

手性化合物 $[\text{Co}(\text{L}/\text{D-thr})_3] \cdot 4.5\text{H}_2\text{O}$ 的合成、结构以及圆二色性

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摘要: 合成了 2 个基于手性配体 *L*-和 *D*-苏氨酸(*L/D-thr*)的 $\text{Co}(\text{III})$ 配合物的对应异构体 $[\text{Co}(\text{L-thr})_3] \cdot 4.5\text{H}_2\text{O}$ (*L-1*)和 $[\text{Co}(\text{D-thr})_3] \cdot 4.5\text{H}_2\text{O}$ (*D-1*), 并对 2 个化合物进行了单晶 X 射线衍射、红外、热重、紫外可见光谱以及 CD 谱性质研究。晶体结构分析表明, 2 个化合物分别结晶在四方晶系 $P4_32_12$ 和 $P4_12_12$ 手性空间群。固体 CD 谱测试进一步证实 2 个化合物具有手性。

关键词: 圆二色; 手性; 氨基酸

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Syntheses, Structures and Circular Dichroism Spectroscopy of Chiral Complexes $[\text{Co}(\text{L}/\text{D-thr})_3] \cdot 4.5\text{H}_2\text{O}$

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Abstract: A couple of enantiomer $[\text{Co}(\text{L-thr})_3] \cdot 4.5\text{H}_2\text{O}$ (*L-1*) and $[\text{Co}(\text{D-thr})_3] \cdot 4.5\text{H}_2\text{O}$ (*D-1*) consisting the $\text{Co}(\text{III})$ ion, based on chiral ligand *L/D*-threonine (*L/D-thr*), were prepared and characterized by single-crystal X-ray structure analysis, IR, thermogravimetric analysis, solid-state UV-Vis spectra and circular dichroism analysis. Complexes *L-1* and *D-1* crystallize in tetragonal system $P4_32_12$ and $P4_12_12$, respectively. Moreover, the circular dichroism analysis of complexes *L-1* and *D-1* was measured with chirality, and the CD spectra of the enantiomer show change under the magnetic field inducing. CCDC: 1556561, *L-1*; 1556562, *D-1*.

Keywords: circular dichroism; chiral; amino acid

0 Introduction

The homochirality of life, one of the great mysteries in science, has become a pressing problem in the field of biochemistry. Current life forms could exist in a world where chirality of monomers such as natural amino acids and sugars forming the biological building blocks of proteins and polysaccharides^[1-3]. Chirality is present in biological machinery exten-

sively, but only one enantiomer of chiral amino acids is included in proteins^[2,4-6]. Therefore, a tremendous amount of work and interest focus on finding out the reason of this bias for one enantiomer^[4]. This further relates to the origin of life beings^[7-11].

It is known that circular dichroism (CD) is the most powerful implement for probing the chirality of matter^[7,12-13]. Natural circular dichroism (NCD) related to natural optical activity is characterized as different

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absorption when chiral media are crossed by left (LCP) and right (RCP) circularly polarized lights. This effect is a consequence of lack of mirror symmetry^[14-15]. Another effect of resemblant phenomenology is magnetic circular dichroism (MCD), where LCP and RCP are differentially absorbed when chiral objects subject to a magnetic field^[16-20]. The chiral systems present different optical properties for light propagating parallel or antiparallel to the magnetic field direction^[21-23]. For a given relative direction of magnetic field, the enantiomers exhibit the opposite signs. This effect results from the breaking of the time-inversion symmetry of the medium^[14,16-18,21,24-26]. Magnetic induction of chiroptical response of chiral matter may be a plausible candidate for elucidating the homochirality of life^[1,27-32]. Consequently, chemical, biological, and physical scientists pay considerable attention on synthesis and characterization on the chiroptical activity of chiral compounds. At the meantime, we focus our attention on exploring the change of chiroptical features under the condition of the magnetic field and without magnetic field.

