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A single-helix coordination polymer with mixed ligands $[Zn_2(phen)_2(e,a\text{-}cis\text{-}1,4\text{-}chdc)_2(H_2O)_2]_n$ (phen = 1,10-phenanthroline; chdc = cyclohexanedicarboxylate)

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Abstract

A coordination polymer with mixed ligands $[Zn_2(phen)_2(e,a\text{-}cis\text{-}1,4\text{-}chdc)_2(H_2O)_2]_n$ (chdc = cyclohexanedicarboxylic acid; phen = 1,10-phenanthroline) was prepared under hydrothermal conditions and characterized by elemental analyses, IR spectra, TG analysis, and single-crystal X-ray diffraction analysis. X-ray crystal structural analyses reveal that **1** and **2** are isomorphic and belong to the monoclinic system. $C_{40}H_{36}Zn_2N_4O_{10}$, $P2_1/c$, $a = 10.084(2)$ Å, $b = 8.9072(18)$ Å, $c = 20.276(4)$ Å, $\beta = 99.92(3)°$, $V = 1793.9(6)$ Å^3, $Z = 1$. In the structures of **1**, the 1,4-chdc ligand possesses only one kind of *e*,*a*-*cis*-conformation although there are both *cis*- and *trans*-conformations in the raw material. Two oxygen atoms of one carboxyl in 1,4-chdc ligand and another oxygen atom of contraposition carboxyl link adjacent Zn atoms into an infinite 1D zigzag chain. The most attractive structural feature of **1** is that it exhibits an infinite chiral chain-like structure with 2_1 helices along the *b*-axis. In addition, the right- and left-handed chains are alternate. Meanwhile, the adjacent chains of **1** is linked via hydrogen bonds into 2D network structures, which further form 3D frameworks via π–π interactions of 1,10-phen.

Keywords: Mixed ligands; Chiral; Helical chain; 3D network

1. Introduction

Over the past decade, helical structures have received much attention in coordination chemistry and materials chemistry because helicity is an essence of life and is also important in advanced materials such as optical devices, enantiomer separation, chiral synthesis, ligand exchange, and selective catalysis [1–5]. Consequently, many single-, double- and higher-order stranded helical complexes have been generated by self-assembly processes [6–10]. Most of recent studies in this area are involved with the construction from d^{10} transition metal ions and functional ligands [11–16]. The octahedral metal complexes coordinated with chelating ligands have been considered promising owing to their inherently chiral centers [17,18]. 1,4-Cyclohexanedicarboxylic acid (chdcH2) possesses a chair-type structure with *cis*- and *trans*-conformations (Scheme 1). Thus, it can connect metal ions in different directions. Hence, chdc may be a good candidate for the construction of chiral coordination polymers. We report here the preparations and crystal structure characterizations of a helical coordination polymer $[Zn_2(phen)_2(e,a\text{-}cis\text{-}1,4\text{-}chdc)_2(H_2O)_2]_n$ (**1**). It should be pointed out that the 1,4-chdc ligands in the product **1** possesses only one kind of *e*,*a*-*cis*-conformation.

2. Experimental

All reagents were purchased commercially and used without further purification. Deionized water was used

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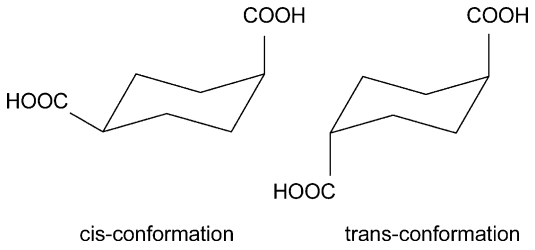

Scheme 1. The conformations of 1,4-cyclohexanedicarboxylic acid.

for the hydrothermal synthesis. The hydrothermal reaction was performed in a 15 mL Teflon-lined stainless steel autoclave at 180 °C under autogenous pressure. Elemental analyses (C, H and N) were performed on a Perkin–Elmer 2400 CHN Elemental Analyzer. Zn element is determined by ICP-AES analysis. The infrared spectras of the compound was obtained on an Alpha Centaurt FT/IR spectrometer with pressed KBr pellets in the 4000–500 cm^{-1} region.

