Syntheses, Structures and Luminescence Properties of Two Cd(II) Complexes Based on 2-((1*H*-1,2,4-Triazol-1-yl)methyl)-1*H*-benzimidazole and Aromatic Polycarboxylate Ligands

Xiuxiu Wang, Xiao Han, Zhun Qiao, Guanghua Jin, and Xiangru Meng

The College of Chemistry and Molecular Engineering, Zhengzhou University, Zhengzhou 450052, P. R. China

Reprint requests to Prof. Xiangru Meng. Fax: +86-0371-67783126. E-mail: mxr@zzu.edu.cn

Z. Naturforsch. **2012**, *67b*, 783 – 790 / DOI: 10.5560/ZNB.2012-0159
Received May 4, 2012

Two new Cd(II) complexes, $\{[Cd(m\text{-bdc})(tmb)(H_2O)]\cdot CH_3OH\}_n$ (**1**) and $\{[Cd(t\text{-bdc})(tmb)(H_2O)]\cdot 2H_2O\cdot DMF\}_n$ (**2**), have been prepared by using 2-((1*H*-1,2,4-triazol-1-yl)methyl)-1*H*-benzimidazole (tmb) as a ligand in the presence of 1,3-benzenedicarboxylic acid (m-H_2bdc) or 1,4-benzenedicarboxylic acid (t-H_2bdc). Single-crystal X-ray diffraction exhibits that complex **1** displays a 2D structure constructed by tmb ligands in *trans* conformation and carboxylate groups in a chelating mode. The 2D structure of complex **2** is different from that of **1**, in that the tmb ligands are in *cis* conformation, and the carboxylate groups are in both unidentate or chelating coordination mode at the Cd(II) centers. The luminescence properties of **1** and **2** in the solid state at room temperature have been studied.

Key words: Cd(II) Complex, 2-((1*H*-1,2,4-Triazol-1-yl)methyl)-1*H*-benzimidazole, Crystal Structure, Luminescence, Benzenedicarboxylate

Introduction

The structures of metal-organic frameworks (MOFs) are affected by the choice of the coordination geometry of metal centers, the coordination behavior of the multifunctional organic ligands and auxiliary ligands, the reaction temperature, the pH values, and the solvent system [1, 2]. The selection of the organic ligand plays an important role in the construction of complexes because the change in the type of bridging units, the flexibility of the molecular backbone, the conformational preference, and the symmetry of organic ligands can lead to remarkable classes of materials bearing diverse architectures and functions [3, 4]. For example, multifunctional *N*-heterocyclic ligands 1,2-bis(4-pyridyl)-ethane [5, 6], 1,2-di(4-pyridyl)ethenes [7], 1,3-bi(4-pyridyl)propane [8 – 10] *etc.* can coordinate to transition metal ions to produce unique structural motifs with beautiful aesthetics and useful functional properties. Furthermore, MOFs based on aromatic polycarboxylic acid ligands, such as 1,2-benzenedicarboxylic, 1,3-benzenedicarboxylic, 1,4-benzenedicarboxylic, 1,3,5-benzenetricarboxylic, and 1,2,4,5-benzenetetracarboxylic acid have been widely studied because of the diversity of coordination modes and the pH-sensitivity of the carboxylate groups [11]. Aromatic polycarboxylic acids can be partially or fully deprotonated to adopt different coordination modes in their reactions with metal ions, and they can act not only as hydrogen bond acceptors but also as hydrogen bond donors to form supramolecular structures or allow for guest structures by hydrogen bonding interactions [12].

Cd(II) ions are able to coordinate simultaneously to both oxygen- and nitrogen-containing ligands. A great number of Cd(II) complexes containing both aromatic carboxylates and *N*-heterocyclic ligands have been reported [11]. For this contribution we chose the flexible *N*-heterocyclic ligand 2-((1*H*-1,2,4-triazol-1-yl)methyl)-1*H*-benzimidazole (tmb) as the bridging ligand and 1,3-benzenedicarboxylic (m-H_2bdc) or 1,4-benzenedicarboxylic acid (t-H_2bdc) as auxiliary ligands in order to construct d^{10} transition metal complexes, and to explore mixed-ligand Cd(II) complexes constructed from aromatic carboxylate and *N*-heterocyclic ligands. Herein, we report the crystal structures and luminescence properties of two new complexes, $\{[Cd(m\text{-bdc})(tmb)(H_2O)]\cdot CH_3OH\}_n$ (**1**) and $\{[Cd(t\text{-bdc})(tmb)(H_2O)]\cdot 2H_2O\cdot DMF\}_n$ (**2**).

