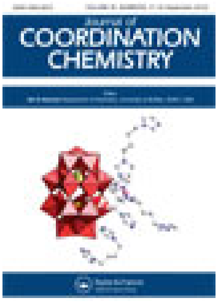
This article was downloaded by: [Renmin University of China]
On: 13 October 2013, At: 10:38
Publisher: Taylor & Francis
Informa Ltd Registered in England and Wales Registered Number: 1072954 Registered office: Mortimer House, 37-41 Mortimer Street, London W1T 3JH, UK



Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/gcoo20

Syntheses, crystal structures, and fluorescent properties of two Cd(II) complexes based on 2,2′-(ethane-1,2-diyl)bis(1H-imidazole-4,5-dicarboxylic acid)

Ting Li [a] , Yu Xiu [a] , Xiao Su [a] & Xiang-Ru Meng [a]
[a] The College of Chemistry and Molecular Engineering, Zhengzhou University , Zhengzhou 450001 , P.R. China

Accepted author version posted online: 11 Jul 2012.Published online: 24 Jul 2012.

To cite this article: Ting Li , Yu Xiu , Xiao Su & Xiang-Ru Meng (2012) Syntheses, crystal structures, and fluorescent properties of two Cd(II) complexes based on 2,2′-(ethane-1,2-diyl)bis(1H-imidazole-4,5-dicarboxylic acid), Journal of Coordination Chemistry, 65:17, 3111-3121, DOI: 10.1080/00958972.2012.710901

To link to this article: http://dx.doi.org/10.1080/00958972.2012.710901

PLEASE SCROLL DOWN FOR ARTICLE

Taylor & Francis makes every effort to ensure the accuracy of all the information (the “Content”) contained in the publications on our platform. However, Taylor & Francis, our agents, and our licensors make no representations or warranties whatsoever as to the accuracy, completeness, or suitability for any purpose of the Content. Any opinions and views expressed in this publication are the opinions and views of the authors, and are not the views of or endorsed by Taylor & Francis. The accuracy of the Content should not be relied upon and should be independently verified with primary sources of information. Taylor and Francis shall not be liable for any losses, actions, claims, proceedings, demands, costs, expenses, damages, and other liabilities whatsoever or howsoever caused arising directly or indirectly in connection with, in relation to or arising out of the use of the Content.

This article may be used for research, teaching, and private study purposes. Any substantial or systematic reproduction, redistribution, reselling, loan, sub-licensing, systematic supply, or distribution in any form to anyone is expressly forbidden. Terms &

Journal of Coordination Chemistry
Vol. 65, No. 17, 10 September 2012, 3111–3121

Syntheses, crystal structures, and fluorescent properties of two Cd(II) complexes based on 2,2′-(ethane-1, 2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid)

TING LI, YU XIU, XIAO SU and XIANG-RU MENG*

The College of Chemistry and Molecular Engineering,
Zhengzhou University, Zhengzhou 450001, P.R. China

(*Received 25 November 2011; in final form 7 May 2012*)

Two new complexes, $[Cd_2(H_4ebidc)_2(CH_3OH)_4] \cdot 2CH_3OH$ (**1**) and $\{[Cd(Cl)(I)(H_6ebidc)_{1/2}] \cdot 1/2bbe \cdot H_2O\}_n$ (**2**) ($H_6ebidc = 2,2'$-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid), bbe = 1,2-bis(2-benzimidazolyl)ethane), are obtained through self-assembly of H_6ebidc with Cd(II). Single-crystal X-ray diffraction shows that **1** has a binuclear structure and each tridentate chelating ligand coordinates to two Cd(II) ions with μ_2-O. Complex **2** displays a 1-D chain structure and each tetradentate ligand bridges two Cd(II) ions in chelating fashion. Fluorescent properties have also been determined.

Keywords: Cadmium complex; Crystal structure; Fluorescent property

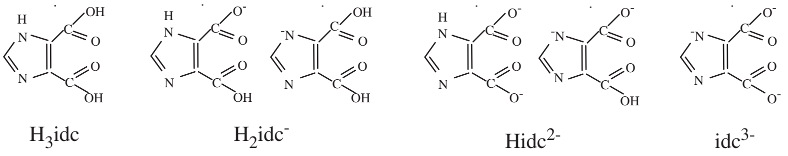
1. Introduction

Metal-organic frameworks (MOFs) are of interest for intriguing structures and potential applications in ion exchange, molecular recognition and separation, heterogeneous catalysts, gas sorption and storage, drug delivery and medical imaging and optical, magnetic, and porous materials [1–14]. Though a large number of complexes have been reported, synthetic strategies remain a long-term challenge because the structure of the resultant framework is influenced by many factors. Key factors are to choose metal ions with suitable coordination geometries and to rationally design ligands. Cadmium ion is a favorable building block or connecting node for complexes for ease to coordinate to N and O-containing ligands and closed-shell d^{10} Cd–Cd interactions can often give intriguing supramolecular motifs and properties [15, 16]. Multifunctional organic ligands play an important role in directing the extended structure of the complexes [17–22]. Thus, deliberate selection of multifunctional ligands to prepare interesting polymeric frameworks is an attractive topic.

---

*Corresponding author. Email: mxr@zzu.edu.cn

Journal of Coordination Chemistry
ISSN 0095-8972 print/ISSN 1029-0389 online © 2012 Taylor & Francis
http://dx.doi.org/10.1080/00958972.2012.710901



Scheme 1. The existing modes of H_3idc at different pH values.

