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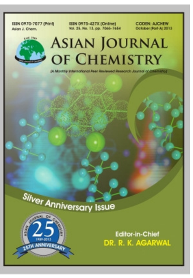

Synthesis, Crystal Structure and Luminescent Property of Cadmium(II) Complex Assembled by Sebacic Acid

YI QIN[1], XIAO-JU CHEN[2], WEI-JI HU[1] and GUO-LIANG ZHAO[1,2,*]

[1]Xingzhi College, Zhejiang Normal University, Jinhua 321004, P.R. China
[2]College of Chemistry and Life Science, Zhejiang Normal University, Jinhua 321004, P.R. China

*Corresponding author: Fax: +86 579 82282269; Tel: +86 579 82282061; E-mail: sky53@zjnu.cn

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A cadmium(II) complex $[Cd_2L_2(phen)_4(H_2O)]\cdot 5H_2O$ (**1**) assembled by flexible ligand sebacic acid ($C_{10}H_{18}O_4$, H_2L) and neutral N-based ligand 1,10-phenanthroline (phen), has been hydrothermally synthesized and characterized by elemental analysis, IR and TG. The single-crystal X-ray diffraction studies demonstrated that the complex is crystallize in triclinic, P_i space group, with a = 1.15341(2), b = 1.34483(2), c = 2.10931(3) nm, α = 92.0120(10)º, β = 94.1770(10)º, γ = 91.8060(10)º, V = 3.2592(3) nm^3, Z = 2, $C_{68}H_{76}N_8O_{14}Cd_2$, M_r = 1454.17, $F_{(000)}$ = 1496, D_c = 1.482 g/cm^{-3}, $\mu(M_0K_\alpha)$ = 0.724 mm^{-1}. The final R = 0.0433 and wR = 0.1122 for 11469 observed reflections with $I > 2\sigma(I)$. The dual-nuclei bridge structure complex was formed by sebacic acid. The water dimer stay at the lattice space firmly through the hydrogen bonding. The luminescent property in solid state of complex **1** was also studied and discussed. CCDC: 877979.

Key Words: Sebacic acid, Flexible ligand, Cadmium complex, Crystal structure, Luminescent property.

INTRODUCTION

The design and synthesis of metal-organic compounds has attracted much attention due to their diverse topologies and potential applications in catalysis, molecular recognition, magnetism, electrochemisty, *etc.*[1-5]. With strong coordination ability and varieties of coordination modes, the rigid ligand is easy to form grid, brick wall, honeycomb and diamond-like shape network[6-9], so a great deal of work were focus on the rigid ligand. Compared with the rigid ligand, the long flexible multi-function ligand tend to form unique interpenetrating and entangled architectures, such as catenanes and rotaxanes structures[10-12]. At the same time, the flexible ligand is easy to adjust and modify, can easily bring in all kinds of coordination unit. Additionally, owing to the coordination modes can spread or concentration, rich variety of complexes based on flexible ligands can obtained. Therefore, the study on flexible ligands have made a great progress in recent years[13-15]. We have made great effort on the study of flexible carboxylic ligand complexes[16-18].

On the other hand, polynuclear d^{10} metal complexes have attracted considerable interest recently because of their photoluminescent properties[19-21]. In this paper, one novel cadmium complex $[Cd_2L_2(phen)_4(H_2O)]\cdot 5H_2O$ has been synthesized based on sebacic acid ligand and characterized by infrared spectroscopy, elemental analysis and X-ray crystallographically. As a continuation of our search, the solid luminescent property was also studied and discussed.

EXPERIMENTAL

All the reagents and solvents used were of commercially available quality and without purified before using. FTIR spectra were recorded on a Nicolet NEXUS 670 FTIR spectrophotometer using KBr discs in the range of 4000-400 cm^{-1}. Elemental analysis was performed on C, H, N elemental analyzer, Elementar Vario EL III. A Mettler Toledo thermal analyzer TGA/SDTA 851^e was used to carry out the thermoanalytical analysis with a heating rate of 10 ºC min^{-1} from 30-800 ºC in air atomsphere. Fluorescent spectrum were recorded at room temperature on an Edinburgh FL920 phosphorimeter.