Experimental Section

All chemicals were of reagent grade quality obtained from commercial sources and used without further purification. The ligand 2-((1*H*-1,2,4-triazol-1-yl)methyl)-1*H*-benzimidazole (tmb) was synthesized as reported previously [13]. Carbon, hydrogen and nitrogen analyses were carried out on a Flash EA 1112 elemental analyzer. IR data were recorded on a Bruker Tensor 27 spectrophotometer with KBr pellets in the 400 – 4000 cm^{-1} region. Steady-state luminescence measurements were performed using a Fluoro Max-P spectrofluorimeter at room temperature in the solid state.

Synthesis of $\{[Cd(m\text{-bdc})(tmb)(H_2O)]\cdot CH_3OH\}_n$ (1)

A mixture of ligand tmb (0.05 mmol), $CdCl_2\cdot 2.5H_2O$ (0.05 mmol), 1,3-benzenedicarboxylic acid (m-H_2bdc) (0.05 mmol), H_2O (6 mL), CH_3OH (2 mL), and DMF (1 mL) was poured into a Parr Teflon-lined stainless-steel vessel (25 mL). Then the vessel was sealed and heated to 120 °C for 3 d. The autoclave was cooled to room temperature at a rate of 10 $°C\cdot h^{-1}$. Crystals of $\{[Cd(m\text{-bdc})(tmb)(H_2O)]\cdot CH_3OH\}_n$ suitable for X-ray analysis were collected. Yield: 51 %. – Anal. for $C_{19}H_{19}CdN_5O_6$ (525.79): calcd. C 40.40, H 3.65, N 13.32; found C 40.66, H 3.51, N 13.49. – FT-IR (KBr, cm^{-1}): ν = 3410 (m), 3118 (s), 1607 (s), 1548 (s), 1515 (s), 1462 (m), 1444 (s), 1398 (m), 1378 (s), 1284 (m), 1226 (m), 1120 (s), 1024 (s), 844 (m), 739 (s), 671 (m).

Synthesis of $\{[Cd(t\text{-bdc})(tmb)(H_2O)]\cdot 2H_2O\cdot DMF\}_n$ (2)

The preparation of **2** was similar to that of **1** except that 1,4-benzenedicarboxylic acid (t-H_2bdc) was used instead of 1,3-benzenedicarboxylic acid. Crystals of $\{[Cd(t\text{-bdc})(tmb)(H_2O)]\cdot 2H_2O\cdot DMF\}_n$ suitable for X-ray analysis were obtained. Yield: 57 %. – Anal. for $C_{21}H_{26}CdN_6O_8$ (602.88): calcd. C 41.83, H 4.36, N 13.94; found C 41.64, H 4.47, N 13.78. – FT-IR (KBr, cm^{-1}): ν = 3372 (m), 3146 (m), 1669 (s), 1566 (s), 1499 (m), 1463 (m), 1384 (s), 1367 (s), 1287 (m), 1276 (m), 842 (m), 751 (s).

Single-crystal structure determination

Suitable single crystals of **1** and **2** were carefully selected and glued to thin glass fibers. X-Ray data collections were performed on a Rigaku Saturn 724 CCD area detector equipped with a graphite monochromator (MoK_α radiation; λ = 0.71073 Å; operating at 50 kV and 40 mA). The data were collected in the ω-scan mode at a temperature of 293(2) K. The crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz and polarization effects. The structures were solved by Direct Methods and completed by dif-

Complex	**1**	**2**
Empirical formula	$C_{19}H_{19}CdN_5O_6$	$C_{21}H_{26}CdN_6O_8$
Formula weight	525.79	602.88
Temperature, K	293(2)	293(2)
Crystal size, mm^3	0.19 × 0.18 × 0.15	0.20 × 0.17 × 0.16
Crystal system	triclinic	triclinic
Space group	$P\bar{1}$	$P\bar{1}$
a, Å	8.1745(16)	10.237(2)
b, Å	10.034(2)	11.057(2)
c, Å	13.195(3)	11.529(2)
α, deg	107.10(3)	93.36(3)
β, deg	97.84(3)	95.30(3)
γ, deg	96.55(3)	108.21(3)
Volume, Å^3	1011.1(4)	1228.9(4)
Z	2	2
Calculated density, g cm^{-3}	1.73	1.63
Absorption coefficient, mm^{-1}	1.1	0.9
$F(000)$, e	528	612
θ range for data collection, deg	2.15 – 26.00	2.37 – 25.50
hkl range	$\pm 10, -12 \rightarrow 11, \pm 16$	$\pm 12, -13 \rightarrow 12, -10 \rightarrow 13$
Reflections collected / unique / R_{int}	10987 / 3966 / 0.0470	11816 / 4480 / 0.0225
Data / ref. parameters	3966 / 282	4480 / 325
Final $R1$ / $wR2$ [$I > 2\,\sigma(I)$]	0.0500 / 0.1073	0.0256 / 0.0643
Final $R1$ / $wR2$ (all data)	0.0566 / 0.1126	0.0292 / 0.0663
Goodness-of-fit on F^2	1.121	1.034
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.81 / −0.97	0.47 / −0.48

