

研究简报

配合物 $[\text{CdCl}(\text{HL})(\text{dpp})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ 的合成、 晶体结构与荧光性能研究

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Synthesis, Crystal Structure and Luminescent Property of $[\text{CdCl}(\text{HL})(\text{dpp})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$

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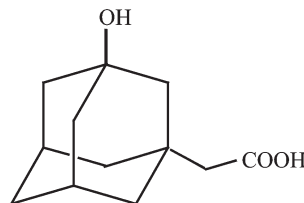
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Abstract: Under hydrothermal condition, the reaction of 3-hydroxy-1-adamantaneacetic acid (H_2L) with CdCl_2 and 1,3-di-4-pyridylpropane (dpp) has afforded a new Cd(II) compound, $[\text{CdCl}(\text{HL})(\text{dpp})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (**1**), which was structurally characterized by single-crystal X-ray diffraction analysis. The crystal is triclinic, space group $P\bar{1}$ with $a=1.091\ 0(1)$ nm, $b=1.131\ 8(1)$ nm, $c=1.246\ 4(1)$ nm, $\alpha=88.52(1)^\circ$, $\beta=71.34(1)^\circ$, $\gamma=68.11(1)^\circ$, $V=1.345\ 2(1)$ nm³, $Z=2$, $M_r=591.40$, $F(000)=608$, $D_c=1.460$ g·cm⁻³, $\mu=0.947$ mm⁻¹, the final $R=0.040\ 1$ and $wR=0.104\ 0$ for 4 950 observed reflections ($I>2\sigma(I)$). Complex **1** consists of one-dimensional chains deriving from $\text{CdCl}(\text{HL})(\text{H}_2\text{O})$ units linked by dpp ligands, and lattice water molecules decorate between the chains. The O—H···O and O—H···Cl hydrogen bonds lead to the formation of a 2D layer structure. CCDC: 756099.

Key words: Cd(II) complex, 3-hydroxy-1-adamantaneacetic acid, crystal structure, luminescent property

Since the discovery of adamantane in 1930^[1], adamantane and its derivatives have been widely investigated. Some complexes with adamantane^[2-3], adamantane-thiol^[4-5], and adamantanecarboxylic acids^[6-11] have been prepared and studied. However, the complexes based on 3-hydroxy-1-adamantaneacetic acid (H_2L) ligand have never been reported so far. The ligand might be utilized as a linker in the construction of coordination polymers. In addition, long flexible ligands have the ability to produce unique structural motifs^[12-13], the 1,3-di-4-pyridylpropane (dpp) ligand has been proven to be

a good candidate for the organization of polymeric because of its length and flexibility^[14-16]. We combined H_2L and dpp as a mixed ligand system to react with CdCl_2 under hydrothermal condition, obtaining a new Cd(II) compound, $[\text{CdCl}(\text{HL})(\text{dpp})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (**1**). In



Scheme 1 3-hydroxy-1-adamantaneacetic acid (H_2L)

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this paper, we report the synthesis, crystal structure and luminescent property of the title compound.

1 Experimental

1.1 Reagents and measurements

All solvents and chemicals were used without further purification. Elemental analyses were carried out using a Perkin-Elmer 2400 II elemental analyzer. The diffraction data were collected on a Bruker APEX II single-crystal X-ray diffractometer. IR spectra were measured in KBr pellets on a Nicolet 5DX FTIR spectrometer. The thermogravimetric measurements were performed on preweighed samples in an oxygen stream using a Netzsch STA449C apparatus with a heating rate of $10\text{ }^\circ\text{C} \cdot \text{min}^{-1}$. The excitation and luminescence spectra were performed on a HITACHI-F-2500 fluorescence spectrometer in solid state at room temperature.

1.2 Synthesis of the complex

$[\text{CdCl}(\text{HL})(\text{dpp})(\text{H}_2\text{O})]_n \cdot n\text{H}_2\text{O}$ (**1**)

A mixture of H_2L (0.210 g, 1.0 mmol), $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ (0.228 g, 1.0 mmol), dpp (0.099 g, 0.5 mmol) and Na_2CO_3 (0.053 g, 0.5 mmol) were dissolved in 18 mL distilled water. The solution was heated to 433 K for 72 h and then cooled to room temperature over 3 days. Colorless single crystals of **1** were obtained by slow evaporation of the filtrate over a few days (yield 48.1% based on HL). Anal. Calcd. (%) for $\text{C}_{25}\text{H}_{35}\text{CdClN}_2\text{O}_5$: C, 50.66; H, 5.96; N, 4.73. Found(%): C, 50.60; H, 5.98; N, 4.76. IR (KBr, cm^{-1}): 3 283s, 2 932s, 1 613s, 1 540s, 1 432s, 1 339m, 1 311m, 1 247m, 1 227m, 1 147m, 1 047m, 1 015m, 807m, 603m, 519m.

