



苯丙烯酸桥联的双核镉配合物 $[\text{Cd}(\text{cinnamato})_2(\text{Phen})]_2$ 的水热合成和晶体结构

唐斯萍

(衡阳师范学院化学与材料科学系, 衡阳 421008)

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Hydrothermal Synthesis and Crystal Structure of a Dinuclear Cadmium Complex Bridged by Cinnamic Acid

TANG Si-Ping

(Department of Chemistry and Materials Science, Hengyang Normal University, Hengyang, Hunan 421008)

Abstract: A cadmium complex $[\text{Cd}(\text{cinnamato})_2(\text{Phen})]_2$ was synthesized by the reaction of cinnamic acid, phenanthroline (phen), and $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. It crystallizes in triclinic, space group $P\bar{1}$, with $a=1.142\ 1(13)$ nm, $b=1.157\ 6(13)$ nm, $c=2.106\ 1(2)$ nm, $\alpha=80.307(2)^\circ$, $\beta=77.334(2)^\circ$, $\gamma=71.630(2)^\circ$, $V=2.563\ 4(5)$ nm³, $D_c=1.521$ g·cm⁻³, $Z=2$, $M_r=586.90$, $\mu=0.891$ mm⁻¹, $F(000)=1\ 184$, the final $R=0.031\ 7$, $wR=0.067\ 5$. The crystal structure shows that the cadmium ion is coordinated with two nitrogen atoms from one phen molecule and five oxygen atoms respectively from three cinnamic acids, giving a pentagonal bipyramid coordination geometry. CCDC: 687380.

Key words: cadmium(II) complex; crystal structure; hydrothermal synthesis

In recent years, cadmium complexes have become an attractive research field because of their potential applications in many fields, such as materials, medicine, molecular electrochemistry and biochemistry^[1-4]. So far, to the best of our knowledge, with aromatic carboxylic acid as ligands have been intensively studied^[5-9]. In order to obtain novel functional carboxyl cadmium complexes and investigate their structure-function relationship, we have chosen cinnamic acid and phen as ligands and investigated their reaction with $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$. We report herein the synthesis and crystal structure of the Cd(II) compound, $[\text{Cd}(\text{cinnamato})_2(\text{Phen})]_2$, **1**.

1 Experimental

1.1 Materials and instruments

All the reagents and solvents were used as commercial sources without further purification. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The IR spectra were recorded on FTIR-8700 spectrophotometer using KBr discs. Cyclic voltametric was measured on a LK98 electrochemical analysis system.

1.2 Synthesis of the title compound

A mixture of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.191 g, 0.5 mmol),

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E-mail: tsp00@163.com

作者: 唐斯萍, 女, 32 岁, 讲师; 研究方向: 生物无机及配位化学。

cinnamic acid (0.152 g, 1 mmol), NaOH (0.041 g, 1 mmol), phen (0.101 g, 0.5 mmol) and H₂O (10 mL, 0.55 mmol) was heated in a 23 mL capacity Teflon-lined reaction vessel at 160 °C for 6 days, the reaction mixture was cooled to room temperature over a period of 40 h. The product was collected by filtration, washed with H₂O and air-dried, Yield: 0.15 g (44%). Anal. Calcd. for C₃₀H₂₂CdN₂O₄ (%): C 61.34, H 3.75, N 4.77; Found (%): C 61.82, H 3.32, N 4.92. Main IR bands (cm⁻¹): 3 435 (vw, br), 1 620(s), 1 515(s), 1 459(s), 1 426(m, br), 850 (m), 727(w), 624(w), 448(w).

1.3 Crystal structure determination

A suitable block colorless crystal with dimensions of 0.24 mm × 0.16 mm × 0.12 mm was selected for structure analysis. The data were collected on a Bruker Smart 1000 CCD diffractometer with a Mo K α radiation (λ = 0.071 073 nm) at 294(2) K by using an φ - ω scan

mode in the range of 1.00° < θ < 25.02°. A total of 13 368 reflections were collected and corrected by SADABS, of which 8988 were independent (R_{int} = 0.023 3), 6 132 were observed ($I > 2\sigma(I)$) and used for the refinement. The structure was solved by direct methods and subsequent difference Fourier syntheses. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were introduced geometrically. The final refinement converged to R = 0.031 7, wR = 0.067 5 ($w = 1/[\sigma^2(F_o^2) + (0.030 2P)^2 + 0.189 4P]$, where $P = (F_o^2 + 2F_c^2)/3$, S = 1.027, $(\Delta/\sigma)_{\text{max}}$ = 0.000. The highest and lowest residual peaks in the final difference Fourier map are 274 and -409 e·nm⁻³, respectively. All calculations were performed with SHELXTL-2000 package. Relative structure parameters are given in Table 1. The selected bond lengths and bond angles are listed in Table 2.