Table 1. Crystallographic data and structure refinement details for **1** and **2**.

ference Fourier syntheses and refined by full-matrix least-squares using the SHELXS/L-97 program package [14]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned geometrically and refined using a riding model. The hydrogen atoms were assigned with common isotropic displacement parameters and included in the final refinement by using geometrical restraints. Crystallographic crystal data and structure processing parameters for complexes **1** and **2** are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table 2. Hydrogen bond parameters are listed in Table 3.

CCDC 877998 (**1**) and 877999 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallo-

Table 2. Selected bond lengths (Å) and angles (deg) for **1** and **2** with estimated standard deviations in parentheses[a].

	Complex **1**		
Cd1–N4$^{\#1}$	2.312(4)	Cd1–O4$^{\#2}$	2.392(4)
Cd1–N1	2.340(4)	Cd1–O1	2.481(3)
Cd1–O2	2.341(4)	Cd1–O3$^{\#2}$	2.544(3)
Cd1–O5	2.366(3)	O1–Cd1–O3$^{\#2}$	176.09(12)
N4$^{\#1}$–Cd1–N1	86.26(13)	N4$^{\#1}$–Cd1–O2	144.96(13)
N1–Cd1–O2	93.02(14)	N4$^{\#1}$–Cd1–O5	86.05(12)
N1–Cd1–O5	170.14(12)	O2–Cd1–O5	96.81(13)
N4$^{\#1}$–Cd1–O4$^{\#2}$	137.44(13)	N1–Cd1–O4$^{\#2}$	93.54(14)
O2–Cd1–O4$^{\#2}$	77.60(12)	O5–Cd1–O4$^{\#2}$	87.97(14)
N4$^{\#1}$–Cd1–O1	92.10(13)	N1–Cd1–O1	101.81(14)
O2–Cd1–O1	53.73(12)	O5–Cd1–O1	84.63(14)
O4$^{\#2}$–Cd1–O1	129.20(12)	N4$^{\#1}$–Cd1–3$^{\#2}$	85.86(12)
N1–Cd1–O3$^{\#2}$	81.40(13)	O2–Cd1–O3$^{\#2}$	128.72(12)
O5–Cd1–O3$^{\#2}$	91.90(12)	O4$^{\#2}$–Cd1–O3$^{\#2}$	52.25(11)
	Complex **2**		
Cd1–O3	2.3098(17)	Cd1–O2	2.374(2)
Cd1–O5	2.322(2)	Cd1–N1	2.381(2)
Cd1–N4$^{\#1}$	2.328(2)	Cd1–O1	2.479(2)
O3–Cd1–O5	100.01(7)	O3–Cd1–N4$^{\#1}$	142.32(7)
O5–Cd1–N4$^{\#1}$	81.00(8)	O3–Cd1–O2	83.40(7)
O5–Cd1–O2	88.20(8)	N4$^{\#1}$–Cd1–O2	134.11(7)
O3–Cd1–N1	83.40(7)	O5–Cd1–N1	166.32(7)
N4$^{\#1}$–Cd1–N1	88.23(8)	O2–Cd1–N1	105.38(8)
O3–Cd1–O1	134.28(7)	O5–Cd1–O1	93.86(8)
N4$^{\#1}$–Cd1–O1	82.68(7)	O2–Cd1–O1	53.55(7)
N1–Cd1–O1	93.08(8)		

[a] Symmetry transformations used to generate equivalent atoms: **1**: $^{\#1}$ $x+1, y, z$; $^{\#2}$ $x, y-1, z$; **2**: $^{\#1}$ $-x+1, -y+2, -z+2$.

Table 3. Hydrogen bonds for **1** and **2**[a].

D–H···A	*d*(D–H) (Å)	*d*(H···A) (Å)	*d*(D···A) (Å)	(D–H···A)(deg)
		Complex **1**		
O6–H6···O3$^{\#3}$	0.82	1.84	2.658(5)	172.3
N5–H5A···O6$^{\#5}$	0.86	1.89	2.716(5)	159.9
O5–H1W···O2$^{\#6}$	0.85	1.89	2.691(5)	155.6
O5–H2W···O4$^{\#7}$	0.85	1.94	2.702(5)	148.4
		Complex **2**		
O5–H2W···O6	0.85	1.90	2.731(3)	166.8
O6–H3W···O7	0.85	2.04	2.816(4)	151.8
O7–H5W···O8	0.85	1.87	2.716(4)	176.5
O7–H6W···O2	0.85	1.92	2.752(3)	164.5
N2–H2A···O3$^{\#4}$	0.86	1.95	2.760(3)	156.3
O5–H1W···O4$^{\#5}$	0.85	1.94	2.789(3)	174.3
O6–H4W···O7$^{\#6}$	0.85	2.03	2.864(4)	167.3

