

二维含镧链异核金属化合物的合成、结构和磁性研究

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摘要: 水热法合成了 3 个层状异核金属化合物 $[\text{Ln}(\text{idaH})\text{M}(\text{ida})_2]_n \cdot 0.5n\text{H}_2\text{O}$ (H_2ida =亚氨基二乙酸, $\text{Ln}=\text{Nd}$, $\text{M}=\text{Co}$ (**1**); $\text{Ln}=\text{La}$, $\text{M}=\text{Co}$ (**2**); $\text{Ln}=\text{La}$, $\text{M}=\text{Ni}$ (**3**)). 进行了晶体结构测定, 红外光谱分析、能谱分析与磁性能分析。3 个化合物除金属原子不同外具有相同的结构, 其晶体都属于单斜晶系, $C2/c$ 空间群。单晶结构表明该结构含有由十配位的 Ln 通过羧基氧连接而成的链, 六配位的 3d 金属(Co 、 Ni)交替地处在链的两边, 形成了带状结构, 带状链通过配体连成二维结构, 通过氢键形成三维骨架。

关键词: 晶体结构; 镧链; 二维层状; 磁性

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2D Heterometallic Complexes with Infinite Ln Chains: Synthesis, Crystal Structure and Magnetic Properties

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Abstract: Three 2D sandwich-like layer heterometallic complexes, formulated as $[\text{Ln}(\text{idaH})\text{M}(\text{ida})_2]_n \cdot 0.5n\text{H}_2\text{O}$, (H_2ida =iminodiacetic acid, $\text{Ln}=\text{Nd}$, $\text{M}=\text{Co}$ (**1**); $\text{Ln}=\text{La}$, $\text{M}=\text{Co}$ (**2**); $\text{Ln}=\text{La}$, $\text{M}=\text{Ni}$ (**3**)) have been synthesized under hydrothermal reaction condition and characterized by X-ray diffraction single-crystal structure analysis, IR spectroscopy, elemental analysis, TGA analysis, XPS techniques and magnetic analysis. The Ln atoms are ten-coordinated and linked up into chains by carboxylic oxygen atoms, which are engrafted by six-coordinated 3d transition metal atoms on both sides to give rise to belt-like chains. The belt-like chains are linked up into 2D network by ida ligands and further extended into 3D open-framework by strong hydrogen-bond interactions. CCDC: 694953, **1**; 694954, **2**; 694955, **3**.

Key words: crystal structure; lanthanide-chain; 2D-layer; magnetic property

0 Introduction

In recent years, studies on coordination polymers built up from lanthanide transition metals and multifunctional organic ligands represent a significant

field. The synthesis of such heterometallic complexes has been rapidly developed, where the compounds possess tremendous potential applications in the area of catalysis, separation, magnetism and optoelectronic domain^[1,2].

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Owing to the large ionic radii and the large coordination spheres, the earth elements tend to form isolate structures or multi-dimensional frameworks with most organic ligands. Multi-dimensional frameworks based on Ln-cluster or Ln-chain structures have been reported^[3-10], which has contributed greatly to the understanding of how to build such solid-state structures. However, many such studies have been focused on discrete complexes, therefore, how to explore new building principles so as to design and build versatile architectures with specific properties, such as superconducting and magnetic properties, still remain as a great challenge for chemists.

Lanthanide/transition metal complexes are good models for investigating the nature of the magnetic exchange interactions between 3*d* and 4*f* metal ions in magnetic materials. Since lanthanides show strong affinity towards oxygen donors, the iminodiacetic acid, which can be tuned in designing new metal-organic framework structures because of more coordinated atoms and coordinated patterns^[11], is employed as an organic ligand to the construction of the target architecture.

We have successfully synthesized three two-dimensional open framework mixed metal complexes with one-dimensional lanthanide oxygen networks: [Ln(idaH)M(ida)₂]_{*n*}·0.5*n*H₂O (H₂ida=iminodiacetic acid) (Ln=Nd, M=Co (**1**); Ln=La, M=Co (**2**); Ln=La, M=Ni (**3**)). The structure of the similar compound has been reported in 2004^[8,9] and 2007^[10], but the magnetic properties of them have never been explored. We present here the synthesis, structure and magnetic properties of these three compounds.