CCDC: 687380.

Table 1 Crystal data and structure parameters for the title complex

Empirical formula	C ₃₀ H ₂₂ CdN ₂ O ₄	Z	2
Formula weight	586.9	Absorption coefficient / mm ⁻¹	0.891
Temperature / K	294(2)	$F(000)$	1 184
Crystal system	Triclinic	Crystal size / mm	0.24 × 0.16 × 0.12
Space group	$P\bar{1}$	θ / (°)	1.0 to 25.02
a / nm	1.142 1(13)	Limiting indices	$-13 \leq h \leq 13, -13 \leq k \leq 9, -24 \leq l \leq 24$
b / nm	1.157 6(13)	Reflections collected / unique (R_{int})	13 368 / 6 132 (0.023 3)
c / nm	2.106 1(2)	Data / restraints / parameters	8 988 / 0 / 667
α / (°)	80.307(2)	Goodness of fit on F^2	1.027
β / (°)	77.334(2)	Final R indices (all data)	R_1 = 0.058 2, wR_2 = 0.079 9
γ / (°)	71.630(2)	Final R indices [$I > 2\sigma(I)$]	R_1 = 0.031 7, wR_2 = 0.067 5
V / nm ³	2.563 4(5)	Largest diff. peak and hole / (e·nm ⁻³)	274 and -409
D_c / (g·cm ⁻³)	1.521		

Table 2 Selected bond lengths (nm) and bond angle (°)

Cd(1)-O(1)	0.247 0(2)	Cd(1)-N(1)	0.238 3(3)	Cd(2)-O(8)	0.246 0(2)
Cd(1)-O(2)	0.227 9(2)	Cd(1)-N(2)	0.234 2(3)	Cd(2)-O(5)#2	0.234 5(2)
Cd(1)-O(3)	0.232 4(2)	Cd(2)-O(5)	0.232 2(2)	Cd(2)-N(3)	0.234 0(3)
Cd(1)-O(3)#1	0.234 5(2)	Cd(2)-O(6)	0.258 8(2)	Cd(2)-N(4)	0.237 5(3)
Cd(1)-O(4)	0.260 1(2)	Cd(2)-O(7)	0.229 2(2)		
O(2)-Cd(1)-O(3)	90.51(8)	N(1)-Cd(1)-O(1)	80.66(9)	O(7)-Cd(2)-N(4)	95.94(10)
O(2)-Cd(1)-N(2)	167.91(9)	O(3)-Cd(1)-O(1)	134.96(8)	O(5)-Cd(2)-N(4)	139.00(9)
O(3)-Cd(1)-N(2)	100.69(9)	N(2)-Cd(1)-O(1)	117.23(9)	N(3)-Cd(2)-N(4)	70.76(10)
O(2)-Cd(1)-O(3)#1	102.83(9)	O(3)#1-Cd(1)-O(1)	87.26(8)	O(5)#2-Cd(2)-N(4)	142.80(9)
O(3)-Cd(1)-O(3)#1	71.93(9)	O(7)-Cd(2)-O(5)	91.40(8)	O(7)-Cd(2)-O(8)	55.12(9)
N(2)-Cd(1)-O(3)#1	85.13(10)	O(7)-Cd(2)-N(3)	166.44(10)	O(5)-Cd(2)-O(8)	135.02(8)

Continued Table 2

O(2)-Cd(1)-N(1)	97.77(10)	O(5)-Cd(2)-N(3)	100.41(9)	N(3)-Cd(2)-O(8)	117.66(9)
O(3)-Cd(1)-N(1)	137.58(9)	O(7)-Cd(2)-O(5)#2	103.98(9)	O(5)#2-Cd(2)-O(8)	86.61(8)
N(2)-Cd(1)-N(1)	70.89(10)	O(5)-Cd(2)-O(5)#2	72.26(9)		
O(3)#1-Cd(1)-N(1)	143.90(9)	N(3)-Cd(2)-O(5)#2	86.11(9)		

#1: $-x+1, -y+1, -z+1$; #2: $-x+1, -y, -z$.

