基于二乙醇胺配体的[Dy₂Co₈]型配合物的合成、晶体结构和磁性分析

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摘要：以二乙醇胺为配体合成了一种具有[Dy₂Co₈]核结构的配合物[Dy₂Co₈(L)₄(HL)₄(HCOO)₄(OH)₂Cl₂(CH₃OH)₂]Cl₂·4CH₃OH·2H₂O (**1**)(H₂L=二乙醇胺)，并对其进行了 X 射线单晶衍射、红外光谱、元素分析和磁性表征。该配合物属于三斜晶系，$P\bar{1}$ 空间群。晶体学数据：a=1.160 4(8) nm，b=1.322 7(9) nm，c=1.465 3(9) nm，α=71.181(7)°，β=67.638(7)°，γ=65.939(7)°。在晶体结构中，每一个 Dy(Ⅲ)都是九配位，而每一个 Co(Ⅱ)均为六配位。

关键词：二乙醇胺；晶体结构；镝-钴配合物；磁性

Synthesis, Crystal Structure and Magnetism of a [Dy₂Co₈] Core Complex with Diethanolamine Ligand

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Abstract: A new [Dy₂Co₈] core Complex [Dy₂Co₈(L)₄(HL)₄(HCOO)₄(OH)₂Cl₂(CH₃OH)₂]Cl₂·4CH₃OH·2H₂O (**1**) (H₂L= diethanolamine) was prepared and characterized by single crystal X-ray diffraction, FTIR spectra, elemental and magnetic analysis. It crystallizes in the triclinic system, space group $P\bar{1}$. X-ray diffraction analysis reveals that each Dy(Ⅲ) was nine-coordinated and each Co(Ⅱ) ion displays distorted octahedral coordination environment. CCDC: 1576526.

Keywords: diethanolamine; crystal structure; dysprosium-cobalt complex; magnetic properties

0 Introduction

The study of 3*d*-4*f* heterometallic complexes is an active area of research in contemporary coordination chemistry because of their potential applications in various fields such as non-linear optical materials, luminescence, molecular adsorption and magnetism[1-4]. Importantly, some of these 3*d*-4*f* heterometallic complexes behave single-molecule

magnets (SMMs) properties. Most notable in this vein is the research on polynuclear metal complexes, many of which display fascinating molecular structures and, more importantly, interesting magnetic properties due to the unique exchange interactions between the metal ions[5-10]. Over recent years, many examples with SMM behavior of 3*d*-4*f* compounds involving cobalt(Ⅱ) ion have been reported[11-15]. It is meaningful to continue to construct and study the magnetism of Co-Ln based

molecular cluster. Using bridging ligands to bind $3d$ and $4f$ paramagnetic building blocks is the main synthetic plan to develop discrete polynuclear complexes and improve magnetic properties for $3d$-$4f$ complexes. Diethanolamine was usefully selected to construct molecular clusters because of its intrinsic nature, such as having more coordination sites and good flexibility[16-18]. In this paper, we report the synthesis, structure and preliminary magnetic studies for a new type of [Dy$_2$Co$_8$] complex [Dy$_2$Co$_8$(L)$_4$(HL)$_4$(HCOO)$_4$(OH)$_2$Cl$_2$(CH$_3$OH)$_2$]Cl$_2$·4CH$_3$OH·2H$_2$O using diethanolamine as the ligand.

1 Experimental

1.1 Material and methods

All starting reagents were of A.R. grade and used as purchased without further purification. IR spectrum was recorded as KBr discs on a Shimadzu IR-408 infrared spectrophotometer in the 4 000~600 cm^{-1} range. Analyses of C, H and N were determined on a Perkin-Elmer 240 Elemental analyzer. Thermogravimetric analysis (TGA) experiments were carried out on a NETZSCH STA 449F3 thermal analyzer from 40 to 800 ℃ under N$_2$ at a heating rate of 10 ℃·min^{-1}. Powder X-ray diffraction (PXRD) determinations was performed on an X-ray diffractometer (D/max 2500 PC, Rigaku) with Cu $K\alpha$ radiation (λ=0.154 06 nm). The crushed single crystalline powder samples were scanned at 40 kV (generator voltage) and 40 mA (tube current) from 5° to 50° with a step of 0.1°·s^{-1}. The magnetic susceptibility measurements was measured over the temperature range of 2~300 K with a Quantum Design MPMS-XL7 SQUID magnetometer using an applied magnetic field of 2 000 Oe.