1 Experimental section

1.1 Materials and instrumentation

All chemicals were of reagent grade and used without further purification. Elemental analyses were performed on a vario EL III CHNOS Elemental Analyzer. Infrared spectrum was recorded in range of 4 000~450 cm⁻¹ on a FTS-40 spectrophotometer using pressed KBr pellets. Thermogravimetric analysis was performed on a NETZSCH STA 449C thermal analyzer under nitrogen atmosphere from 30 °C to 1 000 °C at a heating rate of

10 K·min⁻¹. XPS measurements were acquired using PHI Quantum 2000 Scanning ESCA Microprobe. Al Kα radiation (1 486.60 eV) was used, and the pressure in the measurement chamber was less than 5×10⁻⁷ Pa. All XPS spectra were corrected using the C1s peak at 284.8 eV. The magnetic susceptibilities were measured on a model CF-1 superconducting extracting sample magnetometer in the 2~300 K temperature range with an applied field of 0.5 T, the powdered sample were kept in the capsule for weighing.

1.2 Preparation of [Nd(idaH)Co(ida)₂]_{*n*}·0.5*n*H₂O (**1**)

Nd₂O₃ (0.5 mmol) and Co(OAc)₂·4H₂O (1 mmol), H₂ida (3 mmol) were mixed in 8 mL water and diluted HNO₃ to adjust pH to 4.5, then the mixture was sealed in a 20 mL stainless steel reactor with Teflon liner and heated at 140 °C for 4 d. Amaranthine crystals of **1** were isolated by mechanical separation and washed by water in 65% yield based on Nd. Anal. calcd. for **1**: (%): C 23.77; H 2.82; N 6.94. Found (%): C 23.38; H 2.76; N 6.72. IR (KBr, cm⁻¹): 1 385s, 1 117s, 988w, 945w, 917w, 780w, 726w, 618s.

1.3 Preparation of [La(idaH)Co(ida)₂]_{*n*}·0.5*n*H₂O (**2**)

The synthesis method is similar to that for complex **1** by using La₂O₃ instead of Nd₂O₃. Purple crystals of **2** were obtained in high yield (90% based on La). Anal. calcd. for **2**: (%): C 23.98; H 2.85; N 7.00. Found (%): C 23.36; H 2.98; N 7.13. IR (KBr, cm⁻¹): 1 385s, 1 124 m, 1 107m, 1 090m, 988w, 945w, 917w, 780w, 726w.

1.4 Preparation of [La(idaH)Ni(ida)₂]_{*n*}·0.5*n*H₂O (**3**)

The synthesis method is similar to that for complex **1** by using La₂O₃ instead of Nd₂O₃ and Ni(OAc)₂·4H₂O instead of Co(OAc)₂·4H₂O. Blue crystals of **3** were isolated by mechanical separation and washed by water in 70% yield based on La. Anal. calcd. for **3**: (%): C 23.99; H 2.85; N 7.00. Found (%): C 23.54; H 2.90; N 7.21. IR (KBr, cm⁻¹): 1 385s, 1 117s, 994w, 950w, 918w, 780w, 732w, 622w.

1.5 Single-crystal structure determination

Data collections for the three compounds were performed on a Rigaku Mercury CCD diffractometer

with graphite-monochromatic Mo $K\alpha$ radiation ($\lambda = 0.071\ 073\ \text{nm}$) at 293 K. The data sets were corrected by CrystalClear program^[12]. The structures were solved by direct method, and were refined on F^2 by full-matrix least-squares methods with SHELX-97 program package^[13]. All atoms except hydrogen atoms were refined anisotropically, while the hydrogen atoms were located

geometrically.

The crystallographic data and structural refinement parameters for three compounds are summarized in Table 1, and the selected bond lengths and bond angles are listed in Table 2. Table 3 shows the hydrogen-bonding geometry for complexes **1**~**3**.

CCDC: 694953, **1**; 694954, **2**; 694955, **3**.