Amino acids are known to play a vital role in biochemistry and life sciences^[3,33-34]. Threonine, which is one of twenty kinds of Amino acids, has a potential application in medicine, chemical reagents and food enhancer. *L*-threonine is found to be a part of several proteins of human being such as hemoglobin, insulin, β -lactoglobulin and γ -globulin^[35]. Furthermore, metal-containing metalloproteins bonded to amino acid residues play pivotal roles in biological systems, especially cobalt-containing metalloproteins^[36-40]. Cobalt, instead of other metal ions, has been employed to gather information about the change of metal sites in proteins during protein function^[39]. Moreover, cobalt atom, which is mostly six-coordinated, can be easy to coordinate with the rich O and N atoms of threonine to form the mononuclear chiral compound. This simple system can eliminate many effects of complicated factor and predigest our investigation the chiral response to magnetic field.

With the consideration above in mind, we choose cobalt bonded to amino acid threonine (*L/D*-threonine)

to successfully get a simple chiral Co-containing system, which is helpful to understanding the correlation of structure-property and figuring out whether the chirality could be alternated under the induction of the magnetic field. In the present report, oxidation of Co(II) to Co(III) in the presence of *L/D*-threonine and $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{pyr})_3](\text{ClO}_4)$ produced chiral mononuclear Co(III) enantiomer, $[\text{Co}(\text{L-thr})_3] \cdot 4.5\text{H}_2\text{O}$ (**L-1**) and $[\text{Co}(\text{D-thr})_3] \cdot 4.5\text{H}_2\text{O}$ (**D-1**). To the best of our knowledge, although early papers have focused on mononuclear Cobalt (III) *L*-threonine complexes about Λ and $\Lambda\beta$ isomers for the basic research, which have been isolated using different methods^[41-42], void information exists about MCD in the enantiomer. It is surprising that we observe the change of the compared NCD and MCD in the diamagnetic Co(III) system.

1 Experimental

1.1 Reagents and physical measurements

All the reagents and solvents were of reagent grade and used as commercially purchased without further purification.

The elemental analyses (C, H and N) were performed on a Perkin-Elmer Model 240C elemental analyzer. The Co elemental analyses were determined by the Leaman inductively coupled plasma (ICP) spectrometer. Infrared spectra ($400\sim 4\,000\text{ cm}^{-1}$) were measured on a Perkin-Elmer Fourier transform infrared (FTIR) spectrophotometer using KBr pellets (Fig.S1~S2, supporting information). Thermogravimetric analyses (TGA) were performed on a Perkin-Elmer TG-7 analyzer in flowing nitrogen atmosphere from room temperature to $800\text{ }^\circ\text{C}$ with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. Powder X-ray diffraction (PXRD) measurements were assessed on a Siemens D5005 diffractometer with Cu $K\alpha$ ($\lambda=0.154\,184\text{ nm}$) in 2θ range of $5^\circ\sim 50^\circ$ at room temperature. The XRD accelerating voltage and emission current were 40 kV and 30 mA, respectively.

1.2 Synthesis of complexes **L-1** and **D-1**

A mixture of *L*-threonine (0.059 g, 0.5 mmol), $\text{Co}(\text{Ac})_2 \cdot 4\text{H}_2\text{O}$ (0.25 g, 1 mmol) and $[\text{Mn}_3\text{O}(\text{O}_2\text{CMe})_6(\text{pyr})_3](\text{ClO}_4)$ (0.087 g, 0.1 mmol) in 40 mL of aqueous

solution was heated at 85 °C for 3 h. After the mixture was stirred at room temperature overnight, it was filtered. The filtrate was allowed to stand for several days. The red, rod-like, diffraction quality single crystals of *L*-**1** were collected, washed with a small volume of water (Yield: 65% based on Co). Anal. Calcd.(%): Co 11.92, C 29.16, H 6.73, N 8.50; Found (%): Co 11.38, C 29.71, H 6.47, N 8.45. Complex *D*-**1** was prepared in a procedure similar to that of *L*-**1**, except that *D*-threonine was used instead of *L*-threonine (Yield: 60 % based on Co). Anal. Calcd.(%): Co 11.92, C 29.16, H 6.73, N 8.50; Found(%): Co 11.02, C 29.62, H 6.24, N 8.20.

