

对称性破缺:手性高氯酸乙酸·二(乙二胺)合锌(II)的合成与结构

欧光川* 李治章 张 敏 袁先友*
(湖南科技学院生命科学与化学工程系,永州 425199)

摘要: 用简单的非手性原料醋酸锌和乙二胺在高氯酸钠的甲醇溶液中反应,反应过程中发生了对称性破缺现象,得到了一对对映体 Δ -*cis*-[Zn(en)₂Ac][ClO₄] (Δ -**1**) 和 Λ -*cis*-[Zn(en)₂Ac][ClO₄] (Λ -**1**) (en=乙二胺, Ac⁻=醋酸根)。用元素分析、红外光谱、CD 光谱和 X-ray 单晶衍射对产物进行了表征。X-ray 单晶衍射结果表明配合物 Δ -**1** 和 Λ -**1** 中的锌(II)离子均与 2 个乙二胺上的 4 个氮原子和醋酸根上的 2 个氧原子顺式配位,形成六配位畸变的八面体构型。 $\{\Delta$ -*cis*-[Zn(en)₂Ac]⁺和 $\{\Lambda$ -*cis*-[Zn(en)₂Ac]⁺单体通过氢键作用分别形成具有右手和左手双螺旋的一维链。用 X-ray 单晶衍射和 CD 光谱确定了配合物的手性特征。

关键词: 对称性破缺; 锌配合物; 晶体结构; CD 光谱; 手性

中图分类号: O641.24[†]

文献标识码: A

文章编号: 1001-4861(2014)06-1459-05

DOI: 10.11862/CJIC.2014.187

Symmetry Breaking: Synthesis, Crystal Structure of Chiral Acetatobis(diaminoethane)zinc(II) Perchlorate

OU Guang-Chuan* LI Zhi-Zhang ZHANG Min YUAN Xian-You*

(Department of Biology and Chemistry, Hunan University of Science and Engineering, Yongzhou, Hunan 425199, China)

Abstract: The reaction of zinc acetate with diaminoethane and sodium perchlorate gave two chiral complexes Δ -*cis*-[Zn(en)₂Ac][ClO₄] (Δ -**1**) and Λ -*cis*-[Zn(en)₂Ac][ClO₄] (Λ -**1**) (en=diaminoethane, Ac⁻=Acetic anion) in the absence of any chiral source, and the spontaneous chiral symmetry breaking occurs during the reaction. The products were characterized by elemental analysis, IR, circular dichroism (CD) spectra. Single crystal X-ray diffraction analyses indicated that the central Zn(II) atoms in Δ -**1** and Λ -**1** display a distorted six-coordinate octahedral coordination geometry by coordination with four nitrogen atoms of two diaminoethane ligands, and two oxygen atoms of Ac⁻ in the *cis*-position. It was found that the monomers of $\{\Delta$ -*cis*-[Zn(en)₂Ac]⁺ and $\{\Lambda$ -*cis*-[Zn(en)₂Ac]⁺ are connected through the intermolecular hydrogen bonds to generate one-dimensional double-stranded chains with right-handed and left-handed double-helicity. The chiral natures of Δ -**1** and Λ -**1** are confirmed by the results of X-ray diffraction and CD spectra measurements. CCDC: 957460, Δ -**1**; 957461, Λ -**1**.

Key words: symmetry breaking; zinc(II) complex; crystal structure; CD spectra; chirality

The research of origin of biomolecular homochirality is a fascinating challenge in science^[1]. Symmetry breaking is the common phenomena in various biology systems and in nature. It is very

important to investigate the mechanism of spontaneous symmetry breaking in the process of molecule crystallization without any enantiopure chiral auxiliary, which could provide some new evidences for

收稿日期: 2013-10-08。收修改稿日期: 2013-12-14。

湖南省大学生研究性学习和创新性实验计划(No.2013-191), 湖南省教育厅项目(No.13B029, 13A030), 湖南省“十二五”重点建设学科(No.2011-76), 湖南省科技创新团队(No.2012-318), 湖南省科技计划(No.2013FJ3004)和湖南科技学院英才计划资助项目。

