ISSN 1070-3284, Russian Journal of Coordination Chemistry, 2021, Vol. 47, No. 1, pp. 75–80. © Pleiades Publishing, Ltd., 2021.

Two Cd(II) Coordination Compounds Based on the Flexible N-Bridging Ligands: Syntheses, Crystal Structures and Luminescent Properties

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Received March 4, 2020; revised March 30, 2020; accepted March 31, 2020

Abstract—Two coordination compounds, $Cd_2(Ptt)_2Cl_4(H_2O)_2$ (**I**) and $[Cd(Dpb)_2Cl_2]_n \cdot nH_2O$ (**II**) (Ptt = 3-(pyrid-2-yl)-5-(1H-1,2,4-triazol-3-yl)-1,2,4-triazolyl), Dpb = 1,4-bis(pyridin-3-ylmethoxy)benzene), were synthesized from hydro-solvothermal technique. Their structures have been characterized by infrared spectra, elemental analyses, single crystal X-ray diffraction analyses (CIF files CCDC nos. 1903141 (**I**), 1903138 (**II**)) and thermogravimetric analyses. Compound **I** is a dinuclear structure and **II** is a 1D chain. Moreover, the luminescent properties of **I** and **II** have been investigated with fluorescent spectra in the solid state, the two compounds display a strong fluorescent emission at room temperature and have potential applications as fluorescent-emitting materials.

Keywords: hydro-solvothermal technique, crystal structure, luminescent property

DOI: 10.1134/S1070328421010073

INTRODUCTION

During the last few decades, the design and synthesis of metal-organic coordination compounds have attracted increasing interest not only because of their rich structural diversity [1–4] but also owing to their tremendous potential applications in various field such as gas storage [5], catalysis [6], ion-exchange [7], magnetism [8], luminescence [9], nonlinear optics [10], drug delivery [11] and so on. Although the self-assembly of metal ion and organic linker under hydrothermal condition has become a general route to obtain such materials. However, the rational predict and control the framework of a given crystalline product remains a great challenge in crystal engineering [12].

It is well-know that many factors can affect the structural features of coordination compounds, such as the metal salts, organic ligands, solvents, metal-ligand ratio, temperature and so on [13, 14]. Amongst, the rational selection of organic ligands is important for the assembly of coordination compound. The N-bridging ligands have been frequently used for the constructing coordination compounds with diverse structures and properties [15–17]. Among the N-bridging ligands, the flexible 4-bis(pyridin-3-ylmethoxy)benzene (Dpb) and 3-(pyrid-2-yl)-5-(1H-1,2,4-triazol-3-yl)-1,2,4-triazolyl (Ptt) are good candidates for the construction of coordination compounds. The Dpb possesses the rotating $-O-CH_2$ group and the neutra pyridine moieties, which can exhibit a great variety of coordination modes. On the other hand, The Ptt ligand possess multiple nitrogen-containing, which can mediate coordination needs of the metal centers and consequently generate more meaningful architectures. Moreover, the large aromatic system of Dpb and Ptt ligands can provide potential supramolecular recognition sites for $\pi-\pi$ aromatic stacking and hydrogen-bond interactions to form supramolecular structures.

In the present paper, two coordination compounds have got by choosing the Dpb and Ptt as ligands, we demonstrated the hydro-solvothermal synthesis, single crystal structures and fluorescent properties of Cd(II)-based compounds $Cd_2(Ptt)_2Cl_4(H_2O)_2$ (**I**) and $[Cd(Dpb)_2Cl_2]_n \cdot nH_2O$ (**II**). In compound **I**, the nitrogen atoms of two Ptt ligands coordinate to Cd(II) atoms to form a mononuclear unit, two mononuclear units are bridged by coordination chlorine atoms to form dinuclear structure. Compound **II** shows a one dimensional chain which was formed by the nitrogen atoms of Dpb ligand coordinating to Cd(II) atom. Meanwhile, the luminescence properties of **I** and **II** were also investigated.