In recent years, N-heterocyclic carboxylates have attracted interest in preparation of new MOFs and a number of complexes have been synthesized using different nitrogen/oxygen donors, such as pyridine carboxylic acid [23, 24], pyrazole carboxylic acid [25, 26], and imidazole carboxylic acid [27, 28]. For example, research based on the assembly of metal-organic complexes from 4,5-imidazoledicarboxylic acid (H_3idc) has been extensively carried out [29–31]; since H_3idc has six potential donors, it can be partially or fully deprotonated to generate H_2idc^-, $Hidc^{2-}$, and idc^{3-} at different pH values (scheme 1) and shows various coordination modes [32–35]. In contrast, complexes containing the N-heterocyclic carboxylate 2,2′-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid) (H_6ebidc) have been scarcely reported until now.

As a derivative of H_3idc, 2,2′-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid) (H_6ebidc) has abundant nitrogen/oxygen donors and possesses interesting structural features. First, there are 12 potential donors in the free ligand. Second, H_6ebidc can remove one to six protons forming $H_n$ebidc ($n = 0$, 1, 2, 3, 4, and 5). Thus, one may expect that deprotonated $H_n$ebidc exhibits various coordination modes. Third, H_6ebidc offers tunability of structural frameworks owing to the presence of the ethanediyl spacer. Fourth, H_6ebidc can act as both hydrogen bond acceptors and donors due to amino group of imidazole ring and carboxyl group. We have focused our attention on synthesis, structure, and properties of complexes with H_6ebidc, a number of complexes containing this ligand have been prepared [36, 37]. Here, through reactions of H_6ebidc with Cd(II) salts, we obtain two new complexes, $[Cd_2(H_4ebidc)_2(CH_3OH)_4]\cdot 2CH_3OH$ (**1**) and $\{[Cd(Cl)(I)(H_6ebidc)_{1/2}]\cdot 1/2bbe\cdot H_2O\}_n$ (**2**). IR and fluorescent properties are also investigated.

2. Experimental

2.1. *General information and materials*

All chemicals are of AR grade and used without purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets from 400–4000 cm^{-1}. Elemental analyses were carried out on a FLASH EA 1112 elemental analyzer. Steady state fluorescence measurements were performed using a Hitachi F-4500 spectrofluorimeter at room temperature in the solid state. TG measurements were performed by heating the sample from 30°C to 837°C at 10°C min^{-1} in air on a NETZSCH STA 409 PC/PG differential thermal analyzer. 2,2′-(Ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid) (H_6ebidc) and 1,2-bis(2-benzimidazolyl)ethane hydrochloride (bbe · HCl) are synthesized according to the literature method [38].

2.2. *Synthesis of* $[Cd_2(H_4ebidc)_2(CH_3OH)_4]\cdot 2CH_3OH$ *(1)*

An aqueous solution (3 mL) of $Cd(NO_3)_2\cdot 3H_2O$ (0.05 mmol) was added dropwise to a methanol solution of H_6ebidc (0.05 mmol) with filtering to give a clear solution at room temperature. Colorless crystals suitable for X-ray analysis were obtained four weeks later. Anal. Calcd for $C_{15}H_{20}CdN_4O_{11}$ (%): C, 33.05; H, 3.71; N, 10.28. Found (%): C, 33.35; H, 3.77; N, 10.12. IR (KBr, cm^{-1}): 3430(m), 3122(m), 1696(m), 1537(s), 1357(s), 1250(m), 1162(m), 1094(m), 1056(m), 975(w), 943(w), 833(m), 780(s), 748(m), 667(m).

2.3. *Synthesis of* $\{[Cd(Cl)(I)(H_6ebidc)_{1/2}]\cdot 1/2bbe\cdot H_2O\}_n$ *(2)*

An aqueous solution (3 mL) of CdI_2 (0.05 mmol) was added dropwise to a methanol solution of H_6ebidc (0.05 mmol), then a methanol solution (3 mL) of bbe · HCl (0.05 mmol) was added dropwise into the above mixture and filtered to give a clear solution at room temperature. Colorless block crystals suitable for X-ray analysis were obtained five weeks later. Anal. Calcd for $C_{14}H_{14}CdClIN_4O_5$ (%): C, 28.33; H, 2.38; N, 9.45. Found (%): C, 28.55; H, 2.41; N, 9.36. IR (KBr, cm^{-1}): 3461(w), 2930(w), 1706(m), 1624(m), 1572(m), 1531(s), 1483(s), 1442(m), 1394(m), 1287(w), 1117(m), 761(s), 654(w), 486(w).

2.4. *Single-crystal structure determination*

A suitable single crystal of each complex was carefully selected and glued to a thin glass fiber. Crystal structure determinations by X-ray diffraction were performed on a Rigaku Saturn 724 CCD area detector with a graphite monochromator for the X-ray source (Mo-Kα radiation, $\lambda = 0.71073$ Å) operating at 50 kV and 40 mA. The data were collected in ω scan mode at 293(2) K with crystal-to-detector distance of 45 mm. An empirical absorption correction was applied and data were corrected for Lorentz-polarization effects. The structures were solved by direct methods and completed by difference Fourier syntheses and refined by full-matrix least-squares using SHELXS-97 [39]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were positioned geometrically and refined using a riding model. All hydrogen atoms were assigned with common isotropic displacement factors and included in the final refinement by using geometrical restraints. Crystallographic parameters and structural refinement for the complexes are summarized in table 1. Selected bond lengths and angles are listed in table 2. Hydrogen bonds are listed in table 3.