*通讯联系人。E-mail: ouguangchuan@gmail.com, yuanxianzhangmin@163.com

exploring the origins of life. Though spontaneous resolution, known as the segregation of enantiomers upon crystallization, was first discovered by Louis Pasteur^[2] over 100 years ago when he manually separated left-handed from right-handed crystals of sodium ammonium tartrate, and the mechanism of spontaneous symmetry breaking in the process of chiral molecule crystallization were supposed^[3-7], it can not be predicted in advance. Recently, many examples of chiral symmetry breaking have been reported^[8-15].

Although the title complexes were prepared 40 years ago by Curtis^[16], the chiral symmetry breaking phenomenon cannot be put forward, and the laws of physics determining the processes are not yet fully understood. Herein, we reported on the chiral symmetry breaking of the zinc acetate with diaminoethane and sodium perchlorate, and two one-dimensional hydrogen bonded homochiral double-stranded helical chains of Δ -*cis*-[Zn(en)₂Ac][ClO₄] (Δ -**1**) and Λ -*cis*-[Zn(en)₂Ac][ClO₄] (Λ -**1**).

1 Experimental

1.1 Materials and general methods

All the chemicals were commercially sourced and used without further purification. Elemental analyses were determined using an Elementar Vario EL elemental analyzer. IR spectra were recorded in the 4 000~400 cm⁻¹ region using KBr pellets and a Bruker EQUINOX 55 spectrometer. The solid (KCl pellets) circular dichroism (CD) spectra were recorded on a JASCO J-810 spectropolarimeter.

1.2 Synthesis of Δ -*cis*-[Zn(en)₂Ac][ClO₄] (Δ -**1**) and Λ -*cis*-[Zn(en)₂Ac][ClO₄] (Λ -**1**)

To a stirred solution of zinc acetate dihydrate

(0.219 g, 1 mmol) in 10 mL of methanol was added dropwise a methanol solution (10 mL) of diaminoethane (0.120 g, 2 mmol) and sodium perchlorate (0.367 g, 3 mmol). The solution was filtered and evaporated slowly at room temperature. After several weeks, colorless block crystals of Δ -**1** and Λ -**1** were obtained. Anal. Calcd. for C₆H₁₉ClN₄ZnO₆(%): C, 20.94; H, 5.56; N, 16.28. Found (%): C, 20.43; H, 5.72; N, 16.42. IR (KBr, cm⁻¹): 3 290 (s), 2 948 (w), 1 562 (vs), 1 413 (s), 1 116 (m), 1 024 (s), 630 (s), 518 (m).

1.3 Crystal structure determination

Single-crystal data for Δ -**1** and Λ -**1** were collected on a Bruker Smart Apex II diffractometer, with Mo K α radiation (λ =0.071 073 nm). The empirical absorption corrections were applied using the SADABS program^[17]. Both structures were solved using direct methods, which yielded the positions of all non-hydrogen atoms. These were refined first isotropically and then anisotropically. Hydrogen atoms attached to carbon atoms were located geometrically and refined using the riding model, and the hydrogen atoms attached to nitrogen were located from the difference maps and refined with isotropic thermal parameters. All calculations were performed using the SHELXTL system of computer programs^[18]. For Δ -**1** and Λ -**1**, C6 atom is disordered over two symmetry related sites (occupancies 0.535(16):0.465(16) for Δ -**1**, 0.641(15):0.359(15) for Λ -**1**). The crystallographic data for Δ -**1** and Λ -**1** are summarized in Table 1. Selected bond lengths and angles are listed in Table 2. Hydrogen bond parameters are given in Table 3.

CCDC: 957460, Δ -**1**; 957461, Λ -**1**.