Synthesis of the complex: A mixture of $CdCl_2\cdot 6H_2O$ (1.0 mmol, 0.2284 g), sebacic acid (1.0 mmol, 0.2022 g), 1,10-phen (1.0 mmol, 0.1984 g), NaOH (2.0 mmol, 0.0800 g) and 18 mL of 3:1 H_2O/ethanol (v/v) was placed in a Parr Teflon lined stainless steel vessel (25 mL) and then the vessel was sealed and heated to 160 ºC for 72 h. After the reactant mixture was slowly cooled to room temperature over 3 d, colourless block crystals were obtained and washed with water. Elemental analysis calcd. (%) for $C_{68}H_{76}N_8O_{14}Cd_2$: C, 56.10; H, 5.28; N, 7.74. Found (%): C 56.21, H 5.27, N 7.70. IR (KBr, ν_{max}, cm^{-1}): 3423(s), 3054(m), 2925(s), 2851(s), 1621(s), 1516(s), 1461(m), 1425(s), 1406(s), 1303(m), 1240(m), 1189(m), 932(w), 854(s), 727(s), 679(w), 645(w).

X-Ray crystallography: The block crystal of the synthesized cadmium(II) complex sized in 0.218 mm × 0.167 mm × 0.088 mm was selected for structure analyses. The diffraction data was collected on a Bruker SMART APEX II CCD diffractomerer equipped with a graphite-momochromatized MoK_{α} radiation ($\lambda = 0.071073$ nm) at 296(2) K. Data intendity was corrected by Lorenta-polarization factors and empirical absorption. The structure was solved with direct methods and expanded with difference Fourier techniques. Except the hydrogen atoms on oxygen were located from the difference Fourier maps, the other hydrogen atoms were generated geometrically, the non-hydrogen atoms were refined anisotropically. All structure analysis and refinement were performed using SHELXS-97[22] and SHELXL-97[23] program package, Experimental details for X-ray data collection are presented in Table-1 and the selected bond lengths and angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR THE COMPLEX

Empirical formula	$C_{68}H_{76}N_8O_{14}Cd_2$
Formula weight	1454.17
Temperature (K)	296(2)
Wavelength (nm)	0.071073
Crystal system	Triclinic
Space group	P_i
a (nm)	1.15341(2)
b (nm)	1.34483(2)
c (nm)	2.10931(3)
α (º)	92.0120(10)
α (º)	94.1770(10)
γ (º)	91.8060(10)
V (nm^3)	3.25923(9)
Z	2
D_c (g cm^{-3})	1.482
Absorption coefficient (mm^{-1})	0.724
$F_{(000)}$	1496
Crystal size (mm)	0.202 × 0.192 × 0.168
Theta range for data collection (º)	0.97 to 25.00
Limiting indices	-13 ⇐ h ⇐ 13, -15 ⇐ k ⇐ 15, -25 ⇐ l ⇐ 25
Reflections collected/unique	44986 / 11469 [$R_{(int)}$ = 0.0411]
Completeness to theta = 27.52 (%)	99.9
Max. and min. transmission	0. 938 and 0. 865
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	11469/2/828
Goodness-of-fit on F^2	1.098
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0433$, $wR_2 = 0.1122$
R indices (all data)	$R_1 = 0.0631$, $wR_2 = 0.1240$
Largest diff. peak and hole (e nm^{-3})	771 and -568

RESULTS AND DISCUSSION

IR spectrum: For the IR spectrum of the present cadmium complex, there is a broad strong peak observed at near 3423 cm^{-1}, which corresponds to the stretching vibrations of O-H of water molecules. The attendance of broad bond at 3054 cm^{-1} indicating the existance of hydrogen bonds between water. The complex shows the typical anti-symmetric (1621cm^{-1}) and symmetric (1425 cm^{-1}) stretching bands of carboxylate groups. The absence of the characteristic bond around 1700 cm^{-1} attributed to the protonated carboxylic group indicate that the present deprotonation of H_2L ligand. In addition, the peak at about 645 cm^{-1} is associated with the coordinated water.

TABLE-2
SELECTED BOND LENGTHS (nm) AND ANGLES (º)

