Four Co^{II}-Gd^{III} mixed-metal phosphonate clusters as molecular magnetic refrigerants

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Abstract

The building of 3d-Gd clusters are very essential in the fields of magnetic refrigerants. Three bulky phosphonic acids: (9-methyl-9H-fluoren-9-yl)phosphonic acid (RPO_3H_2), (2,7-di-tert-butyl-9-methyl-9H-fluoren-9-yl)phosphonic acid ($R'PO_3H_2$), and (9-(sec-butyl)-2,7-di-tert-butyl-9H-fluoren-9-yl)phosphonic acid ($R''PO_3H_2$) have been employed to construct four Co^{II}-Gd^{III} clusters $[Co^{II}_2Gd^{III}_3(OH)(RPO_3)_2(^tBuCO_2)_8(^tBuCO_2H)_2(C_5H_5N)(H_2O)_2] \cdot 2H_2O \cdot ^tBuCO_2H$ (1), $[Co^{II}_4Gd^{III}_3(OH)_2(RPO_3)_2(^tBuCO_2)_{11}(py)(CH_3CN)(H_2O)_2] \cdot CH_3CN$ (2), $[Co^{II}_3Gd^{III}_3(OH)_2(R'PO_3)_2(^tBuCO_2)_9(^tBuCO_2H)(H_2O)_2] \cdot ^tBuCO_2H \cdot 2CH_2Cl_2$ (3) and $[Co^{II}_3Gd^{III}_3(R''PO_3)_2(^tBuCO_2)_5(CH_3CN)(H_2O)_4] \cdot ^tBuCO_2H \cdot 3CH_3CN$ (4) under ambient condition. Clearly, the varied hindrance of fluorenyl groups are responsible for the formation of various clusters. Single crystal analysis indicates that the metal ions arrange in one plane in each cluster. Magnetic studies show that the entropy changes are 18.3, 19.8, 20.0 and 9.6 J kg⁻¹ K⁻¹ for 1–4, respectively, from which we can see these values are nearly proportional to the percentage of the gadolinium in the core.

Introduction

The design and synthesis of heterometallic transition metal clusters are motivated not only by their intriguing properties but also their potential applications as functional materials.^[1] The magnetocaloric effect (MCE) describes the change of magnetic entropy (ΔS_m) following a change of the applied magnetic field (ΔH) and has potential technological use in cooling applications.^[2] The very large MCE observed in some molecular coordination clusters suggests they are potential candidates to replace the expensive and rare helium-3.^[2] Former studies on magnetocaloric clusters

focus on the 3d clusters such as $\{\text{Mn}_{12}\}$,^[3] $\{\text{Fe}_8\}$,^[4] and $\{\text{Mn}_{19}\}$.^[5] The isothermal entropy change can be maximized by incorporation of Gd^{III} ions into the molecules as it provides the largest entropy per single ion.^[6] Recently, Gd^{III} ions have been doped in the clusters and isolated 3d-4f clusters such as $\{\text{Mn}_4\text{Gd}_4\}$,^[7] $\{\text{Ni}_6\text{Gd}_6\}$,^[8] $\{\text{Cu}_5\text{Gd}_4\}$ ^[9] and $\{\text{Ni}_{12}\text{Gd}_{36}\}$ ^[10] for the searching of cryogenic magnetic refrigeration materials with better performance.

