClO4)3(CF3SO3)2 | EtOH | 45 | 3 |
| 3 | **2** | 2:1:2.5:12 | [CoII3GdIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5 | EtOH | 81 | 2 |
| 4 | **3** | 2:1:2.5:12 | [CoII3YIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5 | EtOH | 77 | 5 |
| 5 | **4** | 2:1:2.5:12 | [NiII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5 | EtOH | 69 | 3 |
| 6 | **4** | 2:1:2.5:2.5 | [NiII3DyIII4(µ3-OH)6(**L1**)6(H2O)](ClO4)6 | EtOH | 5 | 25 |
| 7 | **4’** | 2:1:2.5:2.5 | [NiII3DyIII4(µ3-OH)6(**L1**)6(H2O)](ClO4)6 | MeOH | 12 | 38 |
| 8 | **5** | 2:1:2.5:12 | [NiII3GdIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5) | EtOH | 71 | 2 |
| 9 | **6** | 2:1:2.5:12 | [NiII3YIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5 | EtOH | 68 | 7 |



**Figure 1.** Molecular structure of **4**. Color code; green: NiII; light blue: DyIII; yellow: carbon; pale blue: nitrogen; red: oxygen; yellow: Sulphur; fluorine: light green.

**ESI-MS Studies.** To further confirm the identity of the reported compounds, we performed a broad electrospray ionization mass spectrometry for compounds **2**, **3**, **4**, **5** and **6**. We observed three main regions for the analogues showing three distinct fragments in each region, perfectly corresponding to the tetracationic, tricationic and dicationic fragments respectively; [M3Ln4(µ3-OH)6(C19H18N3O3)6(CF3SO3)]4+, [M3Ln4(µ3-OH)6(C19H18N3O3)6(CF3SO3)3]3+ and [M3Ln4(µ3-OH)6(C19H18N3O3)6(CF3SO3)4]2+ (Fis S1-S5). Conversely the **6** analogue only demonstrates the [Ni3Y4(µ3-OH)6(C19H18N3O3)6(CF3SO3)4]2+ fragment (Fig S3). Values assigned to these fragments corresponding to CC are shown in Table 2. Each of these fragments corresponds to the [M3Ln4(µ3-OH)6(L6)] core with additional OTf counter ions.

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| **Table 2.** m/z fragment vales for reported MII3LnIII4 CC. | | | |
| Compound | [M3Ln4(µ3-OH)6(C19H18N3O3)6(CF3SO3)4]2+ /m/z | [M3Ln4(µ3-OH)6(C19H18N3O3)6(CF3SO3)3]3+ /m/z | [M3Ln4(µ3-OH)6(C19H18N3O3)6(CF3SO3)]4+ /m/z |
| **2** | 1762.06 | 1125.39 | 807.06 |
| **3** | 1624.03 | 1038.02 | 761.19 |
| **4** | 1771.14 | 1132.07 | 774.82 |
| **5** | 1760.61 | 1124.41 | 768.09 |
| **6** | 1624.09 | N/A | N/A |

**Thermogravimetric analysis.** TGA measurements were performed to examine the thermal stability of selected compounds. In the cases of **2** and **6** (Figs S6 – S7, ESI), the first mass loss corresponds to the loss of the counter-anions. The stability of the remaining core is then retained up to the region of ~300 °C, where gradual decomposition takes place. The final residue fits well to the analogous oxide [Co3Gd4O9 for **2** calculated (24.86%) found (24.14%) and Ni3Y4O9 for **6** calculated (19.05%) found (19.43%)].

**Topological features.** There are few examples of 3d/4f disk-like CCs reported in the literature. The first reported examples demonstrating the disk-like or **3,6M7-1**[62] topology were the MnIV6Ce disks reported by Christou et al.[63,64] These were followed by CuII6PrIII,[65] MnII3LnIII4,[66] CuII5LnIII2,[67] CoII3DyIII4,[57] and CoII2DyIII5[59] examples (Table 3). The seven previous reported examples of 3d/4f **3,6M7-1** CCs are shown (Table 3 entries 1-7) and to the best of our knowledge (**4-6**) are the first examples of NiII/LnIII CCs of this topology. Whereas **3** and **2** are the first examples of CoII/YIII and CoII/ GdIII discs respectively, whilst both are also the fourth and fifth examples of CoII/LnIII disks. There are three configurations for the 3d and 4f cation nodes within the disk, dependent on the 3d and 4f ratio. The first (3/4, A Figure 2) incorporates the presence of an Ln node in the center of the disk. This configuration is found in all MII3LnIII4 (Table 3 entries 1, 6, 7 and 8) and all form [MnII3LnIII4(µ3-O)6] cores. The next (5/2 or 2/5 B Figure 2) configuration involves CuII5LnII2 and CoII2DyIII5 (Table 3 Entries 2 and 7). The Ln or the Co nodes can be found in the periphery sandwiched between two 3d nodes each side, with a central Cu or Dy node, respectively. The last (6/1, C Figure 2) configuration is seen in MnIV6CeIV and CuII6Pr CCs; the 3d ions form the periphery and the 4f ion occupies the central node. With this report, Schiff Base ligands (H**L1** and H3**L3**) have been the most successful in synthesizing 3d/4f **3,6M7-1** CCs, however these are limited to the MII/LnIII valences. Whereas ligands containing carboxylic acid groups have been used to form unique MnIV/LnIV clusters as well as the MII/LnIII valences. Though it is evident there are distinct types of **3,6M7-1** CCs it is difficult to relate these to the types of ligand with the limited number of examples. None of the previously reported examples have been investigated for the magnitude of their MCE, whereas CoII3DyIII4, CuII5DyIII2, CuII5HoIII2 were found to have SMM properties at low energy barriers.