Table 1 Crystal data and structure determination summaries for **1**, **2** and **3**

Compound	1	2	3
Formula	C ₁₂ H ₁₇ NdCoN ₃ O _{12.50}	C ₁₂ H ₁₇ LaCoN ₃ O _{12.50}	C ₁₂ H ₁₇ LaNiN ₃ O _{12.50}
Formula weight	606.46	601.13	600.91
Crystal size / mm	20×15×10	25×18×15	30×15×10
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	<i>C2/c</i>	<i>C2/c</i>	<i>C2/c</i>
<i>a</i> / nm	0.971 8(3)	0.969 800(10)	0.977 0(2)
<i>b</i> / nm	2.408 7(6)	2.414 79(2)	2.404 6(7)
<i>c</i> / nm	0.856 5(2)	0.859 8	0.856 7(2)
β / (°)	114.991(3)	114.888(5)	114.892(2)
<i>V</i> / nm ³	1.817 1(8)	1.826 60(2)	1.825 7(8)
<i>Z</i>	4	4	4
<i>D_c</i> / (g·cm ⁻³)	2.217	2.186	2.186
μ / mm ⁻¹	3.813	3.29	3.414
<i>T</i> / K	293(2)	293(2)	293(2)
λ (Mo $K\alpha$) / nm	0.071 073	0.071 073	0.071 073
<i>F</i> (000)	1 188	1 176	1 180
Reflections collected	7 033	6 961	6 961
Unique reflections (<i>R_{int}</i>)	2 090 (0.020 0)	2 100 (0.020 9)	2 088 (0.023 4)
Reflections observed (<i>I</i> >2 σ (<i>I</i>))	2 016	2 042	2 042
Parameters	138	138	138
<i>S</i> on <i>F</i> ²	1.063	1.007	1.09
<i>R</i> ₁ [<i>I</i> >2 σ (<i>I</i>)] ^a	0.020 1	0.016 8	0.018 2
<i>wR</i> ₂ [<i>I</i> >2 σ (<i>I</i>)] ^b	0.052 8	0.042 8	0.046 4
<i>R</i> ₁ (all data) ^a	0.021 4	0.017 5	0.018 9
<i>wR</i> ² (all data) ^b	0.053 6	0.043 2	0.046 8
$\Delta\rho_{\text{min}}$ and $\Delta\rho_{\text{max}}$ / (e·nm ⁻³)	695 and -477	864 and -508	652 and -624

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|; ^b wR = [\sum w(F_o^2 - F_c^2)^2 / \sum w(F_o^2)^2]^{1/2}.$$

Table 2 Selected geometric parameters (nm, °) for compounds **1**~**3**

Compound 1					
Nd(1)-O(5) ^{#1}	0.242 65(19)	Nd(1)-O(5)	0.270 3(2)	Co(1)-O(1)	0.209 39(19)
Nd(1)-O(2) ^{#1}	0.254 3(2)	Nd(1)-O(6)	0.274 3(2)	Co(1)-N(1)	0.215 8(2)
Nd(1)-O(1)	0.258 22(19)	Co(1)-O(3)	0.206 4(2)		
O(1)-Nd(1)-O(5)	64.74(6)	O(5)-Nd(1)-O(6)	47.63(5)	O(3)-Co(1)-N(1)	80.88(9)
O(5) ^{#3} -Nd(1)-O(5)	164.78(8)	O(3)-Co(1)-O(1)	95.04(9)	O(1)-Co(1)-N(1)	79.81(8)
O(1)-Nd(1)-O(6)	80.79(6)	O(1) ^{#3} -Co(1)-O(1)	83.70(10)	N(1) ^{#3} -Co(1)-N(1)	117.45(13)

Continued Table 2

Compound 2					
La(1)-O(5) ^{#1}	0.244 07(14)	La(1)-O(5)	0.271 26(15)	Co(1)-O(1)	0.209 44(15)
La(1)-O(2) ^{#1}	0.256 20(15)	La(1)-O(6)	0.276 35(15)	Co(1)-N(1)	0.216 01(18)
La(1)-O(1)	0.259 89(14)	Co(1)-O(3)	0.206 33(16)		
O(1)-La(1)-O(5)	64.84(5)	O(5)-La(1)-O(6)	47.38(4)	O(3)-Co(1)-N(1)	81.03(7)
O(5) ^{#3} -La(1)-O(5)	164.58(7)	O(3)-Co(1)-O(1)	95.05(6)	O(1)-Co(1)-N(1)	79.81(6)
O(1)-La(1)-O(6)	80.70(5)	O(1) ^{#3} -Co(1)-O(1)	83.99(8)	N(1) ^{#3} -Co(1)-N(1)	117.14(10)
Compound 3					
La(1)-O(5) ^{#1}	0.244 32(16)	La(1)-O(5)	0.269 08(16)	Ni(1)-O(1)	0.205 68(16)
La(1)-O(2) ^{#1}	0.256 78(16)	La(1)-O(6)	0.277 36(16)	Ni(1)-N(1)	0.209 7(2)
La(1)-O(1)	0.260 00(16)	Ni(1)-O(3)	0.204 63(17)		
O(1)-La(1)-O(5)	64.86(5)	O(5)-La(1)-O(6)	47.44(4)	O(3)-Ni(1)-N(1)	82.92(7)
O(5) ^{#3} -La(1)-O(5)	162.98(7)	O(3)-Ni(1)-O(1)	92.05(7)	O(1)-Ni(1)-N(1)	81.51(7)
O(1)-La(1)-O(6)	82.52(5)	O(1) ^{#3} -Ni(1)-O(1)	85.01(9)	N(1) ^{#3} -Ni(1)-N(1)	112.44(11)