3. Results and discussion

3.1. *Crystal structures of* $[Cd_2(H_4ebidc)_2(CH_3OH)_4]\cdot 2CH_3OH$ *(1)*

H_6ebidc reacts with $Cd(NO_3)_2\cdot 3H_2O$ to give **1** at room temperature. Single crystal X-ray analysis reveals that it crystallizes in triclinic space group $P\bar{1}$. As shown in figure 1(a), each H_4ebidc^{2-} coordinates to Cd(II) in Mode I (scheme 2), in which N1 and N3 coordinate to Cd1 and O7 coordinates to Cd1 and Cd1A. Two μ_2-O (O7 and O7A) bridge two Cd(II) ions forming a binuclear unit $[Cd_2(H_4ebidc)_2(CH_3OH)_4]$ with

Table 1. Crystal data and structural refinement of **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{15}H_{20}CdN_4O_{11}$	$C_{14}H_{14}CdClIN_4O_5$
Formula weight	544.75	593.04
Temperature (K)	293(2)	293(2)
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$C2/c$
Unit cell dimensions (Å, °)		
a	9.4118(19)	25.848(5)
b	9.815(2)	9.2368(18)
c	11.773(2)	17.416(4)
α	77.04(3)	90
β	77.79(3)	94.41(3)
γ	72.30(3)	90
Volume (Å^3), Z	997.6(4), 2	4145.9(14), 8
Calculated density (Mg m^{-3})	1.814	1.900
Absorption coefficient (mm^{-1})	1.163	2.701
F(000)	548	2272
Crystal sizes (mm^3)	$0.18 \times 0.17 \times 0.14$	$0.21 \times 0.12 \times 0.09$
Independent reflection	$R(\text{int}) = 0.0384$	$R(\text{int}) = 0.0798$
Data/restraints/parameters	3683/1/281	3808/0/235
Goodness-of-fit on F^2	1.025	1.090
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0490$ $wR_2 = 0.1079$	$R_1 = 0.0883$ $wR_2 = 0.2244$
R indices (all data)	$R_1 = 0.0610$ $wR_2 = 0.1176$	$R_1 = 0.1325$ $wR_2 = 0.2581$

Table 2. Selected bond lengths (Å) and angles (°) for **1** and **2**.

1			
Cd(1)–O(7)#1	2.249(3)	Cd(1)–N(1)	2.252(4)
Cd(1)–O(9)	2.335(4)	Cd(1)–O(10)	2.371(4)
Cd(1)–N(3)	2.411(4)	Cd(1)–O(7)	2.422(4)
O(7)#1–Cd(1)–N(1)	132.79(14)	O(7)#1–Cd(1)–O(9)	103.00(16)
N(1)–Cd(1)–O(9)	96.31(16)	O(7)#1–Cd(1)–O(10)	82.28(15)
N(1)–Cd(1)–O(10)	86.11(16)	O(9)–Cd(1)–O(10)	169.77(15)
O(7)#1–Cd(1)–N(3)	134.55(14)	N(1)–Cd(1)–N(3)	89.57(15)
O(9)–Cd(1)–N(3)	84.19(16)	O(10)–Cd(1)–N(3)	85.89(15)
O(7)#1–Cd(1)–O(7)	68.06(14)	N(1)–Cd(1)–O(7)	157.60(14)
O(9)–Cd(1)–O(7)	84.25(14)	O(10)–Cd(1)–O(7)	89.73(14)
N(3)–Cd(1)–O(7)	68.16(13)		
2			
Cd(1)–N(2)	2.264(8)	Cd(1)–O(1)	2.417(9)
Cd(1)–Cl(1)	2.500(3)	Cd(1)–Cl(1)#1	2.651(3)
Cd(1)–I(1)	2.722(2)		
N(2)–Cd(1)–O(1)	72.2(3)	N(2)–Cd(1)–Cl(1)	138.2(3)
O(1)–Cd(1)–Cl(1)	89.8(2)	N(2)–Cd(1)–Cl(1)#1	96.0(2)
O(1)–Cd(1)–Cl(1)#1	156.5(3)	Cl(1)–Cd(1)–Cl(1)#1	85.92(10)
N(2)–Cd(1)–I(1)	105.9(2)	O(1)–Cd(1)–I(1)	99.5(3)
Cl(1)–Cd(1)–I(1)	114.24(12)	Cl(1)#1–Cd(1)–I(1)	103.33(12)
Cd(1)–Cl(1)–Cd(1)#1	94.08(10)		

Symmetry transformations used to generate equivalent atoms: for **1**: #1: $-x+1$, $-y+2$, $-z+1$; for **2**: #1: $-x+1/2$, $-y+5/2$, $-z$.

Table 3. Hydrogen bonds of **1** and **2**.

