Dalton Transactions

PAPER

Cite this: *Dalton Trans.*, 2014, **43**, 9136

Received 18th February 2014,
Accepted 20th March 2014

DOI: 10.1039/c4dt00515e

www.rsc.org/dalton

Octanuclear [$Ni^{II}_4Ln^{III}_4$] complexes. Synthesis, crystal structures and magnetocaloric properties†‡

Traian D. Pasatoiu,[a] Alberto Ghirri,[b] Augustin M. Madalan,[a] Marco Affronte*[b] and Marius Andruh*[a]

Two original heterooctanuclear [$Ni^{II}_4Ln^{III}_4$] complexes (Ln^{III} = Sm^{III}, Gd^{III}) have been obtained starting from the [Ni^{II}(valpn)(H_2O)$_2$] mononuclear precursor [H_2valpn = 1,3-propanediylbis(2-iminomethylene-6-methoxy-phenol)] and the corresponding lanthanide nitrates, in the presence of azide anions, through slow capture of atmospheric CO_2. Three weak and competitive exchange interactions, J_{GdGd}, J_{GdNi}, J_{NiNi}, make the ground state of this magnetic system degenerate at cryogenic temperature and zero field. This, along with the high spin of Gd^{III}, lead to a significant magnetocaloric effect spread in the temperature range 1 to 20 K (ΔS_m[0–7 T, 3.5 K] = 19 J kg^{-1} K^{-1}).

Introduction

An important research topic in molecular magnetism is represented by the synthesis of heterometallic complexes containing both paramagnetic 3d and 4f ions. The interaction between d and f spin carriers within the same molecular entity leads to interesting magnetic properties. Moreover, 3d–4f complexes have been intensively studied in order to reveal the factors governing the nature and magnitude of the exchange interaction between lanthanides and various 3d metal ions.[1] The interest for 3d–4f heteronuclear complexes grew rapidly after Gatteschi's report on the ferromagnetic interaction between adjacent Cu^{II} and Gd^{III} ions in trinuclear $Cu^{II}Gd^{III}Cu^{II}$ complexes.[2] Nowadays, the revival of 3d–4f combined chemistry arises from to the discovery of molecular nanomagnets (single-molecule magnets, SMMs, and single-chain magnets, SCMs),[1a,b,3] and from their significant magnetocaloric effect (MCE).[4] On one hand, the design of 3d–4f molecular nanomagnets requires the use of lanthanide ions exhibiting a high anisotropy, the best candidates being Tb^{III}, Dy^{III}, and Ho^{III} ions.[3] On the other hand, in order to generate molecular compounds with a large magnetocaloric effect,[4] ions with high spin and low magnetic anisotropy are necessary, such as the isotropic Gd^{III} ion. MCE is an intrinsic property to any magnetic material and is related to the change of the magnetic entropy, $-\Delta S_m$, once it is exposed to a magnetic field. When the magnetic field is switched off, if the demagnetization process occurs without any heat flow from the environment, a drop (ΔT_{ad}) of the temperature of the system is observed. This behaviour can be exploited for magnetic refrigeration.[5] A prerequisite for achieving a large MCE is a highly degenerate magnetic ground state and an easy lift of this degeneration by the application of an external magnetic field which, in turns, induces a large variation of the entropy.[6] Although attention of chemists was mostly oriented towards lanthanide compounds and alloys, due to their large magnetic entropy changes,[5] heterometallic 3d–4f polynuclear complexes were also shown to exhibit a magnetic refrigerant behaviour.[7]

In previous papers we have shown that binuclear [Ni^{II}(valpn)Ln^{III}] complexes, apart from their interest for the investigation of the Ni^{II}–Ln^{III} exchange interactions,[8] can be employed as precursors for obtaining high-nuclearity clusters and coordination polymers with interesting magnetic properties (valpn^{2-} is a Schiff-base compartmental ligand resulted from the condensation of *o*-vanillin with 1,3-propanediamine).[9] Herein we present two novel octanuclear clusters, [$Ni^{II}_4Ln^{III}_4$], which are obtained by reacting the binuclear [$Ni^{II}Ln^{III}$] precursors with sodium azide and through the simultaneous fixation of atmospheric CO_2 (Ln = Sm, Gd). The magnetothermal properties of the gadolinium derivative have been investigated. The reaction between coordination compounds and atmospheric CO_2 was first observed with several transition metal complexes,[10] resulting in carbonato-bridged complexes. More recently, several 4f,[11] and 3d–4f complexes[12] have been shown to be able to capture atmospheric CO_2, resulting in a quite rich variety of carbonato-complexes.

---

[a] *Inorganic Chemistry Laboratory, Faculty of Chemistry, University of Bucharest, Str. Dumbrava Rosie nr. 23, 020464-Bucharest, Romania. E-mail: marius.andruh@dnt.ro*
[b] *C.N.R. – Institute of NanoSciences S3 and Dipartimento di Scienze Fisiche, Informatiche e Matematiche, Università di Modena e Reggio Emilia, Via G. Campi 213/A, 41100 Modena, Italy. E-mail: marco.affronte@unimore.it*

† Dedicated to Professor Francesc Lloret on the occasion of his 60th birthday.

‡ Electronic supplementary information (ESI) available. CCDC 986980 and 986981. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c4dt00515e

Experimental

Materials

The chemicals used, *o*-vanillin, 1,3-diaminopropane, sodium azide, $Sm(NO_3)\cdot 6H_2O$, $Gd(NO_3)_3\cdot 6H_2O$, as well as all the solvents were purchased from commercial sources. The mononuclear complex, [Ni(valpn)], was prepared as follows: 10 mmol 1,3-propylenediamine and 20 mmol triethylamine were added under stirring to 50 mL THF solution containing 20 mmol *o*-vanillin. After 30 minutes, an aqueous solution (50 mL) containing 10 mmol $Ni(NO_3)\cdot 6H_2O$ is added. The resulting mixture is stirred for an hour, then 500 mL H_2O were added to facilitate the precipitation of the mononuclear complex. The light green solid obtained is filtered and dried. In order to synthesize $[Ni^{II}Ln^{III}]$ (Ln^{III} = Sm, Gd), the method we have previously described[8a] was used: 4 mmol of $Ln(NO_3)_3\cdot 6H_2O$ are added to a suspension containing 4 mmol [Ni(valpn)] in 20 mL acetonitrile. The reaction mixture is stirred for about 20 minutes and then let to slowly evaporate at room temperature.