1.3 X-ray crystallography

A colorless single crystal with dimensions of $0.37\text{ mm} \times 0.20\text{ mm} \times 0.04\text{ mm}$ was mounted on a diffractometer equipped with a graphite-monochromatic Mo $K\alpha$ radiation ($\lambda=0.071\,073\text{ nm}$) for data collection at 296(2) K in the range of $1.73^\circ \leq \theta \leq 27.58^\circ$. The total 22 831 reflections with 6 167 independent ones ($R_{\text{int}}=0.034\,7$) were obtained, of which 4 950 observed reflections with $I>2\sigma(I)$ were used to solve the structure. The data intensity was corrected by Lorentz-polarization factor and empirical absorption on the SADABS program^[17].

The structure was solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELX-97 program^[18]. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms attached to carbon were located by geometrical calculations, while those to oxygen were located from difference Fourier maps. The final cycle of full-matrix least-squares refinement based on 313 variable parameters gave $R=0.040\,1$, $wR=0.104\,0$ ($w=1/[\sigma^2(F_o^2)+(0.052\,6P)^2+0.466\,7P]$, where $P=(F_o^2+2F_c^2)/3$), $(\Delta/\sigma)_{\text{max}}=0.000$ and $S=1.111$. The maximum and minimum peaks on the final difference Fourier map are $1\,054$ and $-405\text{ e} \cdot \text{nm}^{-3}$, respectively. The guest H_2O molecule is disordered over two positions and the site occupancy factors refined to $0.83:0.17$. Further details for crystallographic data and refinement conditions are summarized in Table 1. The selected bond lengths and bond angles are given in Table 2. The hydrogen bond lengths and bond angles are shown in Table 3.

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Table 1 Crystal data and structure parameters for the title complex

Empirical	$\text{C}_{25}\text{H}_{35}\text{CdClN}_2\text{O}_5$	Absorption coefficient / mm^{-1}	0.947
Formula weight	591.40	Crystal color	Colorless
Crystal system	Triclinic	Crystal dimension / mm	$0.37 \times 0.20 \times 0.04$
Space group	$P\bar{1}$	θ range / $^\circ$	$1.73 \sim 27.58$
a / nm	1.091 0(1)	Reflections collected	22 831
b / nm	1.1318(1)	Unique reflections (R_{int})	6 167 (0.034 7)
c / nm	1.246 4(1)	Data with $I>2\sigma(I)$	4950
α / $^\circ$	88.52(1)	Parameters refined	313
β / $^\circ$	71.34(1)	R , wR ($I>2\sigma(I)$)	0.0401, 0.1040
γ / $^\circ$	68.11(1)	R , wR (all reflections)	0.053 3, 0.110 0
V / nm^3	1.345 2(1)	Goodness-of-fit (on F^2)	1.111

Continued Table 1

Z	2	$\Delta\rho_{\max}, \Delta\rho_{\min} / (\text{e} \cdot \text{nm}^{-3})$	1 054, -405
$D_c / (\text{g} \cdot \text{cm}^{-3})$	1.460	$(\Delta/\sigma)_{\max}$	0.000
$F(000)$	608		

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

Cd(1)-O(2)	0.230 2(3)	Cd(1)-N(1)	0.238 1(2)	Cd(1)-Cl(1)	0.247 5(1)
Cd(1)-O(1W)	0.233 5(3)	Cd(1)-O(1)	0.251 2(2)	Cd(1)-N(2)#1	0.230 5(2)
O(2)-Cd(1)-N(2)#1	142.46(8)	O(2)-Cd(1)-O(1W)	90.76(11)	N(2)#1-Cd(1)-O(1W)	89.33(9)
O(2)-Cd(1)-N(1)	87.88(9)	N(2)#1-Cd(1)-N(1)	88.62(6)	O(1W)-Cd(1)-N(1)	174.67(7)
O(2)-Cd(1)-Cl(1)	111.28(7)	N(2)#1-Cd(1)-Cl(1)	106.24(5)	O(1W)-Cd(1)-Cl(1)	91.46(7)
N(1)-Cd(1)-Cl(1)	93.83(5)	O(2)-Cd(1)-O(1)	53.63(9)	N(2)#1-Cd(1)-O(1)	89.28(7)
O(1W)-Cd(1)-O(1)	82.12(9)	N(1)-Cd(1)-O(1)	92.94(7)	Cl(1)-Cd(1)-O(1)	163.20(7)

Symmetry codes: #1: $x-1, y+1, z$.

