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Preparation, characterization and fluorescence of two cadmium compounds with different extended structures

Z.-L. Yao[2], Y.-P. Pei[1], Z.-Y. Luo[1], R.-H. Hu[1], Y.-X. Yang[1], Wen-Tong Chen[1]*

[1]*Institute of Applied Chemistry, School of Chemistry and Chemical Engineering, Jiangxi Province Key Laboratory of Coordination Chemistry, Jinggangshan University, Ji'an, Jiangxi 343009, China*

[2]*Biology and Chemistry Engineering Department, Fuqing Branch of Fujian Normal University, Fuqing, Fujian 350300, P.R. China*

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Two cadmium compounds, $[Cd_2Cl_4(2,2'\text{-bipy})]_n$ (**1**) and $[CdCl_2(2,2'\text{-bipy})]_n$ (**2**) (bipy = bipyridine) with different extended structures, have been obtained from hydrothermal reactions and structurally characterized by X-ray single-crystal diffraction. Compound **1** is characterized by a three-dimensional (3D) structure and the cadmium ion is coordinated by three chloride ions and one nitrogen atom to yield a tetrahedron. Differently, compound **2** features a one-dimensional (1D) structure and the cadmium ion is coordinated by four chloride ions and two nitrogen atoms to yield an octahedron. Fluorescence investigation shows that compound **1** displays an emission in the ultraviolet region, while compound **2** exhibits an emission in the green region.

Keywords: crystal, cadmium, extended structure, fluorescence, hydrothermal reaction

INTRODUCTION

Because of the intrinsic aesthetic appeal and the various applications, metal halide bipyridine compounds have recently gained more and more interest [1-23]. The pyridyl rings of the bipyridine are characteristic of a delocalized π-system. Therefore, bipyridine is a useful ligand for preparing light emitting compounds which can be applied in many fields such as organic light emitting diodes, chemical sensors and solar energy conversion. To our knowledge, a large amount of metal halide bipyridine compounds have been reported so far [1]. However, the group-12 (IIB) metal halide bipyridine compounds are still relatively rare. Actually, the IIB metal halide bipyridine compounds can usually exhibit useful fluorescence and photoelectric properties. Furthermore, 2,2′-bipyridine is a bifunctional ligand and it can act as a bidentate ligand to coordinate the metal ions. Our recent efforts in synthesizing IIB metal halide bipyridine compounds are mainly aimed at the systems containing the 2,2′-bipyridine. In this paper, we report the preparation, crystal structures and fluorescence of two cadmium compounds $[Cd_2Cl_4(2,2'\text{-bipy})]_n$ (**1**) and $[CdCl_2(2,2'\text{-bipy})]_n$ (**2**) (bipy = bipyridine) which are synthesized from hydrothermal reactions. It is noteworthy that both compounds show totally different extended structures, although they a have similar molecular formula.

EXPERIMENTAL

Materials and instrumentation

All chemicals and reagents employed are purchased and used as received without purification. Fluorescence studies are performed with solid state samples at room temperature on a computer-controlled JY FluoroMax-3 spectrometer.

Synthesis of $[Cd_2Cl_4(2,2'\text{-bipy})]_n$ (1).

A mixture of $CdCl_2$ (1 mmol, 183 mg) and 2,2'-bipy (0.5 mmol, 78 mg) are stirred and dissolved in 1 mL ethanol and 9 mL distilled water at an ambient temperature. Then, the mixture is heated at 180 °C for 10 days in a 25 mL teflon-lined stainless steel autoclave. Colorless block crystals of compound **1** are obtained and dried in air.

Synthesis of $[CdCl_2(2,2'\text{-bipy})]_n$ (2).

This compound is prepared by mixing $CdCl_2$ (1 mmol, 183 mg), 2,2'-bipy (1 mmol, 156 mg), 3 mL ethanol and 7 mL distilled water in a 25 mL Teflon-lined stainless steel autoclave and heated at 180 °C for 10 days. After being slowly cooled down to room temperature at 6 K/h, colorless crystals are collected.

X-ray structure determination.

