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一个手性四核铜配合物的合成、结构和 CD 光谱

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摘要:香草醛和 *L*-2-氨基-3-苯基-1-丙醇缩合得到的手性希夫碱配体(*L*-H_2vap)与 $Cu(ClO_4)_2\cdot 6H_2O$,$Gd(NO_3)_3\cdot 6H_2O$ 和三乙胺在 4-羟基苯甲酸的存在下反应得到 *L*-$[Cu_4(Hvap)_2(vap)_2(MeOH)_2](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**)。通过元素分析、红外、热重分析和固体 CD 光谱对 **1** 结构进行了表征,并通过 X-射线单晶衍射确定其单晶结构,结果表明 **1** 属于单斜晶系,$P2_1$ 手性空间群,Z=2,包含船型 $\{Cu_4O_4\}$结构。**1** 的 Cu_4 簇通过配体、溶剂分子和高氯酸根离子的氧原子间的氢键沿 *b* 轴形成超分子链。固体 CD 光谱证实了 **1** 的手性。

关键词:手性多核配合物;四核铜(Ⅱ)配合物;晶体结构;CD 光谱

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Synthesis, Structure and CD Spectra of a Chiral Tetranuclear Copper(Ⅱ) Complex

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Abstract: Chiral Schiff-based ligand *L*-H_2vap, derived from the condensation of *o*-vanillin and *L*-2-amino-3-phenyl-1-propanol, reacts with $Cu(ClO_4)_2\cdot 6H_2O$, $Gd(NO_3)_3\cdot 6H_2O$ and triethylamine in the presence of 4-hydroxybenzoid acid to give *L*-$[Cu_4(Hvap)_2(vap)_2(MeOH)_2](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**). The structure of **1** was characterized by EA, IR, TGA, solid-state CD spectra and the single-crystal X-ray diffraction analyses. The X-ray diffraction analyses reveal that the complex crystallize in the monoclinic system, chiral space group $P2_1$ with Z=2, containing a boat-shaped $\{Cu_4O_4\}$ structure. Cu_4 clusters in **1** are connected through intermolecular hydrogen bonding to form supramolecular chains along *b* axis. The solid-state CD spectra comfirm the chiral nature of **1**. CCDC: 883888.

Key words: chiral polynuclear complex; copper(Ⅱ) complex; crystal structure; CD spectra

0 Introduction

During the past decade, chiral polynuclear complexes have become rather charmful because of their useful properties, such as ferroelectric and nonlinear optical properties[1-4]. Generally, the use of chiral ligands is the most effective way to prepare such complexes to ensure the chirality of the final

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products[5-7]. Schiff-based ligands are good candidates for they are easy to possess chirality by the condensation of aldehyde molecules with chiral amine molecules or chiral aldehyde molecules with amine molecules[8-11]. We are interested in chiral polynuclear chemistry, especially 3*d*-4*f* polynuclear clusters. Very recently, we have found that chiral Schiff-based ligand *L*-H_2vap is a good ligand to constrcut chiral polynuclears[12], but failed to introduce lanthanide ions into the final clusters. As a following work, we tried to introduce lanthanide ions by the addition of 4-hydroxybenzoid acid and the replacement of $Cu(Ac)_2\cdot H_2O$ by $Cu(ClO_4)_2\cdot 6H_2O$ through the similar procedure. Finally, a similar complex *L*-$[Cu_4(Hvap)_2(vap)_2(MeOH)_2](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (**1**) was obtained. It seems such copper(Ⅱ) tetranuclear is the stablest structure in the system. Herein, we reported the synthesis, EA, IR, TGA and solid-state CD spectra of complex **1**.