$[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Sm(H_2O)_3(\mu\text{-}CO_3)Sm(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2]$ $(N_3)_2\cdot 12H_2O$ **1** and $[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Gd(H_2O)_3(\mu\text{-}CO_3)Gd(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2]$-$(N_3)_2\cdot 10H_2O\cdot CH_3CN$ **2** were prepared as follows: a solution containing 0.1 mmol NaN_3 dissolved in 10 mL H_2O was added to a solution containing 0.1 mmol of the corresponding $[Ni^{II}(valpn)Ln^{III}]$ (Ln^{III} = Sm, Gd) heterodinuclear complex dissolved in 20 mL acetonitrile. The reaction mixture was stirred for 30 minutes and then filtered. Several days later, the slow vaporization of the solvent yielded green crystals of the octanuclear complexes. Yields: 20% for **1**, and 22% for **2**. Calcd: 30.05 C; 4.20 H; 14.82% N. Found: 30.1 C; 4.1 H; 14.8% N for **1**. Calcd: 30.64 C; 4.14 H; 14.73% N. Found: 30.4 C; 3.9 H; 14.5% N for **2**.

X-Ray structure determination

Single crystals suitable for X-ray diffraction studies were obtained by slow vaporization, as described above. Data were collected at 293 K on a STOE IPDS II diffractometer using graphite-monochromated Mo Kα radiation (λ = 0.71073Å). The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2. The non-H atoms were refined with anisotropic displacement parameters. The crystallographic data are collected in Table 1. CCDC reference number: 986980, 986981.

Physical measurements

The IR spectra were recorded on KBr pellets on a JASCO FTIR 4100 spectrophotometer in the 4000–400 cm^{-1} range.

The magnetic characterization was performed on microcrystalline powders of **2** by means of a Quantum Design PPMS-7 T. Susceptibility measurements were performed with an ac excitation field of 10 Oe and frequency 90, 1730 and 9300 Hz. Magnetization measurements were carried out with a 7 T superconducting coil and dc extraction technique. Heat capacity was measured in the temperature range of 0.3–20 K by means of a Quantum Design ^{3}He refrigerator, using the relaxation method and two-tau fitting. In this case, microcrystalline samples were pressed in thin pellets having a mass of about 2 mg.

Table 1 Crystallographic data, details of data collection and structure refinement parameters for compounds **1** and **2**

Compound	1	2
Chemical formula	$C_{78}H_{130}N_{33}O_{47}Ni_4Sm_4$	$C_{80}H_{129}N_{33}O_{45}Ni_4Gd_4$
M (g mol^{-1})	3104.38	3136.83
Temperature (K)	293	293
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$
a (Å)	13.1410(4)	13.1507(7)
b (Å)	23.4741(8)	23.5171(14)
c (Å)	19.0068(5)	18.9619(10)
α (°)	90.00	90.00
β (°)	91.216(2)	91.06
γ (°)	90.00	90.00
V (Å^3)	5861.8(3)	5863.3(6)
Z	2	2
D_c (g cm^{-3})	1.759	1.764
μ (mm^{-1})	2.696	2.953
F(000)	3116	3092
Refinement on	F^2	F^2
Goodness-of-fit	1.068	0.850
Final R_1, wR_2 [$I > n\sigma(I)$]	0.0600, 0.1490	0.0521, 0.0893
R_1, wR_2 (all data)	0.0768, 0.1589	0.1134, 0.1023
Largest diff. peak and hole (e Å^{-3})	2.448, −1.883	1.482, −0.775

Results and discussion

The aim of this work is to check whether our strategy for designing high-nuclearity clusters and coordination polymers, starting from heterodimetallic complexes, can be applied in order to organize binuclear high spin $[Ni^{II}Ln^{III}]$ species into complexes with an important magnetocaloric effect. The self-assembly processes between preformed $[Ni^{II}Ln^{III}]$ complexes (Ln = Sm, Gd) and the azide anion, in the presence of carbonate anions (resulted from the fixation of atmospheric CO_2), afforded two novel octanuclear clusters $[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Sm(H_2O)_3(\mu\text{-}CO_3)Sm(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2]$-$(N_3)_2\cdot 12H_2O$ **1** and $[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Gd(H_2O)_3(\mu\text{-}CO_3)$-$Gd(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2](N_3)_2\cdot 10H_2O\cdot CH_3CN$ **2**. The carbonato ligand is formed during the slow crystallization process, a phenomenon observed with other 3d–4f complexes as well.[12] The infrared spectrum of **2** (Fig. S1‡) gives some useful information. First of all, we notice characteristic bands of the carbonato ligand at 1467 and 1074 cm^{-1}; the absorption band at 1528 cm^{-1} is assigned to the ν(C–O) stretching vibrations, while the π(C–O) out-of-plane bending vibration appears as a weak absorption band at 852 cm^{-1}.[13] The intense band located at 2033 cm^{-1} is due to the azido ligands. We also mention that the characteristic bands of the nitrato ligands are no more observed and this confirms that the nitrato groups from the binuclear precursors have been replaced by the azido and carbonato ligands.

Description of the structures

X-ray diffraction measurements indicated the two complexes are isomorphous and crystallize in a monoclinic space group (Table 1). Their structure consists of octanuclear cationic units (Fig. 1), uncoordinated azide anions, and solvent molecules (H_2O in crystal **1**, respectively H_2O and CH_3CN in crystal **2**). The gadolinium derivative is particularly interesting from the magnetic point of view, while the first compound was synthesized in order illustrate that the absorption of the CO_2 from the air is a general reaction within this system. They have the following compositions: $[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Sm(H_2O)_3(\mu\text{-}CO_3)Sm(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2](N_3)_2{\cdot}12H_2O$ **1** and $[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Gd(H_2O)_3(\mu\text{-}CO_3)Gd(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2](N_3)_2{\cdot}10H_2O{\cdot}CH_3CN$ **2**. Since the two structures are very similar, only the one of the gadolinium derivative, **2**, will be discussed here.