The X-ray single-crystal data set of both compounds are measured on a Rigaku Mercury CCD X-ray area detector with graphite monochromatic Mo-*K*α radiation (λ = 0.71073 Å). Their data reduction and empirical correction

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* To whom all correspondence should be sent:
E-mail: cwtqq@aliyun.com

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absorption are performed with the CrystalClear software. Crystal structures for both compounds are solved by the direct methods and refined by full-matrix least-squares techniques against F^2 with the Siemens SHELXTL^{TM} Version 5 crystallographic software package. Non-hydrogen atoms are found based on the difference Fourier maps, while the hydrogen atoms are symmetrically generated and allowed to ride on the parent atoms. The crystal data and structural refinement parameters are presented in Table 1. Selected bond lengths and angles are given in Table 2. CCDC No. 1416689 (**1**) and 1416690 (**2**).

RESULTS AND DISCUSSION

The ORTEP figure displaying the molecular structure of compound **1** is shown in Figure 1.

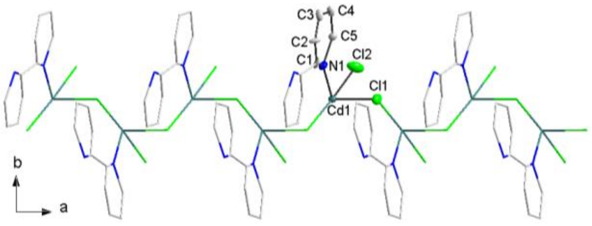

Fig. 1. An ORTEP figure showing the molecular structure of compound **1** (hydrogen atoms were omitted for clarity)

The X-ray single-crystal diffraction results reveal that the molecular structure of compound **1** is characterized by a three-dimensional (3D) structure. All of the crystallographically independent atoms are located on the general positions. The cadmium ion is coordinated by three chloride ions and one nitrogen atom to yield a tetrahedron. The bond length of Cd-N is 2.208(2) Å, while the Cd-Cl bond lengths are between 2.5185(16) Å and 2.6722(13) Å. These bond lengths are normal and comparable with those previously reported [1-8]. The bond angle of N-Cd-N is 69.18(7)°. The bond angles of N-Cd-Cl and Cl-Cd-Cl are in the wide range of 85.70(6)°–160.069(12)° and 84.35(8)°–178.694(2)°, respectively. The result of the bond valence calculation reveals that the cadmium ion is in the +2 oxidation state (Cd1: 1.7) [1]. The pyridyl rings of 2,2'-bipy are perfectly coplanar with the nitrogen atoms pointing in opposite directions. The 2,2'-bipy of compound **1** acts as a bidentate ligand binding to two cadmium(II) ions. The deviation of the atoms of the pyridyl rings is -0.099 Å – +0.081 Å apart from their average ring plane. The molecules of compound **1** interlink two neighboring ones via the chloride ions to form an infinite chain running along the *a* axis (Figure 1). The chains further interconnect together to yield a three-dimensional (3D) framework, as given in Figure 2.

Table 1. Crystallographic data and structural refinement parameters for **1** and **2**

Compound	**1**	**2**
Empirical formula	C10 H8 Cd2 Cl4 N2	C10 H8 Cd Cl2 N2
Color and Habit	colorless block	colorless block
Crystal Size (mm)	0.14 0.10 0.08	0.12 0.08 0.05
Crystal system	monoclinic	monoclinic
Space group	*I*2/*a*	*C*2/*c*
a (Å)	7.1691(4)	17.52(2)
b (Å)	9.3087(5)	9.290(10)
c (Å)	16.4175(12)	7.165(9)
β (°)	93.1810(10)	110.897(14)
V (Å^3)	1093.93(12)	1090(2)
Formula weight	522.78	339.48
Z	4	4
Theta range (°)	5.41 – 25.02	4.98 – 25.00
Reflections collected	1734	3455
Independent, observed reflections (R_{int})	526, 513 (0.0196)	884, 433 (0.0577)
Density(cal.) (g/cm^3)	3.174	2.665
Absorption coefficient (mm^{-1})	4.838	5.405
Temperature(K)	296(2)	296(2)
F(000)	984	790
$R1$, $wR2$	0.0695, 0.1642	0.0866, 0.1353
Goodness-of-fit	1.018	0.645
Largest and Mean Delta/Sigma	0, 0	0.004, 0
$\Delta\rho$ (max, min) (e/Å^3)	1.265, -0.858	1.779, -0.872