Bond	Length	Bond	Length
Cd(1)-O(5) 2.995(4)	0.2285(3)	Cd(2)-O(1W)	0.2344(3)
Cd(1)-O(2) 2.995(4)	0.2322(4)	Cd(2)-N(5)	0.2373(3)
Cd(1)-N(4) 2.578(3)	0.2423(3)	Cd(2)-N(7)	0.2386(3)
Cd(1)-N(2)	0.2427(3)	Cd(2)-N(8)	0.2388(4)
Cd(1)-N(3)	0.2436(3)	Cd(2)-O(4')	0.2406(15)
Cd(1)-N(1)	0.2451(3)	Cd(2)-N(6)	0.2437(3)
Cd(2)-O(4)	0.2307(10)	–	–
Angle	**(º)**	**Angle**	**(º)**
O(5)-Cd(1)-O(2)	90.72(12)	O(4)-Cd(2)-N(7)	85.8(3)
O(5)-Cd(1)-N(4)	166.78(10)	O(1W)-Cd(2)-N(7)	95.03(12)
O(2)-Cd(1)-N(4)	94.36(12)	N(5)-Cd(2)-N(7)	152.63(13)
O(5)-Cd(1)-N(2)	90.33(11)	O(4)-Cd(2)-N(8)	110.2(3)
O(2)-Cd(1)-N(2)	166.26(12)	O(1W)-Cd(2)-N(8)	161.08(12)
N(4)-Cd(1)-N(2)	87.62(10)	N(5)-Cd(2)-N(8)	94.10(12)
O(5)-Cd(1)-N(3)	124.48(11)	N(7)-Cd(2)-N(8)	69.70(12)
O(2)-Cd(1)-N(3)	81.50(12)	O(1W)-Cd(2)-O(4')	91.4(3)
N(4)-Cd(1)-N(3)	68.44(10)	N(5)-Cd(2)-O(4')	124.8(4)
N(2)-Cd(1)-N(3)	86.62(10)	N(7)-Cd(2)-O(4')	80.2(4)
O(5)-Cd(1)-N(1)	79.62(11)	N(8)-Cd(2)-O(4')	96.7(3)
O(2)-Cd(1)-N(1)	125.30(12)	O(4)-Cd(2)-N(6)	156.6(2)
N(4)-Cd(1)-N(1)	87.50(10)	O(1W)-Cd(2)-N(6)	79.52(12)
N(2)-Cd(1)-N(1)	68.33(10)	N(5)-Cd(2)-N(6)	69.41(12)
N(3)-Cd(1)-N(1)	146.18(11)	N(7)-Cd(2)-N(6)	87.69(11)
O(4)-Cd(2)-O(1W)	78.7(3)	N(8)-Cd(2)-N(6)	88.48(11)
O(4)-Cd(2)-N(5)	121.1(3)	O(4')-Cd(2)-N(6)	164.2(4)
O(1W)-Cd(2)-N(5)	95.28(12)	–	–

Structural description: The crystal structure of the present cadmium complex is shown in Fig. 1 (three O atoms (O1, O3, O4) and three C atoms (C3, C8, C9) are disorder, in order to make it clear, we don't show it). Which reveals that the complex crystallizes in P_i space group. Each asymmetric unit consists of two independent Cd(II), two L^{2-} ligand, four phen, one crystaled water and five free water. This dual-nuclei was bridged by one sebacic acid (L^{2-}) ligand. Both Cd(1) and Cd(2) have hexacoordinated octahedral coordination fashion and in similar coordination environment. Cd(1) atom is coordinated with two O atoms from two different L^{2-} ligand (Cd1-O 0.2323(3) and 0.2285(3) nm) and four N donor of two independent phen ligand (Cd1-N 0.2423(3)-0.2451(3) nm). While Cd(2) is coordinated by one carboxylate oxygen atom from L_2^- ligand, four N from two phen ligand (Cd2-N 0.2373(3)-0.2437(3) nm) and one water (Cd2-O1W 0.2344(3) nm), which is similar to the reported complex[24]. The O-Cd-N angles range from 79.62(11)-166.26(12)º and N-Cd-N angles range from 68.33(10)-152.63(13)º. The selected important bond parameters are given in Table-1.

Significantly, hydrogen bonding interactions play vital role in the assembly of supramolecular architectures, there are plentiful hydrogen bonds among the water (Table-2). Which link the adjacent four molecules forming a two-fold 1D corrugated chain with non-interpenetrated along the b axis (Fig. 2). The mode of connection is depicted in Fig. 3. Hydrogen-bonding association generates a cyclic 4- and 7-membered rings consisting of carboxyl and water centers (Table-3). These rings make the molecules running along b axi direction to form

