异金属簇{LnCu₃}低温磁制冷性能

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摘要：基于对已报道 Gd-Cu 配合物的文献调研，发现一类{LnCu₃}簇合物(Ln=Gd(**1**), Tb(**2**), Dy(**3**))，其 Cu^{II} 离子被 Gd^{III} 离子有效分隔且分子内部仅拥有铁磁相互作用，因而对其进行了低温磁制冷性能研究。在已报道实验方法上加以改进，用一锅法制备出一系列异金属{LnCu₃}簇合物 (Ln=Gd(**1**), Tb(**2**), Dy(**3**))，并运用元素分析、红外、单晶/粉末 X-射线衍射等方法对其进行表征，以证明其同构性及相纯度。低温磁热效应的研究结果表明簇合物 **1-3** 在 ΔH=0~7 T 下的最大磁熵变值($-\Delta S_m$)分别为 16.1 (2 K), 6.9 (5 K)和 8.1 (5 K) J·kg^{-1}·K^{-1}。簇合物 **1** 与已报道的 Gd-Cu 簇合物的磁熵变对比再次证明了弱铁磁相互作用在 3d-4f 分子磁制冷剂设计中起到重要的作用。

关键词：低温磁制冷；磁热效应；磁熵变；铁磁相互作用
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Cryogenic Magnetic Refrigeration Properties of Heterometallic {LnCu₃} Cluster Family

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Abstract: Based on the survey of Gd-Cu complexes in literatures, a family of {LnCu₃} clusters (Ln=Gd (**1**), Tb (**2**), Dy (**3**)) were selected to study the magnetocaloric effect (MCE) at low temperature due to their isolated Gd-Cu arrangement as well as the pure intramolecular ferromagnetic coupling. A modified one-pot synthetic method based on the reported result was developed to simplify the reaction procedure. Elementary analyses, IR, single crystal/powder X-ray diffraction measurements were carried out to determine the isomorphism and phase purity. Studies of MCEs indicate that complexes **1~3** have a maximum magnetic entropy change ($-\Delta S_m$) of 16.1 (2 K), 6.9 (5 K) and 8.1 (5 K) J·kg^{-1}·K^{-1} for ΔH=0~7 T, respectively. Comparison of the MCE for {GdCu₃} with the reported Gd-Cu clusters emphasizes the importance of weak ferromagnetic interactions in designing of 3d-4f molecular coolers.

Key words: cryogenic magnetic refrigeration; magnetocaloric effect; magnetic entropy change; ferromagnetic interaction

0   Introduction

Cryogenic molecular coolers refer to a family of clusters which can be used for cooling applications by means of magetocaloric effect (MCE) at both low- and ultra-low-temperatures [1-4]. Studies in this field have rapidly developed over the past ten years [5-9]. The performance of magnetic refrigerant can be evaluated

in terms of magnetic entropy change ΔS_m, which is related to $-R\ln(2S+1)$, where R is the gas constant and S is the spin state. Much attention has been paid to Gd-based systems because of the high spin state $S=7/2$ of Gd^{III} ion [10-12], and many of them show excellent performance, even comparable to that of the commercial cooler $Gd_3Ga_5O_{12}$ (GGG) [13]. As progress moves far ahead, researchers start to realize the importance of magnetic coupling in designing better coolant. At the very beginning, ferromagnetic interactions, which can result in the appearance of low-lying excited states, were considered to be good for observing an enhanced MCE [14]. However, later studies indicated that ferromagnetic coupling among the spin carriers would lower the maximum $-\Delta S_m$ value due to the removal of spin degeneracy[15]. Finally a balance was built that a weak ferromagnetic interaction is favoured to obtain better refrigeration performance over a wide temperature and field range. Gd $\cdots$ Gd magnetic interactions are generally weak because of the "buried" $4f$ orbitals, hence $3d$ ions could be introduced for stronger exchange interactions. On the other hand, couplings among 3d ions are always strongly antiferromagnetic, which would significantly reduce the $-\Delta S_m$ value [16]. Hence, structural topologies such as M-Gd-M (M =transition metal ions) arrangements are needed[1].

Thus we have surveyed numbers of Ln-Cu complexes and selected a family of {LnCu₃} clusters $[LnCu_3(H_2edte)_3(NO_3)][NO_3]_2 \cdot 0.5MeOH$ (H₂edte=2′,2,2-(ethane-1,2-diyldinitrilo)tetra-ethanol; Ln =Gd (**1**); Tb (**2**); Dy(**3**))[17] to study their cryogenic MCE, evaluate and analyse the role of ferromagnetic interactions in molecular cooler design.