D–H···A	d(D–H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D–H···A) (°)
1				
O(6)–H(6)···O(8)	0.85	1.62	2.468(6)	178.7
O(3)–H(3)···O(2)	0.84	1.63	2.478(6)	179.6
N(4)–H(4A)···O(1)#2	0.86	2.09	2.902(6)	157.6
N(2)–H(2A)···O(11)#2	0.86	1.89	2.716(9)	159.7
O(11)–H(11)···O(2)#3	0.85	2.55	3.398(15)	179.2
O(9)–H(9)···O(4)#4	0.85	2.03	2.753(6)	142.7
O(10)–H(10)···O(5)#5	0.85	1.92	2.741(6)	160.8
2				
N(1)–H(1)···O(5)	0.86	2.04	2.86(2)	157.8
O(2)–H(2)···O(4)	0.82	1.74	2.485(13)	149.3
O(3)–H(3)···O(5)	0.85	2.35	3.19(2)	179.6
O(5)–H(5B)···I(1)#2	0.85	2.94	3.78(2)	171.4
N(3)–H(3A)···O(1)#4	0.86	1.98	2.834(11)	174.3

Symmetry transformations used to generate equivalent atoms: for **1**: #2: $x+1, y, z$; #3: $-x, -y+1, -z+2$; #4: $-x+1, -y+1, -z+2$; #5: $-x+2, -y+2, -z+1$; for **2**: #2: $-x+1/2, -y+3/2, -z$; #4: $x, y-1, z$.

Cd···Cd distance of 3.873 Å. Each Cd(II) is six-coordinate and features a distorted octahedral coordination geometry. The equatorial plane is formed by two nitrogen atoms (N1 and N3) and two oxygen atoms (O7 and O7A) from two H_4ebidc^{2-} groups (mean deviations from plane of 0.0918 Å), while the vertices are occupied by two oxygen atoms (O9 and O10) from two methanol groups with the O9–Cd1–O10 bond angle of 169.77(15)°. As shown in figure 1(b), intramolecular O–H···O hydrogen bonds between carboxyl/carboxylate groups stabilize the molecular configuration. There are five kinds of intermolecular hydrogen bonds in **1**. Nitrogen (N4) of H_4ebidc^{2-} forms hydrogen bonds (N4···O1: 2.902 Å) with carboxylate oxygen (O1) of H_4ebidc^{2-}. Nitrogen (N2) of H_4ebidc^{2-} forms hydrogen bonds (N2···O11: 2.716 Å) with oxygen atoms (O11) of uncoordinated methanol. Oxygen (O11) forms hydrogen bonds (O11···O2: 3.398 Å) with carboxylate oxygen (O2) of H_4ebidc^{2-}. There are also O–H···O hydrogen bonds (O9–H9···O4: 2.753 Å, 142.7°; O10–H10···O5: 2.741 Å, 160.8°) between neighboring binuclear units $[Cd_2(H_4ebidc)_2(CH_3OH)_4]$. Thus, N–H···O hydrogen bonds along with O–H···O hydrogen bonds link binuclear unit $[Cd_2(H_4ebidc)_2(CH_3OH)_4]$ and uncoordinated methanol into the 2-D structure (figure 1c).

3.2. *Crystal structures of* $\{[Cd(Cl)(I)(H_6ebidc)_{1/2}]\cdot 1/2bbe\cdot H_2O\}_n$ (**2**)

When bbe · HCl is added into the mixture of H_6ebidc and CdI_2, a new 1-D complex, **2**, with a different structure than **1** is obtained. There is one Cd(II), one chloride, one iodide anion, a half of H_6ebidc, a half of uncoordinated bbe, and one uncoordinated water in the asymmetric unit of **2**. As shown in figure 2(a), the coordination number of Cd(II) and the coordination mode of H_6ebidc are different from those in **1**. Each Cd(II) is five-coordinate by one nitrogen and one oxygen from the same H_6ebidc, two bridging chlorides and one terminal iodide forming a distorted square pyramidal geometry. The square is completed by O1, N2, Cl1, and Cl1A (mean deviations from plane of

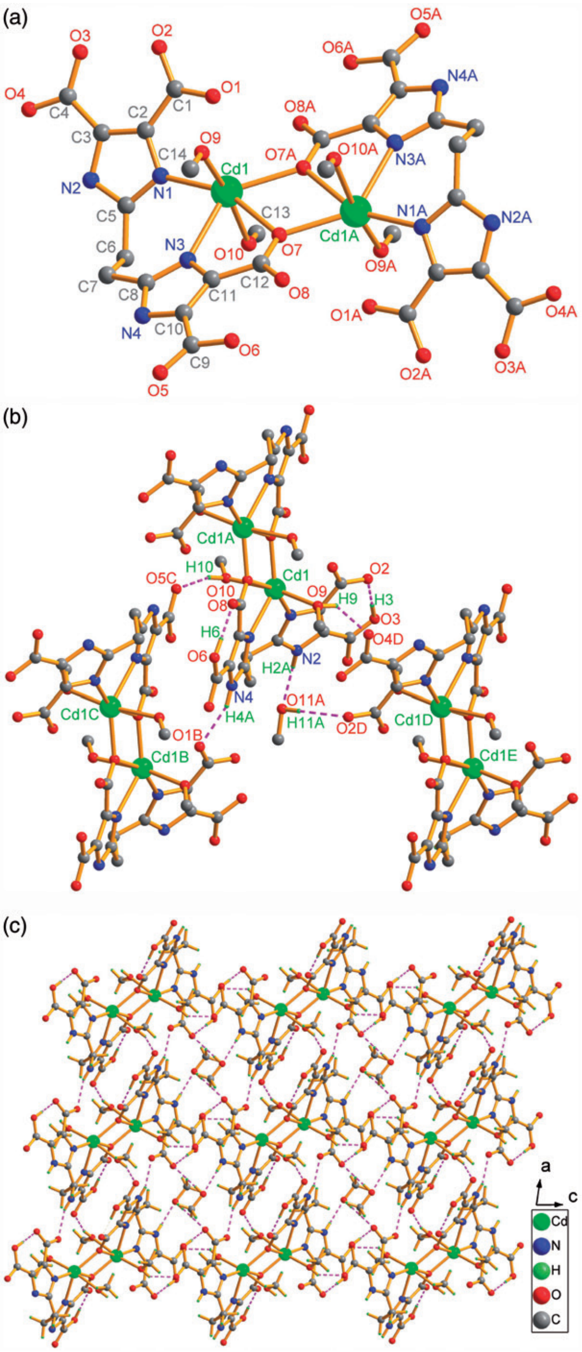
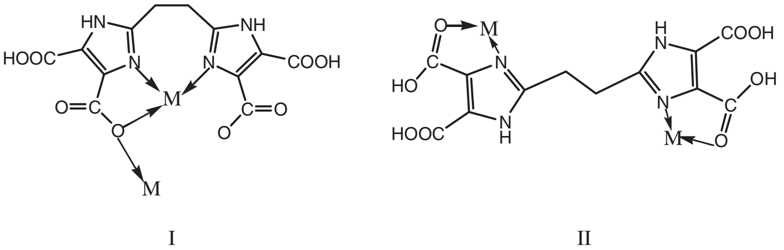


