A homochiral hexagadolinium phosphonate cluster with a large magnetocaloric effect

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Abstract

A homochiral hexagadolinium phosphonate cluster designated as \( R/S^- [\text{Gd}_6(\text{pmhpH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_8] \cdot 19\text{H}_2\text{O} \) (\( R/S^-1 \)) was successfully obtained and analyzed using single crystal X-ray diffraction crystallography, IR spectrum, TG analysis and magnetic testing. The cluster, shaped like a lantern, is constructed from \{\text{GdO}_8\} polyhedra and \{\text{PO}_3\text{C}\} tetrahedra surrounded by eight pmhpH\(^2^-\) ligands. Within the structure, two types of gadolinium ions with different coordination modes are observed. Each Gd(III) ion is bound to two carboxylate oxygens and six phosphonate oxygens from the coordinated pmhpH\(^2^-\) ligands. Circular dichroism spectra confirmed that \( R/S^-1 \) exists as a pair of enantiomers. Moreover, the cluster exhibits high thermal stability, decomposing at temperatures exceeding 335°C. Notably, the magnetic measurements revealed that compound \( R-1 \) exhibits a good magnetocaloric effect (MCE) with a maximum entropy change of \(- \Delta S_{\text{m}} = 36.84 \text{ J kg}^{-1} \text{ K}^{-1} \) at \( T = 2\text{K} \) and \( \Delta H = 7 \text{ T} \).

1. Introduction

Lanthanide clusters, featuring with atomically precise structure, nanoscale molecular particle sizes and abundant 4f metal centers nanoscale dimensions, have exhibit remarkable optical, electrical, magnetic and catalytic properties in the fields of physics, chemistry and materials, garnering extensive attention.\(^1–10\) Particularly intriguing are the Gd(III)-based clusters, renowned for their exceptional magnetic refrigerant capabilities. This allure stems from the small magnetic anisotropy of Gd(III) ions, coupled with their substantial ground state spins (7 unpaired electrons within the 4f electron shell) and low spin excited states. While substantial strides have been taken in the design and fabrication of high-nuclearity Gd(III) cluster materials with massive MCE\(^11–20\), challenges persist. These include limited magnetic entropy variation and reduced thermal conductivity at low magnetic fields, impeding practical applications.

On the other hand, chirality is a universal phenomenon in nature and plays an important role in chemistry, biology and materials science.\(^21–25\) Chiral lanthanide clusters will provide a platform for molecular-based materials with coordination between chirality and magnetism and exhibit great application prospects in the fields of three-dimensional displays, spintronic devices and magneto-optical memories.\(^26–30\) Recently, Liang’s group have in situ synthesized homochiral dysprosium-oxo clusters with threonine Schiff bases.\(^27\) Zou and coworker have designed and synthesized pinwheel/twist-shaped chiral lanthanide clusters with rotor structures by an annular/linear growth mechanism.\(^28\) Besides, they constructed dysprosium clusters by regulating the hydroxyl coordination sites at different positions on the ligands\(^29\) and carefully regulating the hydrolysis of lanthanide metal ions and the resulting hydrolysis products, which provides a method for the creation of chiral high-nucleation lanthanide clusters with unique forms.\(^30\) Su and co-worker synthesized a pair of axially dodecanuclear metal clusters via the bottom-up synthetic strategy, which can be as fluorescence sensor for enantioselective
sensing.[31] Kong’ group report the molecular self-assembly of hydroxido-bridged \( \{ \text{Ln}_5 \text{Ni}_6 \} \) (\( \text{Ln}^{3+} = \text{Dy}^{3+}, \ Y^{3+} \)) metal cluster, which provide the first experimental observation of intense multimetal site MChD signals in the visible–near-infrared region.[32] Nonetheless, the precise prediction and controlled development of homochiral polynuclear Ln-complexes, and achieving the coupling effect of chirality and magnetism is still a challenge.