Table 2. Some bond lengths (Å) and angles (º)

Compound **1**

Cd(1)-N(1)	2.208(2)	N(1)-Cd(1)-Cl(1)	89.56(7)
Cd(1)-Cl(1)	2.5877(13)	Cl(2)-Cd(1)-Cl(1)	177.39(5)
Cd(1)-Cl(1)#1	2.6722(13)	N(1)-Cd(1)-Cl(1)#1	82.65(7)
Cd(1)-Cl(2)	2.5185(16)	Cl(2)-Cd(1)-Cl(1)#1	84.91(6)
N(1)-Cd(1)-Cl(2)	88.21(7)	Cl(1)-Cd(1)-Cl(1)#1	96.15(4)

Symmetry codes: #1 *x*-1/2, -*y*+2, *z*.

Compound **2**

Cd(1)-N(1)	2.3220(18)	Cl(1)-Cd(1)-Cl(1)#1	103.40(8)
Cd(1)-N(1)#1	2.3220(18)	N(1)-Cd(1)-Cl(1)#2	95.38(6)
Cd(1)-Cl(1)	2.5422(17)	N(1)#1-Cd(1)-Cl(1)#2	85.70(6)
Cd(1)-Cl(1)#1	2.5422(17)	Cl(1)-Cd(1)-Cl(1)#2	94.83(8)
Cd(1)-Cl(1)#2	2.752(2)	Cl(1)#1-Cd(1)-Cl(1)#2	84.35(8)
Cd(1)-Cl(1)#3	2.752(2)	N(1)-Cd(1)-Cl(1)#3	85.70(6)
N(1)-Cd(1)-N(1)#1	69.18(7)	N(1)#1-Cd(1)-Cl(1)#3	95.38(6)
N(1)-Cd(1)-Cl(1)	160.069(12)	Cl(1)-Cd(1)-Cl(1)#3	84.35(8)
N(1)#1-Cd(1)-Cl(1)	94.61(7)	Cl(1)#1-Cd(1)-Cl(1)#3	94.83(8)
N(1)-Cd(1)-Cl(1)#1	94.61(7)	Cl(1)#2-Cd(1)-Cl(1)#3	178.694(2)

Symmetry codes: #1 -*x*+1, *y*, -*z*+3/2; #2 *x*, -*y*+1, *z*+1/2; #3 -*x*+1, -*y*+1, -*z*+1.

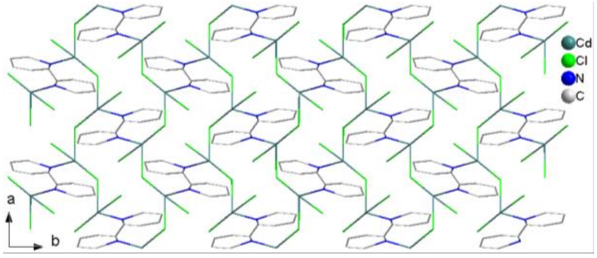

Fig. 2. A packing figure of compound **1** viewed down along the *c* axis.