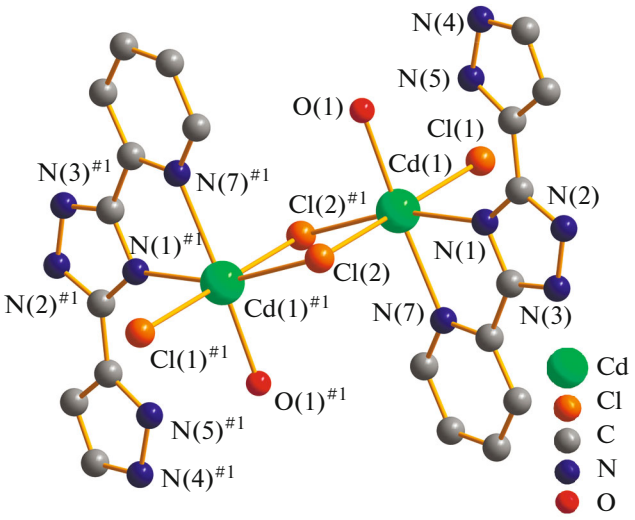

Fig. 1. Coordination environment of the Cd(II) atom in **I**.

EXPERIMENTAL

Materials and methods. All chemicals and reagents were purchased from Jinan Henghua Sci. & Tec. Co. Ltd. and with the purity of the samples are 98%. Elemental analyses (C, H, N) were determined with a Vario EL III elemental analyzer. Infrared spectra were recorded on a Bruker EQUINOX55 spectrometer as KBr pellets in the range of 4000–400 cm^{-1}. Fluorescence spectra were performed on a Hitachi F-4500 fluorescence spectrophotometer at room temperature. Thermal gravimetry analyses (TGA) were carried out with a Universal V2.6 DTA system at a heating rate of 10°C/min in a nitrogen atmosphere.

Synthesis of compound I. A mixture of Ptt (0.013 g, 0.05 mmol), $CdCl_2{\cdot}2.5H_2O$ (0.012 g, 0.05 mmol) was put in a solution of water, DMF and C_2H_5OH (10 mL, $V_{H_2O} : V_{DMF} : V_{C_2H_5OH} = 2 : 1 : 3$) and stirred for 30 min at the room temperature, then sealed in a 25 mL Teflon-lined stainless steel container, which was heated to 150°C for 4 h and kept under autogenous pressure at 150°C for 3 days. After cooling to room temperature at a rate of 2°C per hour, the colorless block-shaped crystals were collected by filtration and washed with deionized water and left to air-dry. Yield was ~52% based on Cd.

For $C_{20}H_{12}N_{12}O_2Cl_4Cd_2$

Anal. calcd., %	C, 29.30	H, 1.47	N, 20.51
Found, %	C, 29.21	H, 1.53	N, 20.47

IR (KBr, ν cm^{-1}): 3403 s,1591 m, 1544 w, 1460 s, 1271 w, 1206 m, 1037 w, 980 m, 896 w, 698 m, 614 m, 548 w, 501 w.

Synthesis of compound II. Compound **II** was synthesized similar to that of **I**, except changing the Ptt to Dpb (0.013 g, 0.05 mmol). The crystals were filtered and washed with deionized water and left to aie-dry. Yield was 42% based on Cd.

For $C_{36}H_{32}N_4O_4Cl_2Cd$

Anal. calcd., %	C, 56.30	H, 4.20	N, 7.30
Found, %	C, 56.79	H, 3.25	N, 7.28

IR (KBr, ν cm^{-1}): 3450 s, 3056 , 1657 w, 1601 m, 1515 s, 1422 s, 1366 m, 1338 w, 1216 s, 1103 m, 1047 s, 802 s, 689 s, 633 m, 511 w.

X-ray crystallography. Intensity data were collected on a Bruker Smart APEX II CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at room temperature. Empirical absorption corrections were applied by the SADABS program. The structure was solved by direct methods [18] and refined by the full-matrix least-squares based on F^2 using SHELXTL-97 program [19]. All non-hydrogen atoms were refined anisotropically and the hydrogen atoms of organic ligands were generated geometrically. Crystal data and structural refinement parameters for **I**, **II** are summarized in Table 1 and selected bond distances and bond angles are listed in Table 2.