1 Experimental

1.1 General procedures

All of the chemicals are commercially available and used without further purification. All the reactions were carried out under aerobic conditions. Elemental analyses were determined using Elementar Vario EL elemental analyzer. The IR spectra were recorded in the 4 000~400 cm^{-1} region using KBr pellets and a Bruker EQUINOX 55 spectrometer. Thermal gravimetric analysis (TGA) data were collected on a Netzsch TG-209 instrument under nitrogen atmosphere in the temperature range of 20~800 ℃ with a heating rate of 10 ℃·min^{-1}. The solid-state circular dichroism (CD) spectra were recorded with KCl pellets on the same spectropolarimeter.

1.2 Syntheses of *L*-$[Cu_4(Hvap)_2(vap)_2(MeOH)_2](ClO_4)_2\cdot 2MeOH\cdot H_2O$ (1)

Caution! Perchlorate salts of metal complexes with organic ligands are potentially explosive. They should be handled with care and prepared only in small quantities.

The addition of $Cu(ClO_4)_2\cdot 6H_2O$ (371 mg, 1.0 mmol) and $Gd(NO_3)_3\cdot 6H_2O$ (451 mg, 1.0 mmol) to a stirred solution of *o*-vanillin (3-methoxy-4-hydroxybenzaldehyde) (152 mg, 1.0 mmol), *L*-2-amino-3-phenyl-1-propanol (152 mg, 1.0 mmol) and triethylamine (101 mg, 1.0 mmol) in methanol (40 mL) produce dark green solution. After stirring at about 50 ℃ for 40 min, 4-hydroxybenzoid acid (138 mg, 1.0 mmol) and then triethylamine (303 mg, 3.0 mmol) were added to the solution, following a continuous heating about 5 h. The resulting solution was allowed to cool down to room temperature, then filtered and the filtrate was evaporated slowly at room temperature. After two weeks, green rhombus crystals of **1** (81 mg, 18.5%) isolated from the solution. Anal. Calcd. for $Cu_4C_{72}H_{90}N_4O_{26}Cl_2$ (%, taking in H_2O, $1H_2O$, FW=1 752.59): C, 49.34; H, 5.18; N, 3.20. Found(%): C, 49.17; H, 5.09; N, 3.53. IR (KBr, cm^{-1}): 3 538, 3 331, 3 063, 3 028, 2 930, 2 836, 1 629, 1 604, 15 46, 1 496, 1 470, 1 458, 1 411, 1 377, 1 326, 1 296, 1 251, 1 221, 1 085, 1 052, 975, 926, 856, 780, 736, 702, 654, 624, 587, 509, 472, 447.

1.3 Crystal structure determination

Single-crystal data for **1** were collected at 173 K on a Bruker Smart 1000 CCD diffractometer with Mo $K\alpha$ radiation (λ=0.071 073 nm). The empirical absorption corrections were applied using the SADABS program[13]. The structures were solved using direct method, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. All the hydrogen atoms of the ligands were placed in calculated positions with fixed isotropic thermal parameters and included in structure factor calculations in the final stage of full-matrix least-squares refinement. All calculations were performed using the SHELXTL-97 system of computer programs[14]. The detailed crystallographic data are listed in Table 1 and the selected bond lengths and angles are included in Table 2.

CCDC: 883888.

2 Results and discussion

2.1 Preparation chemistry

The reaction of *o*-vanillin and *L*-2-amino-3-phenyl-1-propanol with $Cu(ClO_4)_2\cdot 6H_2O$ (371 mg, 1.0 mmol), $Gd(NO_3)_3\cdot 6H_2O$ and triethylamine in the

Table 1　Crystal data and structure refinements for complex 1

Formula	$Cu_4C_{72}H_{88}N_4O_{25}Cl_2$	V / nm^3	3.889 7(11)
Formula weight	1 734.52	Z	2
Temperature / K	173(2)	D_c / (g·cm^{-3})	1.481
Crystal size / mm	0.41×0.33×0.28	Reflections / Unique	16 644 / 12 915
Crystal system	Monoclinic	R_{int}	0.081 8
Space group	$P2_1$	Flack parameter	0.01(2)
a / nm	1.422 0(2)	GOF on F^2	1.007
b / nm	1.351 2(2)	R_1 ($I\geqslant 2\sigma(I)$)	0.0812
c / nm	2.035 1(3)	wR_2 ($I\geqslant 2\sigma(I)$)	0.2005
β / (°)	95.887(3)		