[a] Symmetry transformations used to generate equivalent atoms: **1**: $^{\#3}$ $x-1, y, z$; $^{\#5}$ $-x+1, -y+1, -z$; $^{\#6}$ $-x+3, -y+1, -z+1$; $^{\#7}$ $-x+3, -y+2, -z+1$; **2**: $^{\#4}$ $-x+2, -y+2, -z+2$; $^{\#5}$ $-x+1, -y+1, -z+2$; $^{\#6}$ $-x+1, -y+1, -z+1$.

graphic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Results and Discussion

*IR spectra of complexes **1** and **2***

The IR spectra exhibit absorption bands at 3410 cm^{-1} for **1** and at 3372 cm^{-1} for **2** associated with the stretching vibrations of the hydroxyl groups, and absorption bands at 3118 cm^{-1} for **1** and at 3146 cm^{-1} for **2** attributed to Ar-H stretching vibrations [15]. The absorption band observed at 1669 cm^{-1} is corresponding to the non-coordinated DMF molecule [16]. Furthermore, the absorption bands at 1607, 1548, 1462, and 1444 cm^{-1} for **1** and at 1566, 1499 and 1463 cm^{-1} for **2** originate from C=C and C=N stretching vibrations [17, 18]. The absorption bands at 739 cm^{-1} for **1** and at 751 cm^{-1} for **2** can be assigned to characteristic stretching vibrations of *o*-phenylene [19]. The absorption band at 671 cm^{-1} for **1** can be attributed to the stretching vibrations of *m*-phenylene, and that at 842 cm^{-1} for **2** corresponds to the stretching vibrations of *t*-phenylene [20]. Separations (Δ) between ν_a(COO) and ν_s(COO) are different for the unidentate, chelating (bidentate) and bridging complexation. In **1**, the separation (Δ) between ν_a(COO) and ν_s(COO) is 53 cm^{-1} (1515, 1462 cm^{-1}), and the carboxylate groups are thus chelating the Cd(II) center. In **2**, unidentate and chelating carboxylate groups are mixed; the unidentate carboxylate group shows ν_a(COO) and ν_s(COO) at 1566 and 1384 cm^{-1} ($\Delta = 182$ cm^{-1}) [20], while the chelating carboxylate group displays ν_a(COO) and ν_s(COO) at 1499 and 1463 cm^{-1} ($\Delta = 32$ cm^{-1}), respectively. The above analyses are confirmed by the determination of the molecular structure.

*The structure of $\{[\mathrm{Cd}(m\text{-bdc})(\mathrm{tmb})(\mathrm{H_2O})]\cdot\mathrm{CH_3OH}\}_n$ (**1**)*

Single-crystal X-ray analysis has revealed that complex **1** crystallizes in the triclinic space group $P\bar{1}$ with