Phosphonic acid of the general formula RPO_3H_2 (R = alkyl or aryl) have been proved to be ideal for the construction of molecular coordination clusters.^[11] Employing $^t\text{BuPO}_3\text{H}_2$, PhPO_3H_2 and $\text{PhCH}_2\text{PO}_3\text{H}_2$ as ligands, Zheng isolated several 3d-4f phosphonate clusters with large MCE.^[12] When R is methyl, phenyl, n-hexyl, benzyl or n-octyl, five Wells-Dawson cages were obtained that could function as molecular refrigerants.^[13] Recently, two $\text{Co}^{\text{II}}_4\text{Gd}^{\text{III}}_6$ clusters bearing fluorenyl and carbazolyl phosphonate groups have been constructed by us.^[14] The structural diversity may be due to ligand's solubility and bonding flexibility. Interestingly, we observed a larger MCE in the helmet-like cluster $[\text{Co}^{\text{II}}_4\text{Gd}^{\text{III}}_6(\text{FlumePO}_3)_3(^t\text{BuCO}_2)_{14}(\mu_3\text{-OH})_6(\text{H}_2\text{O})_2(\text{CH}_3\text{CN})]$ because of the large Gd^{III} /ligand mass ratio. A natural extension to these studies is the investigation of the coordination chemistry of analogous organic molecules in which the R group is replaced by an alternative bulky group.^[15] In this regard, we choose three phosphonic acids to react them with the preformed precursors $[\text{Co}^{\text{II}}_2(\mu\text{-OH}_2)(^t\text{BuCO}_2)_4] \cdot (^t\text{BuCO}_2\text{H})_4$ Co_2 ,^[16] $[\text{Co}_9(^t\text{BuCO}_2\text{H})_4(\text{O})_3(\text{OH})_3(^t\text{BuCO}_2)_{12}]$ Co_9 ,^[17] and $[\text{Gd}_2(^t\text{BuCO}_2)_6(^t\text{BuCO}_2\text{H})_6]$ Gd_2 ,^[18] and successfully isolated four clusters with four different classes in terms of structural features. Their applications as magnetic refrigerants were studied.

Scheme 1 Coordination modes of the phosphonates. Labeled with Harris Notation.

Experimental Section

(9-methyl-9H-fluoren-9-yl)phosphonic acid (RPO_3H_2), (2,7-di-tert-butyl-9-methyl-9H-fluoren-9-yl)phosphonic acid ($R'PO_3H_2$), and (9-(sec-butyl)-2,7-di-tert-butyl-9H-fluoren-9-yl)phosphonic acid ($R''PO_3H_2$) were prepared according to the literature method.^[19] All other starting materials were purchased as reagent grade and used without further purification. Elemental analyses were performed on a Perkin Elmer 240C elemental analyzer. The IR spectra were obtained as KBr disks on a VECTOR 22 spectrometer. The magnetic susceptibility data were obtained on a microcrystalline sample, using a Quantum Design MPMS-XL7 SQUID magnetometer. Diamagnetic corrections were made for both the sample holder and the compound estimated from Pascal's constants.^[20]

Table 1. Crystallographic data for compounds **1–4**

	1	2	3	4
Formula	$C_{176}H_{278}Co_4Gd_6N_2O_{66}P_4$	$C_{92}H_{138}Co_4Gd_3N_3O_{32}P_2$	$C_{100}H_{163}Cl_2Co_3Gd_3O_{32}P_2$	$C_{88}H_{141}Co_3GdN_4O_{22}P_2$
<i>M</i>	4781.12	2567.46	2658.68	2003.03
Crystal system	Orthorhombic	Monoclinic	Triclinic	Triclinic
Space group	P2(1)2(1)2(1)	P2(1)/n	P $\bar{1}$	P $\bar{1}$
<i>a</i> /Å	22.261(3)	14.4084(10)	15.713(3)	13.4207(10)
<i>b</i> /Å	27.256(3)	28.2465(19)	16.239(3)	16.2792(12)
<i>c</i> /Å	37.179(4)	27.8048(18)	26.064(5)	27.525(2)
α /°	90	90	76.881(4)	96.6010(17)
β /°	90	94.4000(3)	88.303(5)	100.6610(15)
γ /°	90	90	71.614(4)	114.1360(15)
<i>V</i> /Å ³	22558(5)	11282.8(13)	6140(2)	5270.0(7)
<i>Z</i>	4	4	2	2
<i>D_c</i> /Mg m ⁻³	1.408	1.511	1.438	1.262
μ /mm ⁻¹	2.125	2.411	2.130	1.178
<i>F</i> (000)	9712	5188	2712	2096
Total/Unique reflections	97183 / 39039	105161 / 19206	37122 / 20249	70694 / 18427
<i>R</i> _{int}	0.0668	0.0432	0.0288	0.0367
GooF on <i>F</i> ²	1.082	1.144	1.039	1.111
<i>R</i> ₁ , <i>wR</i> ₂ ^a [<i>I</i> > 2σ(<i>I</i>)]	0.0591, 0.1453	0.0425, 0.1024	0.0475, 0.1254	0.0701, 0.2099
<i>R</i> (all data)	0.0917, 0.1695	0.0658, 0.1225	0.0531, 0.1302	0.0911, 0.2428
Largest diff. peak and hole (e. Å ⁻³)	1.086, -0.756	1.343, -0.984	2.936, -2.105	2.209, -1.061