^{#1} $-x+1, -y, -z$; ^{#2} $x, -y, z+1/2$; ^{#3} $-x+1, y, -z+1/2$.

Table 3 Hydrogen-bonding geometry for complexes **1-3**

	D-H...A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^{\circ})$
Compound 1	N(1)-H(1A)···O(4) ^{#4}	0.091 0	0.202 8	0.293 0	170.88
	N(2)-H(2A)···O(4) ^{#5}	0.090 0	0.193 3	0.277 4	154.96
Compound 2	N(1)-H(1A)···O(4) ^{#4}	0.090 9	0.202 0	0.292 3	171.35
	N(2)-H(2A)···O(4) ^{#5}	0.090 0	0.193 1	0.277 5	155.51
Compound 3	N(1)-H(1A)···O(4) ^{#4}	0.090 0	0.200 3	0.290 0	174.58
	N(2)-H(2A)···O(4) ^{#5}	0.090 0	0.193 0	0.277 5	155.75

^{#4} $x-1/2, -y+1/2, z-1/2$; ^{#5} $x-1, y, z-1$.

2 Results and discussion

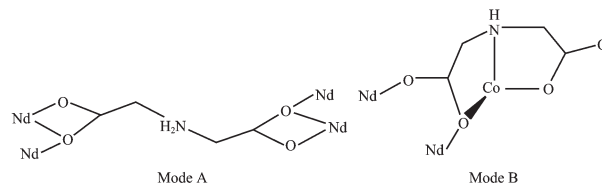
2.1 Synthesis

In order to construct $3d-4f$ heterometallic structures, cobaltic acetate or falcial acetate was adopted as a $3d$ -component, lanthanide nitrate as a $4f$ -component, and aminodiacetate as an organic ligand which shows good coordinating appetency to lanthanide and transition metals. The acidity of the mixed solution must be adjusted carefully to $\text{pH}=4.5$ by adding diluted HNO_3 and the pH of the final solution was changed to 4.9 after heated at 140°C for four days. All complexes were obtained in high yield.

2.2 Crystal structures

The title compounds are iso-structural, so only compound **1** is chosen to represent the detailed structure discussion.

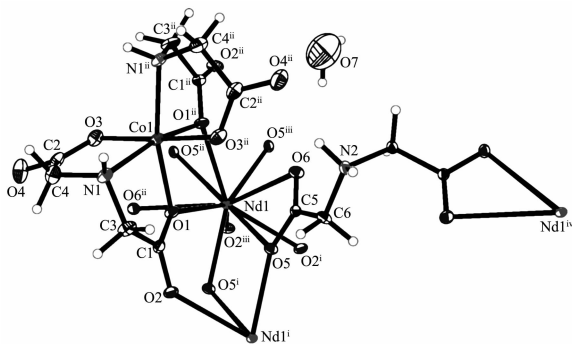
The structure of **1** contains Nd and Co atoms which are all coordinated by ida ligands in two modes as in Scheme 1.