The construction of the centrosymmetric octanuclear complex can be described as resulting by connecting two $\{Ni_2Gd_2\}$ moieties through the 1,3-azido bridge that links the nickel ions; each tetranuclear moiety is constructed from two binuclear {Ni(valpn)Gd} entities bridged by a carbonato ligand, which interacts solely with the gadolinium ions. Within the octanuclear unit, there are two types of Ni^{II} ions, Ni1 and Ni2, both being hexacoordinated. The equatorial plane of the Ni1 ion is occupied by donor atoms of the valpn ligand [Ni1–N1 = 2.027(7), Ni1–N2 = 2.023(9), Ni1–O2 = 2.043(6), Ni1–O3 = 2.050(6) Å], while two azido ligands are coordinated into the axial positions. One of them behaves like a terminal ligand [Ni1–N6 = 2.093(10) Å], while the second one forms a $\mu_{1,3}$-N_3 bridge between two Ni1 ions [Ni1–N9 = 2.211(9) Å]. The intermetallic Ni1⋯Ni1′ separation has a value of 6.007 Å ($' = -x, 2 - y, 1 - z$). The axial positions of Ni2 ions are occupied by one nitrogen atom coming from a terminal azido ligand [Ni2–N12 = 2.220(9)] and by one nitrogen atoms coming from another terminal azido ligand or the oxygen atom of one aqua ligand [Ni2–N15/O32 = 2.191(9) Å, the N15 and O32 were restrained in the crystal structure refinement to occupy the same crystallographic position with site occupancies factors of 0.5 each]. The equatorial coordination sites are occupied by four atoms of the $valpn^{2-}$ Schiff-base ligand [Ni2–N3 = 2.024(9), Ni2–N4 = 2.006(10), Ni2–O6 = 2.032(7), Ni2–O7 = 2.031(6) Å]. The two Ni2 ions within the octanuclear unit are placed at a distance of 24.459 Å.

The gadolinium ions are located in the outer compartment of the $valpn^{2-}$ ligand and are nine-coordinated by oxygen atoms. The Gd1 ions are surrounded by four oxygen atoms of the Schiff-base ligand [Gd1–O1 = 2.544(6), Gd1–O2 = 2.360(6), Gd1–O3 = 2.389(6), Gd1–O4 = 2.556(6) Å], three oxygen atoms belonging to aqua ligands [Gd1–O12 = 2.439(8), Gd1–O13 = 2.467(8), Gd1–O14 = 2.460(7) Å], and two oxygen atoms coming from a carbonato bridge [Gd1–O9 = 2.486(7), Gd1–O10 = 2.415(7) Å].

The Gd2 ion is coordinated to four oxygen atoms of the $valpn^{2-}$ ligand [Gd2–O5 = 2.560(7), Gd2–O6 = 2.370(6), Gd2–O7 = 2.398(7), Gd2–O8 = 2.545(7) Å], three aqua ligands [Gd2–O15 = 2.424(8), Gd2–O16 = 2.432(8), Gd2–O17 = 2.461(7) Å], and two oxygen atoms from the bridging carbonato ligand which displays a two-(η^3 chelation) [Gd2–O9 = 2.465(7), Gd2–O11 = 2.456(6) Å]. The separation between the carbonato-bridged Gd^{III} ions is Gd1⋯Gd2 = 4.942 Å. The distances between the metal ions within the binuclear {NiGd} units are: Ni1⋯Gd1 = 3.538 and Ni2⋯Gd2 = 3.523 Å. The intramolecular Gd1⋯Gd1′ and Gd2⋯Gd2′ ($' = -x, 2 - y, 1 - z$) separations, are 10.016 and 19.610 Å, respectively. Selected bond distances and angles for **1** and **2** are given in Tables 2 and 3, respectively.

Magnetic properties

The ac susceptibility of **2** have been measured between 2 and 300 K (Fig. 2). The room temperature value of the $\chi_M T$ product, 36.8 cm^3 mol^{-1} K, corresponds to the one expected for the eight non-interacting ions (four Ni^{II} and four Gd^{III}): 36.3 cm^3 mol^{-1} K, assuming $g_{Ni} = 2.2$ and $g_{Gd} = 2$. The $\chi_M T$ product is constant down to 50 K, then it increases, reaching ~37.5 cm^3 mol^{-1} K at 8 K. Below this temperature, $\chi_M T$ decreases abruptly reaching ~33 cm^3 mol^{-1} K at 1.8 K. The spin Hamiltonian for

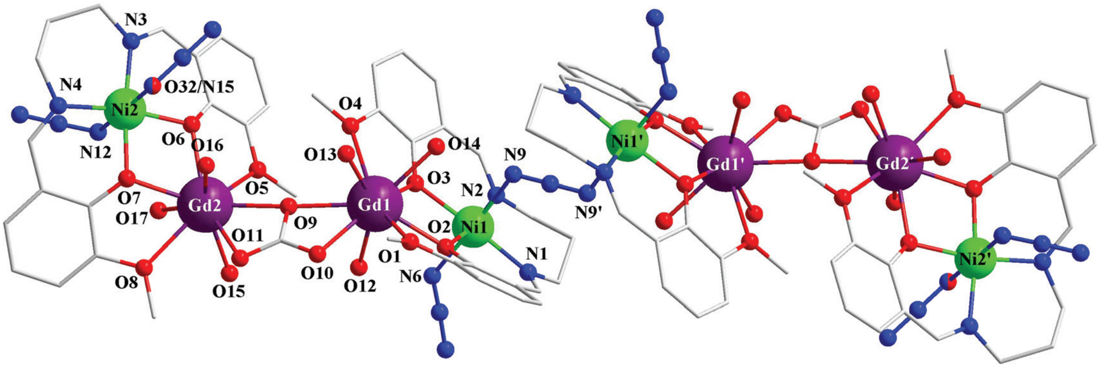

Fig. 1 View of the octanuclear cationic species $[[(N_3)_{1.5}(H_2O)_{0.5}Ni(valpn)Gd(H_2O)_3(\mu\text{-}CO_3)Gd(H_2O)_3(valpn)Ni(N_3)(\mu_{1,3}\text{-}N_3)_{0.5}]_2]^+$ in **2** ($' = -x, 2 - y, 1 - z$).