1.3 Details of X-ray crystallography

Single-crystal X-ray diffraction data for complexes *L*-**1** and *D*-**1** were measured on a Bruker SMART

APEX CCD area detector diffractometer using graphite monochromated Mo *K* α radiation (λ =0.071 073 nm) at 153 K. Structure solution (direct methods) and the refinement of full-matrix least-squares were carried out using the SHELXTL software package^[43-45]. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms attached to carbon and nitrogen atoms were placed in geometrically calculated positions. For both complexes *L*-**1** and *D*-**1**, the hydrogen atoms on one non-coordinated H₂O molecule were not located. Crystallographic and refinement details for the two complexes are summarized in Table 1. Selected bond lengths and angles are listed in Table S1~S2 (Supporting information).

CCDC: 1556561, *L*-**1**; 1556562, *D*-**1**.

Table 1 Crystallographic data and structure refinement summary for complexes *L*-**1** and *D*-**1**

	<i>L</i> - 1	<i>D</i> - 1
Formula	C ₂₄ H ₆₆ Co ₂ N ₆ O ₂₇	C ₂₄ H ₆₆ Co ₂ N ₆ O ₂₇
Formula weight	988.67	988.67
Space group	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2
Crystal system	Tetragonal	Tetragonal
<i>a</i> / nm	1.440 00(6)	1.439 80(9)
<i>b</i> / nm	1.440 0	1.439 8
<i>c</i> / nm	1.977 00(9)	1.977 20(12)
<i>V</i> / nm ³	4.099 5(4)	4.098 8(6)
<i>Z</i>	4	4
<i>D</i> _c / (g·cm ⁻³)	1.599	1.599
<i>F</i> (000)	2 080	2 080
θ range / (°)	1.75~26.03	1.75~26.038
Unique reflections (<i>R</i> _{int})	0.038	0.04 32
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b [<i>I</i> >2 σ (<i>I</i>)]	0.029 5, 0.071 4	0.031 0, 0.074 1
<i>R</i> ₁ ^a , <i>wR</i> ₂ ^b (all data)	0.033 1, 0.073 3	0.035 5, 0.076 5
GOF on <i>F</i> ²	1.047	1.059

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_c|; ^b wR_2 = [\sum w(|F_o| - |F_c|)^2 / \sum w(F_o^2)]^{1/2}; w = 1/\sigma(F_o)^2.$$

2 Results and discussion

2.1 Synthesis

Heating aqueous solution mixture of *L*-threonine, Co(Ac)₂·4H₂O and [Mn₃O(O₂CMe)₆(pyr)₃]ClO₄ in the molar ratio of 5:10:1 afforded red rod-like crystals of [Co(*L*-thr)₃] $\cdot$ 4.5H₂O (*L*-**1**). The complex [Co(*D*-thr)₃] $\cdot$ 4.5H₂O (*D*-**1**) was prepared in a procedure similar to

that of *L*-**1**, except that *D*-threonine was used instead of *L*-threonine. Although the element of [Mn₃O(O₂CMe)₆(pyr)₃]ClO₄ do not appear in the crystal structure of complexes *L*-**1** and *D*-**1**, its presence in the reaction mixture is essential to generate the crystal product with a good quality. Single crystal X-ray diffraction studies reveal that both enantiopure complexes *L*-**1** and *D*-**1** are isolated by enantioselective synthesis in

the presence of enantiopure chiral species, which crystallize in chiral space groups $P4_32_12$ and $P4_12_12$, with the absolute structure parameters of $-0.002\ 0(15)$ and $-0.002\ 0(16)$, respectively. In each compound, one asymmetric unit contains $[\text{Co}(\text{III})(L\text{-thr})_3]$ or $[\text{Co}(\text{III})(D\text{-thr})_3]$ (Fig.1a~1b).

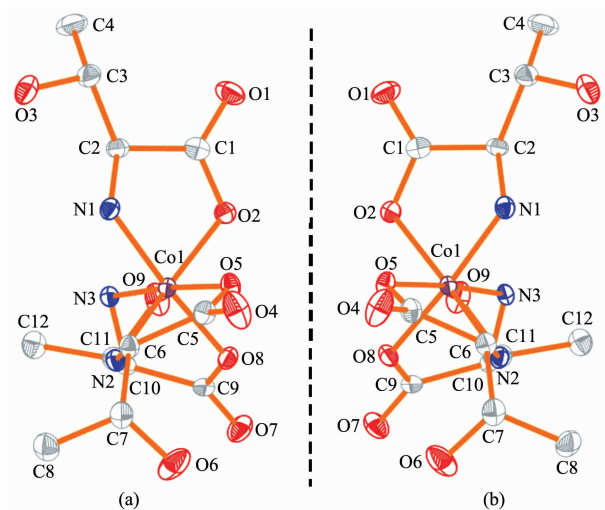


Fig.1 Ellipsoid of $[\text{Co}(\text{III})(L\text{-thr})_3]$ in L -1 (a) and $[\text{Co}(\text{III})(D\text{-thr})_3]$ in D -1 (b) along a axis, and the probability is 50%