1.2 Synthesis of the title complex

To a stirred solution of DyCl$_3$·6H$_2$O (0.3 mmol, 113 mg) and CoCl$_2$·6H$_2$O (1 mmol, 238 mg) in CH$_3$OH (15 mL) was added diethanolamine (2 mmol, 210 mg). After 15 min, CH$_3$ONa (1 mmol, 54 mg) were added to the above solution, and the resulting mixture was stirred for 6 h to give a dark-red solution that was filtered. The dark-red filtrate was then left undisturbed for 1 week. Dark-red, cube-shaped crystals were retrieved in 40% yield (based on Dy). Anal. Calcd. for C$_{42}$H$_{110}$Cl$_4$Co$_8$Dy$_2$N$_8$O$_{34}$ (%): C, 22.83; H, 5.02; N, 5.07. Found(%): C, 22.87; H, 5.01; N, 5.14.

1.3 X-ray structure determination

Single-crystal X-ray diffraction data of complex **1** was collected on a Bruker SMART APEX Ⅱ diffractometer equipped with a graphite-monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) at room temperature by using an ω-2θ scan mode. The structure was solved by directmethods with SHELXS-97 program[19] and refined by full-matrix least-squares techniques on F^2 with SHELXL-97[20]. All non-hydrogen atoms were refined anisotropically. H atoms attached to C were placed geometrically and allowed to ride during subsequent refinement with an isotropic displacement parameter fixed at 1.2 times U_{eq} of the parent atoms. H atoms bonded to N or O atoms were first located in difference Fourier maps and then placed in the calculated sites and included in the refinement. The crystallographic data and selected bond lengths and angles are listed in Table 1 and Table 2, respectively.

CCDC: 1576526.

Table 1　Crystal data and structure refinement for 1

Empirical formula	C$_{42}$H$_{110}$Cl$_4$Co$_8$Dy$_2$N$_8$O$_{34}$	Z	1
Formula weight	2 201.55	D_c / (g·cm^{-3})	1.956
Crystal size / mm	0.15×0.14×0.12	μ(Mo $K\alpha$) / mm^{-1}	3.928
Temperature / K	296(2)	F(000)	1 098
Crystal system	Triclinic	θ range / (°)	2.491~25.997
space group	$P\overline{1}$	Reflection collected	28 782
a / nm	1.160 4(8)	Independent reflection (R_{int})	7 318 (0.051 1)
b / nm	1.322 7(9)	Data, restrain, parameter	7 318, 38, 442
c / nm	1.465 3(9)	Limiting indices (h, k, l)	−14~14, −16~16, −18~18

续表 1

α / (°)	72.181(7)	$R_1, wR_2 [I>2\sigma(I)]$	0.056 1, 0.153 1
β / (°)	67.638(7)	R_1, wR_2 (all data)	0.077 7, 0.199 6
γ / (°)	65.939(7)	S on F^2	1.147
V / nm³	1.869(2)	Largest diff. peak and hole / (e·nm⁻³)	3 700 and −2 392

Table 2　Selected bond lengths (nm) and bond angles (°) of 1

|					
Dy(1)-O(9)	0.229 7(5)	Co(3)-O(4)	0.188 0(6)	Co(2)-O(10)	0.194 1(6)
Dy(1)-O(12)	0.237 8(6)	Co(3)-N(2)	0.192 8(9)	Co(2)-N(3)	0.196 3(8)
Dy(1)-O(7)	0.240 3(8)	Co(1)-O(9)	0.205 8(6)	Co(4)-O(2)	0.206 0(6)
Dy(1)-O(4)	0.240 4(6)	Co(1)-O(8)	0.208 8(7)	Co(4)-Cl(1)	0.236 9(4)
O(9)-Dy(1)-O(12)	125.6(2)	O(9)-Co(1)-O(8)	94.9(3)	N(2)-Co(3)-N(1)	100.0(4)
O(9)-Dy(1)-O(7)	76.4(2)	O(12)-Co(2)-O(11)	177.3(3)	O(2)-Co(4)-O(6)	150.0(3)
O(12)-Dy(1)-O(7)	119.5(3)	O(4)-Co(3)-O(2)	175.5(3)		
O(7)-Dy(1)-O(4)	72.6(2)	O(4)-Co(3)-N(2)	86.6(3)		