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| **Table 3.** Reported 3d/4f CCs with **3,6M7-1** topology. | | | | |
| Entry | Formula | Metals | Ligand | Ref | |
| 1 | [MnII3LnIII4(Piv)12(**L2**)2(H2O)3]·H2O  Ln= La, Pr, Nd, Gd | MnII/LnIII | H3**L2** | [66] | |
| 2 | [CuII5LnIII2(**L3**)2(µ3-OH)4(μ-OH2)2(μ- OAc)2(OAc)2(OH2)2](NO3)2(H2O)2  Ln=Y, Lu, Dy, Ho, Er, Yb | CuII/LnIII | H3**L3** | [67] | |
| 3 | [MnIVCeIV6O9(**L4**)9(H2O)2(MeOH)](ClO4) | MnIV/CeIV | H**L4** | [63] | |
| 4 | [Mn6CeO9(O2CR)9(X)(H2O)2]*y*+ (R = Me (**L4**), X = NO3-, *y* = 0 (**2)**; R = Me (**L5**), X = MeOH, *y* = +1 (**3)**; R = Et, X = NO3-, *y* = 0 | MnIV/CeIV | H**L4**, H**L5** | [64] | |
| 5 | [CuII6PrIII(**L6**)6][PrIII(H2O)10].14H2O | CuII/PrIII | H3**L6** | [65] | |
| 6 | [CoII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](ClO4)5 | CoII/LnIII | H**L1** | [57] | |
| 7 | [CoII2DyIII5(µ3-OH)6(**L1**)2(Piv)8(NO3)4]. 4CH3CN | CoII/LnIII | **HL1** | [59] | |
| 8 | [CoII3LnIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5  Ln= Gd, Y | CoII/LnIII | H**L1** | This Work | |
| 9 | [NiII3LnIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5  Ln=Dy, Gd, Y | NiII/LnIII | H**L1** | This Work | |



**Scheme 2.** Ligands used in the synthesis of 3d/4f **3,6M7-1** CCs

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| **A** | **B** | **C** |

**Figure 2.** Configurations (**A**, **B** and **C**) of 3d/4f nodes for reported **3,6M7-1** CCs. Green and light blue nodes correspond to 3d and 4f ions, respectively.