Organophosphonic acid ligand has a versatile coordination mode, which can make metal organophosphonate coordination polymers with 0D, 1D, 2D and 3D structures through the coordination of various metal ions, which has potential application prospects in ion exchange, catalysis, optics, biology and magnetic.[33–42] However, Among the numerous metal phosphonates reported so far, many are layered materials, while lanthanide clusters based on phosphonates are limited, chiral phosphonates lanthanide clusters are extremely scarce. In this context, we chose a chiral amino acid phosphonic acid as ligand to react with the rare earth metal Gd(III) salt at room temperature, obtaining a new homochiral gadolinium phosphate cluster \( R[\text{Gd}_6(\text{pmhpH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_8]\cdot19\text{H}_2\text{O} \) (Fig, 1a). The cluster can be visualized as a “lantern-like” cage formed by six \( \{ \text{GdO}_8 \} \) polyhedra and eight \( \{ \text{CPO}_3 \} \) tetrahedra. The structure exhibits two types of gadolinium ions with different coordination modes. At the caps of the upper and lower ends of the cage, the Gd6(III) centres adopt an eight-coordinated distorted tetragonal antiprism geometry, while the middle Gd3(III) ions are eight-coordinated in a snub diphenoiod coordination geometry. Each Gd is coordinated by two carboxylate oxygens and six phosphate oxygens from the coordinated pmhpH\(^2-\) ligands. Magnetic investigations show that it exhibits a good MCE with \( -\Delta S_{\text{m}}^{\text{max}} = 36.84 \text{ J kg}^{-1} \text{ K}^{-1} \) at \( T = 2\text{K} \) and \( \Delta H = 7 \text{ T} \).

2. Experimental section

2.1. Materials and physical measurements

\((R)-\text{phosphonomethylhomoproline (pmhpH}_3\) was prepared by reactions of \((R)-\text{pipecolic acid}, \text{diethyl phosphite}, \) and paraformaldehyde, according to literature methods.[43] All other starting materials were reagent grade and used as purchased without further purification. The elemental analyses were performed in a PE240C elemental analyzer. The infrared spectra were recorded on a VECT0R 22 spectrometer with pressed KBr pellets. TGA was performed in nitrogen in the temperature range 25–800°C at a heating rate of 5°C min\(^{-1}\) on a Mettler Toledo TGA/DSC instrument. CD spectra were measured on a JASCO J-720W spectrophotometer at room temperature. The magnetic susceptibility data were obtained on polycrystalline samples using a Quantum Design SQUID VSM system.

2.2. Synthesis

2.2.1. Synthesis of \((R)-\text{phosphonomethylhomoproline (pmhpH}_3\)
The mixture solution of \((R)\)-pipecolic acid (50 mmol, 6.49 g), diethyl phosphite (75 mmol, 6.34 g) and hydrochloric acid (50 mL 6.0 M) in 100 mL three-necked flask was refluxed at 75°C in oil bath. After 1 hour, 2.32 g (75 mmol) of paraformaldehyde are added portion wise and the mixture was refluxed for an additional 12 hours. Then, the reaction solution was completely evaporated to dryness with a rotary evaporator, to which cold ethanol (100 mL) was added with stirring. A large number of white crystals were obtained. Finally, the product was filtrated, washed with ethanol and dried to give a white powder about 8.50 g. Yield: ca. 80% (based on \((R)\)-pipecolic acid). Anal. calcd for \(C_7H_{14}NO_5P\) (%): C, 37.87; H, 6.30; N, 6.39. Found: C, 37.67; H, 6.32; N, 6.27.

\[
\text{IR (KBr, cm}^{-1}\text{)}: 3408(s), 3062(m), 2950(w), 2873(w), 2785–2098(br), 1722(s), 1456(m), 1365(m), 1317(s), 1232(m), 1170(s), 1122(m), 1043(s), 932(m), 795(w), 757(m), 675(w), 580(w), 444(w).
\]

2.2.2 Synthesis of \(R/S\)-[Gd\(_6\)(pmhpH)\(_8\)(NO\(_3\))\(_2\)(H\(_2\)O)\(_8\)]·19H\(_2\)O

Syntheses of \(R\)-1. Gd(NO\(_3\))\(_3\)·6H\(_2\)O (0.1 mmol, 0.0458 g) and \(R\)-pmhpH\(_3\) (0.3 mmol, 0.0675 g) were dissolved in 10 mL deionized water, then adjusted to pH = 3.0 with 0.5 M NaOH solution. After evaporation at room temperature for two weeks, colorless bulk crystals were obtained. Yield: 43% (based on Gd). Elemental analysis calcd for \(C_{56}H_{112}N_{10}O_{54}P_8Tb_6\) (%): C, 18.84; H, 4.84; N, 3.89. Found: C, 18.91; H, 4.99; N, 3.94. IR (KBr, cm\(^{-1}\)): 3408(br), 3012(w), 2952(w), 2866(w), 2746(w), 2689(w), 2640(w), 2544(w), 1643(s), 1396(s), 1361(w), 1336(w), 1294(w), 1242(w), 1203(s), 1169(s), 1036(s), 1001(m), 972(m), 934(m), 870(w), 812(w), 775(m), 690(w), 592(m), 559(m), 524(w), 505(m), 476(w), 432(m).