Figure 1. (a) Coordination environment of Cd(II) center in **1** with atom numbering scheme. Uncoordinated methanol groups and hydrogen atoms are omitted for clarity (A: $1-x$, $2-y$, $1-z$); (b) view of hydrogen bonds in **1** (A: $1-x$, $2-y$, $1-z$; B: $-x$, $2-y$, $1-z$; C: $-1+x$, y, z; D: x, $1+y$, $-1+z$; E: $1-x$, $3-y$, $-z$); and (c) view of the 2-D structure of **1** supported by hydrogen bonds.



Scheme 2. Two coordination modes of H_6ebidc in **1** and **2**.

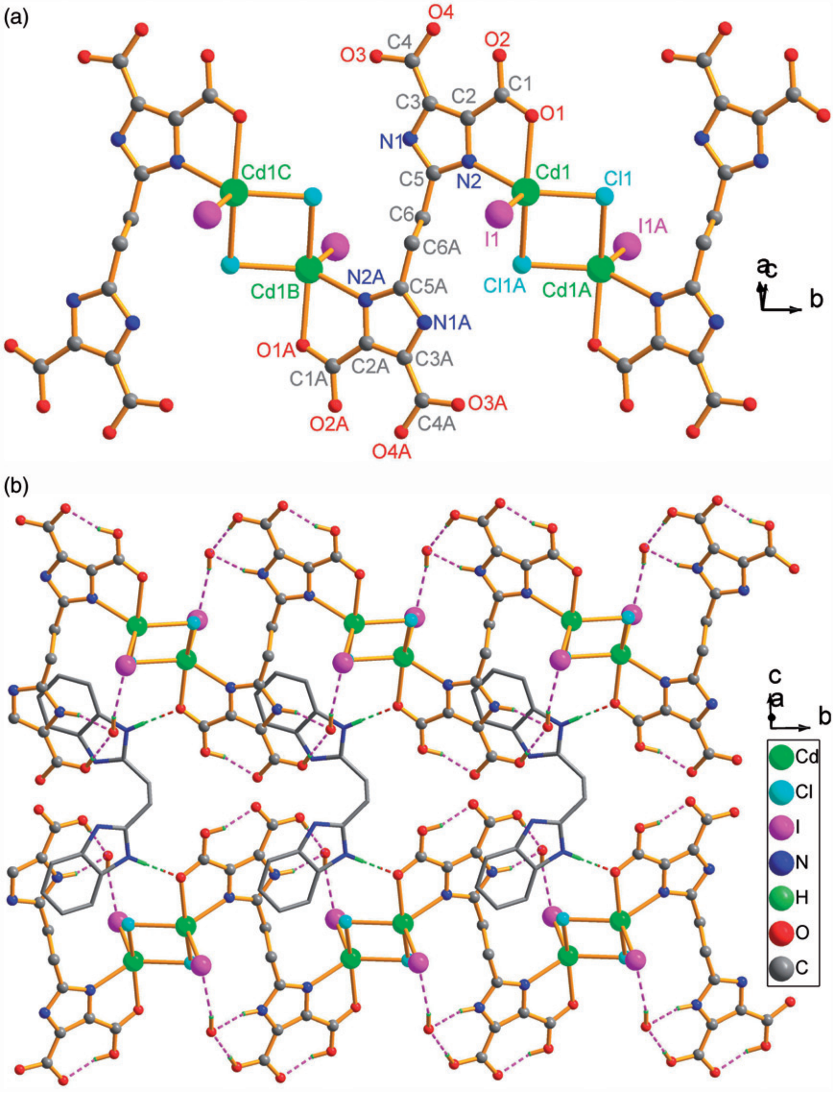


Figure 2. (a) View of the molecular structure of **2** with atom numbering scheme. Uncoordinated water molecules, uncoordinated bbe, and hydrogen atoms are omitted for clarity (A: $0.5 - x$, $2.5 - y$, $-z$; B: $0.5 - x$, $1.5 - y$, $-z$; C: x, $-1 + y$, z) and (b) view of the 2-D structure of **2** supported by hydrogen bonds.