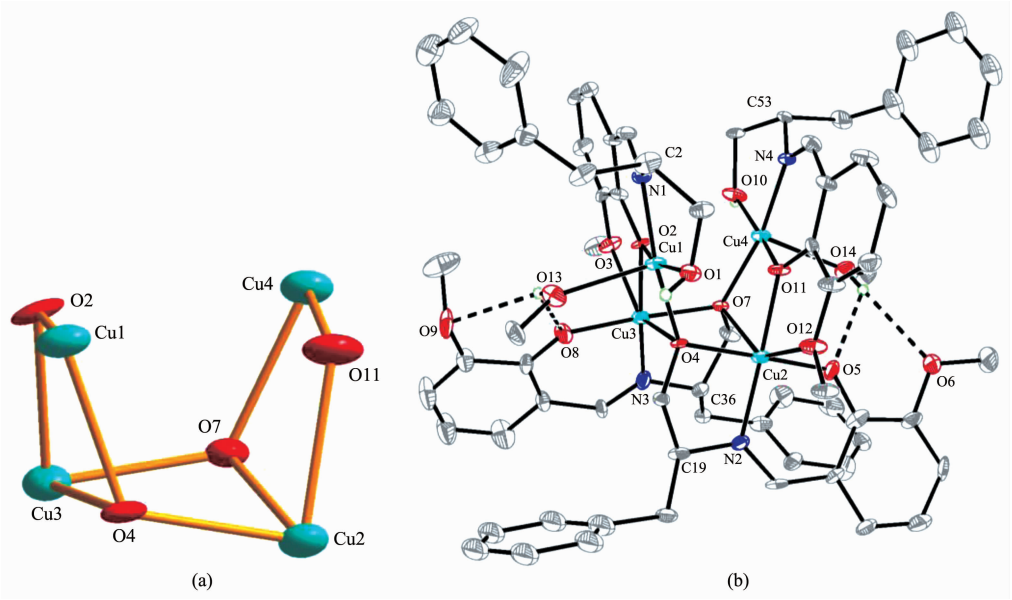
Table 2　Selected bond lengths (nm) and angles (°) for complex 1

Cu2-N2	0.196 2(9)	Cu1-O2	0.193 8(7)	Cu3-O8	0.188 3(8)
Cu2-O4	0.198 7(8)	Cu1-O4	0.192 7(7)	Cu4-N4	0.194 0(9)
Cu2-O5	0.190 2(8)	Cu1-O13	0.229 5(9)	Cu4-O7	0.193 2(7)
Cu2-O7	0.244 2(8)	Cu3-N3	0.193 4(10)	Cu4-O10	0.197 6(8)
Cu2-O11	0.199 1(7)	Cu3-O2	0.198 0(7)	Cu4-O11	0.192 9(7)
Cu2-O12	0.238 7(8)	Cu3-O3	0.239 9(8)	Cu4-O14	0.230 8(9)
Cu1-N1	0.196 3(9)	Cu3-O4	0.247 3(8)		
Cu1-O1	0.201 8(7)	Cu3-O7	0.194 4(7)		
Cu1-O4-Cu2	121.019(4)	Cu1-O2-Cu3	107.079(4)	Cu2-O7-Cu4	91.202(3)
Cu1-O4-Cu3	90.65(3)	Cu3-O7-Cu4	120.999(4)	Cu2-O11-Cu4	106.690(3)
Cu2-O4-Cu3	92.329(3)	Cu2-O7-Cu3	94.341(3)		
Cu1…Cu3	0.315 18(19)	Cu2…Cu3	0.323 41(20)	Cu1…Cu4	0.383 08(20)
Cu1…Cu2	0.340 66(19)	Cu2…Cu4	0.314 52(16)	Cu3…Cu4	0.337 21(20)