Supplementary material for complexes has been deposited with the Cambridge Crystallographic Data Centre (CCDC nos. 1903141 (**I**), 1903138 (**II**); deposit@ccdc.cam.ac.uk or http://www.ccdc. camac.uk).

RESULTS AND DISCUSSION

Single-crystal X-ray analysis reveals that compound **I** displays a dinuclear structure, as shown in Fig. 1. The asymmetric unit of **I** contains two crystallographic independent Cd^{2+} cation, two Ptt ligands, two coordination water molecules and four chlorine atoms. The Cd(1) is hexa-coordinated by two nitrogen atoms (N(1), N(7)) from one Ptt ligand, one oxygen atom (O(1)), from coordination water and three chlorine atoms ((Cl(1), Cl(2), Cl(2)$^{\#1}$)) from $CdCl_2{\cdot}2.5H_2O$ with a distorted octahedral geometry. The Cd(2) has the same coordination geometry with Cd(1). The Cd–O bond length is 2.244(3) Å, the Cd–Cl bond lengths are in the range of 2.5498(13)–2.7527(15) Å and the Cd–N bond lengths are in the range of 2.374(4)–2.384(4) Å which are comparable to the reported values in Cd(II) complexes [20, 21]. The Ptt ligands coordinate to Cd(II) atoms to form mononuclear units and two mononuclear units are bridged by two coordination chlorine atoms (Cl(2), Cl(2)$^{\#1}$) to form a dinuclear structure.

The asymmetric unit of **II** consists of one Cd^{2+} cation, four Dpb ligands and two coordination chlorine atoms. The Cd(II) atom of **II** shows a similar distorted octahedral coordination geometry to Cd(1) in compound **I** (Fig. 2a). Each Dpb ligand coordinates to Cd(II) atom with its nitrogen atoms by anticoordination mode and the adjacent Cd(II) atoms are further

Table 1. Crystallographic data and structural refinement parameters for **I** and **II**

Parameter	Value	
	I	**II**
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a, Å	8.5160(8)	7.7362(10)
b, Å	15.1641(13)	9.6584(13)
c, Å	10.7868(11)	12.440(2)
α, deg	90	107.316(2)
β, deg	95.365(2)	104.417(2)
γ, deg	90	100.572(2)
V, Å^3	1386.9(2)	825.4(2)
Z	2	1
ρ_{calcd}, g cm^{-3}	1.961	1.545
μ, mm^{-1}	1.963	0.870
F(000)	792	390
Reflections collected	6876	4145
Unique reflections	2437	2886
Independent parameters	181	214
S on F^2	1.048	1.044
R_1, wR_2 ($I > 2\sigma(I)$)	0.0383, 0.0971	0.0418, 0.1152
R_1, wR_2 (all data)	0.0515, 0.1031	0.0431, 0.1167
$\Delta\rho_{min}/\Delta\rho_{max}$, e Å^{-3}	0.638/−0.615	1.240/− 0.716

bridged by the Dpb ligands to form a one dimensional chain (Fig. 2b).

The luminescent compounds, especially those with d^{10} transition-metal ions compounds are well known for their potential in a variety of applications [22–25], including photochemistry or light-emitting diodes (LEDs). In order to clarify the structural modification effects of the ligands on the photoluminescent properties of coordination compounds, the photoluminescence properties of **I**, **II** and free ligand were studied in the solid state at room temperature (Fig. 3). The Ptt ligand exhibits intense emissions bands at ~307.4 and 454.3 nm upon excitation at 280 nm which can be assigned to the ligand-centered charge transitions, that is, the $\pi^* \rightarrow n$ and $\pi^* \rightarrow \pi$ transitions. The emission spectra of **I** displays the bimodal emissions at 393 and 447 nm upon excitation at 280 nm, which can be attributed to the ligand-to-metal charge transfer (LMCT) and intraligand $\pi^* \rightarrow \pi$ transition, respectively (Fig. 3a). Upon excitation at 280 nm, the compound **II** exhibits emission band at ~465 nm, while the Dpb ligand exhibits no obvious emission (Fig. 3b). The enhancement of luminescence of the compound **II** may be attributed to ligand coordination to the Cd(II) centers, which effectively increases the rigidity of the coordination polymers and reduces the loss of energy by radiationless decay [26].

