研究简报

一维链状柔性羧酸镉配位聚合物[Cd(*p*-BDOA)·2H$_2$O]$_n$的合成、结构与性质研究

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Synthesis, Crystal Structure and Properties of a 1-D Cd(Ⅱ) Coordination Polymer [Cd(*p*-BDOA)·2H$_2$O]$_n$ Constructed by Flexible Carboxylic Acid

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Abstract: A novel 1-D Cd(Ⅱ) coordination polymer, [Cd(*p*-BDOA)·2H$_2$O]$_n$ (**Ⅰ**) (*p*-BDOA^{2-}=benzene-1,4-dioxyacetate dianion) has been synthesized and characterized by elemental analysis, IR, PL, TG and X-ray single crystal diffraction. The Crystal crystallizes in monoclinic system, the space group is *C*2/*c*, with the crystal cell parameters *a*=1.175 1(1) nm, *b*=0.551 0(1) nm, *c*=1.827 7(2) nm, *β*=96.14(2)°, and *V*=1.176 6(3) nm^3, M_r=372.60, *R*=0.045 9, *wR*=0.127 9. The Cd(Ⅱ) ion has a trigonal prism coordination configuration that defined by four carboxyl O atoms from two different *p*-BDOA^{2-} ligands and two water molecules. Adjacent Cd(Ⅱ) ions are linked by carboxylate groups with the bidentate coordination mode, giving rise to a chain structure with the adjacent Cd…Cd distance of 1.526 3(5) nm. Furthermore, such chains are linked by hydrogen bonds to form supramolecular network. The results of PL and TG show that the complex exhibits intense fluorescent emissions and its chain skeleton is thermally stable up to 419 K. CCDC: 220443.

Key words: Cd(Ⅱ) complex; benzene-1,4-dioxyacetic acid; crystal structure

0 Introduction

The construction of supramolecular architectures and investigation of their properties are a rapidly growing area of research[1~3]. The judicious choice of suitable ligand is an important factor that greatly influences the structure of the coordination architecture and functionality of the complex formed[4,5]. As a building block, *p*-phenylenedioxydiacetic acid (*p*-BDOAH$_2$) has versatile coordination modes and hydrogen bonding. Thus, *p*-BDOAH$_2$ could be regarded as an excellent candidate for the construction of supramolecular complexes. As a contribution to the field, we have recently reported the crystal structures of some mononuclear

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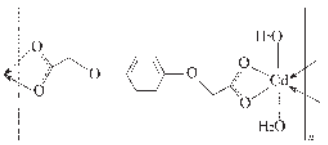
complexes and 1-D or 2-D polymers incorporating with *m*- or *p*-$BDOAH_2$, in which the carboxylate group acts as counter-ion in Mg(Ⅱ) complex, or only one of two oxyacetate groups is involved in coordination in the Co(Ⅱ) complex, as well as it functions as bidentate and tridentate bridging fashions in the Cd(Ⅱ), Cu(Ⅱ) and Mn(Ⅱ) complexes[6~10]. In order to gain further insight into the metal-binding modes of the *p*-$BDOAH_2$ ligand, we introduced the Cd(Ⅱ) ion into the coordination system of the *p*-$BDOAH_2$ ligand, and producing a new 1-D chain polymer, $[Cd(p\text{-}BDOA)\cdot 2H_2O]_n$ (**Ⅰ**). Herein, we report the synthesis, structure and properties of the above coordination polymer.



1 Experimental

1.1 Reagent and apparatus

The *p*-$BDOAH_2$ was prepared following the method described for the synthesis of benzene-1,2-dioxyacetic acid by Mirci [11]. Selected IR data (KBr pellet, cm^{-1}): for *p*-$BDOAH_2$, ν(OH) 3 435(w, br); ν(C=O) 1 728(m); ν_{asym}(COC) 1 234(m); ν_{sym}(COC) 1 077(s). All other chemicals were reagent grade and used received. Elemental analyses was performed on a CARLO ERBA 1106 analyzer. The IR spectra were recorded on a BRUKER EQUINOX 55 FTIR spectrometer using KBr pellet. Thermogravimetry (TG) and differential analysis (DTA) were measured on a PERKIN ELMER TG/DTA 6300 thermal analyzer under static air condition at a heating rate of 10 ℃·min^{-1}. The solid-state fluorescent spectra were acquired on a PERKIN ELMER LS 55 spectrometer.

1.2 Synthesis of $[Cd(p\text{-}BDOA)\cdot 2H_2O]_n$

The title complex was prepared by the addition of $Cd(NO_3)_2\cdot 4H_2O$ (6.16 g, 20 mmol) and NaOH (1.60 g, 40 mmol) to a hot aqueous solution of *p*-$BDOAH_2$ (4.52 g, 20 mmol), respectively, and filtered. Colorless prism single crystals were obtained from the filtrate at room temperature over several days. Selected IR data (KBr pellet, cm^{-1}): ν(OH) 3 400(w, br); ν_{asym}(OCO) 1 614(m); ν_{sym}(OCO) 1 429(s); ν_{asym}(COC) 1 223(m); ν_{sym}(COC) 1 074(s). Anal. Calcd. for $C_{10}H_{12}O_8Cd$ (%): C, 32.23; H, 3.25; Found (%): C, 32.29; H, 3.22.