Table 2 Selected bond distances and angles for compound **1**

Ni1–N1	2.016(5)	N2–Ni1–N1	97.0(3)	O2–Sm1–O3	67.34(15)	O6–Sm2–O7	67.26(16)
Ni1–N2	2.032(6)	N2–Ni1–O2	170.0(2)	O2–Sm1–O10	109.20(17)	O6–Sm2–O15	133.7(2)
Ni1–N6	2.111(6)	N1–Ni1–O2	91.2(2)	O3–Sm1–O10	148.35(18)	O7–Sm2–O15	129.4(2)
Ni1–N9	2.190(6)	N2–Ni1–O3	91.3(2)	O2–Sm1–O12	72.4(2)	O6–Sm2–O16	79.0(2)
Ni1–O2	2.059(4)	N1–Ni1–O3	171.4(2)	O3–Sm1–O12	73.9(2)	O7–Sm2–O16	70.07(19)
Ni1–O3	2.049(4)	O2–Ni1–O3	80.34(18)	O10–Sm1–O12	75.2(2)	O15–Sm2–O16	144.4(2)
Ni2–N3	2.014(7)	N2–Ni1–N6	92.0(3)	O2–Sm1–O14	76.91(16)	O6–Sm2–O11	146.07(18)
Ni2–N4	2.020(6)	N1–Ni1–N6	92.0(3)	O3–Sm1–O14	73.52(16)	O7–Sm2–O11	114.76(16)
Ni2–N12	2.196(6)	O2–Ni1–N6	93.4(2)	O10–Sm1–O14	137.76(18)	O15–Sm2–O11	73.4(2)
Ni2–N15	2.206(7)	O3–Ni1–N6	90.1(2)	O12–Sm1–O14	141.70(19)	O16–Sm2–O11	71.1(2)
Ni2–O6	2.042(5)	N2–Ni1–N9	89.6(3)	O2–Sm1–O13	131.49(18)	O6–Sm2–O17	76.49(19)
Ni2–O7	2.025(5)	N1–Ni1–N9	88.7(2)	O3–Sm1–O13	130.76(18)	O7–Sm2–O17	74.10(17)
Ni2–O32	2.206(7)	O2–Ni1–N9	84.9(2)	O10–Sm1–O13	76.4(2)	O15–Sm2–O17	70.6(2)
Sm1–O1	2.556(5)	O3–Ni1–N9	88.9(2)	O12–Sm1–O13	148.2(2)	O16–Sm2–O17	142.22(19)
Sm1–O2	2.382(4)	N6–Ni1–N9	178.2(3)	O14–Sm1–O13	70.08(17)	O11–Sm2–O17	137.4(2)
Sm1–O3	2.398(4)	N4–Ni2–N3	97.7(3)	O2–Sm1–O9	143.12(16)	O6–Sm2–O9	104.72(16)
Sm1–O4	2.562(5)	N4–Ni2–O6	171.0(3)	O3–Sm1–O9	109.95(15)	O7–Sm2–O9	144.95(16)
Sm1–O9	2.500(5)	N3–Ni2–O6	91.1(3)	O10–Sm1–O9	52.73(16)	O15–Sm2–O9	81.8(2)
Sm1–O10	2.445(5)	N4–Ni2–O7	89.6(2)	O12–Sm1–O9	71.8(2)	O16–Sm2–O9	74.92(19)
Sm1–O12	2.435(6)	N3–Ni2–O7	172.6(2)	O14–Sm1–O9	139.30(17)	O11–Sm2–O9	52.66(16)
Sm1–O13	2.455(5)	O6–Ni2–O7	81.52(19)	O13–Sm1–O9	79.73(18)	O17–Sm2–O9	139.26(17)
Sm1–O14	2.477(5)	N4–Ni2–O32	92.2(3)	O2–Sm1–O1	62.88(15)	O6–Sm2–O8	127.75(17)
Sm2–O5	2.570(5)	N3–Ni2–O32	86.8(3)	O3–Sm1–O1	126.65(15)	O7–Sm2–O8	62.73(17)
Sm2–O6	2.381(5)	O6–Ni2–O32	90.1(2)	O10–Sm1–O1	69.59(17)	O15–Sm2–O8	74.5(2)
Sm2–O7	2.414(4)	O7–Ni2–O32	93.7(2)	O12–Sm1–O1	107.0(3)	O16–Sm2–O8	97.1(2)
Sm2–O8	2.560(6)	N4–Ni2–N12	89.0(2)	O14–Sm1–O1	77.73(19)	O11–Sm2–O8	72.76(17)
Sm2–O9	2.476(5)	N3–Ni2–N12	92.2(3)	O13–Sm1–O1	75.87(19)	O17–Sm2–O8	76.4(2)
Sm2–O11	2.462(5)	O6–Ni2–N12	88.9(2)	O9–Sm1–O1	121.05(16)	O9–Sm2–O8	124.73(17)
Sm2–O15	2.445(6)	O7–Ni2–N12	87.2(2)	O2–Sm1–O4	127.99(16)	O6–Sm2–O5	62.86(17)
Sm2–O16	2.424(6)	O32–Ni2–N12	178.5(3)	O3–Sm1–O4	63.05(15)	O7–Sm2–O5	125.49(17)
Sm2–O17	2.467(6)	Ni1–O2–Sm1	106.20(19)	O10–Sm1–O4	121.01(17)	O15–Sm2–O5	77.3(2)
		Ni1–O3–Sm1	105.95(19)	O12–Sm1–O4	106.8(3)	O16–Sm2–O5	118.2(2)
		Ni2–O6–Sm2	105.9(2)	O14–Sm1–O4	75.18(18)	O11–Sm2–O5	118.67(17)
		Ni2–O7–Sm2	105.23(19)	O13–Sm1–O4	76.26(19)	O17–Sm2–O5	74.3(2)
				O9–Sm1–O4	71.53(16)	O9–Sm2–O5	70.80(17)
				O1–Sm1–O4	146.27(19)	O8–Sm2–O5	144.6(2)

this system should include three exchange parameters (J_{NiGd}, J_{GdGd}, J_{NiNi}) and this, together with the high spin value of Gd, leads to the huge dimension of the matrix and does not make possible to solve the problem numerically. However, the magnetic behaviour of **2**, depicted in Fig. 2, can be understood, having in mind that: (i) the exchange interaction between phenoxo-bridged $\mathrm{N^{III}}$ and $\mathrm{Gd^{III}}$ ions is in most cases weak ferromagnetic, with J values ranging from 0.2 to ~5 $\mathrm{cm^{-1}}$;[8a,14] (ii) the exchange interaction between the carbonato-bridged $\mathrm{Gd^{III}}$ ions, if any, is very weak;[12d] (iii) the magnetic coupling between $\mathrm{Ni^{II}}$ ions connected by 1,3-azido bridges is, in most cases, antiferromagnetic, with J values as large as -114.5 $\mathrm{cm^{-1}}$;[15] rarely, it was showed to be ferromagnetic.[16] In case of complex **2**, the values for Ni1–N9–N10, Ni1′–N9′–N10, and τ dihedral angles are 121.53, 121.53, and 0°, respectively, which suggests a moderate antiferromagnetic coupling between $\mathrm{Ni^{II}}$ ions.[15c,d] Consequently, the increase of the $\chi_{\mathrm{M}}T$ product below 50 K is probably due to dominant ferromagnetic interactions (characteristic for the $\mathrm{Ni^{II}}$–$\mathrm{Gd^{III}}$ pair); below 10 K, a superposition of the antiferromagnetic interactions mentioned above with the zero field splitting effect associated to the $\mathrm{Ni^{II}}$ ions is likely to occur as shown by the drop of the $\chi_{\mathrm{M}}T$ product in Fig. 2.