Synthesis of [Co^{II}₂Gd^{III}₃(OH)(RPO₃)₂(^tBuCO₂)₈(^tBuCO₂H)₂(py)(H₂O)₂]·2H₂O·^tBuCO₂H (**1**)

Compound **1** was obtained by mixing **Co**₂ (0.0949 g, 0.1 mmol), **Gd**₂ (0.1149 g, 0.075 mmol),

RPO_3H_2 (0.0260 g, 0.1 mmol) and 10 μL pyridine (py) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) (16 mL) and stirred at room temperature for 24 h. The resulting solid was filtered and the violet solution was kept in a vial for ca. two weeks. Purple crystals were collected by filtration, yield: 0.080 g, 35% (based on Gd_2). **Elemental Anal. Calc. for 1**, $\text{C}_{88}\text{H}_{139}\text{Co}_2\text{Gd}_3\text{NO}_{33}\text{P}_2$: C, 44.21; H, 5.86; N, 0.59. Found: C, 44.50; H, 5.61; N, 0.35 %. IR (cm^{-1} , KBr): 2961 (s), 1550 (vs), 1485 (vs), 1425 (vs), 1230 (s), 1132 (s), 1094 (m), 1064 (m), 1043 (m), 1028 (m), 981 (s), 733 (m), 607 (s), 568 (s).

Synthesis of $[\text{Co}^{\text{II}}_4\text{Gd}^{\text{III}}_3(\text{OH})_2(\text{RPO}_3)_2(\text{tBuCO}_2)_{11}(\text{py})(\text{CH}_3\text{CN})(\text{H}_2\text{O})_2]\cdot\text{CH}_3\text{CN}$ (2)

Compound **2** was obtained by mixing Co_2 (0.0949 g, 0.1 mmol), Gd_2 (0.1149 g, 0.075 mmol) and RPO_3H_2 (0.0260 g, 0.1 mmol) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) (16 mL) and stirred at room temperature for 24 h. The resulting solid was filtered and the purple solution was kept in a vial after adding 10 μL pyridine. Two weeks later purple crystals were collected by filtration, yield: 0.159 g, 55% (based on Gd_2). **Elemental Anal. Calc. for 2**, $\text{C}_{92}\text{H}_{138}\text{Co}_4\text{Gd}_3\text{N}_3\text{O}_{32}\text{P}_2$: C, 43.04; H, 5.42; N, 1.64. Found: C, 43.39; H, 5.21; N, 1.39 %. IR (cm^{-1} , KBr): 2962 (s), 1550 (vs), 1485 (vs), 1424 (vs), 1231 (s), 1132 (s), 1093 (m), 1044 (m), 988 (s), 750 (m), 608 (s), 566 (s).