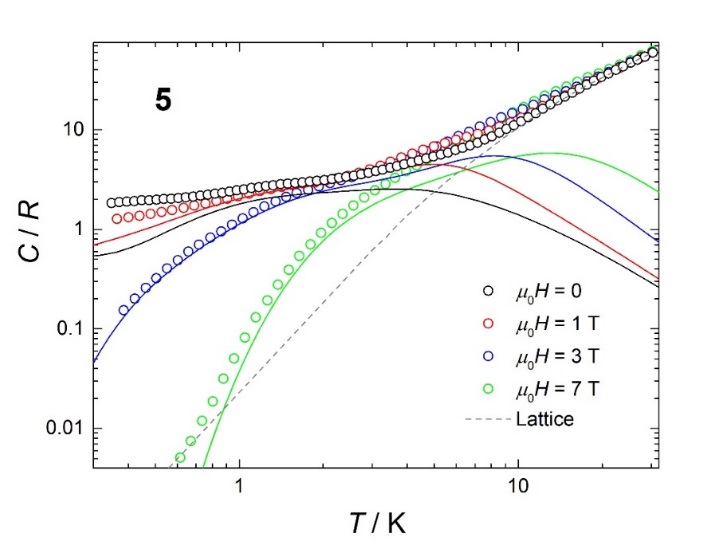
**Magnetic Properties.** Susceptibility measurements were performed for **2**, **4** and **5** and for the Ni-Y complex **6** in order to check the degree of interaction between the d cations, Figure 2. The *χMT* value for **2** at room temperature is 42.87 cm3·mol-1·K, larger than the corresponding spin-only value for three CoII and four GdIII isolated cations of 37.125 cm3·mol-1·K. On cooling the *χMT* value decreases very slightly in the 300-40 K and below this temperature increases continuously up to 60.23 *χMT* cm3·mol-1·K at 2 K. Compound **4** shows a room temperature *χMT* value of 61.43 cm3·mol-1·K that decreases to a minimum value of 57.21 cm3·mol-1·K at 15 K, increasing at lower temperatures up to 98.5 cm3·mol-1·K at 2 K. The initial decrease should be attributed to the depopulation of the Stark levels of the DyIII cation. Compound **5** shows a *χMT* value of 36.09 cm3·mol-1·K at 300 K, somewhat larger than the 34.50 cm3·mol-1·K value expected for three NiII and four GdIII non-interacting cations per molecule, thus suggesting that correlations are sizeable at room temperature. On cooling, the *χMT* product increases slightly in the 300-50 K range and fast below 50 K, reaching the maximum value of 76.2 cm3·mol-1·K at 2.6 K, below which it decays to 75.0 cm3·mol-1·K at 2 K, likely because of weak antiferromagnetic interactions or crystal-field effects. The shape and low-temperature *χMT* values clearly indicate that the dominant interactions are ferromagnetic for the three complexes. Magnetization experiments (Fig. 3 right) show a fast increase at low fields and a further slow increase of the magnetization, reaching quasi saturated values of 28.1 *Nµ*B for **4**, 35.7 *Nµ*B for **2** and 34.9 *Nµ*B for **5,** coherent with the maximum ferromagnetic *S* ground states for **2** and **5** (*S* = 18.5 and 17 respectively). Fit of the experimental data was not possible for the anisotropic Co3Gd4 and Ni3Dy4 complexes **2** and **4**, but a spin-only attempt was performed for the Ni3Gd4 complex **5**. We have also measured the response of the Ni3Y4 complex **6**, that shows a constant *χMT* value of 3.5 cm3·mol-1·K between 300-6 K and a decay below this temperature down to a final value of 2.80 cm3·mol-1·K at 2 K. This measure indicates that there is no interaction between the NiII cations and that complex **6** magnetically behaves as three isolated NiII cations with a *g* value of 2.16. Next, simultaneous fits of *χMT* and *M*(*H*, *T*) data (Fig. 4) were carried out for **5** by using PHI program[68], assuming that only the Ni-Gd and the Gd-Gd pathways are operative and that *g*Ni = 2.16. The best fit, solid lines in Figs. 3 and 4, gives: *J*1(Gd-Gd) = 0.17 cm-1 and *J*2(Ni-Gd) = 0.62 cm-1. It is noteworthy to mention that similar fitting curves of *χMT* and *M*(*H*, *T*) can also be obtained by constraining *J*1(Gd-Gd) and *J*2(Ni-Gd) to be both ferromagnetic and by adding a weak antiferromagnetic effective *zJ* interaction to take into account intermolecular couplings. However, we should safely disregard this second set of parameters because, contrary to the first one, it cannot be used to reproduce satisfactorily the heat capacity results that we report below.



**Figure 3.** Left *χMT* product for **2** (black), **4** (blue) and **5** (red), for applied field 0.1 T. Solid line shows the fit of the experimental data for **5**. Right, magnetization plots for **2** (black), **4** (blue) and **5** (red).



**Figure 4.** Isothermal magnetization curves for *T* = 2−10 K, step 1 K. Solid lines are the best fit curves obtained by using spin-only model and by fixing *g*Ni = 2.16; the coupling constant found from the fitting are *J*1(Gd-Gd) = -0.17 cm-1 and *J*2(Ni-Gd) = 0.62 cm-1.



**Figure 5.** Temperature-dependence of the molar heat capacity, normalized to the gas constant *R*, for **5**, collected for the labelled applied fields. Solid lines are the calculated magnetic contributions for *J*1(Gd-Gd) = -0.17 cm-1 and *J*2(Ni-Gd) = 0.62 cm-1, while dashed line is the non-magnetic lattice contribution.