presence of 4-hydroxybenzoid acid produced **1** reproducibly. We have tried the same procedures without $Gd(NO_3)_3\cdot 6H_2O$ and 4-hydroxybenzoid acid and failed to get products. The reason why this happened has been not clarified yet. It is speculated that both gadolinlium nitrate and 4-hydroxybenzoid acid have played structure-directing-agent roles in the formation of **1**.

2.2　Crystal structure of 1

Single crystal X-ray structural analyses reveal complex **1** crystallizes in monoclinic, chiral space group $P2_1$ with Z=2. As shown in Fig.1, the molecular structure of complex **1** is based on a $\{Cu_4\}^{8+}$ core, similar to that of the copper(Ⅱ) tetranuclear recently reported[12]. Four copper(Ⅱ) atoms are held together by two alkoxide μ_3-O^{2-} atoms from two individual bideprotonated $\eta^1{:}\eta^1{:}\eta^3{:}\mu_3$-$vap^{2-}$ ligands (O4, O7) and two phenoxide μ_2-O^{2-} atoms from two individual monodeprotonated $\eta^2{:}\eta^3{:}\mu_2$-$Hvap^-$ ligands (O2, O11) to form a boat-shaped $\{Cu_4O_4\}$ unit (Fig.1a). The coordination modes of the Schiff-base ligands are shown in Fig.2. Peripheral ligation is provided by two methanol molecules. Cu2 and Cu3 ions are six-coordinated with one nitrogen atom and five oxygen atoms from Schiff-base ligands, adopting a distorted octahedral coordination sphere. The five-coordinated Cu1/Cu4 is surrounded by one oxygen atom from a methanol molecule and one nitrogen atom and three oxygen atoms from Schiff-base ligands, adopting a distorted square-pyramid geometry in which the oxygen atom from methanol molecule locates at the vertex of the distorted square-pyramid. There are intramolecular hydrogen bonding interactions between coordinated methanol molecule and vap^{2-} anions (Fig.



Hydrogen atoms are omitted for clarity except those forming hydrogen bonds; the dotted lines repreasent intramolecular hydrogen bonds (b)

Fig.1 (a) The boat-shaped $\{Cu_4O_4\}$ unit; (b) Molecular structure of **1** with the atom-numbering scheme with thermal ellipsoids at the 30% probability level