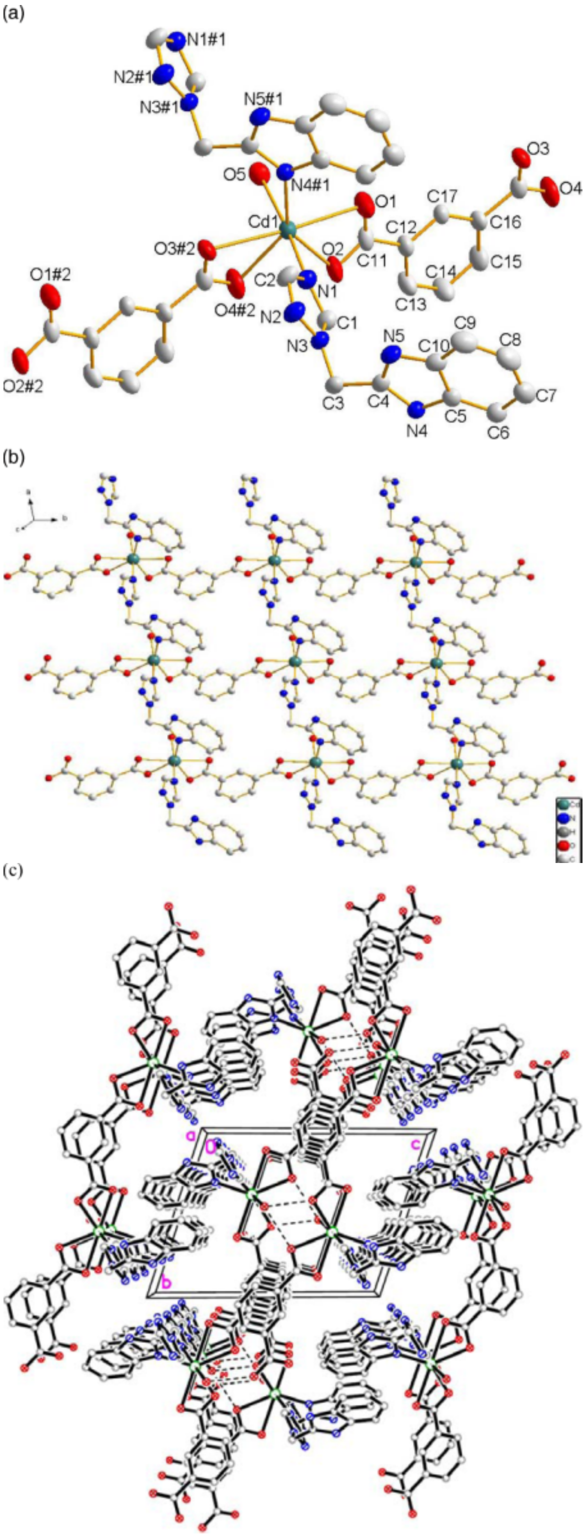

Fig. 1. (a) Coordination environment of Cd(II) in **1** with ellipsoids drawn at the 30 % probability level; hydrogen atoms and free methanol molecules have been omitted for clarity; (b) view of the 2D structure of complex **1**; (c) view of the packing of the building unit of complex **1** in the solid state supported by hydrogen bonds and $\pi\cdots\pi$ interactions.