The field dependence of magnetization $M(H)$ was measured at different temperatures as shown in Fig. 3. At high field and low temperature $M(H)$ tends to reach a value of $\sim 35N_{\mathrm{A}}\mu_{\mathrm{B}}$ although saturation is not completely achieved at 7 T. This is compatible with the 4 spins $S = 7/2$ of $\mathrm{Gd^{III}}$ and 4 spins $S = 1$ of $\mathrm{Ni^{II}}$ per formula unit and indicates that the magnetic field overcomes the weak (anti-)ferromagnetic interactions.

To get more insight we have also measured the specific heat $C(T,H)$ at low temperature in different applied magnetic field (Fig. 4). The $C(T)$ curve in zero field shows a Schottky anomaly with a maximum at 1 K. This anomaly reflects the degeneracy of the ground state due to both the small – but finite – anisotropy of the single $\mathrm{Ni^{II}}$ and $\mathrm{Gd^{III}}$ ions and to the weak and competitive interactions. The Schottky anomaly is progressively shifted towards higher temperatures with the application of magnetic field of increasing strength. For highest fields (*i.e.* 5, 7 T) the maximum disappears but at 15 K the specific heat is higher than in zero field, indicating that a significant amount of magnetic entropy is present at that temperature.

Starting from the specific heat, the change of entropy in magnetic field is evaluated by using the relation: $S(T)_{\mathrm{B}} = \int (C/T)_{\mathrm{B}}\mathrm{d}T + S_0$, where S_0 is an additive constant that accounts for the specific heat curve for $T < 0.3$ K. According to the Maxwell equation, the entropy variation can also be estimated using the magnetization data: $\Delta S_{\mathrm{m}}(T)_{\Delta \mathrm{B}} = \int (\partial M(T,\mathrm{B})/\partial \mathrm{B})_{\mathrm{B}}\,\mathrm{dB}$. In Fig. 5, the ΔS_{m} values obtained with the two different

Table 3 Selected bond distances and angles for compound **2**

Ni1–N1	2.028(7)	N2–Ni1–N1	96.7(3)	O2–Gd1–O3	67.49(18)	O6–Gd2–O7	67.5(2)
Ni1–N2	2.023(8)	N2–Ni1–O2	169.8(3)	O2–Gd1–O10	108.8(2)	O6–Gd2–O15	133.1(2)
Ni1–N6	2.093(10)	N1–Ni1–O2	91.5(3)	O3–Gd1–O10	147.4(3)	O7–Gd2–O15	129.2(3)
Ni1–N9	2.213(9)	N2–Ni1–O3	91.4(3)	O2–Gd1–O12	72.1(2)	O6–Gd2–O16	78.1(2)
Ni1–O2	2.043(6)	N1–Ni1–O3	171.7(3)	O3–Gd1–O12	73.6(3)	O7–Gd2–O16	70.2(2)
Ni1–O3	2.051(6)	O2–Ni1–O3	80.3(2)	O10–Gd1–O12	74.5(3)	O15–Gd2–O16	145.7(2)
Ni2–N3	2.025(9)	N2–Ni1–N6	92.9(4)	O2–Gd1–O14	77.1(2)	O6–Gd2–O11	145.3(2)
Ni2–N4	2.004(9)	N1–Ni1–N6	93.1(4)	O3–Gd1–O14	74.0(2)	O7–Gd2–O11	114.0(2)
Ni2–N12	2.221(9)	O2–Ni1–N6	92.7(3)	O10–Gd1–O14	138.2(2)	O15–Gd2–O11	74.9(2)
Ni2–N15	2.191(9)	O3–Ni1–N6	88.6(3)	O12–Gd1–O14	141.8(2)	O16–Gd2–O11	70.9(2)
Ni2–O6	2.032(7)	N2–Ni1–N9	89.1(3)	O2–Gd1–O13	132.1(2)	O6–Gd2–O17	76.5(2)
Ni2–O7	2.032(6)	N1–Ni1–N9	88.7(3)	O3–Gd1–O13	130.5(2)	O7–Gd2–O17	73.9(2)
Ni2–O32	2.191(9)	O2–Ni1–N9	85.1(3)	O10–Gd1–O13	77.4(3)	O15–Gd2–O17	70.2(2)
Gd1–O1	2.545(6)	O3–Ni1–N9	89.3(3)	O12–Gd1–O13	148.2(3)	O16–Gd2–O17	141.8(2)
Gd1–O2	2.360(6)	N6–Ni1–N9	177.2(4)	O14–Gd1–O13	70.0(2)	O11–Gd2–O17	138.2(2)
Gd1–O3	2.389(6)	N4–Ni2–N3	97.7(4)	O2–Gd1–O9	142.5(2)	O6–Gd2–O9	104.4(2)
Gd1–O4	2.557(6)	N4–Ni2–O6	170.5(3)	O3–Gd1–O9	108.8(2)	O7–Gd2–O9	145.2(2)
Gd1–O9	2.485(7)	N3–Ni2–O6	91.6(3)	O10–Gd1–O9	53.2(2)	O15–Gd2–O9	82.0(2)
Gd1–O10	2.414(7)	N4–Ni2–O7	89.3(3)	O12–Gd1–O9	71.2(2)	O16–Gd2–O9	75.0(3)
Gd1–O12	2.440(8)	N3–Ni2–O7	172.9(3)	O14–Gd1–O9	139.5(2)	O11–Gd2–O9	53.2(2)
Gd1–O13	2.469(8)	O6–Ni2–O7	81.3(3)	O13–Gd1–O9	80.2(2)	O17–Gd2–O9	139.1(2)
Gd1–O14	2.461(7)	N4–Ni2–O32	91.6(4)	O2–Gd1–O1	63.4(2)	O6–Gd2–O8	127.9(2)
Gd2–O5	2.561(7)	N3–Ni2–O32	87.5(4)	O3–Gd1–O1	127.3(2)	O7–Gd2–O8	62.7(2)
Gd2–O6	2.370(6)	O6–Ni2–O32	90.5(3)	O10–Gd1–O1	69.7(2)	O15–Gd2–O8	74.6(3)
Gd2–O7	2.399(6)	O7–Ni2–O32	93.2(3)	O12–Gd1–O1	107.2(3)	O16–Gd2–O8	98.2(3)
Gd2–O8	2.545(7)	N4–Ni2–N12	89.3(3)	O14–Gd1–O1	77.6(2)	O11–Gd2–O8	72.8(2)
Gd2–O9	2.466(6)	N3–Ni2–N12	91.5(3)	O13–Gd1–O1	76.0(2)	O17–Gd2–O8	76.2(2)
Gd2–O11	2.456(6)	O6–Ni2–N12	88.8(3)	O9–Gd1–O1	121.5(2)	O9–Gd2–O8	125.1(2)
Gd2–O15	2.425(7)	O7–Ni2–N12	87.7(3)	O2–Gd1–O4	128.4(2)	O6–Gd2–O5	63.2(2)
Gd2–O16	2.432(8)	O32–Ni2–N12	178.8(4)	O3–Gd1–O4	63.6(2)	O7–Gd2–O5	125.9(2)
Gd2–O17	2.461(7)	Ni1–O2–Gd1	106.7(2)	O10–Gd1–O4	121.0(2)	O15–Gd2–O5	76.5(3)
		Ni1–O3–Gd1	105.4(2)	O12–Gd1–O4	107.7(3)	O16–Gd2–O5	117.6(3)
		Ni2–O6–Gd2	106.1(3)	O14–Gd1–O4	74.8(2)	O11–Gd2–O5	118.9(2)
		Ni2–O7–Gd2	105.0(3)	O13–Gd1–O4	74.8(2)	O17–Gd2–O5	74.4(2)
				O9–Gd1–O4	71.4(2)	O9–Gd2–O5	70.2(2)
				O1–Gd1–O4	145.2(2)	O8–Gd2–O5	144.2(3)