Compound **2** crystallizes in the space group *C*2/*c* of the monoclinic system, while compound **1** crystallizes in the monoclinic *I*2/*a* space group. The Cd(II) ion of compound **2** is located in a special position, while other crystallographically independent atoms reside at general positions. The crystal structure of compound **2** is characteristic of a one-dimensional (1D) chain-like motif comprising of $CdCl_2$(2,2'-bipy) building blocks. As depicted in Figure 3, the cadmium ion of compound **2** is coordinated by four chloride ions and two nitrogen atoms to yield an octahedron. The equatorial plane of this octahedron yields two nitrogen atoms and two chloride ions, while both apical positions are occupied by another two chloride ions. The result of the bond valence calculation reveals that the cadmium ion is in the +2 oxidation state (Cd1: 2.1). Different from compound **1**, both nitrogen atoms of the pyridyl rings of compound **2** point in the same direction and both of them are coordinated to the same cadmium ion. The bond lengths of Cd–N and Cd–Cl in the equatorial plane are 2.3220(18) Å and 2.5422(17) Å, respectively. The bond lengths of the apical Cd–Cl are 2.752(2) Å. The bond distances of Cd–N and Cd–Cl in the coordination sphere of the cadmium ion are normal and comparable with those reported in the references [1, 2, 3, 4]. Each cadmium(II) ion interconnects two neighboring ones through two μ_2-chloride ions to form an infinite 1-D chain-like motif, as displayed in Figure 3. The 2,2'-bipy of compound **2** is a bidentate ligand chelating one cadmium(II) ion, while that of compound **1** acts as a bidentate ligand binding to two cadmium(II) ions. The dihedral angle between the pyridyl rings of the 2,2'-bipy molecule of compound **2** is 7.024(23)º. The 1-D chains stack together via the van der Waals interaction to give a 3-D packing figure, as shown in Figure 4. The reason for the 3D structure and 1D chain in compounds **1** and **2**, respectively, should be ascribed to different coordination modes of the 2,2'-bipy ligand. In compound **1**, two nitrogen atoms of one 2,2'-bipy point to opposite directions that allow the 2,2'-bipy to bind to two different cadmium(II) ions and yield a 3D structure. However, in compound **2**, both nitrogen atoms of one 2,2'-bipy point to the same direction and both of them are coordinated to one same cadmium ion and only form a 1D chain.

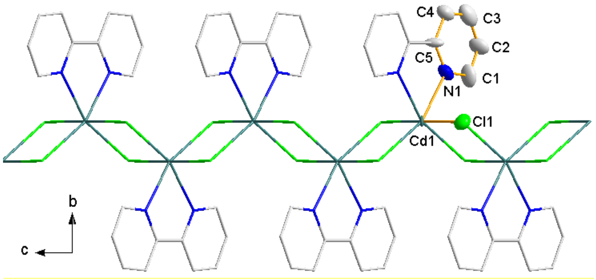

Fig. 3. An ORTEP figure showing the molecular structure of compound **2** (hydrogen atoms were omitted for clarity).

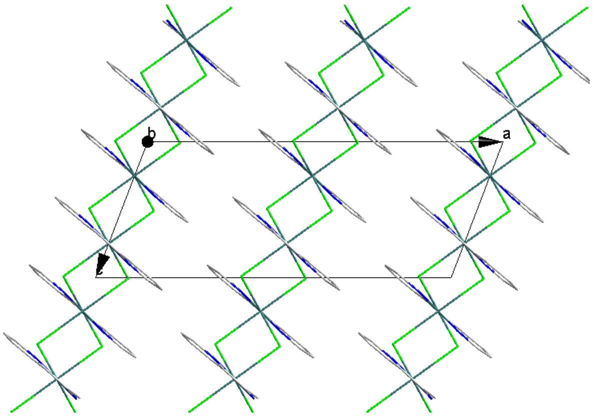

Fig. 4. A packing figure of compound **2** viewed down along the *b* axis

To our knowledge, the 2,2'-bipy and the cadmium ion can generally display fluorescence [5, 6, 7]. Based on this consideration, we deduced the fluorescence spectra for both compounds by using solid-state samples at an ambient temperature. As presented in Figure 5, the excitation spectra of compound **1** shows that the effective energy absorption is dominantly found in the ultraviolet region of 300–350 nm.

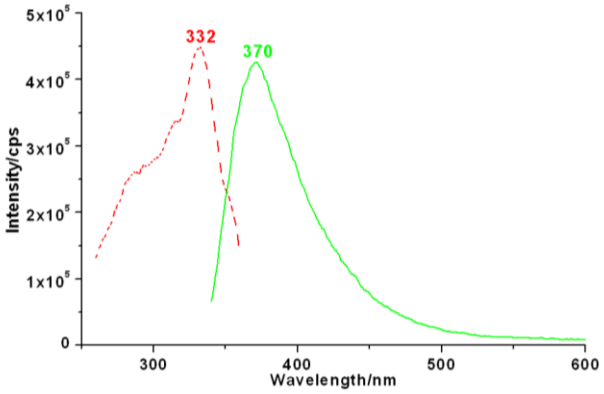

Fig. 5. Solid-state fluorescence spectra of compound **1** under room temperature with the dashed and solid lines representing excitation and emission spectra, respectively.