2　Results and discussion

2.1　Infrared spectrum

The FT-IR spectra of **1** (in KBr) show the bands as follows: 3 400(s), 3 161(s), 2 935(w), 2 870(w), 1 598 (s), 1 346 (s) and 1 042 (s) cm⁻¹. The absorption peak between 1 690 and 1 730 cm⁻¹ is not observed, showing all carboxylic groups are deprotonated[21]. The strong peaks at 1 598 and 1 346 cm⁻¹ are the ν_{as}(COO⁻) and ν_s(COO⁻) stretching mode of the coordinated HCOO⁻ ligand. Peak at 1 042 cm⁻¹ could be attributed to the stretching vibration of C-O bond. In addition, the strong and broad band centered at 3 400 cm⁻¹ for the title compound is attributable to the O-H or N-H stretching vibration on the basis of known structure.

2.2　Structure analysis

The crystal structure of **1** is revealed in Fig.1, and its stacking X-ray structure in Fig.2. The title compound, crystallized as [Dy$_2$Co$_8$(L)$_4$(HL)$_4$(HCOO)$_4$ (OH)$_2$Cl$_2$(CH$_3$OH)$_2$]Cl$_2$·4CH$_3$OH·2H$_2$O, belongs to the triclinic system and $P\bar{1}$ space group. The structure of this complex is centrosymmetric and contains two Dy (Ⅲ) and eight Co (Ⅱ) ions. Each Dy (Ⅲ) was nine-coordinated by nine oxygen atoms with the average Dy-O bond length 0.244 5 nm. Each Co(Ⅱ) ion displays distorted octahedral coordination environment. The ligand diethanolamine plays very important role in construction the structure via bridging and chelating

metal atoms, and the nitrogen atoms only participate the coordination of cobalt atoms. Four coordination modes were found in the structure. In this case, a, b and c present μ_3-η^1:η^2:η^3 coordination mode, while d presents μ_3-η^1:η^1:η^3 coordination mode (Scheme 1). In
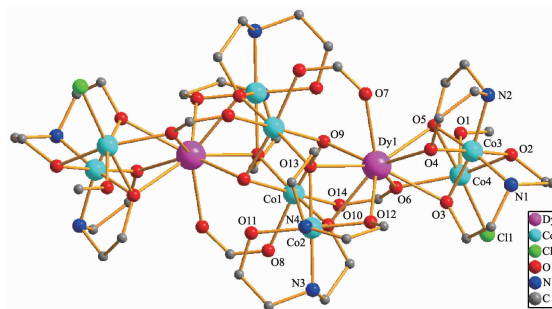
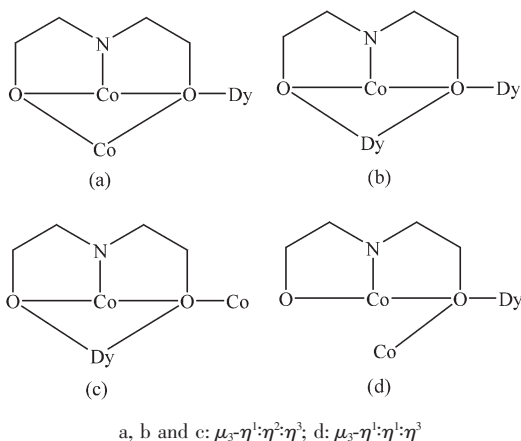Hydrogen atoms, free Cl⁻ and solvent molecules are omitted for clarity

Fig.1　Molecular structure of **1**
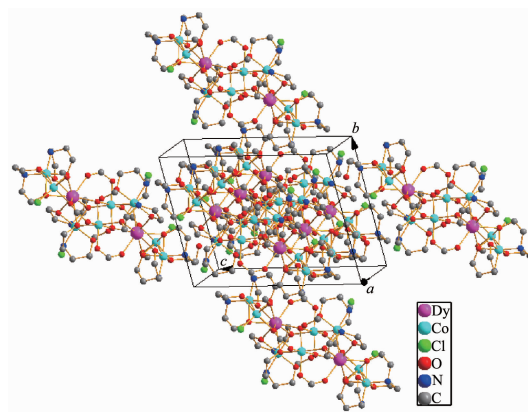

Hydrogen atoms are omitted for clarity

Fig.2　Packing arrangement in a unit cell

the structure two coordination modes of HCOO⁻ were found which mostly come from the oxidation of the solvent methanol (Scheme 2). There are two same μ_3-

(a)　　　　(b)

(c)　　　　(d)

a, b and c: μ_3-η^1:η^2:η^3; d: μ_3-η^1:η^1:η^3

Scheme 1　Different coordination modes of L and HL

OH groups in the structure which bridges two cobalt atoms and one dysprosium atom. Two kinds of Cl⁻ ions were found in the structure, one of which involved in coordination, and another is used to balance the charge. Also, there are four methanol and two water molecules contained in the stucture as the solvent molecules. The existence of some O-H and N-H bonds makes more hydrogen bonds in the structure (Table 3).