Synthesis of $[\text{Co}^{\text{II}}_3\text{Gd}^{\text{III}}_3(\text{OH})_2(\text{R}'\text{PO}_3)_2(\text{tBuCO}_2)_9(\text{tBuCO}_2\text{H})(\text{H}_2\text{O})_2]\cdot\text{tBuCO}_2\text{H}\cdot 2\text{CH}_2\text{Cl}_2$ (3)

Compound **3** was obtained by mixing Co_2 (0.0949 g, 0.1 mmol), Gd_2 (0.1149 g, 0.075 mmol) and $\text{R}'\text{PO}_3\text{H}_2$ (0.0260 g, 0.1 mmol) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) (16 mL) and stirred at room temperature for 24 h. The resulting solid was filtered and the purple solution was kept in a vial for ca. two weeks. Purple crystals were collected by filtration, yield: 0.135 g, 45% (based on Gd_2). **Elemental Anal. Calc. for 3**, $\text{C}_{100}\text{H}_{163}\text{Cl}_2\text{Co}_3\text{Gd}_3\text{O}_{32}\text{P}_2$: C, 45.17; H, 6.18. Found: C, 45.39; H, 5.91 %. IR (cm^{-1} , KBr): 2963 (vs), 1551 (vs), 1485 (vs), 1421 (vs), 1363 (s), 1229 (s), 1143 (s), 1040 (s), 976 (s), 614 (m), 581 (m).

Synthesis of $[\text{Co}^{\text{II}}_3\text{Gd}^{\text{III}}_3(\text{R}''\text{PO}_3)_2(\text{tBuCO}_2)_5(\text{CH}_3\text{CN})(\text{H}_2\text{O})_4]\cdot\text{tBuCO}_2\text{H}\cdot 3\text{CH}_3\text{CN}$ (4)

Compound **4** was obtained by mixing Co_9 (0.2251 g, 0.1 mmol), Gd_2 (0.0306 g, 0.02 mmol) and $\text{R}''\text{PO}_3\text{H}_2$ (0.0414 g, 0.1 mmol) in $\text{CH}_2\text{Cl}_2/\text{CH}_3\text{CN}$ (1:1) (16 mL) and stirred at room temperature for 24 h. The resulting solid was filtered and the purple solution was kept in a vial for ca. two weeks. Purple crystals were collected by filtration, yield: 0.044 g, 56% (based on Gd_2). **Elemental Anal.**

Calc. for 4, $C_{88}H_{141}Co_3GdN_4O_{22}P_2$: C, 52.77; H, 7.10; N, 2.80. Found: C, 52.49; H, 6.90; N, 2.55 %. IR (cm^{-1} , KBr): 2962 (vs), 1872 (vs), 1554 (vs), 1484 (vs), 1423 (vs), 1363 (s), 1228 (s), 1157 (s), 1097 (s), 1064 (s), 1004 (s), 819 (m), 613 (s), 550 (s).

Results and discussion

Synthesis

We have used $[Gd_2(^tBuCO_2)_6(^tBuCO_2H)_6]$ **Gd₂** and two kinds of cobalt, namely, $[Co_2(\mu-OH)_2(^tBuCO_2)_4(^tBuCO_2H)_4]$ **Co₂** and $[Co_9(^tBuCO_2H)_4(O)_3(OH)_3(^tBuCO_2)_{12}]$ **Co₉** as starting materials, to react with three fluorenyl phosphonate ligands to produce four different clusters under ambient conditions. The structural diversity is probably due to the different steric hindrance of the fluorenyl groups although they do not participate in the coordination with metal ions. A clue was found that the ligand with larger hindrance could give a smaller polynuclear core due to the repulsive interactions between the organic groups. The metal source as well as addition of pyridine also contribute to the formation of the final clusters. To our knowledge, clusters **1–4** are additional examples of rare 3d-4f phosphonate clusters bearing bulky organic *R* groups.^[14,15]

Figure 1. a) The structure of **1** in the crystal. Color codes: blue, cobalt; purple, lanthanide; green, phosphorous; yellow, oxygen; gray, carbon; hydrogen atoms and lattice solvent molecules are omitted for clarity. b) The core structure of **1**.