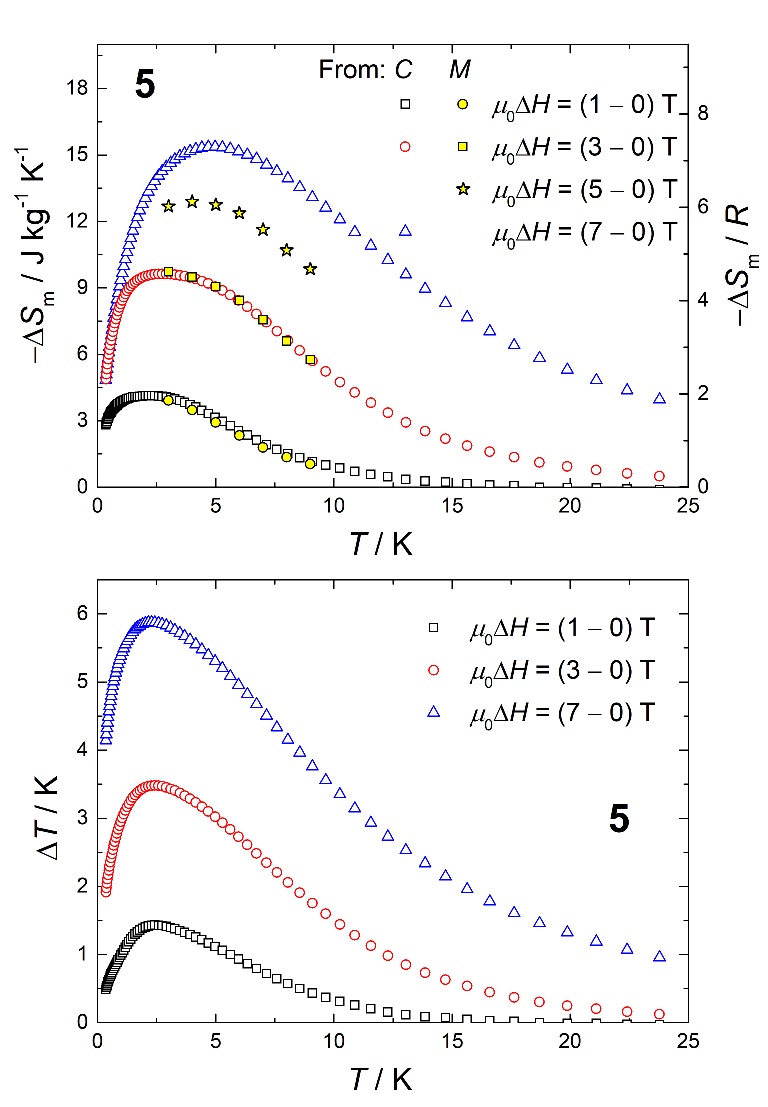
**Heat Capacity.** Figure 5 shows the experimental molar heat capacity *C* for compound **5**, collected for the temperature range 0.35-30 K and for several applied magnetic fields. The heat capacity is best understood by comparing the experimental data with the calculated curves (solid lines) on the basis of the spin-only model and parameters *J*1(Gd-Gd) = -0.17 cm-1 and *J*2(Ni-Gd) = 0.62 cm-1, obtained from fitting the susceptibility and magnetization data. Overall, the agreement is significantly good, with the main discrepancy gradually taking place on increasing *T* above 10-15 K. This discrepancy is due to a non-magnetic contribution that we ascribe to lattice vibrations and can be described by the Debye model (dotted line), which simplifies to a *C*/*R* = *aT* 3 dependence at the lowest temperatures, where *a* = 2.3 x10-2 K-3. The magnetic contribution to the heat capacity is strongly dependent on the applied field, especially for fields larger than 1 T. At the lowest temperatures, the calculated curves deviate from the experimental ones for zero field and less so for *µ*0*H* = 1 T. This is very likely due to weak, though sizeable, magnetic interactions acting between the molecules, probably of dipolar origin, which are not included in our calculations.

**Magnetocaloric Effect.** Finally, we evaluate the MCE for Ni3Gd4, namely, we determine its magnetic entropy change, Δ*S*m, and adiabatic temperature change Δ*T*ad for selected values of the applied field change Δ*H = H* - 0. Note that Δ*S*m can be calculated from the heat capacity and magnetization data by using the relations:

(1)

(2)

where *Sm* is the magnetic entropy and *Cm* is the magnetic heat capacity, which we obtain by subtracting the lattice contribution (dashed line in Figure 5) to the total heat capacity *C*. The adiabatic temperature change can then be obtained straigthforwardly as temperature changes from the entropic data.



**Figure 6**. (Top) Magnetic entropy change *vs T*, for several values of the applied field change Δ*H*, as labelled. These data are calculated by making use of the magnetization and heat capacity data. Vertical axis reports units in Jkg−1K−1 (left) and molar *R* (right). (Bottom) Adiabatic temperature change *vs T* for the labelled applied field change, as obtained from heat capacity data.

The results are shown in Figure 6, where one can notice that the two sets of data for Δ*S*m that we obtain from *C*(*T*,*H*) and *M*(*T*,*H*)are consistent to each other, thus confirming that the procedures used are correct. For **0Δ*H* = 7 T, −Δ*S*m reaches 7.3 *R* = 15.4 Jkg-1K-1 at *T* = 5.0 K, while Δ*T*ad = 5.9 K at *T* = 2.3 K. Magnetic correlations inhibit the system to reach the whole available magnetic entropy that for four GdIII and three NiII ions per molecule amounts to 4*R*ln(2*s*Gd+1) + 3*R*ln(2*s*Ni+1) = 11.62 *R*, where *S*Gd = 7/2 and *S*Ni = 1. The values of Δ*S*m for **5**, when expressed per molar *R*, are similar to the corresponding ones reported for other Ni-Gd compounds,[46,69,70] whereas they compare less favourably when expressed per unit mass, because the metal/non-metal ratio is relatively modest in **5**.

Conclusions

Altering the synthetic procedure of the previously reported heptanuclear disk like CC **1**, a family of isoskeletal compounds formulated [MII3LnIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5] is obtained in higher yields and shorter crystallization times. To the best of our knowledge compounds **4** – **6** represent the first examples of NiII/LnIII CCs derived from this ligand and bearing this disk-like topology. Moreover, **2** and **3** are the first disk-like examples in CoII/ GdIII and CoII/YIII cluster chemistry, respectively. All reported compounds are solution stable and demonstrate three characteristic regions of peaks when analyzed with ESI-MS. The study of their magnetic properties revealed a dominant ferromagnetic coupling, while compound **5** shows magnetocaloric properties at liquid-helium temperatures. The present work illustrates the effectiveness of the proposed synthetic strategy to synthesize polynuclear CCs with fascinating magnetic properties. Ongoing investigations for the synthesis of other polynuclear compounds using this ligand are in progress.