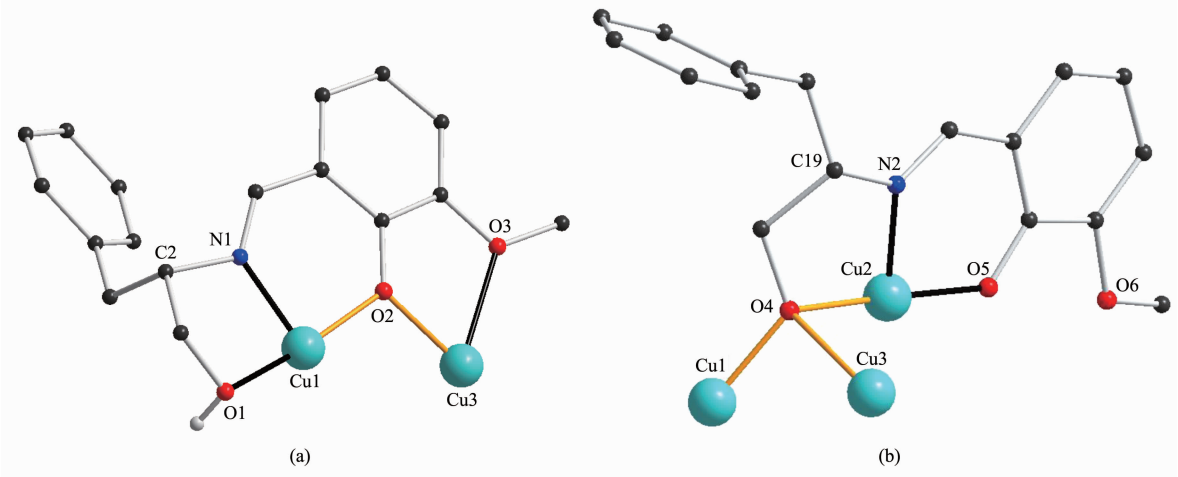


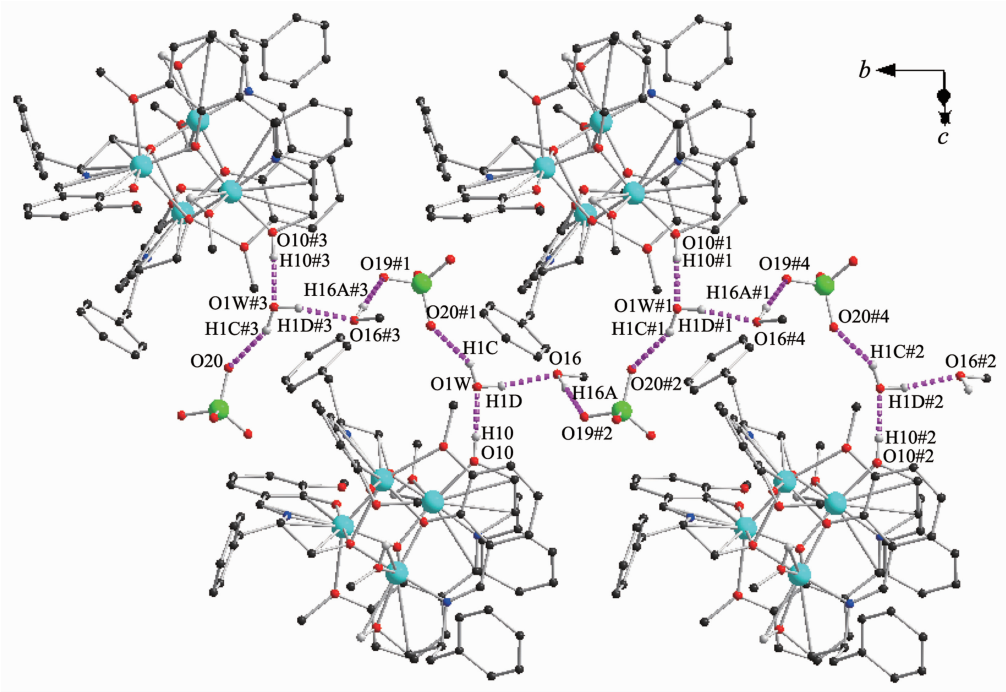
Fig.2 The coordination modes of the $Hvap^-$ (a) and vap^{2-} (b) ligands in **1**

1b and Table 3). Charge balance is afforded by two perchlorate anions in the lattice. Unlike discrete Cu_4 clusters in the complex recently reported[12], such boat-shaped Cu_4 clusters are further connected through intermolecular hydrogen bonding between oxygen atoms of the ligands, solvent molecules and perchlorate anions to form supramolecular chains along *b*-axis (Fig.3, Table 3).

As listed in Table 2, the Cu-N distances are in the normal range. The axial Cu-O distances (0.238 7(8) ~0.247 3(8) nm) of Cu2/Cu3 ion are much longer than the equatorial Cu-O distances (0.188 3(8)~0.199 1(7) nm) due to the Jahn-Teller effect of an octahedral Cu(Ⅱ) ion. As far as Cu1/Cu4 ion is concerned, the Cu-O_{MeOH} bond length (0.201 8(7) and 0.230 8(9) nm) is longer than the squared Cu-O bond lengths (0.192 7 (7) ~0.197 6 (8) nm). Each Cu ⋯ Cu distance is different from other Cu ⋯ Cu distances in the range from 0.314 52(16) to 0.383 08(20) nm, indicative of the unsymmetry nature in the Cu_4 core structure.