Excitation at 370 nm yields a strong band at 332 nm. The peak at 332 nm, is an intensive emission in the ultraviolet region. As for compound **2**, we also measured its fluorescence spectra and the result is shown in Figure 6. As depicted in Figure 6, the excitation spectra of compound **2,** exhibits the effective energy absorption mainly in the ultraviolet region of 350–400 nm. The excitation spectra under the emission of 522 nm display a strong band at 391 nm. By virtue of the excitation peak of 391 nm, we also measured the emission spectra of compound **2** and the result shows an intensive emission peak in the green region with a maximum value of 522 nm.

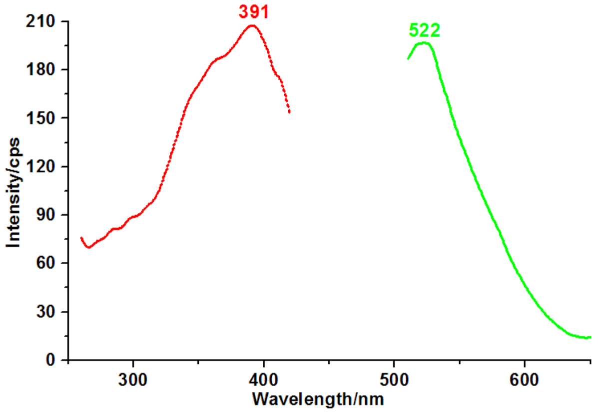

Fig. 6. Solid-state fluorescence spectra of compound **2** under room temperature with the dashed and solid lines representing excitation and emission spectra, respectively.

In summary, two cadmium compounds with different extended structures have been synthesized through hydrothermal reactions and structurally characterized by X-ray single-crystal diffraction. Compound **1** features a 3D structure, while compound **2** is characterized by a 1D motif. The coordination environments of the cadmium ions and the binding modes of the 2,2'-bipy ligand in both compounds are different, which yields different extended structures of the title compounds. Fluorescence investigation shows that the compounds display different fluorescence spectra.

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ПРИГОТВЯНЕ, ОХАРАКТЕРИЗИРАНЕ И ФЛУОРЕСЦЕНЦИЯ НА ДВЕ КАДМИЕВИ СЪЕДИНЕНИЯ С РАЗЛИЧНИ РАЗГЪНАТИ СТРУКТУРИ

Ж.-Л. Яо[2], И.-П. Пей[1], Ж.-И, Луо[1], Р.-Х. Ху[1], И.-С. Яанг[1], Уен-Тонг Чен[1]*

[1]*Институт по приложна химия, Колеж по химия и химично инженерство, Ключова лаборатория по координационна химия в провинция Янгси, Университет Джингангшан, Джиан, Янгси 343009, Китай*
[2]*Департаменъ по химично и биоинженерство, Клон Фуджин на Университета във Фуджиян, Фуджиян 350300, Китай*

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(Резюме)

Две кадмиеви съединения $[Cd_2Cl_4(2,2'\text{-bipy})]_n$ (**1**) и $[CdCl_2(2,2'\text{-bipy})]_n$ (**2**) (bipy = бипиридил) с различни разгънати структури са получени при хидротермални реакции й са структурно охарактеризирани с рентгеноструктурен анализ чрез дифракция на един кристал. Съединение **1** се характеризира с три-измерна (3D) структура, а кадмиевият йон се координира от три хлоридни йона и един азотен атом с получаването на тетраедър. Съединение **2** се характеризира с едно-измерна (1D) структура, а кадмиевият йон се координира с четири хлоридни йона и та азотни атома с получаването на октаедър. Флуоресцентните изследвания показват, че съединение **1** дава емисии в ултравиолетовата област, докато съединение **2** проявява емисии в зелената област на спектъра.