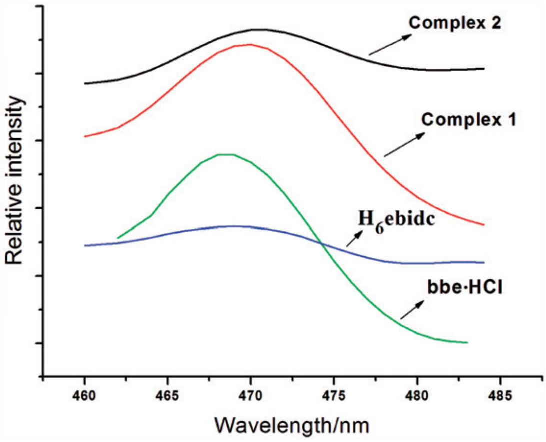


Figure 3. Solid-state emission spectra of free H_6ebidc, bbe · HCl, **1**, and **2** at room temperature.

0.1540 Å) and the vertex is occupied by I^-. Each H_6ebidc in **2** coordinates to Cd(II) in Mode II (scheme 2). O1, O1B, N2, and N2B from the tetradentate H_6ebidc bridge two Cd(II) ions in chelating fashion. As depicted in figure 2(a), the bridging chlorides form a binuclear unit $[Cd_2Cl_2I_2]$ with Cd···Cd distance of 3.771 Å. These $[Cd_2Cl_2I_2]$ units are further connected by H_6ebidc to form the 1-D chain structure. The Cd···Cd distance separated by H_6ebidc is 7.729 Å. There are five kinds of hydrogen bonds in **2**: (a) hydrogen bond of uncoordinated water/iodide (O–I distance: 3.78(2) Å); (b) hydrogen bond of carboxyl/carboxylate (O–O distance: 2.485(13) Å); (c) hydrogen bond of carboxyl O/uncoordinated water (O–O distance: 3.19(2) Å); (d) hydrogen bond of imidazole/uncoordinated water (N–O distance: 2.86(2) Å); and (e) hydrogen bond of benzimidazole groups/carboxyl O (N–O distance: 2.834(11) Å). The 1-D chains are connected by N–H···O hydrogen bonds between benzimidazole and carboxyl O leading to the 2-D structure; other kinds of hydrogen bonds further stabilize the 2-D structure (figure 2b).

3.3. *Fluorescence*

Luminescent properties of complexes with d^{10} metal centers have attracted interest for potential applications in chemical sensors, photochemistry, and electroluminescent displays [40, 41]. In this study, we have investigated the fluorescence of free H_6ebidc, bbe · HCl, **1** and **2** in solid state at room temperature. As shown in figure 3, free H_6ebidc gives an emission band at 469 nm upon excitation at 219 nm and bbe · HCl shows an emission band with a maximum at 471 nm ($\lambda_{ex} = 214$ nm). Both **1** and **2** display emission bands at 470 nm when excited at 218 and 203 nm, respectively. Obviously, the emissions observed are neither MLCT (metal-to-ligand charge transfer) nor LMCT (ligand-to-metal charge transfer) since the Cd^{2+} ions are difficult to oxidize or reduce due to their d^{10} configuration [42]. As a result, the emission band of **1** can be assigned to intraligand fluorescent emissions since a similar emission is also observed for H_6ebidc [43, 44], and the emission band of **2** may be attributed to cooperative effects of the H_6ebidc and bbe · HCl.

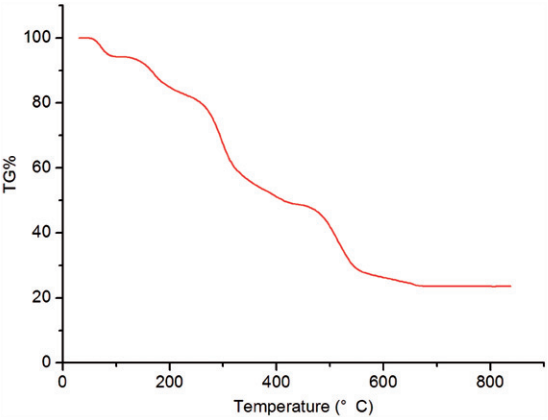


Figure 4. The TG curve of **1** at heating rate of 10°C · min^{-1} in air.

3.4. *Thermogravimetric analysis*

Thermogravimetric analysis (TGA) of **1** was performed by heating the complex from 30°C to 837°C in air. As shown in figure 4, the first mass loss of 5.70% occurs between 55°C and 87°C, corresponding to the release of uncoordinated methanol (Calcd 5.88%). Then a plateau region is observed from 87°C to 133°C. The solid continues to lose mass from 133°C to 258°C corresponding to the release of coordinated methanol. Continuous mass loss from 258°C to 660°C corresponds to the decomposition of H_4ebidc^{2-}. Finally, a plateau occurs from 660°C to 837°C. The residue equals 23.42%, which is attributed to CdO (Calcd 23.57%). The results are in agreement with the aforementioned crystal structure. TGA of complexes containing halogens cannot be performed on a NETZSCH STA 409 PC/PG differential thermal analyzer, so TGA of **2** has not been carried out.