Table 3 Hydrogen bond lengths and bond angles

D-H \cdots A	$d(\text{D-H}) / \text{nm}$	$d(\text{H}\cdots\text{A}) / \text{nm}$	$d(\text{D}\cdots\text{A}) / \text{nm}$	$\angle(\text{DHA}) / (^\circ)$
O(3)-H(3A) \cdots O(2)#3	0.084	0.201	0.281 9(3)	160.4
O(1W)-H(1WB) \cdots O(1)#4	0.085	0.191	0.275 4(3)	171.2
O(1W)-H(1WA) \cdots O(2W)	0.084	0.208	0.275 5(5)	137.6
O(2W)-H(2WA) \cdots O(3)#5	0.089	0.192	0.277 0(6)	158.2
O(2W)-H(2WB) \cdots Cl(1)	0.086	0.273	0.317 9(5)	114.1

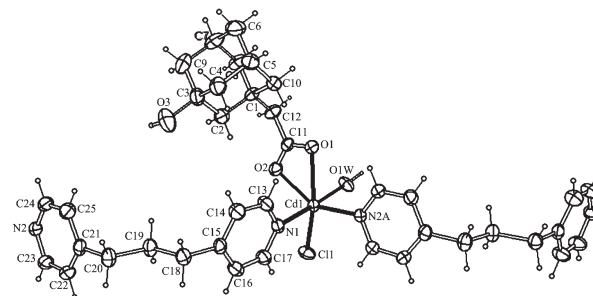
Symmetry codes: #3: $-x+1, -y, -z$; #4: $-x, -y+1, -z$; #5: $x, y+1, z$.

2 Results and discussion

2.1 Crystal structure

The crystal structure of complex **1** is composed of a one-dimensional chain $[\text{CdCl}(\text{HL})(\text{dpp})(\text{H}_2\text{O})]_n$ and lattice water molecules. As shown in Fig.1, the Cd(II) is six coordinated by two oxygen atoms from one chelate carboxyl group of HL, one aqua molecule, one chlorine atom, and two nitrogen atoms from two dpp molecules, giving a distorted octahedral coordination geometry, where Cl(1), N(2)#1, O(1) and O(2) locate at the equator positions, while N(1) and O(1W) occupy the axial positions. Here, bond angles of N(2)#1-Cd(1)-Cl(1), N(2)#1-Cd(1)-O(1), O(2)-Cd(1)-O(1) and O(2)-Cd(1)-Cl(1) are $106.24(5)^\circ$, $89.28(7)^\circ$, $53.63(9)^\circ$ and $111.28(7)^\circ$, respectively. The sum of these angles is 360.43° (close to 360°), suggesting a planar nature of Cl(1), N(2)#1, O(1), O(2) and Cd(1) (plane equation $0.077 0x + 0.862 5y - 0.500 1z = 3.453 7$) with their corresponding deviations from the base plane to be 0.005 4, 0.001 2, 0.021 7, -0.009 5 and -0.000 4 nm. N(1) and O(1W) are away

from the mean plane by -0.238 21 and 0.232 72 nm, respectively. The bond angle defined by the axial atoms of N(1) and O(1W) is $174.67(7)^\circ$.



supramolecular architectures. As shown in Fig.3, it should be noted that there are persistent intermolecular hydrogen bonds involving lattice water molecules and chlorine atoms in the neighboring chains. The $\text{O}-\text{H}\cdots\text{O}$ and $\text{O}-\text{H}\cdots\text{Cl}$ hydrogen bonds link the neighboring chains to yield 2D layer.