Scheme 1 Two coordination modes of ida ligands

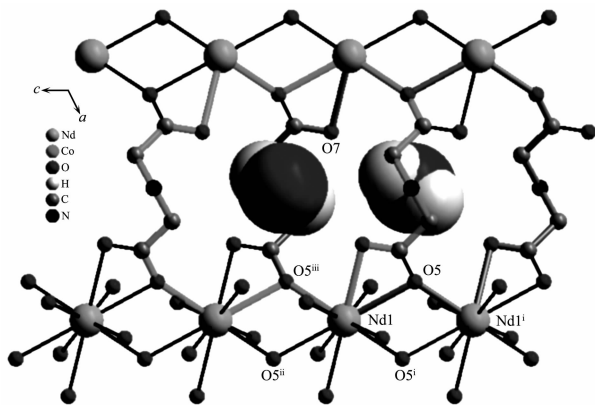
Nd atom is coordinated with ten oxygen atoms from eight different ida ligands in which six oxygen atoms ($\text{O5}^{\text{i}}, \text{O5}^{\text{ii}}, \text{O5}^{\text{iii}}, \text{O5}^{\text{iv}}, \text{O6}, \text{O6}^{\text{ii}}$) (Fig.1) are from four ida ligands in Mode A^[7] while the other four come from four ida ligands in Mode B. The Nd-O bond lengths range from 0.242 65(19) nm to 0.274 3(2) nm and O-Nd-O angles range from $47.63(5)^{\circ}$ to $164.78(8)^{\circ}$, which are all within the normal ranges^[8-10]. Each Nd atom is conne-

cted to generate a one-dimensional chain through sharing of four μ_3 -O. The distance between the adjacent Nd atoms is 0.429 73(10) nm (La \cdots La 0.431 35(0) nm (**2**); 0.429 49(10) nm (**3**)). The Nd-chain is further linked up by ida ligands in Mode A (μ : η^1 - η^2 , η^1 - η^2)^[7] into a two-dimensional structure (Fig.2).



Symmetry code: ⁱ $-x+1, -y, -z$; ⁱⁱ $-x+1, y, -z+0.5$; ⁱⁱⁱ $x, -y, z+0.5$; ^{iv} $x-1, y, z-1$

Fig.1 A segment of the polymeric structure of **1** with displacement ellipsoids at 30% probability



Symmetry code: ⁱ $-x+1, -y, -z$; ⁱⁱ $-x+1, y, -z+0.5$; ⁱⁱⁱ $x, -y, z+0.5$

Fig.2 View of a 2D network derived from 1D Nd-chain linked by ida along the *b* axis, Co-ida groups and all H atoms have been omitted for clarity except for those in free water molecules

Co atoms are engrafted on the both sides of the Nd-chain alternatively via ida ligands in Mode B. Co1 atom is surrounded by four oxygen atoms from two ida dianions in a facial configuration^[14] and accomplished to a heavily distorted octahedral coordination geometry by two nitrogen atoms donors from two iminodiacetate ligands (Table 2).

The Co-N bond length is 0.215 8(2) nm, and Co-O bond lengths between 0.206 4(2) nm and 0.209 39(19) nm. The angles of N-Co-O inside one chelating

iminodiacetate are 80.88(9)° and 79.81° which are part of 5-atom rings of chelating ligand. The angle of N1-Co1-N1ⁱⁱ, the biggest one departure from right angle in octahedron, is 117.45(13)°.

Co1 and Nd1 are linked by two μ_3 -O atoms, O1 and O1ⁱⁱ (symmetry code: ⁱⁱ $1-x, y, 0.5-z$) with the angle of O-Co-O 83.70(10)°, the angle of O-Nd-O 64.74(6)°, and the distance between Co1 and Nd1 0.373 14(11) nm (Co \cdots La 0.374 53(4) nm (**2**); Ni \cdots La 0.371 4(1) nm (**3**)). All the Nd and the Co atoms occupy the special positions across the twofold axis.

The Nd atom exhibits a +III oxidation state and Co atom a +II oxidation state, according to BVS calculation^[15] and XPS analysis. The ida ligand in Mode A is assignment as idaH for fitting the H-bonding pattern and charge balancing. The protonated N atom is located on the twofold axis.

In summary, the coordination polymer has a 2D sandwich-like layer structure as shown in Fig.3. The Nd atoms are linked up into chains by carboxylic oxygen atoms, and these chains are modified to be belts with the two sides decorated alternatively by Co atoms via carboxyl bridges. The belts are further linked up by N-protonated iminodiacetate ligands resulting in 2D network. In the layer there are 20-atom rings (constituted by the four Nd ions and two iminodiacetate units), which are partly occupied by free water