Experimental Section

**Materials**. Chemicals (reagent grade) were purchased from Sigma Aldrich and Alfa Aesar. All experiments were performed under aerobic conditions using materials and solvents as received. *Safety note*: Perchlorate salts are potentially explosive; such compounds should be used in small quantities and handled with caution and utmost care at all times.

**Instrumentation.** IR spectra were recorded over the range of 4000-650 cm-1 on a Perkin Elmer Spectrum One FT-IR spectrometer fitted with a UATR polarization accessory. ESI-MS date were obtained on Bruker Daltonics Fourier transform ion cyclotron (FTICR-MS ) while the EI (at 70 eV) were obtained using Fissions instrument VG Autospec. TGA analysis was performed on a TA Instruments Q-50 model (TA, Surrey, UK) under nitrogen and at a scan rate of 10 °C/min (University of Sussex).

**Magnetic studies.** Variable-temperature and variable-field magnetic studies were performed using a MPMS-5 Quantum Design magnetometer operating at 0.03 T in the 300-2.0 K range and with applied fields up to 5T. Diamagnetic corrections were applied to the observed paramagnetic susceptibility using Pascal’s constants. Heat capacity measurements were carried out by using a Quantum Design PPMS system, equipped with a 3He cryostat. The experiments were performed on a thin pressed pellet (ca. 1 mg) of a polycrystalline sample, thermalized by ca. 0.2 mg of Apiezon N grease, whose contribution was subtracted by using a phenomenological expression.

**Ligand synthesis.** The synthesis of H**L1** was performed following the reported procedure.36

**Preparation of compounds 2 – 6.** Ln(OTf)3 (0.2mmol), Co(NO3)2.6H2O (0.1mmol, 58mg), H**L1** (0.2mmol, 34mg) and Et3N (1.2mmol, 26.8µL) were refluxed for 2h in EtOH (20mL). The reaction mixture was subsequently cooled and filtered. The filtrate was left for slow evaporation between 4-8 days before red crystals suitable for Single X-Ray were collected. These were dried overnight. CHN (**2**) [CoII3GdIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5](expected) C-37.68%, H-3.01%, N-6.60% (observed) C-37.59%, H.3.04%, N-6.71%; A similar procedure was followed for the synthesis of **3** – **6** using the corresponding metal salts. CHN (**3**) [CoII3YIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5] (expected) C-40.62%, H-3.24%, N-7.11% (observed) C-40.71%, H-3.33%, N-7.21%. CHN (**4**); [NiII3GdIII4(µ3-OH)6L6(CF3SO3)](CF3SO3)5) (expected) C-37.71%, H-3.01%, N-6.60% (observed)C-37.82%, H.2.98%, N-6.55%; CHN (**5**) [NiII3DyIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5] (expected) C-37.47%, H-2.99%, N-6.56% (observed) C-37.50%, H-3.09%, N-6.46% ;CHN (**6**) [NiII3YIII4(µ3-OH)6(**L1**)6(CF3SO3)](CF3SO3)5] (expected) C-40.66%, H-3.24%, N-7.12% (observed) C-40.59%, H-3.23%, N-7.15%;

**X-ray Crystallography**. Unit cells (Table S1) for **2**, **5** and **6** (ω- scans) were obtained at the University of Sussex by use of an Agilent Xcalibur Eos Gemini Ultra diffractometer with CCD plate detector under a flow of nitrogen gas at 293(2) K for **2** or 173(2) K for **5** and **6** using Mo Kα radiation (λ = 0.71073 Å). Data for **3, 4** and **4’** were collected at the National Crystallography Service, University of Southampton[71] on a Rigaku FRE+ diffractometer equipped with a HG Saturn 724+ CCD detector under a flow of nitrogen gas at 100(2) K, processed with CrysAlisPro and solved by intrinsic phasing methods with SHELXT.[72] All crystal structures were then refined on Fo2 by full-matrix least-squares refinements using SHELXL.[72] All non-H atoms were refined with anisotropic thermal parameters, and H-atoms were introduced at calculated positions and allowed to ride on their carrier atoms. Geometric/crystallographic calculations were performed using PLATON,[73] Olex2,[74] and WINGX[75] packages; graphics were prepared with Crystal Maker.[76] Crystallographic details are given in Table S1. CCDC 1545359 - 1545361.

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**Keywords:** coordination clusters • magnetic properties • topology • Schiff Base • disk-like

[1] J.-B. Peng, X.-J. Kong, Q.-C. Zhang, M. Orendáč, J. Prokleška, Y.-P. Ren, L.-S. Long, Z. Zheng, L.-S. Zheng, *J. Am. Chem. Soc.* **2014**, *136*, 17938–17941.

[2] C. Papatriantafyllopoulou, E. E. Moushi, G. Christou, A. J. Tasiopoulos, *Chem. Soc. Rev.* **2016**, *45*, 1597–1628.