1 Experimental

1.1 Materials and measurements

All chemicals were analytical grade and commercial available, and were used without further purification. Diffraction intensity data for single crystals of **1**~**3** were collected at 123 (2) K on an Oxford Supernova diffractometer with graphite-monochromated Mo-$K\alpha$ radiation (λ =0.071 073 nm)

using the ω-scan technique. Elemental analyses (C, H and N) were performed on a Perkin-Elmer 240 CHN elemental analyzer. Powder X-ray diffraction patterns were recorded on a D/Max-2500 X-ray diffractometer using Cu-$K\alpha$ radiation (λ =0.154 18 nm). Magnetic measurements were performed on microcrystalline samples using a Quantum Design SQUID-VSM magnetometer. The magnetic data were corrected for the diamagnetic contribution of both the sample holder and the diamagnetic correction estimated using Pascals constants.

1.2 Syntheses of 1~3

1.2.1 $[GdCu_3(H_2edte)_3(NO_3)](NO_3)_2 \cdot 0.5MeOH$ (**1**)

Complex **1** was prepared by a one-pot modified method based on ref 17. To a stirred solution of Cu (NO₃)₂·6H₂O (0.45 mmol) in 5 mL MeOH was added H₄edte (0.25 mmol) and NEt₃ (1.62 mmol) in 5 mL MeCN. The resulting blue solution was stirred for 15 min and then Gd(NO₃)₃·6H₂O (0.20 mmol) in 5 mL MeCN was added and stirred for a further 10 min. The solution was then filtered, sealed in a vial and heated at 60 ℃. Blue rectangular plate-like crystals of **1** suitable for X-ray diffraction were obtained over **1** night, and were collected by filtration. Yield. 43%, based on Gd. Anal. Calcd.for $C_{30.5}H_{68}Cu_3GdN_9O_{21.5}$ (%): C, 29.24; H, 5.47; N, 10.06. Found: C, 29.39; H, 5.81; N, 10.02.

1.2.2 $[TbCu_3(H_2edte)_3(NO_3)](NO_3)_2 \cdot 0.5MeOH$ (**2**)

Complex **2** was synthesized in a procedure analogous to that employed for **1**, except that Tb(NO₃)₃·6H₂O was used in place of Gd(NO₃)₃·6H₂O. Yield. 42%, based on Tb.

Anal. Calcd. for $C_{30.5}H_{68}Cu_3TbN_9O_{21.5}$ (%): C, 29.20; H, 5.46; N, 10.05. Found: C, 29.58; H, 5.79; N, 10.17.

1.2.3 $[DyCu_3(H_2edte)_3(NO_3)](NO_3)_2 \cdot 0.5MeOH$ (**3**)

Complex **3** was synthesized in a procedure analogous to that employed for **1**, except that Dy(NO₃)₃·6H₂O was used instead of Gd(NO₃)₃·6H₂O. Yield. 40%, based on Dy. Anal. Calcd. for $C_{30.5}H_{68}Cu_3DyN_9O_{21.5}$ (%): C, 29.12; H, 5.45; N, 10.02. Found: C, 29.52; H, 5.83; N, 10.39.

Table 1 Crystallographic data of complexes 1~3

Complex	1	2	3
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
T / K	123(2)	123(2)	123(2)
a / nm	0.895 65(1)	0.893 41(5)	0.893 82(5)
b / nm	1.603 81(5)	1.602 98(8)	1.599 76(8)
c / nm	1.634 36(3)	1.631 64(9)	1.630 87(1)
α / (°)	78.853(1)	78.768(5)	79.163(5)
β / (°)	86.254(1)	86.490(5)	85.975(5)
γ / (°)	82.794(2)	82.751(5)	82.859(5)
V / nm^3	2.283 2(3)	2.272 0(2)	2.272 0(2)

1.3 Crystal structure determination

Single-crystal X-ray diffraction analysis, powder X-ray diffraction and elementary analysis data of **1~3** collected at room temperature are shown in Table 1 and Fig.1.