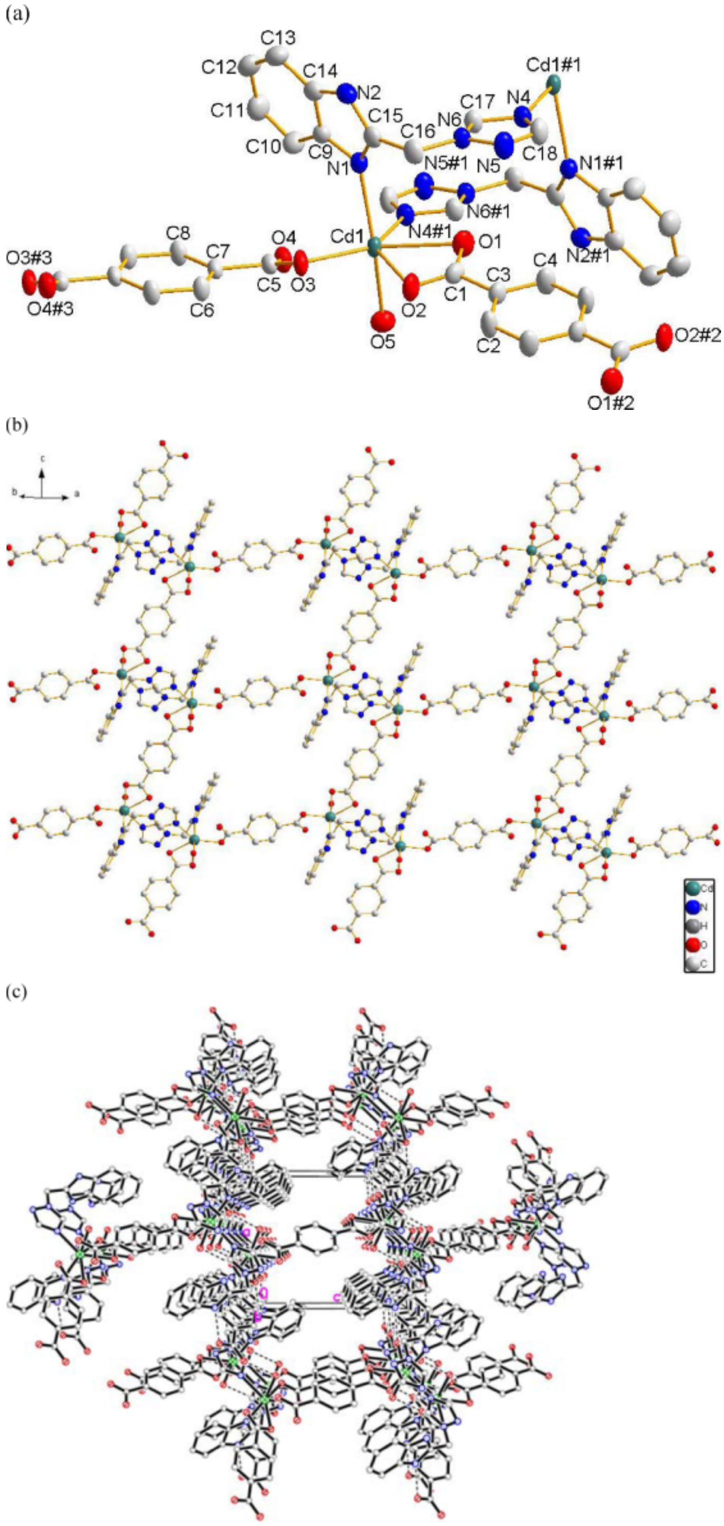

Fig. 2. (a) View of the coordination environment of the Cd(II) center and the dinuclear structure connected by tmb ligands in complex **2** with ellipsoids drawn at the 30 % probability level; hydrogen atoms and free water and DMF molecules were omitted for clarity; (b) view of the 2D network of complex **2**; (c) 3D structure of complex **2** in the solid state supported by hydrogen bonds.

$Z = 2$. As shown in Fig. 1a, the Cd(II) center is hepta-coordinated in a distorted pentagonal-biyramidal geometry. Four O atoms (O1, O2, O3$^{\#2}$, O4$^{\#2}$) from two chelating carboxylate groups as well as one N atom from the benzimidazole ring occupy the equatorial positions (the mean deviation from the plane is 0.1169 Å), and one N atom from a triazole ring together with one O atom from a coordinated water molecule are located in the apical positions (the N1–Cd1–O5 bond angle is 170.14(12)°). The Cd–O and Cd–N distances are in the ranges 2.341(4) – 2.544(3) and 2.312(4) – 2.340(4) Å, and they are similar to the results for other Cd(II) complexes [21 – 24]. The coordinated carboxylate groups are statistically different in that for O1, O2 (or O3$^{\#2}$, O4$^{\#2}$), the Cd–O distances are 2.481(3), 2.341(4) Å (or 2.544(3) and 2.392(4) Å), respectively, suggesting that the pentagonal bipyramid is distorted. In complex **1**, each tmb ligand adopts the *trans* conformation with the N3–C3–C4–N4 torsion angle of –126.9° and links two Cd(II) centers parallel to the crystallographic *a* direction forming a chain (···Cd-tmb-Cd···) (Fig. 1b). The intra-chain Cd···Cd distance *via* the ligand tmb is 8.174 Å. The *m*-H_2bdc ligand is completely deprotonated, and the carboxylate groups coordinated to the Cd(II) centers in the chelating mode. The chains are further linked by the *m*-bdc^{2-} groups parallel to the *b* direction to give rise to a 2D structure of "fields" shape, as shown in Fig. 1b. The distance Cd···Cd *via* the *m*-bdc^{2-} groups is 10.034 Å. In addition, there are $\pi\cdots\pi$ interactions between the benzene rings (the distance between them is 3.449 Å) of the *m*-bdc^{2-} groups in adjacent layers [17]. There are three kinds of hydrogen bonds between coordinating water molecules and carboxylate groups, between non-coordinating water molecules and carboxylate ions, and between N atoms from benzimidazole rings and CH_3OH molecules. The layers are stacked *via* hydrogen bonds, and the $\pi\cdots\pi$ interactions lead to a 3D structure (Fig. 1c).