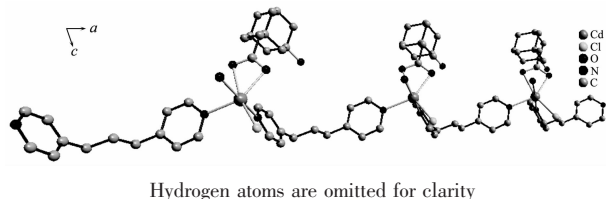


Fig.2 View of one-dimensional chain down the b axis in **1**

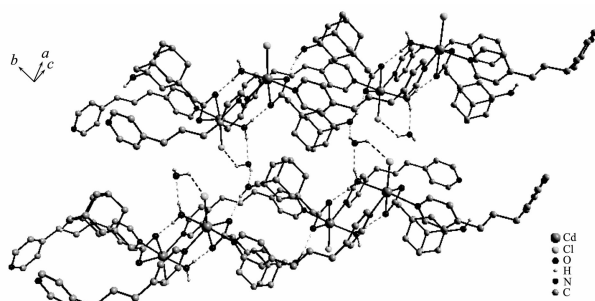


Fig.3 Packing diagram for complex **1**, showing the hydrogen-bonding interactions

2.2 IR spectrum

IR spectrum of complex **1** shows the characteristic bands of the carboxyl group at $1\,613\text{ cm}^{-1}$ for the antisymmetric stretching and at $1\,540\text{ cm}^{-1}$ for the symmetric stretching. The separation (Δ) between $\nu_{\text{asym}}(\text{CO}_2)$ and $\nu_{\text{sym}}(\text{CO}_2)$ of 73 cm^{-1} indicates the presence of chelating coordination mode^[19], which is consistent with the crystal structure. The absence of the expected characteristic bands at $1\,730\sim 1\,690\text{ cm}^{-1}$ attributed to the protonated carboxylate groups accounts for the deprotonation of carboxyl group. The wide absorption peak at about $3\,283\text{ cm}^{-1}$ characterizes the peak of OH group of H_2O and and 3-hydroxy group of HL.

2.3 Thermal property

The sample of complex **1** was heated at a rate of $10\text{ }^\circ\text{C}\cdot\text{min}^{-1}$ under O_2 atmosphere. As shown in Fig.4, the TG diagram reveals decomposition of **1** begins from $83\text{ }^\circ\text{C}$, the first weight loss of 5.5% from 83 to $122\text{ }^\circ\text{C}$ corresponds to the loss of the lattice and coordination water molecules. Then the structure appears to decompose with a total weight loss of 75.9% between

203 and $664\text{ }^\circ\text{C}$, mainly corresponding to loss of the organic ligands and chlorine atom. The final residuals may be CdO (calcd. 21.7%).

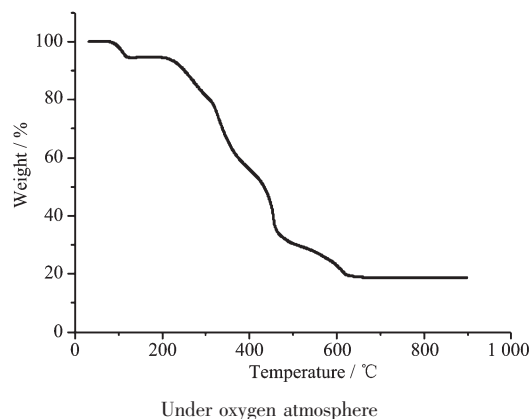


Fig.4 TG diagram for complex **1**

2.4 Luminescent property

The solid-state luminescent property of complex **1** was investigated at room temperature, and the emission spectra are given in Fig.5. Complex **1** exhibit an intense photoluminescence, and the maximum emission wavelength is at 443 nm ($\lambda_{\text{ex}}=353\text{ nm}$). At room temperature, the free HL ligand shows no detectable luminescence and the free dpp ligand display fluorescent properties in the solid state at room temperature with the emission maximum being located at 523 nm ^[20]. Therefore, the emission band of **1** may be mainly ascribed to $\pi-\pi^*$ electronic transition of the ligands^[21-22].

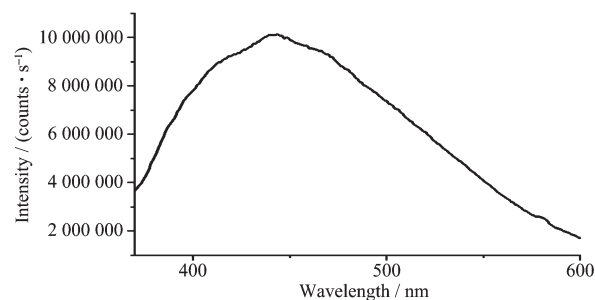


Fig.5 Solid-state luminescent emission spectra of complex **1** at room temperature

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