2.1. Synthesis of $[Zn_2(1,10\text{-phen})_2(e,a\text{-cis-}1,4\text{-chdc})_2(H_2O)_2]_n$ (1)

A mixture of $ZnCl_2 \cdot 6H_2O$ (0.1421 g, 0.6 mmol), 1,4-chdc acid (mixture of *cis* and *trans* 99%) (0.1033 g, 0.6 mmol), 1,10-phen (0.1189 g, 0.6 mmol), and H_2O (8 g, 444.4 mmol) in the mole ratio 1:1:1:741 was adjusted to pH 6.5 by addition of aqueous NaOH solution (6 mol L^{-1}), and heated at 180 °C for 6 days. After the mixture was slowly cooled to room temperature, yellow color crystals of **1** was yielded. Calcd. for $C_{40}H_{36}Zn_2N_4O_{10}$: Zn 14.96%, C 55.40%, H 4.28%, N 6.59%; Found: Zn 15.08%, C 55.68%, H 4.18%, N 6.50%.

2.2. X-ray crystallography

Structure measurement of (**1**) is performed at 293 K on a Rigaku R-AXIS RAPID IP diffractometer with Mo Kα ($\lambda = 0.71073$ Å) radiation, and the ω scan mode in the range of $2.06° < \theta < 27.44°$. Cell parameters were obtained by the global refinement of the positions of all collected reflections. An empirical absorption correction was applied. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL-97 program. All of the nonhydrogen atoms were refined anisotropically. Crystallographic details for the structures of (**1**) is summarized in Table 1. Selected bond lengths and angles for (**1**) are given in Table 2.

The CIF file of (**1**) has been deposited at the Cambridge Crystallographic Data Center and allocated the deposition numbers: CCDC 207778.

Table 1
Crystal data and structure refinement for $[Zn_2(e,a\text{-cis-}1,4\text{-chdc})_2(1,10\text{-phen})_2(H_2O)_2]_n$ (**1**)

Empirical formula	$C_{40}H_{36}Zn_2N_4O_{10}$
Formula weight	850.59
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
A (Å)	10.084(2)
b (Å)	8.9072(18)
c (Å)	20.276(4)
α (°)	90.00
β (°)	99.92(3)
γ (°)	90.00
Volume ($Å^3$)	1793.9(6)
Z	1
Absorption coefficient (mm^{-1})	0.351
$F(000)$	222
Crystal size (mm^3)	$0.52 \times 0.42 \times 0.36$
θ range for data collection (°)	2.04–27.48
Limiting indices	$-13 \le h \le 13, -11 \le k \le 10, -26 \le I \le 26$
Reflections collected	6997
Independent reflections	4119 ($R_{int} = 0.0333$)
Data/restraints/parameters	4119/0/253
Goodnees-of-fit on F^2	0.989
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0523$
	$wR2 = 0.0863$

Table 2
Selected bond lengths (Å) and angles (°) for (**1**)

Bond lengths			
Zn1–O4	2.0466(18)	Zn1–O3	2.0700(19)
Zn1–N2	2.132(2)	Zn1–O1	2.173(2)
Zn1–N1	2.180(2)	Zn1–O2	2.234(2)
O4–C13	1.269(3)	N2–C10	1.328(3)
N2–C12	1.352(3)	O2#1–C20	1.264(3)
N1–1	1.318(3)	N1–11	1.350(3)
O1#1–20	1.245(3)	O5–C13	1.237(3)
C19–C18	1.523(3)	C19–C14	1.531(4)
C14–C15	1.519(3)	C14–C13	1.523(3)
C7–C12	1.395(3)	C7–C8	1.408(4)
Bond angles			
O4–Zn1–O3	92.10(8)	O4–Zn1–N2	91.01(8)
O3–Zn1–N2	108.63(8)	O4–Zn1–O1	89.15(7)
O3–Zn1–O1	148.69(7)	N2–Zn1–O1	102.62(8)
O4–Zn1–N1	167.56(8)	O3–Zn1–N1	88.50(8)
N2–Zn1–N1	77.05(8)	O1–Zn1–N1	96.78(8)
O4–Zn1–O2	99.17(7)	O3–Zn1–O2	89.91(8)
N2–Zn1–O2	158.56(8)	O1–Zn1–O2	59.06(7)
N1–Zn1–O2	93.25(7)	O4#1–Zn1–C20	91.89(7)
O3#1–Zn1–C20	119.29(8)	C13–O4–Zn1	126.46(18)
C10–N2–C12	117.7(2)	C10–N2–Zn1	127.40(18)
C12–N2–Zn1	114.79(16)	C20–O2#1–Zn1	88.31(16)
C1–N1–Zn1	128.51(17)	C11–N1–Zn1	113.00(16)
C20–O1#1–Zn1	91.56(16)	O2#1–C20–Zn1#1	61.79(14)
O1#1–C20–Zn1#1	59.03(14)	C17–C20–Zn1#1	171.48(15)