(a)　　　　(b)

a: μ_3-η^1:η^2; b: μ_2-η^1:η^1
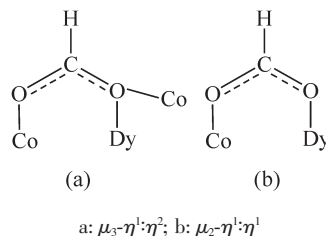
Scheme 2　Different coordination modes of HCOO⁻

Table 3　Hydrogen bond parameters of 1

D–H⋯A	d(D-H) / nm	d(H⋯A) / nm	d(D⋯A) / nm	∠DHA / (°)
O(1W)−H(1WA)⋯O(11)#1	0.096	0.209	0.270 5(11)	120.3
O(16)−H(16C)⋯O(1W)#2	0.096	0.192	0.272 8(17)	140.2
O(15)−H(15C)⋯N(3)#3	0.096	0.222	0.295 0(13)	132.4
C(7)−H(7B)⋯O(1W)#4	0.097	0.261	0.351 1(19)	154.7
C(21)−H(21A)⋯Cl(2)#2	0.096	0.269	0.360(2)	157.3
C(4)−H(4A)⋯Cl(1)	0.097	0.292	0.359 6(12)	127.3
C(6)−H(6A)⋯O(1)	0.097	0.26	0.319 3(15)	119.8
C(16)−H(16B)⋯O(4)	0.097	0.253	0.313 8(12)	120.5
C(14)−H(14A)⋯Cl(2)#1	0.097	0.267	0.361 9(12)	166.8
C(9)−H(9A)⋯O(7)	0.097	0.249	0.307 1(13)	118.2
C(3)−H(3B)⋯Cl(2)#4	0.097	0.291	0.381 7(14)	156.8
C(12)−H(12A)⋯O(14)#1	0.097	0.265	0.330 7(12)	125.4
O(1)−H(1C)⋯O(1W)	0.085	0.196	0.262 1(11)	133.4
O(9)−H(9C)⋯O(11)#1	0.098	0.175	0.262 5(8)	146.6

Symmetry transformations used to generate equivalent atoms: #1: −x+1, −y+1, −z+1; #2: x+1, y, z; #3: x, y, z+1; #4: −x+1, −y, −z+1.

2.3　Thermal stability

　　Thermal stability is an important aspect for the application of coordination compound. Thermogravimetric analysis (TGA) experiments were carried out to determine the thermal stabilities of **1** (Fig.3). TG curves showed the first consecutive step of weight loss was observed in the range of 50~180 ℃, corresponding to the release of solvent molecules (Calcd. 7.4%; Obsd. 6.9%). Then, the continuously weight loss corresponds to the release of ligands (in the range of 180~600 ℃).
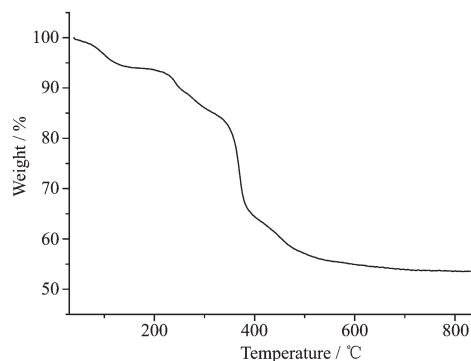

Fig.3　TG curve of complex **1**

Finally, the weight loss ends until heating to 600 ℃ and the total weight loss was about 45%.