Table 1 Crystal data and structure refinements for Δ -**1** and Λ -**1**

Compound	Δ - 1	Λ - 1
Empirical formula	C ₆ H ₁₉ ClN ₄ ZnO ₆	C ₆ H ₁₉ ClN ₄ ZnO ₆
Formula weight	344.07	344.07
Temperature / K	296(2)	296(2)
Crystal size / mm	0.43×0.38×0.16	0.42×0.39×0.25
Crystal system	Tetragonal	Tetragonal
Space group	<i>P</i> 4 ₃ 2 ₁ 2	<i>P</i> 4 ₃ 2 ₁ 2
<i>a</i> / nm	0.958 53(3)	0.958 13(6)

Continued Table 1

b / nm	0.958 53(3)	0.958 13(6)
c / nm	3.082 5(2)	3.079 2(4)
V / nm^3	2.832 1(3)	2.826 7(4)
Z	8	8
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.614	1.617
μ / mm^{-1}	1.947	1.951
$F(000)$	1 424	1 424
Unique refl. (R_{int})	3 248 (0.019 4)	3 225 (0.020 4)
Goodness-of-fit on F^2	1.015	1.068
Final R indices ($I > 2\sigma(I)$)	0.045 7, 0.140 2	0.045 7, 0.134 4
R indices (all data)	0.048 7, 0.145 9	0.048 4, 0.136 5
Absolute structure parameter	0.06(3)	0.03(3)

Table 2 Selected bond distances (nm) and angles ($^\circ$)

$\Delta\text{-1}$					
Zn(1)-N(1)	0.215 4(4)	Zn(1)-N(2)	0.211 5(4)	Zn(1)-N(3)	0.213 4(4)
Zn(1)-N(4)	0.211 1(4)	Zn(1)-O(1)	0.217 3(4)	Zn(1)-O(2)	0.235 2(4)
N(1)-Zn(1)-O(1)	90.00(16)	N(2)-Zn(1)-N(1)	81.57(17)	N(2)-Zn(1)-O(1)	149.13(16)
N(1)-Zn(1)-O(2)	92.16(16)	N(2)-Zn(1)-N(3)	96.02(17)	N(2)-Zn(1)-O(2)	93.07(16)
N(3)-Zn(1)-N(1)	177.53(18)	N(3)-Zn(1)-O(1)	92.35(15)	N(3)-Zn(1)-O(2)	88.48(16)
N(4)-Zn(1)-N(1)	97.99(17)	N(4)-Zn(1)-N(3)	82.14(17)	N(4)-Zn(1)-O(2)	159.53(15)
N(4)-Zn(1)-N(2)	105.94(17)	N(4)-Zn(1)-O(1)	104.62(15)	O(1)-Zn(1)-O(2)	57.44(13)
$\Lambda\text{-1}$					
Zn(1)-N(1)	0.215 2(4)	Zn(1)-N(2)	0.211 4(4)	Zn(1)-N(3)	0.212 8(4)
Zn(1)-N(4)	0.210 9(4)	Zn(1)-O(1)	0.234 3(4)	Zn(1)-O(2)	0.216 9(4)
N(1)-Zn(1)-O(1)	92.08(16)	N(2)-Zn(1)-N(1)	81.53(16)	N(2)-Zn(1)-O(1)	92.92(15)
N(1)-Zn(1)-O(2)	90.22(16)	N(2)-Zn(1)-N(3)	95.70(17)	N(2)-Zn(1)-O(2)	149.13(16)
N(3)-Zn(1)-N(1)	177.23(18)	N(3)-Zn(1)-O(2)	92.25(16)	N(3)-Zn(1)-O(1)	88.18(16)
N(4)-Zn(1)-N(1)	98.16(17)	N(4)-Zn(1)-N(3)	82.45(16)	N(4)-Zn(1)-O(2)	104.67(14)
N(4)-Zn(1)-N(2)	105.92(16)	N(4)-Zn(1)-O(1)	159.64(14)	O(2)-Zn(1)-O(1)	57.51(13)