Syntheses of \(S\)-1. \(S\)-1 was prepared using a similar procedure to \(R\)-1 except that \(R\)-pmhpH\(_3\) was replaced by \(S\)-pmhpH\(_3\). Yield: 51%. Elemental analysis calcd for \(C_{56}H_{112}N_{10}O_{54}P_8Tb_6\) (%): C, 18.84; H, 4.84; N, 3.89. Found: C, 18.88; H, 4.90; N, 3.91. IR (KBr, cm\(^{-1}\)): 3408(br), 3012(w), 2952(w), 2866(w), 2746(w), 2689(w), 2640(w), 2544(w), 1643(s), 1396(s), 1361(w), 1336(w), 1294(w), 1242(w), 1203(s), 1169(s), 1036(s), 1001(m), 972(m), 934(m), 870(w), 812(w), 775(m), 690(w), 592(m), 559(m), 524(w), 505(m), 476(w), 432(m).

2.3. Crystallographic data collection and refinement

Data collections for complex \(R\)-1 was carried out on a Bruker SMART APEX CCD diffractometer equipped with graphite monochromated Mo Ka (\(\lambda = 0.71073\) Å) radiation. Hemispheres of data were collected in the \(\theta\) range of 1.71–26.00°, using a narrow-frame method with scan widths of 0.308° in \(\omega\) and an exposure time of 5 s per frame. The data were integrated using the Siemens SAINT program\(^{[44]}\), with the intensities corrected for the Lorentz factor, polarization, air absorption, and absorption due to variation in the path length through the detector faceplate. Empirical absorption corrections were applied using the SADABS program\(^{[45]}\). The structure was solved by direct methods and refined on \(F^2\) by full-matrix least squares using SHELXTL\(^{[46]}\). All the non-hydrogen atoms were refined anisotropically. All the hydrogen atoms, except those attached to water molecules, were put in calculated positions. The H atoms of water molecules were found from the Fourier maps. All H atoms were refined isotropically with the isotropic
vibration parameters related to the non-hydrogen atoms to which they are bonded. Crystallographic and refinement details are listed in Table S1. Selected bond lengths and angles are collected in Tables S2.

3. Results and discussion

3.1 Crystal Structures of compound

Single crystal X-ray diffraction analysis revealed that compound R-1 crystallizes in the monoclinic space group $P2_1$. Within complex 1, there exists a discrete neutral cluster denoted as $[\text{Gd}_6(\text{pmhpH})_8(\text{NO}_3)_2(\text{H}_2\text{O})_8]$ (1a), accompanied by 19 lattice water molecules. The number of lattice water molecules was determined through elemental and thermal analyses. The crystal structure of 1a consists of six Gd(III) ions, eight chiral ligands pmhpH$^{-1}$, two NO$_3^-$ anions, and eight coordination water molecules. The core of the cluster 1a, can be visualized as a “lantern-like” cage formed by six {GdO$_8$} polyhedra and eight {CPO$_3$} tetrahedra (Fig. 1c, and d). Each pmhpH$^{2-}$ ligand acts as a tetradeinate ligand, coordinating to the gadolinium ions with 3.211 binding modes through one P-O-Gd bond [P–O: 1.490–1.551 Å; Gd–O: 2.328–2.496 Å] and a C-O-Gd bridged linkage [C–O: 1.2041–1.326 Å; Gd–O: 2.328–2.496 Å] (Fig. 1b). Notably, the phosphonate group adopts a 3.211 coordination fashion with the Gd ions (Fig. S1). When viewed from the top (Fig. 1e and f), it can be observed that the four organic ligands in the upper layer do not overlap with the four organic ligands in the lower layer, but rather cross-bed in opposite directions. Compared with $[\text{H}_3\text{O}][\text{Gd}_6(\text{PO}_4)(\text{AnPO}_3)_8(\text{DMF})_6]\cdot 2\text{DMF}\cdot \text{H}_2\text{O}$ cluster previously reported$^{[14]}$, the cage is hollow.