2.4　PXRD results

Powder X-ray diffraction (PXRD) experiment for complex **1** has also been conducted to confirm whether the crystal structures are truly consistent with the bulk materials. The PXRD computer-simulated and experimental patterns of complex **1** are shown in Fig.4. In comparison with the simulated from crystal mode, the bulk-synthesized material and as-grown crystal can be considered homogeneous for complex **1**.
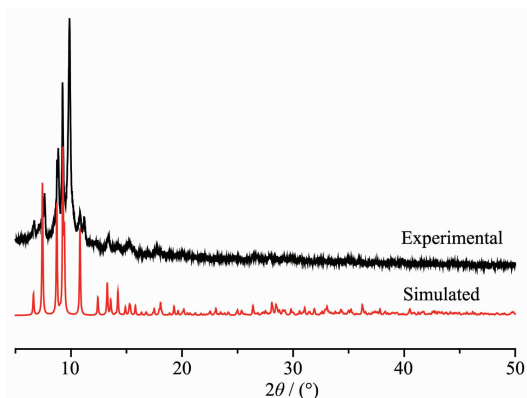

Fig.4　PXRD patterns of **1** measured in air

2.5　Magnetic properties

Temperature-dependent direct current (DC) magnetic susceptibility measurements for **1** was performed at temperatures ranging from 2 to 300 K, under an applied field of 1 000 Oe. The room temperature $\chi_M T$ value (40.81 cm³·mol⁻¹·K) (Fig.5) is slightly smaller than spin only value (43.34 cm³·mol⁻¹·K) for two Dy(Ⅲ) ($^6H_{15/2}$, g=4/3) and eight Co(Ⅱ) (g=2, S=3/2), remaining constant before decreasing from 40.57 cm³·mol⁻¹·K at 100 K to 38.47 cm³·mol⁻¹·K at 15 K indi-

cative of Stark level splitting in the lanthanide ions. Below 15 K, $\chi_M T$ value increases rapidly to 40.05 cm³·mol⁻¹·K at 4.5 K before dropping to 37.09 cm³·mol⁻¹·K at 2 K. The increase of magnetic susceptibility data at low temperature reveals the weak ferromagnetic interactions between metal centers or strong orbital contribution from Co(Ⅱ) ions.

Field-dependent magnetization (M) dada for **1** was collected in the range of 0~5 T at 2~5 K for the title compound (Fig.6). The curves of M vs H exhibit a gradual increase with increasing field strength reaching a saturation M value of 16.5μ_B at 2 K and 5 T, smaller than the theoretical saturated value for two Dy(Ⅲ) and eight Co(Ⅱ) ions. The magnetic anisotropy, together with the strong spin-orbital coupling, should be responsible for the magnetic unsaturation even at 5 T. This suggests the presence of magnetic anisotropy and/or considerable crystal-field effects. AC susceptibility measurement has also been conducted (Fig.7). However, no in-phase and out-of-phase signal could be observed.
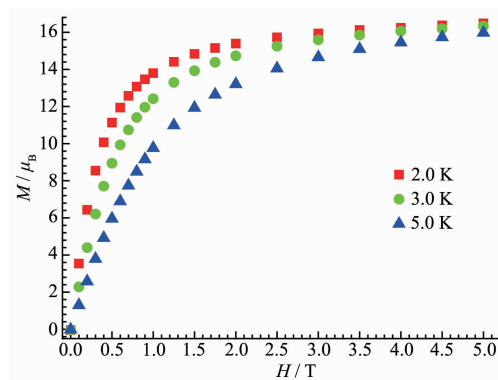

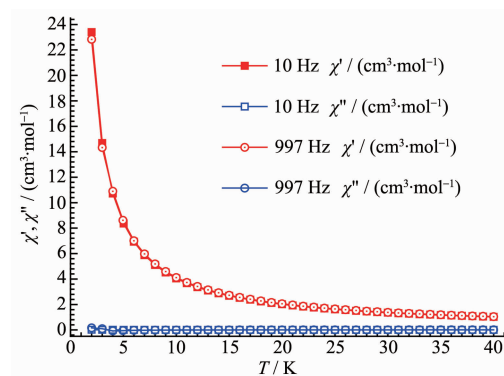Fig.6　Isothermal magnetization curves for **1** collected from 2 to 5 K

Fig.5　$\chi_M T$ versus T plot of **1** under 2 000 Oe DC field

Fig.7　AC susceptibility measurement for **1**

3　Conclusions

In summary, we have successfully prepared an unprecedented $[Dy_2Co_8]$ core complex with diethanolamine as ligand, which have been structurally characterized. In particular, magnetic properties of the title complex was investigated and AC susceptibility measurement revealed that in-phase and out-of-phase signal could not be observed.

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