4. Conclusion

Studies of coordination of H_3idc and structures of the Cd(II) complexes reveal that singly deprotonated H_2idc generally coordinates in the monodentate imidazole-N or N,O-chelate mode [45, 46], the doubly deprotonated Hidc coordinates in the $\mu2$, $\mu3$, or $\mu4$ mode [47–49], and the triply deprotonated idc can coordinate in the $\mu3$, $\mu4$, or $\mu5$ mode [50, 51]. As a derivative of H_3idc, 2,2′-(ethane-1,2-diyl)bis(1*H*-imidazole-4,5-dicarboxylic acid) can provide more coordination modes with the 12 potential donors, forming interesting structures, and can be partially or fully deprotonated to generate anions with one, two, three, four, or five charges at different pH values giving acidity-dependent coordination modes. In this article, we select the flexible N-heterocyclic carboxylate H_6ebidc to self-assemble with Cd(II) and obtained a binuclear complex (**1**) in which tridentate chelating ligand coordinates to two Cd(II) ions with μ_2-O and a 1-D chain complex (**2**) in which each tetradentate ligand bridges two Cd(II) ions in chelating fashion. Our results reveal that introduction of bbe · HCl into the complex can influence the coordination modes of H_6ebidc and the coordination number of the central metal ion, and thus influence the structures of the complexes. As a promising N-heterocyclic carboxylate, H_6ebidc can be potentially utilized in constructing more complexes with charming structures under different conditions.

Supplementary material

Crystallographic data reported in this article have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. CCDC numbers are 855 314 and 855 315. This data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44 1 223 336 033).

Acknowledgments

We gratefully acknowledge the financial support by the National Natural Science Foundation of China (No. J0830412).

References

[1] A.N. Khlobystov, A.J. Blake, N.R. Champness, D.A. Lemenovskii, A.G. Majouga, N.V. Zyk, M. Schröder. *Coord. Chem. Rev.*, **222**, 155 (2001).
[2] B. Moulton, M.J. Zaworotko. *Chem. Rev.*, **101**, 1629 (2001).
[3] O.M. Yaghi, M. O'Keeffe, N.W. Ockwig, H.K. Chae, M. Eddaoudi, J. Kim. *Nature*, **423**, 705 (2003).
[4] R.Q. Zhong, R.Q. Zou, M. Du, N. Takeichi, Q. Xu. *CrystEngComm*, **10**, 1175 (2008).
[5] S.R. Batten, K.S. Murray. *Coord. Chem. Rev.*, **246**, 103 (2003).
[6] S. Takamizawa, E. Nakata, H. Yokoyama, K. Mochizuki, W. Mori. *Angew. Chem., Int. Ed.*, **42**, 4331 (2003).
[7] D.N. Dybtsev, H. Chun, S.H. Yoon, D. Kim, K. Kim. *J. Am. Chem. Soc.*, **126**, 32 (2004).
[8] B. Kesanli, Y. Cui, M.R. Smith, E.W. Bittner, B.C. Bockrath, W.B. Lin. *Angew. Chem., Int. Ed.*, **44**, 72 (2005).
[9] H.L. Jiang, Q. Xu. *Chem. Commun.*, **47**, 3351 (2011).
[10] H.L. Jiang, Y. Tatsu, Z.H. Lu, Q. Xu. *J. Am. Chem. Soc.*, **132**, 5586 (2010).
[11] Y.Q. Lan, H.L. Jiang, S.L. Li, Q. Xu. *Adv. Mater.*, **23**, 5015 (2011).
[12] H.L. Jiang, B. Liu, T. Akita, M. Haruta, H. Sakurai, Q. Xu. *J. Am. Chem. Soc.*, **131**, 11 302 (2009).
[13] X.J. Gu, Z.H. Lu, H.L. Jiang, T. Akita, Q. Xu. *J. Am. Chem. Soc.*, **133**, 11 822 (2011).
[14] P.Z. Li, Y. Maeda, Q. Xu. *Chem. Commun.*, **47**, 8436 (2011).
[15] H.J. Liu, X.T. Tao, J.X. Yang, Y.X. Yan, Y. Ren, H.P. Zhao, Q. Xin, W.T. Yu, M.H. Jiang. *Cryst. Growth Des.*, **8**, 259 (2008).
[16] Q.G. Zhai, X.Y. Wu, S.M. Chen, C.Z. Lu, W.B. Yang. *Cryst. Growth Des.*, **6**, 2126 (2006).
[17] F.N. Dai, J.M. Dou, H.Y. He, X.L. Zhao, D.F. Sun. *Inorg. Chem.*, **49**, 4117 (2010).
[18] P.P. Lima, F.A.A. Paz, R.A.S. Ferreira, V. de Z. Bermudez, L.D. Carlos. *Chem. Mater.*, **21**, 5099 (2009).
[19] B. Chen, N.W. Ockwig, A.R. Millward, D.S. Comreras, O.M. Yaghi. *Angew. Chem. Int. Ed.*, **44**, 1890 (2005).
[20] M. Dincă, J.R. Long. *J. Am. Chem. Soc.*, **127**, 9376 (2005).
[21] A. dos Anjos, A.J. Bortoluzzi, R.H.M.B. Osório, R.A. Peralta, G.R. Friedermann, A.S. Mangrich, A. Neves. *Inorg. Chem. Commun.*, **8**, 249 (2005).
[22] K.T. Holman, H.H. Hammud, S. Isber, M. Tabbal. *Polyhedron*, **24**, 221 (2005).
[23] W. Lin, L. Ma, O.R. Evans. *Chem. Commun.*, 2263 (2000).