Structural description

Single crystal analysis reveals that compound **1** crystallizes in the triclinic space group $P2(1)2(1)2(1)$. There are two $[Co^{II}_2Gd^{III}_3(OH)(RPO_3)_2(^tBuCO_2)_8(^tBuCO_2H)_2(py)(H_2O)_2]$ molecules crystallize in the asymmetry unit and each features a planar structure (Figure 1). This structure can be viewed as three Gd^{III} ions are bridged by two phosphonate groups into a triangle with two sides further connected with the Co^{II} ions. Co1 has a trigonal bipyramidal configuration with O6, O10

and O15 atoms located on the plane, and O2 and N1 atoms in the vertex. Co2 has a distorted octahedral coordination geometry surrounded by O18, O19, O22, O25 and O27 atoms from five pivalates, and O1 from μ_3 -OH. The Co–O distances range from 1.956(10) to 2.231(9) Å, which are consistent with that observed in $\{\text{Co}^{\text{II}}_8\text{Gd}^{\text{III}}_8\}$ ^[12a], $\{\text{Na}_{0.5}[\text{Co}_3(\mu_4\text{-Mtta})_{1.5}(\mu_2\text{-OAc})_3(\mu_3\text{-OAc})(\mu_3\text{-OH})]\}_n$ (Mtta = 5-methyl tetrazolate), and a series of Co clusters based on 5-(pyridin-4-yl)isophthalic acid, 4,4'-{[1,2-Phenylenebis(methylene)]bis(oxy)}dibenzoate and 4,4'-oxydibenzoic acid.^[21] Each Gd^{III} ion is eight-coordinated and can be described as a distorted double-capped trigonal prism, featuring coordination by oxygen atoms from phosphonate, pivalates, OH and H_2O . The Gd–O bond lengths fall in the range of 2.250(8)–2.549(8) Å, which are comparable to those in $\{\text{Gd}_6\}$.^[22] One phosphonate group shows 3.111 coordination mode to coordinate with three Gd^{III} ions, while the other shows 4.221 coordination mode to link four metal centres (Scheme 1).^[23] The pivalate groups exhibit 2.21, 2.11, 1.11 and 1.10 modes.

Figure 2. a) The structure of **2** in the crystal. Color codes: blue, cobalt; purple, lanthanide; green, phosphorous; yellow, oxygen; gray, carbon; hydrogen atoms and lattice solvent molecules are omitted for clarity. b) The core structure of **2**.

Single crystal analysis reveals that compound **2** crystallizes in the monoclinic space group $P2(1)/n$ and features a butterfly structure (Figure 2). This structure can be viewed as the Gd2 atom sites on the head position, and each side of the wing is occupied by one $\{\text{Co}_2\text{Gd}(\text{OH})\}$ unit. Co1 and Co2 have distorted octahedral coordination geometries, while Co3 and Co4 have trigonal bipyramidal configurations. The Co–O distances range from 1.955(5) to 2.375(4) Å, which are consistent with that observed in compound **1**. Each Gd^{III} ion is eight-coordinated and can be described as a distorted

double-capped trigonal prism, featuring coordination by oxygen atoms from phosphonate, pivalates and H₂O. The Gd–O bond lengths fall in the range of 2.313(5)–2.464(4) Å, which are comparable to those in Gd^{III} clusters.^[24] The structure can also be viewed as a triangle {Gd₃O₆} unit connects with a linear {Co₄O₄} unit through phosphonate and carboxylate bridges. The Gd1⋯Gd2 and Gd2⋯Gd3 distances are 3.97 and 3.94 Å, respectively. One phosphonate group shows 4.221 coordination mode to coordinate with two Gd^{III} and two Co^{II} ions, while the other one shows 5.222 coordination mode to link five metal centres (Scheme 1). The pivalate groups exhibit 2.21, 2.11, 1.11 and 1.10 modes.

Figure 3. a) The structure of **3** in the crystal. Color codes: blue, cobalt; purple, lanthanide; green, phosphorous; yellow, oxygen; gray, carbon; hydrogen atoms and lattice solvent molecules are omitted for clarity. b) The core structure of **3**.