In order to examine the thermal stability of the two compounds, their thermal decomposition behavior was investigated at 30–800°C under nitrogen atmospheres using TGA technique (Fig. 4). At first, compound **I** loses two coordination water molecules in interval 185–216°C, and the weight loss found of 4.81% is consistent with that calculated (4.39%). The second stage weight loss can be detected from 216 to 374°C attributed to the loss of four coordinated chlorine atoms (calcd. 17.27%; found 17.67%). Above 374°C, the compound begins to lose its organic ligands and then starts to decompose. In the DSC curve, the sharp exothermic peaks at 216 and 374°C confirms the melting and decomposition point of the studied compound (Fig. 4a).

According to the TG–DSC curve of **II** (Fig. 4b), the weight loss of 9.37% under 220°C is corresponded to the loss of two coordination chlorine atoms (calcd. 9.21%). Then the weight loss of 56.94% between 220 and 310°C was assigned to the decomposition of three quarters of Dpb ligands (calcd. 57.09%) and then the framework began to collapse. The DSC curve of **II** exhibits two endothermic peaks at 220 and 310°C, those peaks are correlated with TGA analysis results.

Table 2. Selected bond distances (Å) and bond angles (deg) for **I** and **II***

Bond	*d*, Å	Bond	*d*, Å
		I	
Cd(1)–O(1)	2.244(3)	Cd(1)–N(1)	2.374(4)
Cd(1)–N(7)	2.384(4)	Cd(1)–Cl(2)	2.5498(13)
Cd(1)–Cl(1)	2.6284(16)	Cd(1)–Cl(2)$^{\#1}$	2.7527(15)
Cl(2)–Cd(1)$^{\#1}$	2.7527(15)		
		II	
Cd(1)–N(2)$^{\#1}$	2.390(4)	Cd(1)–N(2)$^{\#2}$	2.390(4)
Cd(1)–N(1)	2.424(4)	Cd(1)–N(2)$^{\#3}$	2.424(4)
Cd(1)–Cl(1)	2.6038(12)	Cd(1)–Cl(1)$^{\#3}$	2.6038(12)
Cd(1)–N(2)$^{\#4}$	2.390(4)		
Angle	ω, deg	Angle	ω, deg
		I	
O(1)Cd(1)N(1)	96.78(13)	O(1)Cd(1)N(7)	166.73(14)
N(1)Cd(1)N(7)	71.76(14)	O(1)Cd(1)Cl(2)	96.52(10)
N(1)Cd(1)Cl(2)	162.95(10)	N(7)Cd(1)Cl(2)	93.64(10)
O(1)Cd(1)Cl(1)	93.86(12)	N(1)Cd(1)Cl(1)	91.94(10)
N(7)Cd(1)Cl(1)	93.21(11)	Cl(2)Cd(1)Cl(1)	97.77(5)
O(1)Cd(1)Cl(2)$^{\#1}$	84.21(12)	N(1)Cd(1)Cl(2)$^{\#1}$	83.42(10)
N(7)Cd(1)Cl(2)$^{\#1}$	87.76(11)	Cl(2)Cd(1)Cl(2)$^{\#1}$	87.34(5)
Cl(1)Cd(1)Cl(2)$^{\#1}$	174.72(4)	Cd(1)Cl(2)Cd(1)$^{\#1}$	92.66(4)
		II	
N(2)$^{\#1}$Cd(1)N(2)$^{\#2}$	180	N(2)$^{\#1}$Cd(1)N(1)	91.22(14)
N(2)$^{\#2}$Cd(1)N(1)	88.78(14)	N(2)$^{\#1}$Cd(1)N(1)$^{\#3}$	88.78(14)
N(2)$^{\#2}$Cd(1)N(1)$^{\#3}$	91.22(14)	N(1)Cd(1)N(1)$^{\#3}$	180
N(2)$^{\#1}$Cd(1)Cl(1)	89.39(10)	N(2)$^{\#2}$Cd(1)Cl(1)	90.61(10)
N(1)Cd(1)Cl(1)	89.18(10)	N(1)$^{\#3}$Cd(1)Cl(1)	90.82(10)
N(2)$^{\#1}$Cd(1)Cl(1)$^{\#3}$	90.61(10)	N(2)$^{\#2}$Cd(1)Cl(1)$^{\#3}$	89.39(10)
N(1)Cd(1)Cl(1)$^{\#3}$	90.82(10)	N(1)$^{\#3}$Cd(1)Cl(1)$^{\#3}$	89.18(10)
Cl(1)Cd(1)Cl(1)$^{\#3}$	180		