Table 3 Hydrogen bonds for $\Delta\text{-1}$ and $\Lambda\text{-1}$

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
$\Delta\text{-1}$				
N(3)-H(3B) \cdots O(1)A	0.090	0.206	0.291 9(6)	159.1
N(4)-H(4B) \cdots O(2)C	0.090	0.222	0.305 6(6)	154.5
$\Lambda\text{-1}$				
N(3)-H(3C) \cdots O(2)D	0.090	0.204	0.2909(6)	162.2
N(4)-H(4A) \cdots O(1)E	0.090	0.222	0.306 1(6)	155.5

Symmetry transformations used to generate equivalent atoms: A: $-1/2+x, 3/2-y, 1/4-z$; C: $1/2+x, 3/2-y, 1/4-z$; D: $3/2-x, 1/2-y, 1/4-z$; E: $3/2-x, 1/2+y, 1/4-z$.

2 Results and discussion

2.1 Description of the crystal structures

Complexes $\Delta\text{-1}$ and $\Lambda\text{-1}$ are a pair of

enantiomers (Fig.1a, Fig.1b), and crystallize in the chiral space group $P4_32_12$ and $P4_12_12$, with the absolute structure parameters of 0.06(3) and 0.03(3),

respectively. In each complex **Δ -1** and **Λ -1**, one asymmetric unit contains one *cis*-[Zn(en)₂Ac]⁺ and one ClO₄⁻. In each cation, the Zn(II) ion displays a distorted octahedral coordination geometry by coordination with four nitrogen atoms of two diaminoethane ligands, and two carboxylate oxygen atoms of Ac⁻ in *cis*-position (Fig.1). The Zn-N distance (0.211 1(4)~0.215 4(4) nm for **Δ -1**, 0.210 9(4)~0.215 2(4) nm for **Λ -1**) is slightly shorter than the Zn-O distances (0.217 3(4)~0.235 2(4) nm for **Δ -1**, 0.216 9(4)~0.234 3(4) nm for **Λ -1**) (Table 2). In **Δ -1**, the Δ -*cis*-[Zn(en)₂Ac]⁺ monomers are connected through the N-H...O (0.291 9(6) and 0.305 6(6) nm) (Table 3) hydrogen bonds between two carboxylate oxygen atoms (O1 and O2) of Ac⁻ and two primary amines (N3 and N4) of diaminoethane of adjacent Δ -*cis*-[Zn(en)₂Ac]⁺ cation, generating a novel one-dimensional homochiral chain with right-handed and left-handed double-helicity (Fig.2a). Each helix in the right-handed and left-handed helical chain contains two Δ -*cis*-[Zn(en)₂Ac]⁺ monomers, with the same pitch of 0.958 nm and the different helix diameter of 0.275 and 0.465 nm, respectively. In contrast to **Δ -1**, the connection of Λ -*cis*-[Zn(en)₂Ac]⁺ monomers in **Λ -1** through similar intermolecular hydrogen bonds

generates a novel one-dimensional homochiral chain with left-handed and right-handed double-helicity (Fig.2b). The results have demonstrated that hydrogen bonds play a key role in the process of symmetry breaking upon crystallization in the absence of any chiral source, and offer a new evidence for exploring the origins of life.