Compound **3** crystallizes in the triclinic space group *P* $\bar{1}$ and features a planar structure (Figure 3). This structure can be viewed as three Gd^{III} ions are bridged by two phosphonate groups into a triangle with each side further connected with one Co^{II} ions. Co1 and Co3 have the distorted tetrahedral coordination geometries, while Co2 has a distorted octahedral coordination geometry. The Co–O distances range from 1.948(4) to 2.124(4) Å, which are consistent with that observed in {Co^{II}₄Gd^{III}₆}.^[14] Each Gd^{III} ion is eight-coordinated and can be described as a distorted double-capped trigonal prism, featuring coordination by oxygen atoms from phosphonate, pivalates and H₂O. The Gd–O bond lengths fall in the range of 2.290(4)–2.573(4) Å, which are comparable to those in Gd^{III} clusters.^[24] The structure can also be viewed as two {CoGd₂(OH)} triangles connect with each other by sharing one corner. And the third cobalt ion connects with the triangles through the phosphonate groups. One phosphonate group shows 3.221 coordination mode, while the other

shows 4.221 coordination mode to link four metal centres (Scheme 1). The pivalate groups exhibit 2.21, 2.11 and 1.10 modes.

Figure 4. a) The structure of **4** in the crystal. Color codes: blue, cobalt; purple, lanthanide; green, phosphorous; yellow, oxygen; gray, carbon; hydrogen atoms and lattice solvent molecules are omitted for clarity. b) The core structure of **4**.

Compound **4** crystallizes in the triclinic space group $P\bar{1}$ and features a planar structure (Figure 4). Four metal ions arrange in the distorted square-planar geometry. Co1 sites in a tetrahedral geometry coordinated by O2, O5, O10 and O11 atoms from phosphonate and carboxylate groups. Co2 has a square pyramidal geometry with O4, O5, O8 and O9 locates on the plane and O1 in the vertex. Co3 has an octahedral coordination geometry surrounded by O4, O7, O17, O18 and O19 from one pivalate, one phosphonate and three water molecules, and N1 atom from CH_3CN . The Co–O distances range from 1.954(5) to 2.186(5) Å, which are consistent with that observed in cobalt clusters.^[25] The Gd^{III} ion is eight-coordinated in a distorted double-capped trigonal prism, featuring coordination by oxygen atoms from phosphonate, pivalates and H_2O . The Gd–O bond lengths fall in the range of 2.289(4)–2.453(5) Å, which are comparable to those in Gd^{III} clusters.^[24] One phosphonate group shows 3.111 coordination mode, while the other shows 4.221 coordination mode to link four metal centres (Scheme 1). The pivalate groups exhibit 2.11 and 1.11 modes.

It is very interesting to have a comparison on the configurations constructed by the metal ions of the cores in **1-4**. All of the metal ions in **1-4** are located nearly in one plane. Three Co^{II} ions in **3** form a large triangle, in which a small triangle that made up of three Gd^{III} ions was observed. Removing one Co^{II} ion from the Co_3Gd_3 core will give a Co_2Gd_3 core that is similar to that of **1**. Take a close

look at the Gd^{III} ions in **1-3**, we can find the Gd^{III} ions arranged in a triangle in each case. The forming of different cores in **1-4** are mainly due to the varied steric hindrance of the bulky organic ligands.

Magnetic property

The magnetic behaviors of **1-4** were studied on polycrystalline samples using SQUID magnetometer, and the results are summarized in Table 2. The room temperature $\chi_M T$ values were used to calculate the average g -value per cobalt site, using the known ground state ($S = 7/2$) and the Curie constant ($g = 2$) for Gd^{III} ion.^[20] Any interactions between the spins are excluded in this calculation. This gives a range of g -values for the cobalt sites. The g value should be related to the coordination geometry of the Co^{II} ions, with octahedral geometry giving larger value than tetrahedral due to spin-orbit coupling. More sophisticated analysis of the magnetism of such clusters involving ions with orbital component of their magnetism is impossible.^[25]