[3] W.-P. Chen, P.-Q. Liao, Y. Yu, Z. Zheng, X.-M. Chen, Y.-Z. Zheng, *Angew. Chem. Int. Ed.* **2016**, *55*, 9375–9379.

[4] G. E. Kostakis, in *Elsevier Ref. Modul. Chem. Mol. Sci. Chem. Eng.* (Ed.: J. Reedijk), Elsevier, Waltham, MA, **2016**, pp. 1–53.

[5] J. Long, J. Rouquette, J.-M. Thibaud, R. A. S. Ferreira, L. D. Carlos, B. Donnadieu, V. Vieru, L. F. Chibotaru, L. Konczewicz, J. Haines, et al., *Angew. Chem. Int. Ed.* **2015**, *54*, 2236–2240.

[6] J. Jankolovits, C. M. Andolina, J. W. Kampf, K. N. Raymond, V. L. Pecoraro, *Angew. Chem. Int. Ed.* **2011**, *50*, 9660–9664.

[7] F. Evangelisti, R. Moré, F. Hodel, S. Luber, G. R. Patzke, *J. Am. Chem. Soc.* **2015**, *137*, 11076–11084.

[8] P. Buchwalter, J. Rosé, P. Braunstein, *Chem. Rev.* **2015**, *115*, 28–126.

[9] K. Griffiths, P. Kumar, G. R. Akien, N. F. Chilton, A. Abdul-Sada, G. J. Tizzard, S. J. Coles, G. E. Kostakis, *Chem. Commun.* **2016**, *52*, 7866–7869.

[10] R. G. Pearson, *J. Chem. Educ.* **1968**, *45*, 581.

[11] R. E. P. Winpenny, *J. Chem. Soc. Dalt. Trans.* **2002**, 1–10.

[12] J. Ferrando-Soria, A. Fernandez, E. Moreno Pineda, S. A. Varey, R. W. Adams, I. J. Vitorica-Yrezabal, F. Tuna, G. A. Timco, C. A. Muryn, R. E. P. Winpenny, *J. Am. Chem. Soc.* **2015**, *137*, 7644–7647.

[13] J. Wu, L. Zhao, L. Zhang, X.-L. Li, M. Guo, A. K. Powell, J. Tang, *Angew. Chemie Int. Ed.* **2016**, *55*, 15574–15578.

[14] Y.-K. Deng, H.-F. Su, J.-H. Xu, W.-G. Wang, M. Kurmoo, S.-C. Lin, Y.-Z. Tan, J. Jia, D. Sun, L.-S. Zheng, *J. Am. Chem. Soc.* **2016**, *138*, 1328–1334.

[15] T. Pugh, N. F. Chilton, R. A. Layfield, *Angew. Chemie Int. Ed.* **2016**, *55*, 11082–11085.

[16] Y.-S. Ding, N. F. Chilton, R. E. P. Winpenny, Y.-Z. Zheng, *Angew. Chemie Int. Ed.* **2016**, *55*, 16071–16074.

[17] J. J.-L. Liu, Y.-C. Chen, J. J.-L. Liu, V. Vieru, L. Ungur, J.-H. Jia, L. F. Chibotaru, Y. Lan, W. Wernsdorfer, S. Gao, et al., *J. Am. Chem. Soc.* **2016**, *138*, 5441–50.

[18] Y.-C. Chen, J.-L. Liu, L. Ungur, J. Liu, Q.-W. Li, L.-F. Wang, Z.-P. Ni, L. F. Chibotaru, X.-M. Chen, M.-L. Tong, *J. Am. Chem. Soc.* **2016**, *138*, 2829–2837.

[19] A. M. Ako, I. J. Hewitt, V. Mereacre, R. Clérac, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Angew. Chemie Int. Ed.* **2006**, *45*, 4926–4929.

[20] M. Manoli, S. Alexandrou, L. Pham, G. Lorusso, W. Wernsdorfer, M. Evangelisti, G. Christou, A. J. Tasiopoulos, *Angew. Chem. Int. Ed.* **2016**, *55*, 679–684.

[21] A. M. Ako, V. Mereacre, R. Clérac, W. Wernsdorfer, I. J. Hewitt, C. E. Anson, A. K. Powell, *Chem. Commun.* **2009**, 544–546.

[22] T. C. Stamatatos, K. A. Abboud, W. Wernsdorfer, G. Christou, *Angew. Chem. Int. Ed.* **2007**, *46*, 884–888.

[23] R. Modak, Y. Sikdar, G. Cosquer, S. Chatterjee, M. Yamashita, S. Goswami, *Inorg. Chem.* **2016**, *55*, 691–699.

[24] X.-Q. Song, P.-P. Liu, Y.-A. Liu, J.-J. Zhou, X.-L. Wang, *Dalton Trans.* **2016**, *45*, 8154–8163.

[25] L. Zhao, J. Wu, H. Ke, J. Tang, *Inorg. Chem.* **2014**, *53*, 3519–3525.

[26] J. W. Sharples, D. Collison, *Coord. Chem. Rev.* **2014**, *260*, 1–20.