Notably, the structure exhibits two types of gadolinium ions with different coordination modes. At the caps of the upper and lower ends of the cage, the Gd6(III) centres adopt an eight-coordinated distorted tetragonal antiprism geometry, with coordination provided by four oxygen atoms from the PO$_3$ ligands and four oxygen atoms from the terminal H$_2$O ligands (Fig. 2c). In contrast, the middle part of the cage comprises four edge-sharing gadolinium polyhedra, where the four Gd centres are coplanar, forming a {Gd$_4$} rectangular ring. The geometries of GdIII atoms have been confirmed by using the SHAPE program of Alvarez and the corresponding CShM values are listed in Table S3. The middle Gd3(III) ions are all eight-coordinated in a snub diphenoic coordination geometry (Fig. 2b). Each Gd is coordinated by two carboxylate oxygens and six phosphate oxygens from the coordinated pmhpH$^{2-}$ ligands (Fig. 2b). The Gd ions are linked to each other through bridge oxygen atoms from the phosphate ligand, resulting in a square plane arrangement. The distances between Gd···Gd interactions range from 3.952 to 4.000 Å (Fig. 2a). The compound can also be viewed as an elongated tetragonal bipyramidal gadolinium cluster, covered by eight organic phosphonate ligands, with Gd5 and Gd6 occupying the axial sites of the bipyramid, while the rest are located in the equatorial plane (Fig. 2a). The distances between the apical Gd(III) ions and the equatorial Gd(III) ions range from 5.731 to 5.797 Å. All clusters are stacked through weak interactions among molecules, forming a three-dimensional structure (see Fig. S1).
3.2 PXRD pattern, IR spectra and Circular dichroism spectra

Unfortunately, the crystal quality of S-1 is poor, so a detailed crystal structure was not obtained. The structure of S-1 was proved that it is isostructural with R-1 characterized by PXRD, IR and CD spectroscopy. The PXRD pattern shows S-1 that has the same diffraction peaks with that of R-1, indicating they are isostructural (Fig. S2). The experimental PXRD patterns of the two compounds match well with the simulated patterns from the single crystal structures, which indicates that the collected samples are pure phase. Besides, the infrared (IR) spectroscopy measurements were recorded in the range of 400–3800 cm\(^{-1}\). As shown in Fig.S3, the band at 3420 cm\(^{-1}\) could be assigned to the stretching vibration of O-H of water molecular. The band at 1620 cm\(^{-1}\) correspond to the stretching vibration of COO\(^{-}\). The vibration bands at 1120 – 1041 cm\(^{-1}\) are the character stretching vibrations peaks of the phosphonate groups. These bonds shown obviously red shift compared to the IR spectrum of ligand, which is the result of coordination of the metal ion with the ligand. The CD spectra of R-1 and S-1 displayed good mirror symmetry, confirming that they are a pair of enantiomers (Fig. 3). The CD spectrum of R-1 shows two positive Cotton effect signal peaks at 245 nm and 265 nm. The S-isomers display the opposite Cotton effects.

3.3 Thermal stability

The thermal stability of R, S-1 have been investigated under nitrogen atmospheres with slow heating rate of 5°C/min from 25 to 800°C by thermogravimetric analysis (TGA) (Fig. S4). The TGA curve shows two steps of weight loss at the range of 25–800°C. The first weight loss is 20.49% from 25 to 200°C, assigned to the release of 8 lattice water molecules and 19 lattice water molecules. A plateau appears at 200–335°C, and as the temperature rises above 335°C, weightlessness begins again. The second weight loss is 29.78% at the range of 335–800°C, which can be ascribed to the structural collapse. The results indicate that the compounds have good thermal stability until 335°C.

3.4 Magnetic studies

Variable-temperature magnetic susceptibilities for R-1 were measured in the temperature range of 2 – 300 K under a constant magnetic field of 1000 Oe (Fig. 4). The \(\chi_M T\) value at room temperature (300 K) of 47.93 emu K mol\(^{-1}\) is consistent with the expected value of 47.28 emuK mol\(^{-1}\) for six spin-only Gd(III) ions (\(S = 7/2\) and \(g = 2\)). Up cooling from 300 to 50 K, the product \(\chi_M T\) decreases slowly, while until until ca. 50 K \(\chi_M T\) decreases more rapidly. Consistently, fitting the data with Curie-Weiss law in the temperature range of 50–300 K gives Curie constant \(C = 48.23\) cm\(^3\) K mol\(^{-1}\) and, Weiss constant \(\theta = -0.13\) K (Fig. S5). The negative Weiss constant indicated the presence of antiferromagnetic coupling between adjacent Gd(III) centers in R-1. The isothermal field-dependent magnetization \((M - H)\) of R-1 was measured at low temperature (2 – 10 K) (Fig. S6). As shown Fig. S6, at 2K, the magnetization increases abruptly to 41.14 \(\mu B\) at 15 kOe. Above 15 kOe, it smoothly increases and finally reaches 41.58 \(\mu B\) at 70 kOe, which is nearly close to the saturation value of 42 \(\mu B\) for six Gd(III) ions. It indicates the intramolecular antiferromagnetic interaction in R-1 is very weak, so the spins are easily magnetized.\[^{47}\]
The Gd\textsubscript{6} cluster \textbf{R-1} contains isotropic Gd\textsuperscript{III} ions with a large spin ground state and very weak antiferromagnetic interactions between the Gd\textsuperscript{III} ions, which should possess considerable potential for magnetic refrigerants. Therefore, we investigated its magnetocaloric effect (MCE) through calculating the magnetic entropy change $\Delta S_m$ for various field changes and temperatures from the $M(H,T)$ data (Fig. 5). The experimental MCE of \textbf{R-1} was investigated by using multiple temperature data of magnetization to fit the Maxwell equation below: 