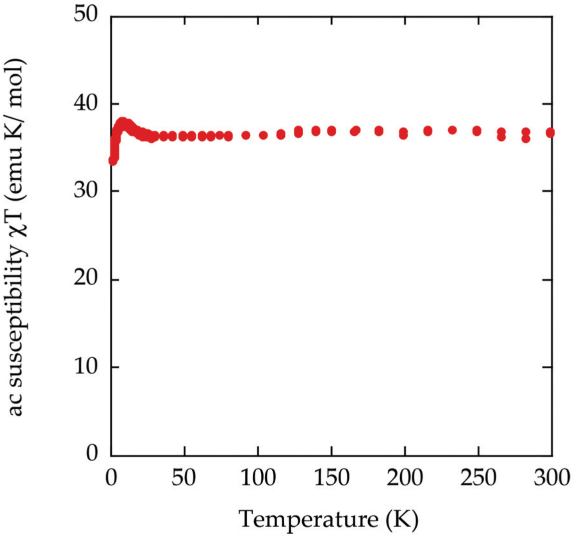

Fig. 2 Temperature dependence of the $\chi_M T$ product for **2**.

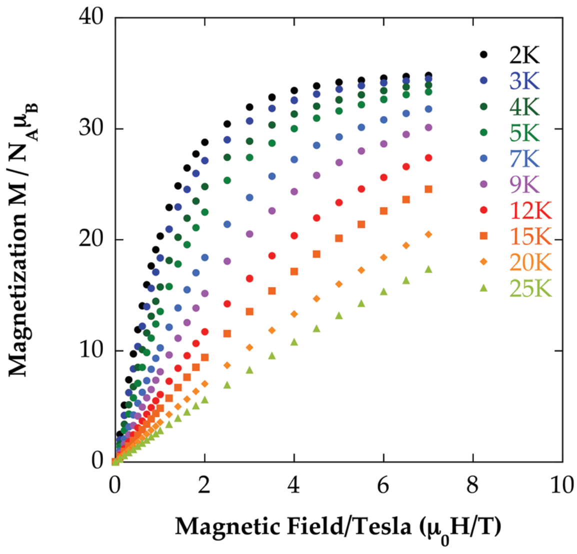

Fig. 3 Isothermal magnetization curves for **2** from 0 to 7 T.

methods compare very well one to another. The peak of $\Delta S_m(T)$ is found at about 3.5 K with a maximum value of $\Delta S_m[0\text{–}7\ \text{T}] = 19\ \text{J kg}^{-1}\ \text{K}^{-1}$. This peak results not particularly pronounced but the entropy variation $\Delta S_m[0\text{–}7\ \text{T}]$ is still large ($>5\ \text{J kg}^{-1}\ \text{K}^{-1}$) at 20 K. Thus while ΔS_m value is comparable to those reported for other molecular Gd^{III} complexes,[4] it turns out that the process of entropy removal is spread over a wider temperature range (1–20 K) in this complex.

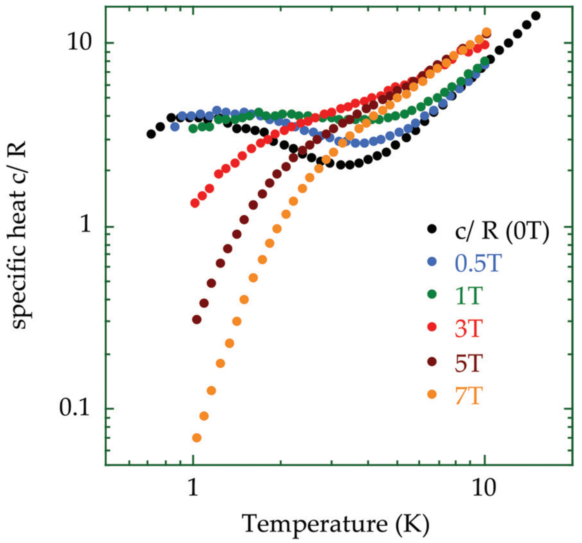

Fig. 4 Temperature dependence of specific heat measured at different applied magnetic fields. The Schottky anomaly at zero field has a maximum at 1 K and it is spread towards higher temperature with increasing magnetic field.