*The structure of {[Cd(t-bdc)(tmb)(H$_2$O)]·2H$_2$O·DMF}$_n$ (**2**)*

Substitution of 1,4-benzenedicarboxylic acid in **2** for 1,3-benzenedicarboxylic acid in **1** results in a different crystal and molecular structure. The single-crystal X-ray analysis shows that the 1,4-benzenedicarboxylate ligand in **2** coordinates with one of its carboxylate groups to one Cd(II) center in a unidentate fashion. The other carboxylate group coordinates to a neighboring Cd(II) center in a chelating coordination mode, whereas in **1** both of the carboxylates of the 1,3-benzenedicarboxylate ligand coordinate to Cd(II) in a chelating fashion. Furthermore, in **2** each tmb ligand coordinates to Cd(II) centers in a *trans* conformation with the N1–C15–C16–N6 torsion angle of 80.0°, while the tmb ligands are coordinated to Cd(II) centers in the *cis* conformation in **1**. Fig. 2a displays the coordination environment of the Cd(II) center. It is hexa-coordinated by four O atoms and two N atoms to give rise to a severely distorted octahedral geometry. The equatorial positions are occupied by three O atoms from one unidentate carboxylate group and one chelating carboxylate group and one N atom from a triazole ring, and the mean deviation from the plane is 0.1521 Å. One O atom from the coordinated water molecule as well as one N atom from a benzimidazole ring occupy the apical positions, and the O5–Cd1–N1 bond angle is 166.32(7)°. The distances Cd–O and Cd–N are in the ranges 2.3098(17) – 2.479(2) and 2.328(2) – 2.381(2) Å, respectively. They are similar to those in **1** and to the results for other Cd(II) complexes [21 – 24]. In **2**, Cd1 and Cd1$^{\#1}$ are bridged by two tmb ligands leading to a dinuclear structure [$Cd_2(tmb)_2$], in which the Cd1···Cd1$^{\#1}$ distance is 6.571 Å as shown in Fig. 2a. The dimers are bridged by unidentate carboxylate groups leading to a chain parallel to the crystallographic *a* direction. These chains are linked by chelating carboxylate groups forming a 2D grid structure as shown in Fig. 2b. Additionally, there are six kinds of hydrogen bonds between the coordinating water molecules and carboxylate groups, between coordinating water molecules and non-coordinating water molecules, between non-coordinating water molecules and carboxylate groups, between non-coordinating water molecules and DMF molecules, between non-coordinating water molecules and non-coordinating water molecules, and between N atoms from benzimidazole rings and carboxylate groups. Through these hydrogen bonds these layers are further stacked into a 3D framework (Fig. 2c).

Luminescence properties

Because metal-organic complexes constructed from d^{10} metal centers and organic ligands are promising candidates for hybrid photoactive materials with potential applications *e. g.* in light-emitting diodes

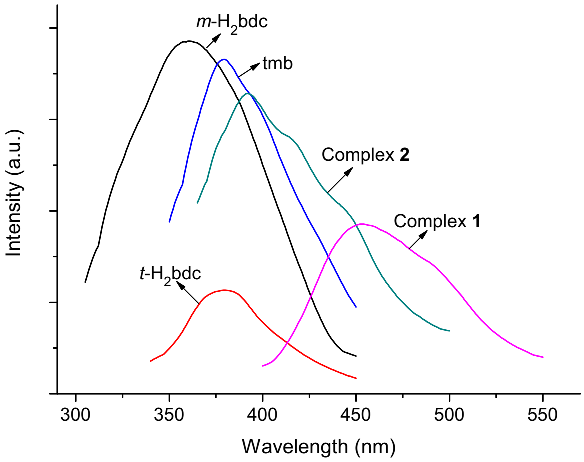

Fig. 3. Solid-state emission spectra of the free ligands, and complexes **1** and **2** at room temperature.

(LEDs) [25–29], the emission spectra of both complexes have been investigated in the solid state at room temperature (Fig. 3). Complexes **1** and **2** show luminescence at 450 nm ($\lambda_{ex} = 389$ nm) and 391 nm ($\lambda_{ex} = 346$ nm), respectively. To further analyze the nature of the emission bands, the luminescence properties of the ligand tmb and of the auxiliary ligands m-H_2bdc and t-H_2bdc have also been investigated in the solid state at room temperature. The emission peaks occur at 378 nm ($\lambda_{ex} = 335$ nm) for tmb, 363 nm ($\lambda_{ex} = 292$ nm) for m-H_2bdc and 384 nm ($\lambda_{ex} = 329$ nm) for t-H_2bdc. Compared to the emission bands of the free ligands, the emissions of complexes **1** and **2** show bathochromic shifts, which may be assigned to intraligand $\pi \rightarrow \pi^*$ transitions, the same as in the free ligands. The N-donor and O-donor ligands contribute to the fluorescence of the two complexes simultaneously [30].

Conclusion

In summary, we have isolated two new complexes resulting from flexible N-heterocyclic ligands and a Cd(II) salt in the presence of 1,3-benzenedicarboxylic or 1,4-benzenedicarboxylic acid. Because of the difference of the auxiliary ligands, the 2-((1H-1,2,4-triazol-1-yl)methyl)-1H-benzimidazole ligand adopts different conformations, which lead to different crystal and molecular structures of **1** and **2**. In complex **1**, tmb ligands coordinate to Cd(II) centers with a *trans* conformation, while a *cis* conformation is adopted to connect to Cd(II) centers in **2**. The present results demonstrate that an auxiliary ligand plays an important role in the construction of the frameworks. If one introduces other auxiliary ligands into the reaction systems, new complexes with interesting structure may be obtained.