2.2 X-ray crystal structures

The cobalt ion displays slightly distorted octahedral coordination geometry by coordination with three N and three O atoms from three L/D -threonine ligands. The Co-O distance is shorter than the Co-N distances in both complexes (Table S1 and S2) (Average Co-O distance: 0.190 7 nm; Co-N distance: 0.193 2 nm). It is noteworthy that the valence of cobalt has been assigned as +3 oxidation state according to

charge balance consideration and crystallographic request as well as confirming by bond valence sum (BVS) calculations^[46-48]. Intermolecular hydrogen bonds play a dominating contribution on forming supramolecular topology (Fig.2a~2b). The hydrogen bonding linked inter-chains for L -1 and D -1 are showing in Fig.S3.

2.3 Thermal stability and PXRD analysis of L -1 and D -1

We recorded IR spectra of the two complexes compared with that of the free ligands L -thr and D -thr. There are three characteristic absorption bands observed for free ligands L/D -thr: the stretching vibration $\nu(\text{N-H})$ at $3\ 027\ \text{cm}^{-1}$, and asymmetric and symmetric stretching vibrations, $\nu_{\text{as}}(\text{COO}^-)$ at $1\ 627\ \text{cm}^{-1}$ and $\nu_{\text{s}}(\text{COO}^-)$ at $1\ 480\ \text{cm}^{-1}$. The enantiomer L -1 and D -1 exhibit similar IR absorptions (Fig.S1~S2). Compared to the ligands L - and D -thr, the two new forming complexes are observed some changes of the characteristic absorption bands (Fig.S1). Therefore, the changes indicate that the coordination to the Co(III) ions are amino nitrogen and carboxylate oxygen of free ligands L -thr/ D -thr to form novel complexes. Thermal stabilities measurements indicate that lattice water molecules are easy to release in the temperature range of $25\sim 104\ ^\circ\text{C}$ for the two compounds (Fig.S4). The phase purity is confirmed by powder X-ray diffraction (PXRD) at room temperature. The experimental patterns of L -1 and D -1 are in fairly good agreement with the simulated ones generated from single-crystal diffraction data (Fig.S5~S6).

2.4 Circular dichroism of L -1 and D -1

Solid-state UV-Vis spectra were recorded for the two complexes L -1 and D -1 at room temperature as shown in Fig.3a. The two complexes show similar absorption bands. There are three peaks at 230, 375, 521 nm. The broad band at 521nm observed for L -1/ D -1 could be attributed to $^1A_{1g} \rightarrow ^1T_{1g}$ transition in a distorted octahedral geometry around Co(III) ion^[49-51]. The two bands with high energy are assigned to ligand to metal transition. In respect that compounds L -1 and D -1 are both insoluble in water and common organic solvents, in order to examine the chiroptical activities,

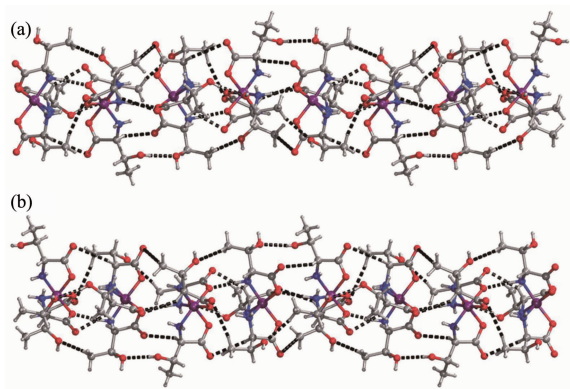


Fig.2 Side view of 1D hydrogen bonding linked chains in L -1 (a) and D -1 (b) along a axis

the solid state circular dichroism (CD) spectra of the two compounds were measured by mixing enantiopure crystal pressed in KBr matrices at room temperature. As shown in Fig.3b, the two compounds show pronounced optical activity in the solid state and afford approximately mirror-image CD spectra of each other. It is found that *L*-1 reveals three negative