2.3 Thermogravimetric analyses

The TGA curve of complex **1** (Fig.4) shows an initial weight loss of 8.69% from room temperature to 120 ℃, corresponding to the removal of four methanol



Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y-1/2$, $-z$; #2: x, $y-1$, z; #3: $-x$, $y+1/2$, $-z$; #4: $-x$, $y-3/2$, $-z$

Fig.3　A view of the fragment of the hydrogen-bonded chain along b axis in **1**

Table 3　Intramolecular hydrogen-bond parameters in complex 1

D–H···A	d(D-H) / nm	d(H···A) / nm	d(D···A) / nm	∠DHA / (°)
O1–H1···O15	0.084	0.180	0.260 0(13)	157.8
O10–H10···O1W	0.084	0.177	0.260 2(13)	169.4
O13–H13A···O8	0.085	0.204	0.266 1(11)	129.3
O13–H13A···O9	0.085	0.245	0.314 0(13)	138.3
O14–H14A···O5	0.085	0.218	0.276 8(11)	126.0
O14–H14A···O6	0.085	0.237	0.302 8(11)	134.6
O15–H15A···O21	0.084	0.199	0.279 7(19)	162.0
O1W–H1C···O20#1	0.086	0.225	0.301 5(19)	149.1
O1W–H1D···O16	0.085	0.192	0.272 4(16)	156.1
O16–H16A···O19#2	0.084	0.201	0.284(2)	175.1

Symmetry transformations used to generate equivalent atoms: #1: $-x$, $y-1/2$, $-z$; #2: x, $y-1$, z.

(two coordinated ones and two lattice ones) and one lattice water molecules (calcd. 8.42%), following a plateau until 210 ℃. Then complex **1** began to decompose upon further heating.

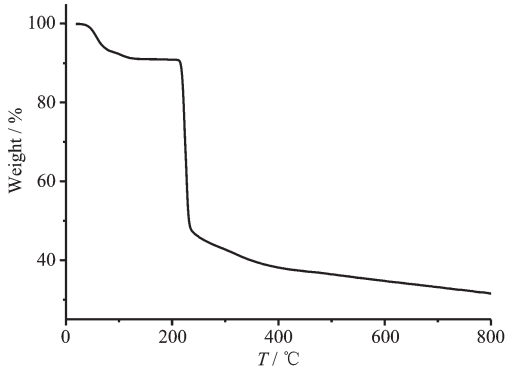


Fig.4　TGA curve of **1**

2.4　CD spectra

Considering that complex **1** is chiral, the solid-state circular dichroism (CD) spectra were recorded to probe the whole chiral nature of the bulk samples. As shown in Fig.5, the results of solid-state circular dichroism (CD) measurements show the chiral nature of complex **1** in crystalline state, revealing that the bulk crystals of complex **1** show a negative Cotton effect at 368 and 582 nm, respectively, indicative of the homochiral nature of complex **1**.

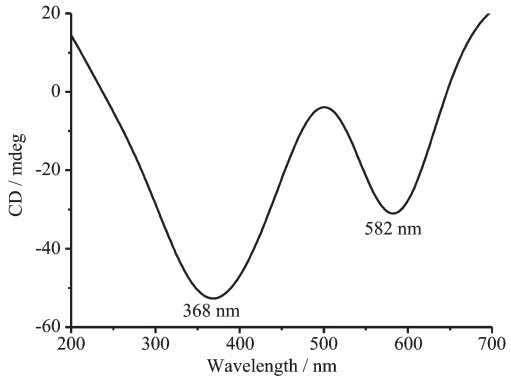


Fig.5 Solid-state CD spectra of **1**

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