$$ -\Delta S_m(T) = \int \left[ \frac{\partial M(T,H)}{\partial T} \right]_H dH. $$

As shown in Fig. 6, $-\Delta S_m$ of \textbf{R-1} increase monotonically with the decrease of temperature and the increase of magnetic field, reaching the maximum value of 36.84 J kg\textsuperscript{-1} K\textsuperscript{-1} at $T = 2K$ and $\Delta H = 7$ T, which is slightly larger than $\{\text{Gd}_6\}$ with smaller ligand/metal ratio (33.5, 35.3 and 35.4 J kg\textsuperscript{-1} K\textsuperscript{-1}),$^{49-51}$ which maybe attribute to the much week antiferromagnetic interaction.

4. Conclusions

In summary, a pair of new chiral lanthanide clusters has been successfully synthesized under evaporation conditions. The prepared Gd-cluster shielded by organic phosphonate ligand R-PO\textsubscript{3}\textsuperscript{2-}. It composed of a lantern-like cage made up of \{GdO\textsubscript{8}\} polyhedra and \{PO\textsubscript{3}C\} tetrahedra. The structure exhibits two types of gadolinium ions with different coordination modes. Each Gd is coordinated by two carboxylate oxygens and six phosphate oxygens from the coordinated pmhp\textsuperscript{2-} ligands. The cluster exhibits high thermal stability and decompose above 335°C. Magnetic studies revealed that the anti-ferromagnetic interactions existed between the adjacent Gd(III) ions in clusters \textbf{R-1}. Moreover, the magnetic measurements show the compound \textbf{R-1} displays good magnetocaloric effect (MCE) with $-\Delta S_{m_{\text{max}}}$ = 36.84 J kg\textsuperscript{-1} K\textsuperscript{-1} at 2K and $\Delta H$= 7 T. This work provides new chiral lanthanide clusters material and lays the foundation for future studies of magnetic chirality.

Declarations

Supporting information The online version contains supplementary material available at https://doi.org/xx.xxxx/x.xxxxx.xxxx.xx.xxx

Author contribution J.G.J and Q.Q.Q. contribute for the main manuscript and preparing the figures and the tables and contribute for the characterization of PXRD, IR, CD test. J.H and M.R contributes for the magnetic property test. Q.W and L.M.Z. contributes for the conception of this manuscript. All authors participated in the discussions, contributed to improving the manuscript, and approved the submitted manuscript.

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Declaration of competing interest The authors declare no competing interests.

Data availability R1 CIF files are available in the Cambridge Structural Database (CSD) and the CCDC number is 2321042

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44. SAINT Program for Data Extraction, Reduction, Siemens Analytical X-ray Instruments, Madison, WI, (1994–1996)

Figures

(a) R-{Gd(pmhpH)_{4}(NO_{3})_{2}(H_{2}O)_{3}}·19H_{2}O (R-1)

(b) (c) (d) (e) (f)
Figure 1

The synthetic route (a) and the building unit (b) of \textbf{R1}; Ball-and-stick and polyhedral representation of 1\textbf{a}. (side view: (c) and (d); top view: (e) and (f)); Color code: N blue balls; O, red balls; C, black balls; \{GaO}_8\ polyhedra, lime; PO_4 tetrahedra, pink; hydrogen atoms and water molecules are omitted for clarity.

Figure 2

Distance analysis of adjacent Gd ions (a) and coordination configuration of Gd3 (b) and Gd6 (c)
Figure 3

The CD spectra of $R, S-1$. 
Figure 4

The $\chi_M$ and $\chi_M T$ vs. $T$ plots for $R-1$
Figure 5

Values of $-\Delta S_m$ calculated from the magnetization data for $R\cdot1$ at various fields (1.0–7.0 T) and temperatures (2.0–10.0 K)

Supplementary Files

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- Gd6S1.docx