* Symmetry codes: $^{\#1}$ $-x, -y+2, -z$ (**I**) . $^{\#1}$ $-x+1, -y, -z+1$; $^{\#2}$ $x-2, y-1, z-1$; $^{\#3}$ $-x-1, -y-1, -z$; $^{\#4}$ $x+2, y+1, z+1$ (**II**).

Thus, two novel coordination compounds have been synthesized and characterized by IR, elemental analysis and single-crystal X-ray diffraction. The compound **I** shows a dinuclear structure and compound **II** displays 1D chain structure. Their structural diversities show that the ligand play a significant role in the structural self-assembly process. The solid-state fluorescent analyses show that compound **I** and **II** exhibit luminescence properties, indicating they may be good candidates as luminescent materials.

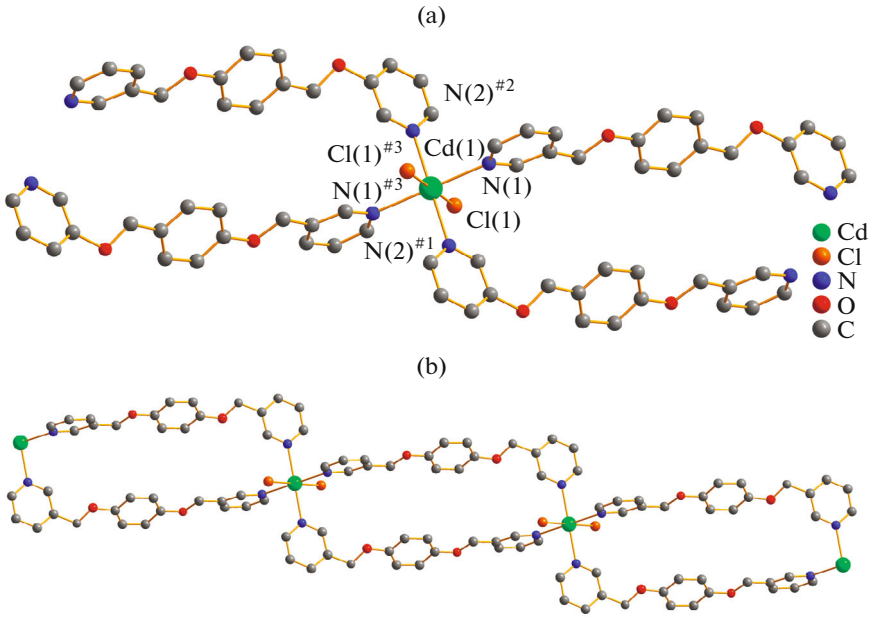

Fig. 2. Coordination environment of the Cd(II) atom in **II** (a); view of the 1D chain of **II** (b).