Table 2. Magnetic data for clusters **1-4**

compound	obs χT at 300 K (cm ³ mol ⁻¹ K)	calcd average g value for Co(II)	obs χT at 2 K (cm ³ mol ⁻¹ K)	obs M at 2 K and 7 T (μ_B)	$-\Delta S_m$ at 2.5 K and 7 T (J kg ⁻¹ K ⁻¹)
1	31.3	2.86	19.6	21.5	18.3
2	35.8	2.55	20.4	23.3	19.8
3	32.2	2.47	18.6	27.5	20.0
4	19.7	2.81	12.1	14.2	9.6

Figure 5. The χT versus T plot of **1–4** under 0.1 T dc field.

For all compounds, the $\chi_M T$ decreases slowly with decreasing temperature down to about 20 K, before decreasing more rapidly (Figure 5). At 1.8 K, the value of $\chi_M T$ is not zero, indicating that paramagnetic states are still populated due to the very weak exchange involving the Gd^{III} ions. The quench of the orbital-contribution also contributes to the decrease of $\chi_M T$ with lowering the temperature because of the Co^{II} ion.^[26] Magnetization measurements were performed in the range of 0–7 T at 2 K (Figure S1). The M values show a steady increase with increasing field, but do not saturate at 7 T. It can be seen that the slopes of M vs H plots are steeper at lower field, indicating that the clusters are easier magnetized, which is critical in magnetic cooling application.

Studies of the ac susceptibilities for **1–3** shows no slow relaxation behavior down to 2 K, so they are not single molecule magnets (Fig. S2-4). Fig. S5 shows the in-phase ($\chi'_M T$) and out-of-phase (χ''_M) signals versus T curves of compound **4**. The showed frequency-dependent out-of-phase signals may be due to the superparamagnetic relaxation of the magnetization of compound **4**. However, no maxima were observed down to 2 K, quantitative estimation of the relaxation kinetics was not possible. The magnetocaloric properties were investigated. The magnetic entropy changes for

changing applied field were calculated indirectly from the magnetization behavior as a function of applied field and temperature (Figure 6) using the standard relationship $\Delta S = \int [\partial M(T, H) / \partial T]_H dH$.^[2] For all clusters, the $-\Delta S$ versus T plots increase gradually from 10 to 2.5 K, reaching a maximum. There is no sign of downturn, which means the maximum should come at a lower temperature for the applied field changes. The lowest maximum $-\Delta S$ is observed in compound **4**. This can be explained by the fact that the entropy change increases with the gadolinium content of the cluster. The showed $-\Delta S$ values are close to that found in other Co-Gd clusters ($11.8 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\{\text{Co}_8\text{Gd}_2\}$, $20.0 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\{\text{Co}_4\text{Gd}_2\}$, $21.1 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\{\text{Co}_8\text{Gd}_4\}$ and $21.4 \text{ J kg}^{-1} \text{ K}^{-1}$ for $\{\text{Co}_8\text{Gd}_8\}$).^[18]

Figure 6. Experimental ΔS_m for **1–4** at various fields and temperatures. Lines are guides to the eye.

Conclusion

The preparation of four $\text{Co}^{\text{II}}\text{--Gd}^{\text{III}}$ clusters by employing bulky phosphonate ligands was performed. The results show that the steric hinderance of the fluorenyl ligands is the key factor for the isolation of clusters. These $\text{Co}^{\text{II}}\text{--Gd}^{\text{III}}$ heterometallic clusters show a potential capability for magnetic cooling at low temperatures. We observe that the entropy change increases with the percentage of gadolinium in the cluster. Our studies on these clusters bearing fluorenyl phosphonate ligands should be advantageous since a wide variety of ligands are available. Further studies on pure Gd^{III}

fluorenyl phosphoante clusters for magnetic refrigeration are underway.

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Appendix A. Supplementary material

CCDC 1482327-1482330 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at <http://>

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