[27] L. Li, Y. Zhang, M. Avdeev, L. F. Lindoy, D. G. Harman, R. Zheng, Z. Cheng, J. R. Aldrich-Wright, F. Li, *Dalton Trans.* **2016**, *45*, 9407–9411.

[28] C. D. Polyzou, A. Baniodeh, N. Magnani, V. Mereacre, N. Zill, C. E. Anson, S. P. Perlepes, A. K. Powell, *RSC Adv.* **2015**, *5*, 10763–10767.

[29] J. A. Sheikh, A. Clearfield, *Inorg. Chem.* **2016**, *55*, 8254–8256.

[30] J.-L. Liu, W.-Q. Lin, Y.-C. Chen, S. Gómez-Coca, D. Aravena, E. Ruiz, J.-D. Leng, M.-L. Tong, *Chem. Eur. J.* **2013**, *19*, 17567–17577.

[31] J. W. Sharples, Y. Zheng, F. Tuna, E. J. L. McInnes, D. Collison, *Chem. Commun.* **2011**, *47*, 7650–7652.

[32] G. Guthausen, J. R. Machado, B. Luy, A. Baniodeh, A. K. Powell, S. Krämer, F. Ranzinger, M. P. Herrling, S. Lackner, H. Horn, *Dalton Trans.* **2015**, *44*, 5032–5040.

[33] Y.-Z. Zheng, M. Evangelisti, F. Tuna, R. E. P. Winpenny, *J. Am. Chem. Soc.* **2012**, *134*, 1057–1065.

[34] R. Sessoli, A. K. Powell, *Coord. Chem. Rev.* **2009**, *253*, 2328–2341.

[35] E. C. Sañudo, L. Rosado Piquer, *Dalton Trans.* **2015**, *44*, 8771–8780.

[36] K. Liu, W. Shi, P. Cheng, *Coord. Chem. Rev.* **2015**, *289*–*290*, 74–122.

[37] J.-L. Liu, J.-Y. Wu, Y.-C. Chen, V. Mereacre, A. K. Powell, L. Ungur, L. F. Chibotaru, X.-M. Chen, M.-L. Tong, *Angew. Chemie Int. Ed.* **2014**, *53*, 12966–12970.

[38] K. C. Mondal, A. Sundt, Y. Lan, G. E. Kostakis, O. Waldmann, L. Ungur, L. F. Chibotaru, C. E. Anson, A. K. Powell, *Angew. Chem. Int. Ed.* **2012**, *51*, 7550–7554.

[39] X.-L. Li, F.-Y. Min, C. Wang, S.-Y. Lin, Z. Liu, J. Tang, *Dalt. Trans.* **2015**, *44*, 3430–3438.

[40] J. Goura, R. Guillaume, E. Rivière, V. Chandrasekhar, *Inorg. Chem.* **2014**, *53*, 7815–7823.

[41] S. K. Langley, D. P. Wielechowski, B. Moubaraki, K. S. Murray, *Chem. Commun.* **2016**, *52*, 10976–10979.

[42] I. A. Kühne, N. Magnani, V. Mereacre, W. Wernsdorfer, C. E. Anson, A. K. Powell, *Chem. Commun.* **2014**, *50*, 1882–1885.

[43] Y.-Z. Zheng, G.-J. Zhou, Z. Zheng, R. E. P. Winpenny, *Chem. Soc. Rev.* **2014**, *43*, 1462–75.

[44] G. Karotsis, M. Evangelisti, S. Dalgarno, E. Brechin, *Angew. Chem. Int. Ed.* **2009**, *48*, 9928–9931.

[45] G. Karotsis, S. Kennedy, S. J. Teat, C. M. Beavers, D. A. Fowler, J. J. Morales, M. Evangelisti, S. J. Dalgarno, E. K. Brechin, *J. Am. Chem. Soc.* **2010**, *132*, 12983–12990.

[46] T. N. Hooper, J. Schnack, S. Piligkos, M. Evangelisti, E. K. Brechin, *Angew. Chem. Int. Ed.* **2012**, *51*, 4633–4636.

[47] J.-D. Leng, J.-L. Liu, M.-L. Tong, *Chem. Commun.* **2012**, *48*, 5286–5288.

[48] S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evangelisti, K. S. Murray, *Chem. Sci.* **2011**, *2*, 1166–1169.

[49] A. Chakraborty, P. Bag, J. Goura, A. K. Bar, J. P. Sutter, V. Chandrasekhar, *Cryst. Growth Des.* **2015**, *15*, 848–857.

[50] J. Goura, V. Mereacre, G. Novitchi, A. K. Powell, V. Chandrasekhar, *Eur. J. Inorg. Chem.* **2015**, *2015*, 156–165.

[51] M. Andruh, *Dalton Trans.* **2015**, *44*, 16633–16653.

[52] J. Wu, L. Zhao, M. Guo, J. Tang, *Chem. Commun.* **2015**, *51*, 17317–17320.

[53] E. C. Mazarakioti, K. M. Poole, L. Cunha-Silva, G. Christou, T. C. Stamatatos, *Dalton Trans.* **2014**, *43*, 11456–11460.