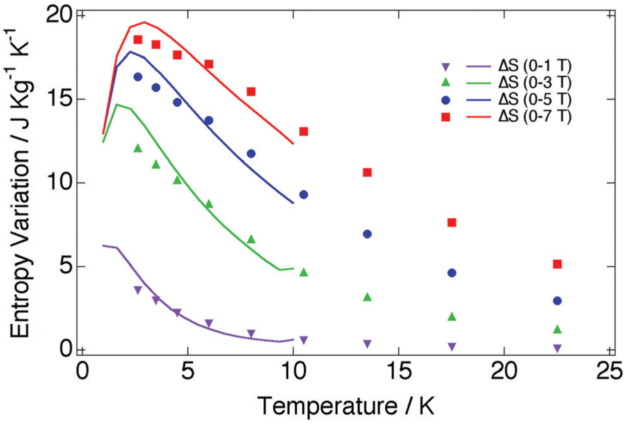

Fig. 5 Entropy variation between 0 T and 7 T calculated from magnetization (markers) and specific heat (lines) data.

Conclusions

In conclusion, we have obtained two novel octanuclear $[Ni^{II}_4\text{-}Ln^{III}_4]$ [Ln = Sm, Gd] molecular clusters through fixation of atmospheric CO_2. The eight metal ions are held together by three different types of bridge: phenoxo, carbonato and azido. The increasing number of such complexes shows that slow crystallization processes in the presence of a basic reagent (*e.g.* triethylamine) favor the absorption of the CO_2, with the formation of carbonato bridged species. The investigation of the magnetic properties of the $[Ni^{II}_4Gd^{III}_4]$ complex reveals a significant magnetocaloric effect ($\Delta S_m[0\text{–}7\ T] = 19\ J\ kg^{-1}\ K^{-1}$).

Acknowledgements

Financial support from the UEFISCDI (grant PNII-ID-PCCE-2011–2-0050) is gratefully acknowledged.

References

1 (*a*) M. Andruh, J.-P. Costes, C. Diaz and S. Gao, *Inorg. Chem.*, 2009, **48**, 3342; (*b*) R. Sessoli and A. K. Powell, *Coord. Chem. Rev.*, 2009, **253**, 2328; (*c*) M. Sakamoto, K. Manseki and H. Okawa, *Coord. Chem. Rev.*, 2001, **219–221**, 379; (*d*) J. S. Miller and D. Gatteschi, *Chem. Soc. Rev.*, 2011, **40**, 3065.

2 A. Bencini, C. Benelli, A. Caneschi, R. L. Carlin, A. Dei and D. Gatteschi, *J. Am. Chem. Soc.*, 1985, **107**, 8128.

3 D. Gatteschi, R. Sessoli and J. Villain, *Molecular Nanomagnets*, Oxford University Press, New York, 2006.

4 (*a*) M. Evangelisti, in *Molecular Magnets, Physics and Applications*, ed. J. Bartolomè, F. Luis and J. F. Fernandez, Springer Verlag, 2014, ISSN 1434-4904, pp. 365–387; (*b*) R. Sessoli, *Angew. Chem., Int. Ed.*, 2011, **50**, 2; (*c*) M. Evangelisti and E. K. Brechin, *Dalton Trans.*, 2010, **39**, 4672; (*d*) A. S. Dinca, A. Ghirri, A. M. Madalan, M. Affronte and M. Andruh, *Inorg. Chem.*, 2012, **51**, 3935.

5 (*a*) C. Zimm, A. Jastrab, A. Sternberg, V. K. Pecharsky, K. A. Gschneidner Jr., M. Osborne and I. Anderson, *Adv. Cryog. Eng.*, 1998, **43**, 1759; (*b*) V. K. Pecharsky and K. A. Gschneidner Jr., *J. Magn. Magn. Mater.*, 1999, **200**, 44; (*c*) K. A. Gschneidner Jr., A. O. Pecharsky and V. K. Pecharsky, in: *Cryocoolers II*, ed. R. S. Ross Jr., Kluwer Academic/Plenum Press, New York, 2001, p. 433.

6 (*a*) M. Manoli, R. D. L. Johnstone, S. Parsons, M. Murrie, M. Affronte, M. Evangelisti and E. K. Brechin, *Angew. Chem., Int. Ed.*, 2007, **46**, 4456; (*b*) M. Evangelisti, A. Candini, A. Ghirri, M. Affronte, E. K. Brechin and E. J. L. McInnes, *Appl. Phys. Lett.*, 2005, **87**, 072504; (*c*) Y.-Z. Zheng, M. Evangelisti, F. Tuna and R. E. P. Winpenny, *J. Am. Chem. Soc.*, 2012, **134**, 1057; (*d*) F.-S. Guo, J.-D. Leng, J.-L. Liu, Z.-S. Meng and M.-L. Tong, *Inorg. Chem.*, 2012, **51**, 405; (*e*) M. Evangelisti, O. Roubeau, E. Palacios, A. Camón, T. Hooper, E. K. Brechin and J. J. Alonso, *Angew. Chem., Int. Ed.*, 2011, **50**, 6606; (*f*) Y.-Z. Zheng, M. Evanghelisti and R. E. P. Winpenny, *Angew. Chem., Int. Ed.*, 2011, **50**, 3692; (*g*) S. K. Langley, N. F. Chilton, B. Moubaraki, T. Hooper, E. K. Brechin, M. Evanghelisti and K. S. Murray, *Chem. Sci.*, 2011, **2**, 1166; (*h*) J.-B. Peng, Q.-C. Zhang, X.-J. Kong, Y.-P. Ren, L.-S. Long, R.-B. Huang, L.-S. Zheng and Z. Zheng, *Angew. Chem., Int. Ed.*, 2011, **50**, 1; (*i*) F.-S. Guo, Y.-C. Chen, J.-L. Liu, J.-D. Leng, Z.-S. Meng, P. Vrábel, M. Orendáč and M.-L. Tong, *Chem. Commun.*, 2012, **48**, 12219.

7 (*a*) R. D. McMichael, R. D. Shull, L. J. Swartzendruber, L. H. Bennett and R. E. Watson, *J. Magn. Magn. Mater.*, 1992, **111**, 29; (*b*) L. H. Bennett, R. D. McMichael,

H. C. Tang and R. E. Watson, *J. Appl. Phys.*, 1994, **75**, 5493; (*c*) M. Evangelisti, A. Candini, A. Ghirri, M. Affronte, S. Piligkos, E. K. Brechin and E. J. L. McInnes, *Polyhedron*, 2005, **24**, 2573; (*d*) R. Shaw, R. Laye, L. Jones, D. Low, C. Talbot-Eeckelaers, Q. Wei, C. Milios, S. Teat, M. Helliwell, J. Raftery, M. Evangelisti, M. Affronte, D. Collison, E. K. Brechin and E. J. L. McInnes, *Inorg. Chem.*, 2007, **46**, 4968.