All results indicate that complexes **1 ~3** synthesized via the one-pot method are essentially isostructural with the reported {LnCu$_3$} clusters[17] and exhibit high purity, which are essential for the subsequent magnetic analysis.
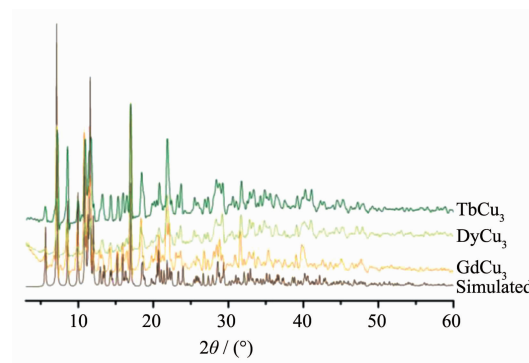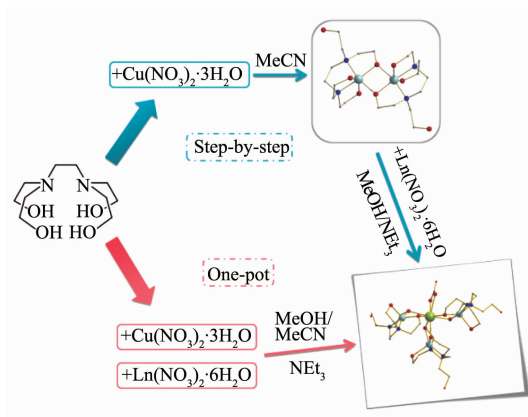

Fig.1　Powder XRD patterns for complexes **1~3**

Scheme 1　Reaction procedures for syntheses of complexes **1~3**　The step-by-step method is from Ref 17

2 Results and discussion

2.1 Syntheses

The title Ln-Cu clusters was synthesized by a step-by-step stop approach by Kettles et al[17]. In the approach, a dimeric Cu^{II} precursor was prepared initially. Then the final products were obtained by

reacting the precursor with corresponding Ln(NO$_3$)$_3$· xH$_2$O salts in MeOH in the presence of NEt$_3$. We modified the method in this work. A one-pot approach was developed to simplify the reaction procedure (Scheme 1). Under mild reaction conditions, large single crystals are formed via self-assembly of the reactants in mixed solvents. MeCN in the system may
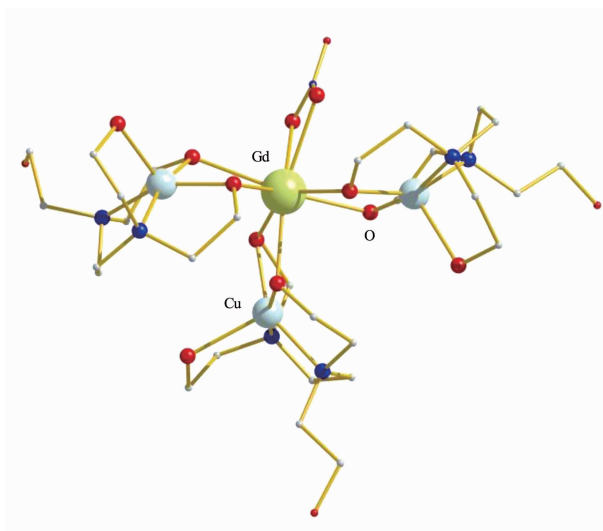
Fig.2　Molecular structure of complex **1**

act as a poor solvent to promote the crystallization.

2.2　Crystal structure

As described in reference 17, complex **1** crystallizes in triclinic space group $P\bar{1}$ and is constituted by the complex cation $[GdCu_3 (H_2edte)_3 (NO_3)]^{2+}$ combining with two nitrate ions for charge balance　(Fig.2). The metallic cation cores consist of one Gd and three Cu ions, overall giving a T shape with Cu ions arranging around the central Gd ion (Fig. 3, left). Three Cu ions in the structure are separated by Gd ion without direct μ-O bridges associated with magnetic couplings (Fig.3, right).
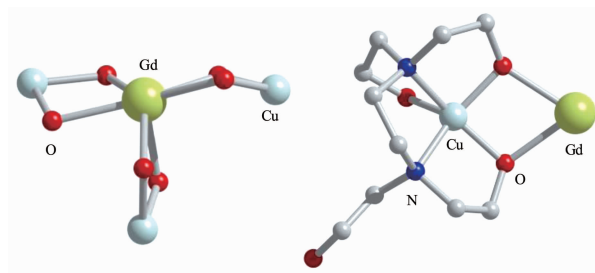
Fig.3　Left: T-shaped metallic cores of {GdCu₃} with μ_2-O bridges; right: Coordination and bridging mode of H_2edte^{2-}

The Gd ion locates on the intersection of the T shape, coordinating to each of the neighbouring Cu ion through two μ_2-OR⁻ groups, affording three CuO_2Gd units, which are favourable for ferromagnetic Cu-Gd interactions arising from the $3d$ $(Cu^{II}) \rightarrow 5d$ (Gd^{III}) electron transfer[18].