1.3 Determination of crystal structure

A colorless single crystal with dimension 0.38 mm × 0.24 mm × 0.18 mm was employed for data collection at 293 K on a RIGAKU RAXIS-RAPID diffractometer with graphite monochromatized Mo $K\alpha$ radiation (λ=0.071 073 nm) in an ω scan mode. A total of 4 210 reflections and 1 321 unique ones were collected in the range of $3.49\leqslant\theta\leqslant27.35°$ with R_{int}=0.031 1, of which 1 249 observed reflections with $I>2\sigma(I)$ were used in the succeeding structural calculations. Lorentz-polarization factor and empirical absorption correction were applied to intensity data. The structure was solved by direct method and subsequent difference Fourier syntheses. The non-hydrogen atoms were refined by full-matrix least-squares techniques on F^2 with anisotropic thermal parameters. The H atoms on carbon were placed in calculated positions with C-H=0.093 nm (aromatic) or 0.097 nm (aliphatic) and $U_{iso}(H)=1.2U_{eq}(C)$ in the riding model approximation, and the H atoms of water molecules were located in difference Fourier maps and refined with O-H distance restraint of 0.085(1) nm and $U_{iso}(H)=1.5U_{eq}(O)$. All calculations were carried out with SHELX-97 program[12].

The Crystal belongs to monoclinic system, the space group is *C*2/*c*, with the crystal cell parameters *a*=1.175 1(1) nm, *b*=0.551 0(1) nm, *c*=1.827 7(2) nm, β=96.14(2)°, and *V*=1.176 6(3) nm^3, M_r=372.60, D_c=2.103 g·cm^{-3}, μ=1.891 mm^{-1}, *F*(000)=736, *R*=0.045 9, *wR*=0.127 9, *S*=1.042, (Δ/σ)=0.000, $\Delta\rho_{max}$=746 e·nm^{-3} and $\Delta\rho_{min}$=−685 e·nm^{-3}.

CCDC: 220443.

2 Results and discussions

2.1 IR spectra

The peak of 1 728 cm^{-1} is observed in IR spectra of the free *p*-$BDOAH_2$ and assigned to ν(C=O) absorption of carboxyl group, but it disappears in the title complex. The peaks of 1 614 and 1 429 cm^{-1} are shown in IR spectra of the complex and attributed to $\nu_{asym}(OCO^-)$ and $\nu_{sym}(OCO^-)$, respectively. The value of $\Delta(OCO^-)$ is 185 cm^{-1}, which is less than 200 cm^{-1}, indicating that the *p*-$BDOAH_2$ ligand is coordinated to the Cd(Ⅱ) atom in the bidentate chelate mode[13]. In addition, the peak of 3 400 cm^{-1} is assigned to O-H vi-

bration, which suggests that water molecule hydrogen bonds occur in the complex.

2.2 Crystal structure

The selected bond distances and angles of the title complex are given in Table 1. The molecular structure of the complex is shown in Fig.1. The Cd(Ⅱ) ion and *p*-BDOA^{2-} ligand lie on special positions with twofold rotation symmetry and inversion center, respectively. The Cd(Ⅱ) ion displays a distorted trigonal prism coordination geometry, comprising four carboxyl O atoms from two bidentate chelate *p*-BDOA^{2-} ligands and two coordinated water molecules [Cd-Ow, 0.219 6(5) nm]. However, in the previously reported Cd(Ⅱ) polymer, [Cd(C$_5$H$_5$N)$_3$(*m*-BDOA)·H$_2$O], the Cd(Ⅱ) ion is a six-coordinated octahedral geometry defined by two carboxyl O atoms from two monodentate *m*-BDOA^{2-} ligands, three pyridine N atoms and one coordinated water molecule[8]. In the title complex, the Cd(Ⅱ) centre with the angles O-Cd(1)-O is range from 55.2(2) to 142.8(2)°, which is probably attributed to the chelate coordination of the *p*-BDOA^{2-} ligand that forms a four-membered ring. The distances of Cd-O (carboxylate) [0.234 7(4)~0.236 4(5) nm] lie within the range of the corresponding bond distances [0.225 1~0.287 9 nm] reported for the normal Cd-carboxylate complexes[14].

The two C-O bond distances of each carboxyl group are nearly identical (Table 1), suggesting the electrons delocalized throughout. The coordinated oxyacetate group and phenyl ring are almost coplanar, with a C3-O3-C2-C1 torsion angle being 172.7(6)°.