2 Results and discussion

2.1 Crystal structure of the title complex

The selected bond lengths and bond angles in Table 2, molecular structure of the title compound is revealed in Fig.1. As shown in Fig.1, the title compound consists of two completely uniform dicadmium molecules. In every unit, the central Cd(II) ion coordinates with two nitrogen atoms from phen, five carboxylic oxygen atoms from three cinnamic acid to give a pentagonal bipyramid coordination geometry. The CdN_2O_5 fragments of two crystallographically independent molecules with the same configurations, around Cd1, O(1), O(3), O(3)#1, N(1) and O(4) locate at the equatorial plane, but O(2) and N(2) occupy the axial positions, which the bond angle of O(2)-Cd(1)-N(2) is $167.91(9)^\circ$. The phen groups exhibit their usual acute N...N distances ($0.272\ 8\sim 0.273\ 4\ \text{nm}$) and N-Cd-N angles ($70.76(10)^\circ\sim 70.89(10)^\circ$), very close to those found in $[\text{Cd}_2(\text{Phen})_4(\text{bmal})_2]\cdot 3\text{H}_2\text{O}$ ^[10]. The bond angles of equatorial plane (O(1)-Cd(1)-N(1), N(1)-Cd(1)-O(4), O(4)-Cd(1)-O(3), O(3)-Cd(1)-O(3)#1 and O(3)#1-Cd(1)-O(1)) are $80.66(9)^\circ$, $85.35(8)^\circ$, $52.24(7)^\circ$, $71.93(9)^\circ$ and $87.26(8)^\circ$, respectively and the sum is 367.44° , suggesting O(1), O(3), O(3)#1, N(1) and O(4) are coplanar. Since the chelating ring contains only four atoms, it is not surprising that the O(4)-Cd(1)-O(3) angles is relatively sharp at 52° . Based on the above analyses, con-

clusion could be drawn that the central Cd(II) ion assumes a distorted pentagonal bipyramid coordination geometry.

Furthermore, In **1**, each ligand adopts two coordinate modes, one is O,O-bidentate chelet mode, the other is tridentate bridging mode. Two Cd^{II} centers are doubly bridged by the cinnamato ligands, forming a dinuclear structure, with the Cd-Cd distance of $0.378\ 0\ \text{nm}$.

2.2 Spectra characteristics and cyclic voltammetry (CV)

The infrared spectra of the title complex has been recorded and some important assignments are shown above. Peaks at $1\ 620$ and $1\ 515\ \text{cm}^{-1}$ could be attributed to $\text{vas}(\text{COO}^-)$ adsorption of completely deprotonic acid, which show that the cinnamato has participated in coordination.

Peaks at $1\ 426$, 850 and $727\ \text{cm}^{-1}$ could be assigned to characteristic peaks of phen. Compared to those of free phen ($1\ 421$, 858 and $725\ \text{cm}^{-1}$), these peaks shift to some extent, indicating that phen has participated in coordination. These attributions are in agreement with structural determination.

The CV curve of the title compound is given in Fig.2. In the CV measurement, tri-electrode system was used with glass/C as working electrode, Pt as auxiliary electrode and SCE as reference electrode. The solvent is the mixture of methanol and water with complex condensation of $1\times 10^{-5}\ \text{mol}\cdot\text{L}^{-1}$. The scanning range is

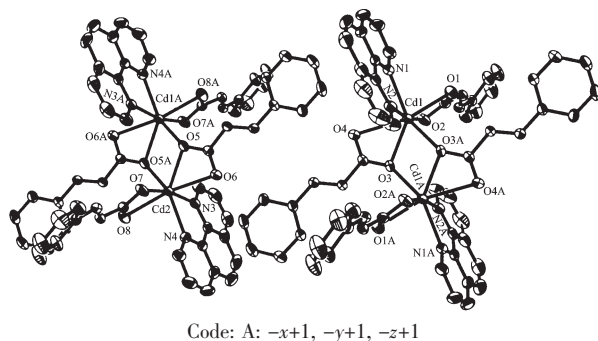


Fig.1 Molecular structure of the title complex

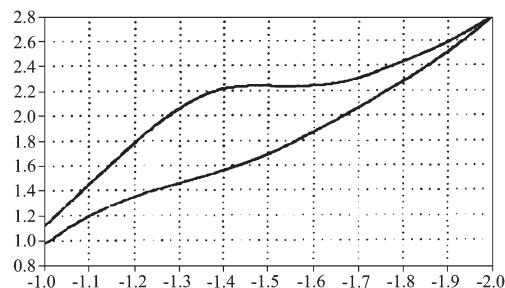


Fig.2 Cyclic voltammogram of the title complex

-1.000~-2.000 V and scanning rate $0.1 \text{ V} \cdot \text{s}^{-1}$. The results show that only one reduction peak occurs (-1.34 V) without the appearance of oxidation peak, so we can deduce that the electron transfer in electrolysis reaction is irreversible.

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