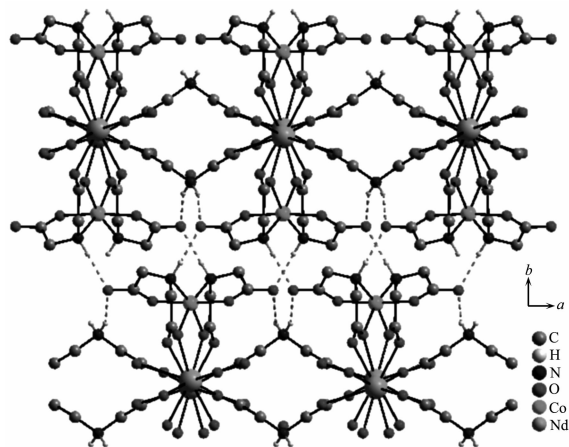


Fig.3 Two-dimensional sandwich-like layer structure viewed along the *c* axis, Broken lines indicate hydrogen bonds, All H atoms have been omitted for clarity except for those engaged in hydrogen bonding

molecules (Fig.2).

There exist strong hydrogen-bond interactions in the complex between O and N ions (Table 3). It is notable that hydrogen-bond interactions between N2 and O4 atoms might play important roles to fix the ida ligand and to provide voids for water molecules. The hydrogen-bond interactions between N1 and O4 atoms finally extend the layers into a three-dimensional open-framework (Fig.3).

2.3 XPS analysis

The binding energies of Co2p were measured to serve as a reference for chemical state identification. A typical Co2p XPS spectrum is presented in Fig.4. It consists of two Co2p_{3/2,1/2} doublets. The components of the main one are located at binding energy values (BE) 779.8 eV and 795.6 eV. The minor doublet represents the satellite lines. Such spectrum shape corresponds to Co(II)^[16-18]. Thus, the Co2p XPS spectra show that the oxidation level of cobalt is mainly + II.

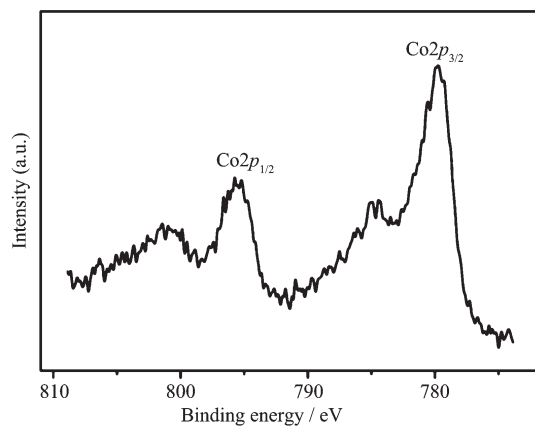


Fig.4 Co2p XPS spectrum of compound 1

2.4 Thermogravimetric analysis

The thermogravimetric analysis (TGA) of the three title complexes is similar (Fig.5). The results indicate that the complexes are steady at the temperature below 390 °C. The mass loss in the range of 100~390 °C corresponds to the water segments in the molecules (calculated for **1**, **2** and **3** are all about 2%, found for **1**: 3%, **2**: 4%, **3**: 2%). The structures were decomposed after 390 °C, the decomposed temperature for complex **3** is slight higher than that for complexes **1** and **2**. The mass loss at 750 °C for complexes **1** and **2** may refer to the phase change of cobalt-oxide. Over 800 °C the mass

does not change obviously. The residual for the complexes is metal oxides (calculated for **1**: 41.4%, **2**: 40.9%, **3**: 40.9%, found for **1**: 41.4%, **2**: 40.6%, **3**: 40.5%).

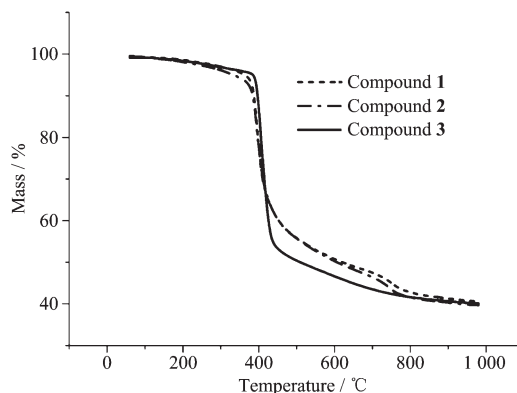


Fig.5 Thermal gravimetric curves of complexes **1**~**3**

2.5 Magnetic properties

Though the structure of La(III)-Co(II) compound bridged via ida ligand was reported, its magnetic chemistry property has not been investigated up to now. The temperature-dependent magnetic susceptibility data of complexes **1**~**3** have been measured in the temperature range of 2~300 K at 5 kOe. The μ_{eff} vs T plots for compounds **1**~**3** are shown in Fig.6. The Curie-Weiss law are obeyed for **1**~**3** with a Curie constant of $C=2.9 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, $\theta=-7.0 \text{ K}$ for **1**, $C=2.5 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, $\theta=-4.3 \text{ K}$ for **2**, and $C=1.1 \text{ cm}^3 \cdot \text{K} \cdot \text{mol}^{-1}$, $\theta=0.83 \text{ K}$ for **3**. These results indicate that there exist weak antiferromagnetic interaction in complexes **1** and **2** and weak ferromagnetic interaction in **3**. The curve μ_{eff} vs T also supports significant contributions of ferromagnetic or antiferromagnetic behaving.