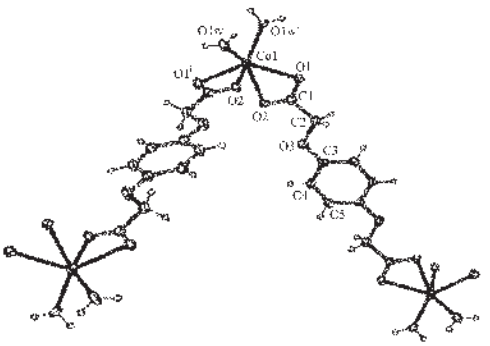


Fig.1 ORTEP plot of the title complex with 30% probability ellipsoid

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

Cd(1)-O(1w)	0.219 6(5)	Cd(1)-O(2)	0.234 7(4)	Cd(1)-O(1)	0.236 4(5)
O(2)-C(1)	0.125 3(7)	O(1)-C(1)	0.125 1(8)		
O(1w)-Cd(1)-O(1w)^{i}	92.3(3)	O(1w)-Cd(1)-O(1)	125.3(2)	O(1w)-Cd(1)-O(2)^{i}	142.8(2)
O(1w)^{i}-Cd(1)-O(1)	88.4(2)	O(1w)-Cd(1)-O(2)	102.3(2)	O(2)i-Cd(1)-O(2)	86.5(2)
O(2)-Cd(1)-O(1)	55.2(2)	O(2)-Cd(1)-O(1)i	89.6(2)		

Symmetry code: ^{i}: $-x$, y, $-z$ + 3/2.

Each *p*-BDOA^{2-} group acts as a bis-bidentate ligand to link two Cd(Ⅱ) ions through the carboxyl O atoms in an *anti-anti* configuration. As a result, a 1-D infinite zigzag chain is formed along the *c*-axis direction (see Fig.2). In the chain, the adjacent Cd⋯Cd distance is 1.526 3(5) nm, somewhat longer than the value of 1.130 4 nm in the 1-D cadmium polymer with the terephthalate ligand[15]. In the title complex, the interval Cd⋯Cd distance within the chain is 2.064 4 (5) nm. Furthermore, the chains are connected through intermolecular hydrogen bonds involving O1, O2, O3 atoms and the coordinated water molecules, yielding hydrogen-bonding supramolecular network (Table 2).

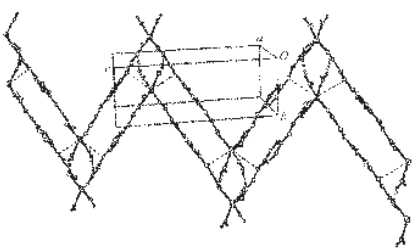


Fig.2 Packing diagram of the title complex (Symmetries see Table 1 and 2)

Table 2 Hydrogen bond lengths (nm) and angles (°) for the title complex

D–H⋯A	*d*(D-H)	*d*(H⋯A)	*d*(D⋯A)	∠(DHA)
O(1w)–H(1w2)⋯O(2)^{ii}	0.085(7)	0.191(5)	0.269 8(7)	153(8)
O(1w)–H(1w2)⋯O(3)^{ii}	0.085(7)	0.261(8)	0.314 2(7)	122(7)
O(1w)–H(1w1)⋯O(1)^{iii}	0.085(4)	0.184(4)	0.268 7(6)	176(8)

Symmetry codes: ^{ii}: x, $y-1$, z; ^{iii}: $x+1/2$, $y-1/2$, z.

2.3 Fluorescent spectra

Excitation (λ=258 nm) of the title complex in the solid state at room temperature produces strong fluorescent emissions at 320 and 422 nm, as shown in Fig.3. It may suggest that these fluorescent emissions come from the p-$BDOA^{2-}$ ligand, since similar emissions are observed for free p-$BDOAH_2$ at 316 and 416 nm. It is noted that the fluorescent intensities of the title complex are slightly stronger than those of the free acid ligand, which probably due to the symmetry decrease and the conformational rigidity enhancement of the coordination polymer compared with the free acid ligand, thereby reducing the loss of energy via non-radiative decay of the intraligand excited state[14,15].

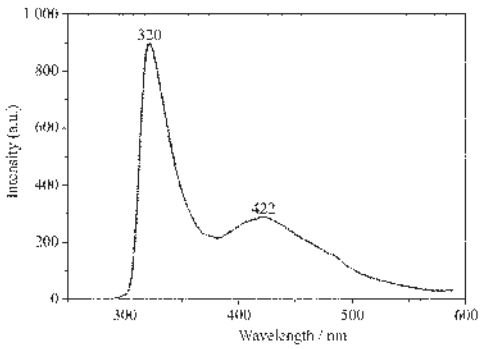


Fig.3 Emission spectrum of the title complex in the solid state at room temperature

2.4 Thermal analysis

The results of TG analysis of the complex exhibit two weight-loss steps. The first weight loss is at the range of 419~460 K in the TG curve, suggesting two coordinated water molecules are lost (found 9.78, calcd. 9.67%), and the corresponding endothermic peak is at 440 K in the DTA curve. The second weight loss occurs from 572 to 844 K in the TG curve with one intense exothermic peak in the DTA curve at 735 K, which is ascribed to the burning organic parts. The final residue may be CdO (found 34.02, calcd. 34.45%).

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