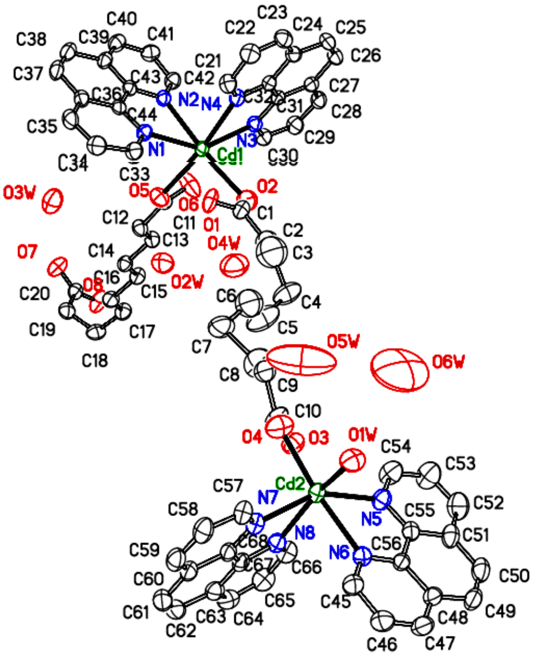


Fig. 1. Thermal eclipse diagram of the nonsymmetrical unit of present Cd(II) complex with ellipsoids at 30 % probability and the hydrogen atoms are omitted

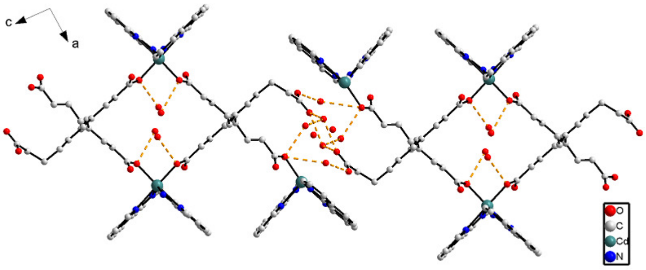


Fig. 2. 1D chain formed by hydrogen-bonding interactions in Cd(II) complex

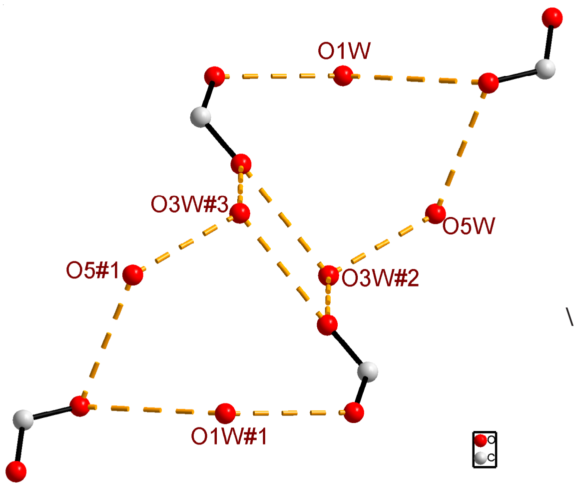


Fig. 3. Hydrogen-bonded model of the water molecules and carboxylic anions symmetry codes: #1 2-x, 3-y, 2-z; #2 -1+ x, 1+y, 1+z; #3 3-x, 1-y, 1-z

a 1D corrugated supramolecular morphology, which can be described as O1W linking the adjacent carboxyl oxygens by hydrogen-bonding interactions, while two pairs of water dimmer filling in each hole. The O···O···O angles range from 125-174.8º, considerably deviating from the preferred ideal tetrahedral geometry of water. Meanwhile, there are infinite parallel aromatic rings from the phen, the π-π stacking interactions also play an important role in stabilizing the supramolecular architecture (Fig. 4).

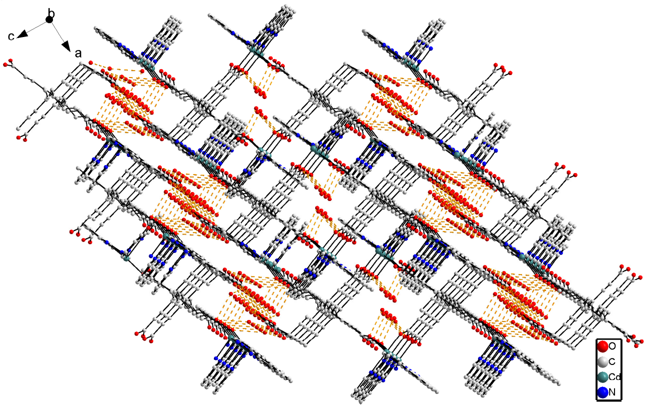


Fig. 4. Packing plot of Cd(II) complex

TG analysis: Thermal stability of the complex **1** was conducted under air atmosphere in the tempreature range of 30-800 ºC with a 10 ºC min^{-1} ramp (Fig. 5). The TG diagram reveals two distinct weight regions. The first weight loss of 7.30 % (calcd. 7.48 %) from 50-91 ºC corresponds to the release of six water molecules. The further decomposition of the organic ligands occurred in the range of 170-480 ºC, the residue weights 17.64 % corresponds to values calculated for CdO 17.66 %.