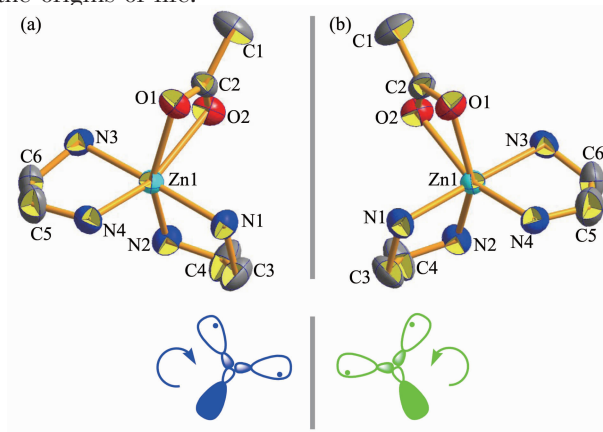
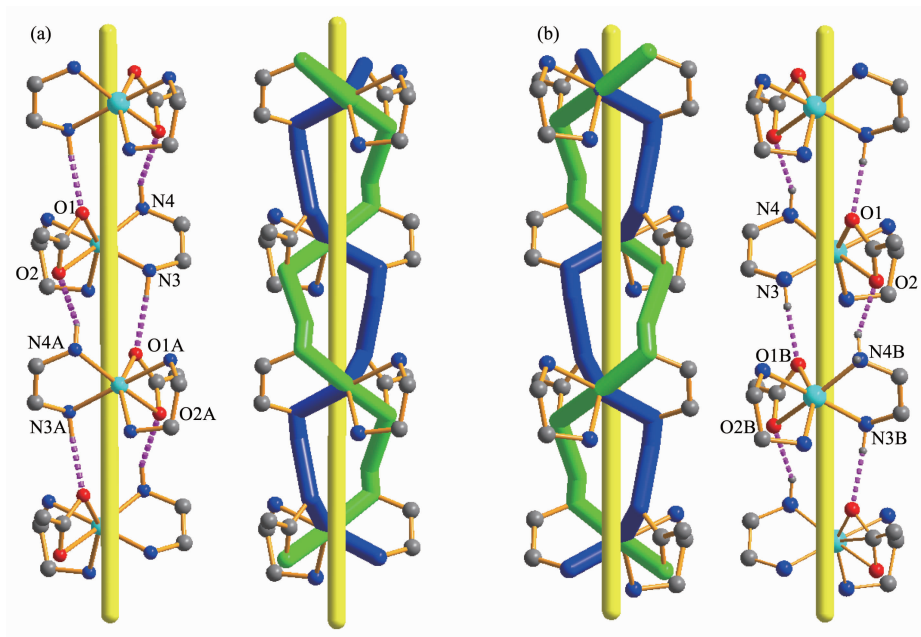


Fig.1 Enantiomers of (a) ORTEP diagram of the asymmetry unit of Δ -*cis*-[Zn(en)(Ac)]⁺ in **Δ -1**, (b) ORTEP diagram of the asymmetry unit of Λ -*cis*-[Zn(en)(Ac)]⁺ in **Λ -1** with 50% probability displacement ellipsoids

2.2 CD spectra

The results of solid CD measurements are



Symmetry codes for the generated atoms: A: 1/2+x, 3/2-y, 1/4-z; B: 3/2-x, 1/2+y, 1/4-z

Fig.2 Side view of (a) one-dimensional hydrogen bonded chain with left-handed and right-handed double-helicity in **Δ -1**, (b) one-dimensional hydrogen bonded chain with right-handed and left-handed double-helicity in **Λ -1**

consistent with the results of X-ray crystal structures. As shown in Fig.3, the five single crystals, which are random picked up from the bulk crystals, show a negative Cotton effect at about $\lambda_{\text{max}}=230$ nm, a positive Cotton effect at about $\lambda_{\text{max}}=290$ and 620 nm. The positive Cotton effect at about 290 nm may be an exciton couplet pattern, corresponding to the amine $\pi-\pi^*$ transition. According to the law of exciton split^[14,19], the absolute configurations of the five single crystals are Δ conformation. The solid CD spectra of the five single crystals show similar dichroic signal, indicating the same chiral natures of the five crystals. Unfortunately the dichroic signal of single crystals with Λ conformation are not obtained. When other eight single crystals, which are random picked up from the bulk crystals, were determined by X-ray diffraction, we find six complexes crystallize in the chiral space group $P4_22_1$, and two complexes crystallize in $P4_22_1$ (Tables 1 and S1). The results of single crystal X-ray diffraction analyses and solid CD spectra indicate symmetry breaking occurs during the reaction of zinc acetate with diaminoethane and sodium perchlorate to generate a pair of enantiomers, in which one enantiomer over the other. The solid state CD spectrum indicate significant chirality manifested throughout the entire polycation structure.