8 (*a*) T. D. Pasatoiu, J. P. Sutter, A. M. Madalan, F. Z. C. Fellah, C. Duhayon and M. Andruh, *Inorg. Chem.*, 2011, **50**, 5890; (*b*) T. D. Pasatoiu, C. Tiseanu, A. M. Madalan, B. Jurca, C. Duhayon, J. P. Sutter and M. Andruh, *Inorg. Chem.*, 2011, **50**, 5879.

9 (*a*) T. D. Pasatoiu, M. Etienne, A. M. Madalan, M. Andruh and R. Sessoli, *Dalton Trans.*, 2010, **39**, 4802; (*b*) T. D. Pasatoiu, M. Etienne, A. M. Madalan, R. Sessoli and M. Andruh, *Rev. Roum. Chim.*, 2012, **57**, 507.

10 (*a*) N. Kitajima, K. Fujisawa, T. Koda, S. Hikichi and Y. Moro-oka, *J. Chem. Soc., Chem. Commun.*, 1990, 1357; (*b*) T. Tanase, S. Nitta, S. Yoshikawa, K. Kobayashi, T. Sakurai and S. Yano, *Inorg. Chem.*, 1992, **31**, 1058; (*c*) M. M. El-Hendawy, N. J. English and D. A. Mooney, *Inorg. Chem.*, 2012, **51**, 5282; (*d*) M. Ito and Y. Takita, *Chem. Lett.*, 1996, 929; (*e*) M. Fondo, N. Ocampo, A. M. García-Deibe, R. Vicente, M. Corbella, M. R. Bermejo and J. Sanmartín, *Inorg. Chem.*, 2006, **45**, 255.

11 (*a*) S. K. Langley, B. Moubaraki and K. S. Murray, *Inorg. Chem.*, 2012, **51**, 3947; (*b*) H. Tian, L. Zhao, Y. N. Guo, Y. Guo, J. Tang and Z. Liu, *Chem. Commun.*, 2012, **48**, 708; (*c*) A. K. Ghosh, M. Pait, M. Shatruk, V. Bertolasic and D. Ray, *Dalton Trans.*, 2014, **43**, 1970; (*d*) J. Vallejo, J. Cano, I. Castro, M. Julve, F. Lloret, O. Fabelo, L. Cañadillas-Delgado and E. Pardo, *Chem. Commun.*, 2012, **48**, 7726.

12 (*a*) S. Sakamoto, S. Yamauchi, H. Hagiwara, N. Matsumoto, Y. Sunatsuki and N. Re, *Inorg. Chem. Commun.*, 2012, **26**, 20; (*b*) B. Zhang, X. Zheng, H. Su, Y. Zhu, C. Du and M. Song, *Dalton Trans.*, 2013, **42**, 8571; (*c*) S. Titos-Padilla, J. Ruiz, J. M. Herrera, E. K. Brechin, W. Wersndorfer, F. Lloret and E. Colacio, *Inorg. Chem.*, 2013, **52**, 9620; (*d*) S. Sakamoto, T. Fujinami, K. Nishi, N. Matsumoto, N. Mochida, T. Ishida, Y. Sunatsuki and N. Re, *Inorg. Chem.*, 2013, **52**, 7218.

13 K. Nakamoto, *Infrared and Raman Infrared and Raman Spectra of Inorganic and Coordination Compounds, Part B, Applications in Coordination, Organometallic, and Bioinorganic Chemistry*, John Wiley & Sons, Inc., Hoboken, New Jersey, 6th edn, 2009.

14 (*a*) J.-P. Costes, F. Dahan, A. Dupuis and J. P. Laurent, *Inorg. Chem.*, 1997, **36**, 4284; (*b*) J.-P. Costes, T. Yamaguchi, M. Kojima and L. M. Vendier, *Inorg. Chem.*, 2009, **48**, 5555; (*c*) J.-P. Sutter, S. Dhers, R. Rajamani, S. Ramasesha, J.-P. Costes, C. Duhayon and L. Vendier, *Inorg. Chem.*, 2009, **48**, 5820; (*d*) P. Khuntia, M. Mariani, A. V. Mahajan, A. Lascialfari, F. Borsa, T. D. Pasatoiu and M. Andruh, *Phys. Rev. B: Condens. Matter Mater. Phys.*, 2011, **84**, 184439; (*e*) V. Chandrasekhar, B. M. Pandian, R. Boomishankar, A. Steiner, J. J. Vittal, A. Houri and R. Clérac, *Inorg. Chem.*, 2008, **47**, 4918; (*f*) N. Bridonneau, L.-M. Chamoreau, P. P. Lainé, W. Wernsdorfer and V. Marvaud, *Chem. Commun.*, 2013, **49**, 9476; (*g*) T. Shiga, N. Ito, A. Hidaka, H. Okawa, S. Kitagawa and M. Ohba, *Inorg. Chem.*, 2007, **46**, 3492; (*h*) M.-G. Alexandru, D. Visinescu, S. Shova, F. Lloret and M. Andruh, *Inorg. Chem.*, 2013, **52**, 11627.

15 (*a*) J. Ribas, M. Monfort, C. Diaz, C. Bastos and X. Solans, *Inorg. Chem.*, 1993, **32**, 3557; (*b*) J. Ribas, A. Escuer, M. Monfort, R. Vicente, R. Cortés, L. Lezama and T. Rojo, *Coord. Chem. Rev.*, 1999, **193–195**, 1027; (*c*) S. S. Massoud, F. A. Mautner, R. Vicente, A. A. Gallo and E. Ducasse, *Eur. J. Inorg. Chem.*, 2007, 1091; (*d*) R. Cortes, K. Urtiaga, L. Lezama, J. L. Pizarro, A. Goñi, M. I. Arriortua and T. Rojo, *Inorg. Chem.*, 1994, **33**, 4009.

16 (*a*) P. S. Mukherjee, S. Dalai, E. Zangrando, F. Lloret and N. R. Chaudhuri, *Chem. Commun.*, 2001, 1444; (*b*) A. Escuer, C. J. Harding, Y. Dussart, J. Nelson, V. McKee and R. Vicente, *J. Chem. Soc., Dalton Trans.*, 1999, 223.