2.3　Magnetic studies

Dc magnetic susceptibility data collected for **1~3** under an applied field of 1 000 Oe over the temperature range of 2~300 K are the same as for the reported ones, exhibiting significant ferromagnetic interactions at low temperatures[17]. The Weiss constant determined over the whole temperature range for **1** is 2.75 K. Such positive value also supports that the magnetic interaction of Gd $\cdots$ Cu is ferromagnetic, which is always the case for the CuO_2Ln unit[18].

In most of the [GdCu] systems reported to date, Cu ions prefer to assemble together through various μ-O bridges although the Gd $\cdots$ Cu coupling is ferromagnetic in most cases, thus affording strong antiferromagnetic or ferrimagnetic interacions between the spin carriers [19-21]. Such phenomenon therefore would lower the total ground spin state S which is crucial for the MCE behaviour. Hence in this case, Cu

ions are fully isolated, giving a cluster that adopts ferromagnetic interactions only between Gd and Cu ions. In thought of these benefits, isothermal magnetization is performed in the temperature range of 2~10 K under the fields 0~7 T were performed to assess the magnetocaloric behaviour of complexes **1~3** (Fig.4).
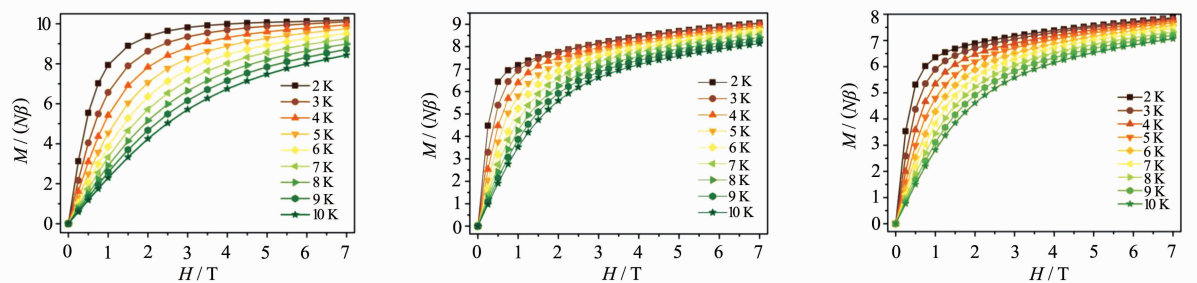

Fig.4　Field-dependent magnetization plots at indicated temperatures for **1** (left), **2** (middle) and **3** (right); Lines are visual guides

The $-\Delta S_m$ data at different magnetic fields and temperatures calculated by using the Maxwell equation $-\Delta S_m \ (T) = \int \ [\partial M(T,H)/T]_H dH$ are given in Fig.5. The maximum magnetic entropy changes for ΔH=0~7 T are 16.1 (2 K), 6.9 (5 K) and 8.1 (5 K) J· kg^{-1}·K^{-1} for **1~3**, respectively. All the $-\Delta S_m$ values are smaller than the expected ones judged by the function of $-\Delta S_m =R \ [n_{Ln}\ln (2S_{Ln}+1) +n_{Cu}\ln (2S_{Cu}+1)]$ for three uncorrelated Cu and one Ln ions (27.9, 27.0 and 25.95 J·kg^{-1}·K^{-1} for **1**, **2** and **3** respectively). However, when the metal ions are ferromagnetically coupled, the total spin lowers to S=10/2 ($S_{Gd}+3S_{Cu}$).
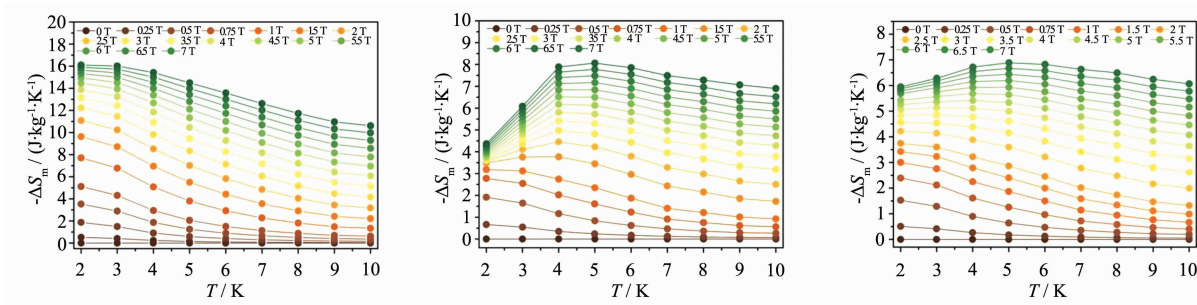