Acknowledgement

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

[1] C. C. Wang, S. M. Tseng, S. Y. Lin, F. C. Liu, S. C. Dai, G. H. Lee, W. J. Shih, H. S. Sheu, *Cryst. Growth & Des.* **2007**, *7*, 1783.
[2] P. Zhang, D. S. Li, J. Zhao, Y. P. Wu, C. Li, K. Zou, J. Y. Lu, *J. Coord. Chem.* **2011**, *64*, 2329.
[3] Y. Wan, L. Zhang, L. Jin, S. Gao, S. Lu, *Inorg. Chem.* **2003**, *42*, 4985.
[4] M. Eddaoudi, J. Kim, J. B. Wachter, H. K. Chae, M. O'Keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 4368.
[5] E. Suresh, M. M. Bhadbhade, *CrystEngComm* **2001**, *3*, 50.
[6] D. Ghoshai, T. K. Maji, G. Mostafa, T. H. Lu, N. R. Chaudhuri, *Cryst. Growth & Des.* **2003**, *3*, 9.
[7] M. C. Brandys, R. J. Puddephatt, *Chem. Commun.* **2001**, 1508.
[8] F. M. Tabellion, S. R. Seidel, A. M. Arif, P. J. Stang, *Angew. Chem. Int. Ed.* **2001**, *40*, 1529.
[9] L. Pan, E. B. Woodlock, X. Wang, K. C. Lam, A. L. Rheingold, *Chem. Commun.* **2001**, 1762.
[10] M. L. Tong, Y. M. Wu, J. Ru, X. M. Chen, H. C. Chang, S. Kitagawa, *Inorg. Chem.* **2002**, *41*, 4846.
[11] J. D. Lin, J. W. Cheng, S. W. Du, *Cryst. Growth & Des.* **2008**, *8*, 3345.
[12] F. Oscar, P. Jorge, C. D. Laura, S. D. Fernando, L. Ana, L. Francesc, J. Miguel, R. P. Catalina, *Cryst. Growth & Des.* **2008**, *8*, 3984.
[13] R. Pellicciari, *Synth. Commun.* **1981**, 629.
[14] G. M. Sheldrick, SHELXS/L-97, Programs for Crystal Structure Determination, University of Göttingen, Göttingen (Germany) **1997**. See also: G. M. Sheldrick, *Acta Crystallogr.* **1990**, *A46*, 467; *ibid.* **2008**, *A64*, 112.
[15] S. X. Yan, D. Zhao, T. Li, R. Wang, X. R. Meng, *J. Coord. Chem.* **2012**, *65*, 945.
[16] J. Q. Chen, Y. P. Cai, H. C. Fang, Z. Y. Zhou, X. L. Zhan, G. Zhao, Z. Zhang, *Cryst. Growth & Des.* **2009**, *9*, 1605.

[17] A. Majumder, V. Gramlich, G. M. Rosair, S. R. Batten, J. D. Masuda, M. S. El Fallah, J. Ribas, J. P. Sutter, C. Desplanches, S. Mitra, *Cryst. Growth & Des.* **2006**, *6*, 2355.
[18] G. H. Jin, Y. Yang, X. L. Zhou, X. R. Meng, *Z. Naturforsch.* **2012**, *67b*, 29.
[19] X. R. Meng, W. Zhou, Y. F. Qi, H. W. Hou, Y. T. Fan, *J. Organomet. Chem.* **2010**, *695*, 766.
[20] K. Nakamoto. *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Part B, 6th ed., John Wiley, Hoboken, New Jersey, **2009**.
[21] F. A. A. Paz, J. Klinowski, *Chem. Commun.* **2003**, 1484.
[22] F. A. A. Paz, J. Klinowski, *Inorg. Chem.* **2004**, *43*, 3948.
[23] F. A. A. Paz, J. Klinowski, *Inorg. Chem.* **2004**, *43*, 3882.
[24] S. Wang, H. Xing, Y. Z. Li, J. F. Bai, Y. Pan, M. Scheer, X. Z. You, *Eur. J. Inorg. Chem.* **2006**, 3041.
[25] B. Valeur, *Molecular Fluorescence: Principles and Applications*, Wiley-VCH, Weinheim, **2001**.
[26] Y. Qiu, Y. Li, G. Peng, J. Cai, L. Jin, L. Ma, H. Deng, M. Zeller, S. R. Batten, *Cryst. Growth & Des.* **2010**, *10*, 1332.
[27] L. L. Liang, S. B. Ren, J. Zhang, Y. Z. Li, H. B. Du, X. Z. You, *Cryst. Growth & Des.* **2010**, *10*, 1307.
[28] L. P. Zhang, J. F. Ma, J. Yang, Y. Y. Pang, J. C. Ma, *Inorg. Chem.* **2010**, *49*, 1535.
[29] W. Liu, L. Ye, X. Liu, L. Yuan, J. Jiang, C. Yan, *CrystEngComm* **2008**, *10*, 1395.
[30] Y. Y. Liu, J. F. Ma, J. Yang, Z. M. Su, *Inorg. Chem.* **2007**, *46*, 3027.