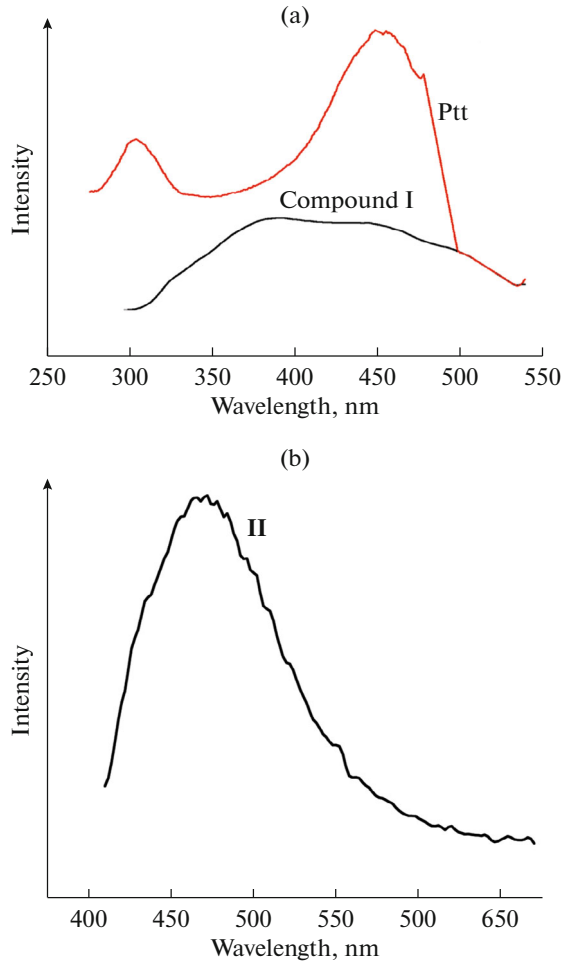

Fig. 3. The solid-state emission spectra: **I** (a) and **II** (b) at room temperature.

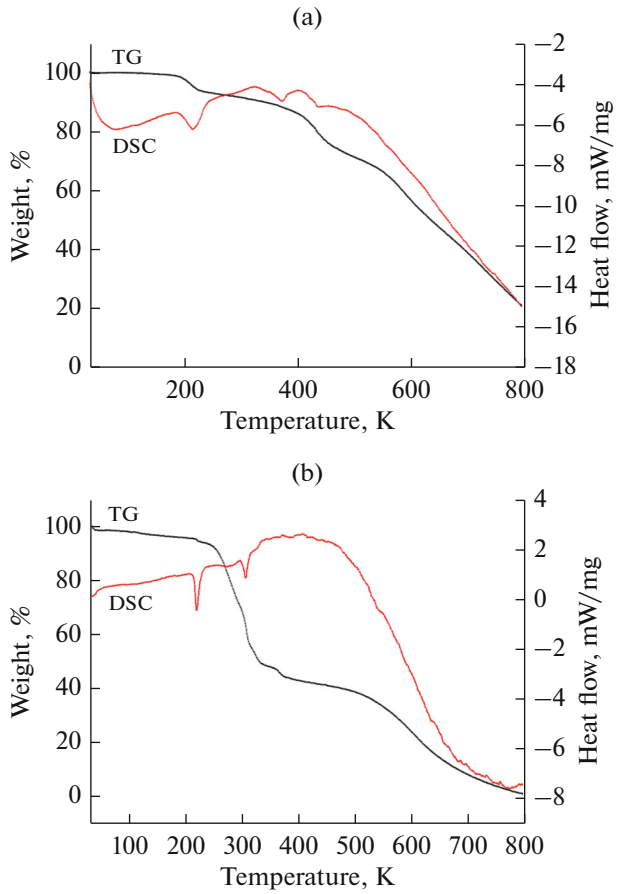

Fig. 4. TGA and DSC curves of complexes **I** (a) and **II** (b).

ACKNOWLEDGMENTS

The authors thank financial assistance from the Key Scientific Research Project of Education Department of Shaanxi Province (17JS027) and this work is also supported by team of syngas catalytic conversion of Shaanxi university of Technology.

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