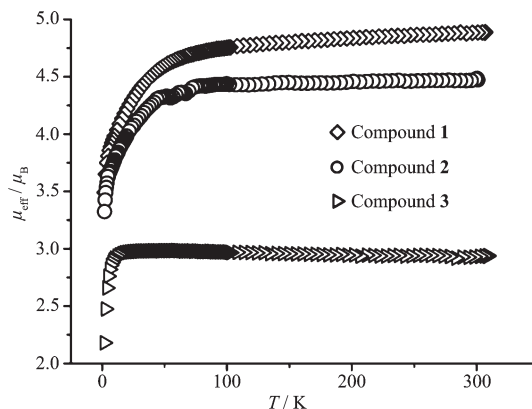


Fig.6 Plots of μ_{eff} vs T for compounds **1**~**3**

Upon cooling, the effective magnetic moment μ_{eff} values are decreased for the complexes **1** and **2**. At 300

K, the μ_{eff} (per Co(II)-Nd(III) unit) is measured to be $4.89\mu_{\text{B}}$ for complex **1**, which is larger than the theoretical value for the spin-only case of Co(II) ($\mu_{\text{eff}} = 3.87\mu_{\text{B}}$, $S=3/2$, $g=2.0$) and smaller than theoretical value for the isolated magnetic center per Nd(III) unit ($5.20\mu_{\text{B}}$), which is calculated according to the Van Vleck formula and includes the contributions from the spin-orbital interactions. The μ_{eff} value for **1** indicates that an intricate orbital contribution is involved for the short separations of Co \cdots Nd and Nd \cdots Nd (0.373 14(11) and 0.429 73(10) nm respectively). For complex **2**, the μ_{eff} values (per Co(II)-La(III) unit) are measured to be $4.48\mu_{\text{B}}$ at 300 K, and upon cooling, is decreased to $3.32\mu_{\text{B}}$ at 2 K, which indicates that the orbital contribution is involved at high temperature.

It should be pointed out that the electrons at 4f of Nd(III) ions gave a significant contributions of antiferromagnetic couplings by comparing the compound **1** with **2**.

For complex **3**, the μ_{eff} values (per Ni(II) unit) remain almost constant in the range of 20~300 K, $2.93\mu_{\text{B}}$ at 300 K and 2.98 at 50 K, which is slight larger than the theoretical values for the spin-only case of uncoupled Ni(II) ion ($\mu_{\text{eff}}=2.83\mu_{\text{B}}$, $S=1$, $g=2.0$) and shows a weak ferromagnetic interaction. The μ_{eff} values decrease rapidly from 20 K upon cooling, to its minimum value of $2.18\mu_{\text{B}}$ at 2 K. This phenomenon possibly results from the contribution of either zero field splitting effects and/or a weak antiferromagnetic interaction.

The nature of the magnetic interactions between the Ln(III) and Co(II) (or Ni(II)) ions cannot be definitively defined because the magnetic behavior of these systems can be affected by many factors, such as the Ln-Ln, Co-Co, and Ln-Co interactions, the ligand-field effects of the Ln(III) ion, and field saturation effects, and the 3d-4f interactions should also be considered.

3 Conclusions

Three M(II)-Ln(III) complexes have been synthesized via self-assembly reaction. They exhibit a sandwich-like layered structure. It has been clearly shown that the Co(II)-La(III) and Co(II)-Nd(III) magnetic couplings are antiferromagnetic. The present research affords new examples showing antiferromagnetic Co(II)-Nd(III) and Co(II)-La(III) couplings and might help elucidate the

intrinsic magnetic coupling between the Co(II) and Ln(III) ions.

It should be emphasized also that iminodiacetic acid is a versatile ligand, which can coordinate in different coordination and available modes to different metals.

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