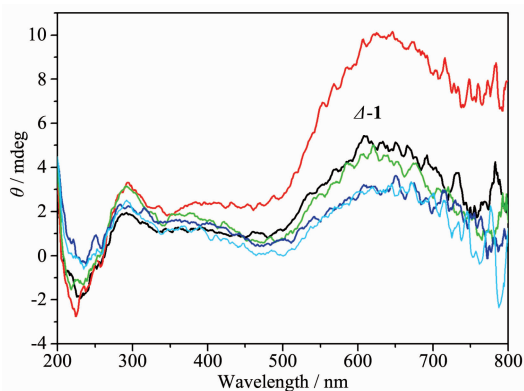


Fig.3 Solid CD spectra of five single crystals with Δ conformation which are random picked up from the bulk crystals

Supporting information is available at <http://www.wjhxxb.cn>: The crystallographic data of other six single crystals (Table S1) have been included.

References:

- [1] Jones N. *Nature*, **2012**, **481**:14-17
- [2] Pasteur L. *Ann. Chim. Phys.*, **1848**, **24**:442-450
- [3] Asakura K, Osanai S, Kondepudi D K. *Chirality*, **2001**, **13**: 435-440
- [4] Asakura K, Kobayashi K, Mizusawa Y, et al. *Physica. D*, **1995**, **84**:72-78
- [5] Asakura K, Inoue K, Osanai S, et al. *J. Coord. Chem.*, **1998**, **46**:159-164
- [6] Asakura K, Kondepudi D K, Martin R. *Chirality*, **1998**, **10**: 343-348
- [7] Asakura K, Ikumo A, Kurihara K, et al. *J. Phys. Chem. A*, **2000**, **104**:2689-2694
- [8] Hou Y, Fang X K, Hill C L. *Chem. Eur. J.*, **2007**, **13**:9442-9447
- [9] ZHANG Hui(章慧), WANG Xian-Ying(王宪营), CHEN Lei-Qi(陈雷奇), et al. *Acta Phys.-Chim. Sin.*(物理化学学报), **2006**, **22**:608-615
- [10] LIN Li-Rong(林丽榕), HU Wang-Xia(胡望霞), MA Jie(马杰), et al. *Acta Chim. Sinica*(化学学报), **2010**, **68**:703-706
- [11] XUAN Wei-Min(宣为民), ZOU Fang(邹方), CHEN Lei-Qi(陈雷奇), et al. *Acta Phys.-Chim. Sin.*(物理化学学报), **2008**, **24**:955-960
- [12] Shen G Y, Liu M R. *Chemistry*, **2013**, **76**:224-230
- [13] Zhang L, Tian Y, Liu M H. *Phys. Chem. Chem. Phys.*, **2011**, **13**:17205-17209
- [14] ZHAO Lei(赵楠), WAN Shi-Gang(万仕刚), CHEN Cheng-Dong(陈成栋), et al. *Acta Phys.-Chim. Sin.*(物理化学学报), **2013**, **29**:1183-1191
- [15] Kang S H, Shan S C, Noorduyn W L. *Adv. Mater.*, **2013**, **25**: 3380-3385
- [16] Curtis N F. *J. Chem. Soc. A*, **1968**:1579-1584
- [17] Sheldrick G M. *SADABS, Program for Empirical Absorption Correction of Area Detector Data*, University of Göttingen, Göttingen, **1996**.
- [18] Sheldrick G M. *Acta Cryst.*, **2008**, **A64**:112-122
- [19] Berova N, Bari L D, Pescitelli G. *Chem. Soc. Rev.*, **2007**, **36**: 914-931