Cotton effects at 296, 369 and 524 nm, respectively. While the *D*-1 shows opposite Cotton effects at the same wavelengths, indicating that the two compounds are enantiomer. Fig.3c shows the result of MCD for the enantiomer *L*-1 and *D*-1. Then, the same disks are put under the 0.7 T magnetic field, which have been employed CD measurement. This feature is observed within the experimental accuracy. It is very interesting to note that the peak at 296 nm has disappeared and new absorption peak has emerged at 420 nm for the enantiomers. To our surprise, when we removed the magnetic field, the CD spectra of the enantiomer have recur as the line shapes of the first CD spectra (Fig.3b and 3d), except that the spectra exhibit slight bathochromic shifts (20 nm) near 316 nm in the UV region.

3 Conclusions

In summary, we synthesize a couple of enantiomers *L*-1 and *D*-1. In order to examine the chiroptical activities, we measured the solid state CD and MCD spectra, which are both of opposite sign for the enantiomers. Compared to the CD spectra, MCD spectra of the enantiomers show new absorption peaks at 420 nm, while the peaks at 296 nm have disappeared. The essence of the alternate signal of the CD spectra with or without magnetic induction is still an open question for the scientists, which is interesting from the viewpoint of possible contribution for explaining the question above mentioned. The further work, which relates to embed other paramagnetic metal ion coordination with the remaining coordination site to isolate homochiral magnetic complexes, is in progress with an eye on their eventual applications in life sciences.

Supporting information is available at <http://www.wjhxsb.cn>

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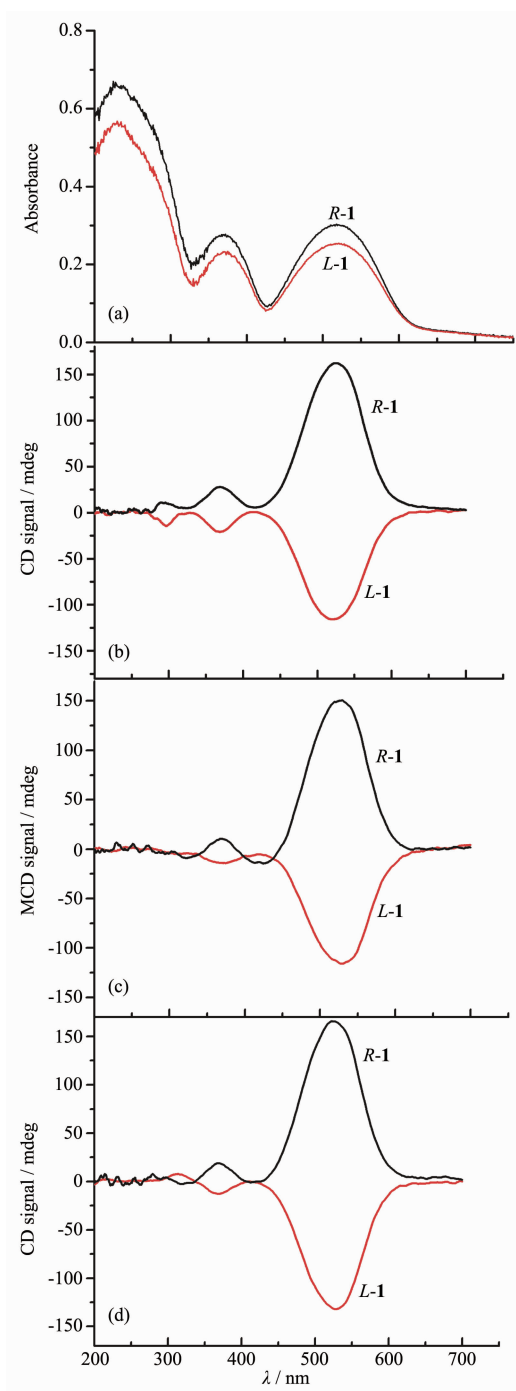


Fig.3 UV-Vis (a), CD (b), MCD (c) and CD (d) spectra of *L*-1 and *D*-1

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