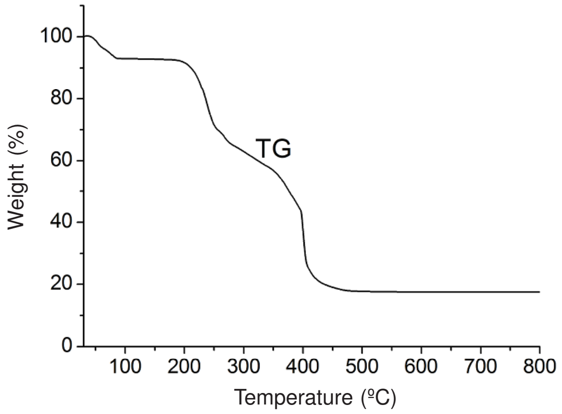


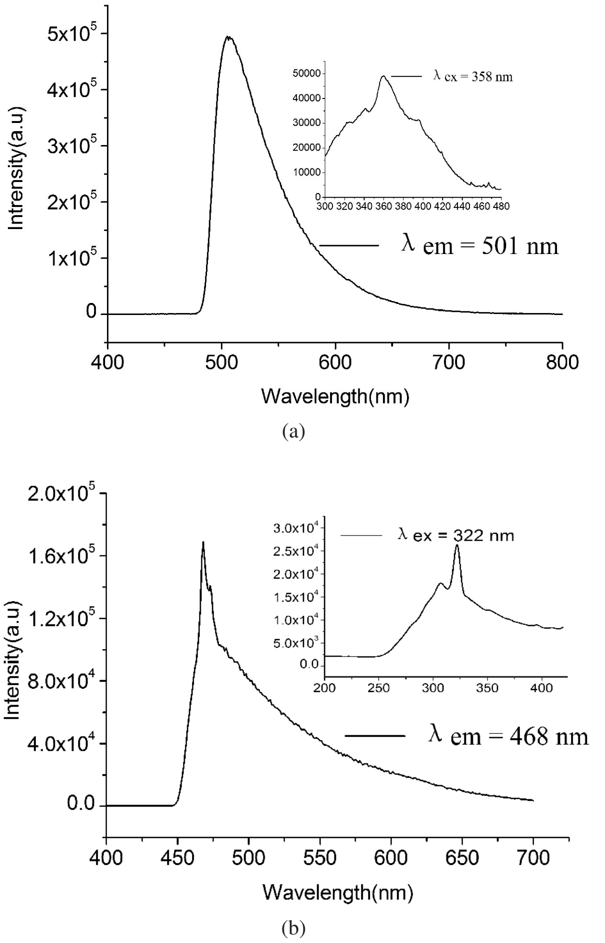
Fig. 5. TG curve for Cd(II) complex

Fluorescent property: Considering the introduction of d^{10} metal polynuclear clusters can improve the luminescent performance of coordination polymers, which have potential applications in chemical sensors, photochemistry and lightemitting diodes (LEDs)[25-26]. As depicted in Fig. 6, complex exhibit fluorescent emission with the maxima at 501 nm (λ_{ex} = 358 nm). Such fluorescence behaviour may be attributed to the intraligand transition of coordinated L ligand, since similar emission at 468 nm (λ_{ex} = 322 nm) was observed for the free L ligand. The red-shifted emissions of complex was attributed to both the deprotonated effect of H_2L and the coordination interactions of the organic ligands to the metal[27]. Which show that the complex may be excellent candidate for potential photoactive material.

TABLE-3
HYDROGEN BOND GEOMETRY FOR TITLE COMPLEX (nm, °)

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠(DHA)
O(1W)-H(1WA)...O(4)	0.085	0.234	0.2948(10)	129.3
O(1W)-H(1WA)...O(5W)	0.085	0.271	0.3316(10)	129.1
O(2W)-H(2WB)...O(5)	0.085	0.200	0.2852(5)	174.8
O(3W)-H(3WA)...O(7)	0.083	0.197	0.2766(6)	160.1
O(3W)-H(3WB)...O(7)[a]	0.082	0.193	0.2726(6)	162.2
O(5W)-H(5WB)...O(3W)[b]	0.085	0.203	0.2612(8)	125.0

Symmetry codes: (a) -x+4, -y+1, -z; (b) x-1, y+1, z+1.



(a)

(b)

Fig. 6. Excitation and emission spectra in the solid state at room temperature: (a) the title complex (b) the H_2L ligand

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