[24] P. Ayyappan, O.R. Evans, W. Lin. *Inorg. Chem.*, **40**, 4627 (2001).
[25] L. Pan, X.Y. Huang, J. Li, Y.G. Wu, N.W. Zheng. *Angew. Chem. Int. Ed.*, **39**, 527 (2000).
[26] L. Pan, N. Ching, X.Y. Huang, J. Li. *Inorg. Chem.*, **40**, 1271 (2001).
[27] P. Mahata, S. Natarajan. *Eur. J. Inorg. Chem.*, 2156 (2005).
[28] D.P. Wang, Y.G. Chen, H.Y. Wang, C.J. Zhang, Q. Tang. *J. Coord. Chem.*, **64**, 2824 (2011).
[29] W.G. Lu, L. Jiang, X.L. Feng, T.B. Lu. *Inorg. Chem.*, **48**, 6997 (2009).
[30] S.R. Freeman, F. Jones, M.I. Ogden, A. Oliviera, W.R. Richmond. *Cryst. Growth Des.*, **6**, 2579 (2006).
[31] Z.G. Gu, M.F. Wang, H.M. Peng, G.Z. Li, X.Y. Yi, X. Gong, H.C. Fang, Z.Y. Zhou, Y.P. Cai. *Inorg. Chem. Commun.*, **13**, 1439 (2010).
[32] Y.Q. Sun, J. Zhang, Y.M. Chen, G.Y. Yang. *Angew. Chem. Int. Ed.*, **44**, 5814 (2005).
[33] Y. Liu, V. Ch. Kravtsov, M. Eddaoudi. *Angew. Chem. Int. Ed.*, **47**, 8446 (2008).
[34] F. Nouar, J. Eckert, J.F. Eubank, P. Forster. *J. Am. Chem. Soc.*, **131**, 2864 (2009).
[35] D.F. Sava, V. Ch. Kravtsov, J. Eckert, J.F. Eubank, F. Nouar, M. Eddaoudi. *J. Am. Chem. Soc.*, **131**, 10 394 (2009).
[36] Y. Wang, X.L. Gao. *Acta Cryst.*, **E67**, m815 (2011).
[37] Y.N. Ding, Syntheses, crystal structures and properties of complexes based on flexible symmetrical imidazole carboxylate ligand or flexible unsymmetrical *N*-heterocyclic ligand. Masters thesis, Zhengzhou University (2011).
[38] H. Schubert, S. Hoffmann, G. Lehmann, I. Barthold, H. Meichsner, H.E. Polster. *Z. Chem.*, **15**, 481 (1975).
[39] G.M. Sheldrick. *Acta Cryst.*, **A64**, 112 (2008).
[40] (a) Q. Wu, M. Esteghamatian, N.X. Hu, Z. Popovic, G. Enright, Y. Tao, M. D'Iorio, S. Wang. *Chem. Mater.*, **12**, 79 (2000); (b) J.E. McGarrah, Y.J. Kim, M. Hissler, R. Eisenberg. *Inorg. Chem.*, **40**, 4510 (2001); (c) G.D. Santis, L. Fabbrizzi, M. Licchelli, A. Poggi, A. Taglietti. *Angew. Chem. Int. Ed.*, **35**, 202 (1996).
[41] (a) J. Yang, Q. Yue, G.D. Li, J.J. Cao, G.H. Li, J.S. Chen. *Inorg. Chem.*, **45**, 2857 (2006); (b) A. Thirumurugan, S. Natarajan. *Dalton Trans.*, 2923 (2004); (c) X.J. Zheng, L.P. Jin, S. Gao, S.Z. Lu. *New J. Chem.*, **29**, 798 (2005); (d) X.J. Zhang, L.P. Jin, S. Gao. *Inorg. Chem.*, **43**, 1600 (2004).
[42] (a) L. Wen, Y. Li, Z. Lu, J. Lin, C. Duan, Q. Meng. *Cryst. Growth Des.*, **6**, 530 (2006); (b) L. Wen, Z. Lu, J. Lin, Z. Tian, H. Zhu, Q. Meng. *Cryst. Growth Des.*, **7**, 93 (2007); (c) J.G. Lin, S.Q. Zang, Z.F. Tian, Y.Z. Li, Y.Y. Xu, H.Z. Zhu, Q.J. Meng. *CrystEngComm*, **9**, 915 (2007).
[43] Y.Y. Liu, J.F. Ma, J. Yang, Z.M. Su. *Inorg. Chem.*, **46**, 3027 (2007).
[44] X.R. Meng, G. Li, H.W. Hou, H.Y. Han, Y.T. Fan, Y. Zhu, C.X. Du. *J. Organomet. Chem.*, **679**, 153 (2003).
[45] D.E. Wang, F. Wang, X.G. Meng, Y. Ding, L.L. Wen, D.F. Li, S.M. Lan. *Z. Anorg. Allg. Chem.*, **634**, 2643 (2008).
[46] R.Q. Fang, X.M. Zhang. *Inorg. Chem.*, **45**, 4801 (2006).
[47] L. Gou, T. Qin, H.M. Hu, X.L. Chen, B.C. Wang, Q.R. Wu, B. Zhang, Z.X. Tang. *J. Coord. Chem.*, **61**, 3943 (2008).
[48] W.L. Liu, L.H. Ye, X.F. Liu, L.M. Yuan, X.L. Lu, J.X. Jiang. *Inorg. Chem. Commun.*, **11**, 1250 (2008).
[49] W.G. Lu, L. Jiang, X.L. Feng, T.B. Lu. *Cryst. Growth Des.*, **8**, 986 (2008).
[50] K. Yang, Z.Z. Wang, Z.H. Liu. *J. Coord. Chem.*, **63**, 2286 (2010).
[51] W.G. Lu, C.Y. Su, T.B. Lu, L. Jiang, J.M. Chen. *J. Am. Chem. Soc.*, **128**, 34 (2006).