Fig.5　Experimental $-\Delta S_m$ obtained from magnetization data at various temperatures and magnetic field changes for **1** (top), **2** (middle) and **3** (bottom). Lines are visual guides

Table 2　$-\Delta S_m$ value based on ΔH at a given temperature for selected Gd-Cu complexes

Complexes	$-\Delta S_m /(J·kg^{-1}·K^{-1})$	T / K	ΔH / T	Magnetic Interaction	Ref.
GdCu$_3$	16.1	2	7	Ferro	This work
Gd$_6$Cu$_3$	34.5	2.1	7	Ferro	[22]
Gd$_4$Cu$_5$	31	3	9	Ferri	[14]
Gd$_2$Cu$_6$	11.9	2	7	Ferri	[23]
Gd$_{15}$Cu$_7$	22.2	2.5	7	Ferri	[24]
Gd$_2$Cu$_8$	12.8	3	7	Ferri	[16]
Gd$_2$Cu$_2$	25.7	2.4	7	Ferri	
Gd$_4$Cu$_8$	13.5	4.5	7	Ferri	[25]
Gd$_9$Cu$_8$	21.4	2.7	7	Ferri	
Gd$_6$Cu$_{12}$	14	4.5	7	Ferri	[20]
Gd$_6$Cu$_{24}$	18.8	2	5	Ferri	[26]
Gd$_{24}$Cu$_{36}$	21	2.1	7	Antiferro	[27]

Hence the maximum magnetic entropy at low temperature decreases to 16.1 $J \cdot kg^{-1} \cdot K^{-1}$ accordingly by adopting the new expression $-\Delta S_m = R\ln(2S+1)$. Such result is consistent with the experimental one, which may be ascribed to the existence of magnetic exchanges and magnetic anisotropies that remove the degeneracy and further split the energy levels of spin multiplets[15]. The $-\Delta S_m$ value of 16.1 $J \cdot kg^{-1} \cdot K^{-1}$ for complex **1** is comparable to those observed for other reported Gd-Cu clusters[14,16,20,22-27]. The MCEs for Gd-Cu molecular magnetic coolants are summarized in Table 2, as well as Figures for the intramolecular magnetic interactions. In these clusters, coupling between Cu ions are always strong antiferromagnetic, overall giving a ferrimagnetic coupling, sacrificing the cooling ability at low temperature. Although ferromagnetic interactions against the good performance of MCEs, it helps to stabilize the $-\Delta S_m$ in a wide temperature range[15]. For **1~3**, their refrigeration ability does not rapidly decrease at high temperature and low field, exhibiting a relative smooth change trend. Furthermore, complex **1** does not show the best magnetic refrigeration performance, but exhibits high atom economy, which is crucial for practical application as well.

3　Conclusions

Based on the survey of Gd-Cu complexes, a family of {LnCu₃} clusters were selected to evaluate their cryogenic MCE owing to the isolated Ln-Cu arrangement as well as the pure ferromagnetic interaction. A modified one-pot synthetic method based on reference[17] was then developed to simplify the reaction procedure. Studies on the cryogenic MCE indicate that complexes **1 ~3** possess the maximum magnetic entropy change ($-\Delta S_m$) of 16.1 (2 K), 6.9 (5 K) and 8.1　(5 K) $J \cdot kg^{-1} \cdot K^{-1}$ for ΔH=0~7 T, respectively. Weak ferromagnetic interactions in the system sacrifice the performance of magnetic refrigeration at low temperature, however, enhance the cooling ability at higher temperature and lower fields. And complex **1** exhibits quit high atom economy, which is crucial for practical application in the future.

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