[54] L.-F. Zou, L. Zhao, Y.-N. Guo, G.-M. Yu, Y. Guo, J. Tang, Y.-H. Li, *Chem. Commun.*  **2011**, *47*, 8659–8661.

[55] L. Zhang, L. Zhao, P. Zhang, C. Wang, S.-W. Yuan, J. Tang, *Inorg. Chem.* **2015**, *54*, 11535–11541.

[56] J. Wu, L. Zhao, L. Zhang, X. L. Li, M. Guo, J. Tang, *Inorg. Chem.* **2016**, *55*, 5514–5519.

[57] E. Loukopoulos, B. Berkoff, A. Abdul-Sada, G. J. Tizzard, S. J. Coles, A. Escuer, G. E. Kostakis, *Eur. J. Inorg. Chem.* **2015**, *2015*, 2646–2649.

[58] E. Loukopoulos, B. Berkoff, K. Griffiths, V. Keeble, V. N. Dokorou, A. C. Tsipis, A. Escuer, G. E. Kostakis, *CrystEngComm* **2015**, *17*, 6753–6764.

[59] B. Berkoff, K. Griffiths, A. Abdul-Sada, G. J. Tizzard, S. J. Coles, A. Escuer, G. E. Kostakis, *Dalton Trans.* **2015**, *44*, 12788–12795.

[60] J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng, Z. Zheng, *Angew. Chem. Int. Ed.* **2011**, *50*, 10649–10652.

[61] Y. Z. Zheng, M. Evangelisti, R. E. P. Winpenny, *Angew. Chemie - Int. Ed.* **2011**, *50*, 3692–3695.

[62] G. E. Kostakis, V. A. Blatov, D. M. Proserpio, *Dalton Trans.* **2012**, *41*, 4634–4640.

[63] A. J. Tasiopoulos, T. A. O’Brien, K. A. Abboud, G. Christou, *Angew. Chem. Int. Ed.* **2004**, *43*, 345–349.

[64] A. J. Tasiopoulos, P. L. Milligan, K. A. Abboud, T. A. O’Brien, G. Christou, *Inorg. Chem.* **2007**, *46*, 9678–96791.

[65] Y.-J. Zhang, B.-Q. Ma, S. Gao, J.-R. Li, Q.-D. Liu, G.-H. Wen, X.-X. Zhang, *J. Chem. Soc. Dalt. Trans.* **2000**, 2249–2250.

[66] J. Liu, C. Ma, H. Chen, M. Hu, H. Wen, H. Cui, C. Chen, *Dalton Trans.* **2013**, *42*, 3787–3790.

[67] V. Chandrasekhar, A. Dey, S. Das, M. Rouzières, R. Clérac, *Inorg. Chem.* **2013**, *52*, 2588–2598.

[68] N. F. Chilton, R. P. Anderson, L. D. Turner, A. Soncini, K. S. Murray, *J. Comput. Chem.* **2013**, *34*, 1164–1175.

[69] A. Hosoi, Y. Yukawa, S. Igarashi, S. J. Teat, O. Roubeau, M. Evangelisti, E. Cremades, E. Ruiz, L. A. Barrios, G. Aromí, *Chem. Eur. J.* **2011**, *17*, 8264–8268.

[70] T. D. Pasatoiu, A. Ghirri, A. M. Madalan, M. Affronte, M. Andruh, *Dalton Trans.* **2014**, *43*, 9136–9142.

[71] S. J. Coles, P. A. Gale, *Chem. Sci.* **2012**, *3*, 683–689.

[72] G. M. Sheldrick, *Acta Crystallogr. Sect. C Struct. Chem.* **2015**, *71*, 3–8.

[73] A. L. Spek, *J. Appl. Crystallogr.* **2003**, *36*, 7–13.

[74] O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard, H. Puschmann, *J. Appl. Crystallogr.* **2009**, *42*, 339–341.

[75] L. J. Farrugia, *J. Appl. Crystallogr.* **2012**, *45*, 849–854.

[76] C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler, J. Van De Streek, *J. Appl. Crystallogr.* **2006**, *39*, 453–457.

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| FULL PAPER | | |
| Text for Table of Contents |  | 3d/4f coordination clusters  *K. Griffiths, C. Harding, V. N. Dokorou, E. Loukopoulos, Stavroula I. Sampani, Alaa Abdul-Sada, G. J. Tizzard,Simon J. Coles, G. Lorusso, M. Evangelisti, A. Esquer\* and G. E. Kostakis\**  Page No. – Page No.  Heptanuclear disk-like MII3LnIII4 (M=Ni,Co) coordination clusters: synthesis, structures and magnetic properties |
|  |

The use of a monoanionic Schiff Base ligand in 3d/4f chemistry yields a family of heptanuclear MII3LnIII4 (M=Ni, Co) disk like coordination clusters. The NiII/LnIII analogues represent the first examples bearing this disk-like topology. Magnetic studies reveal a dominant ferromagnetic coupling, while the NiII3GdIII4 analogue **5** shows magnetocaloric properties at liquid-helium temperatures.