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Synthesis and Crystal Structure of Blue Luminescent Cadmium(II) Coordination Networks with 4,4′-Bis(imidazol-1-ylmethyl)biphenyl from Different Solvent Systems

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Two supramolecular complexes, [Cd(bimb)$_2$Cl$_2$] (1) and [Cd(bimb)(DMF)Cl$_2$]·DMF (2) [bimb = 4,4′-bis(imidazol-1-ylmethyl)biphenyl], were synthesized by reactions of CdCl$_2$·2.5H$_2$O with bimb ligand in ethanol and N,N'-dimethylformamide (DMF), respectively, and their structures were determined by X-ray crystallography. Complex 1 is an infinite 2D grid network bridged by bimb ligands, and the 2D sheets were further linked by C–H···Cl hydrogen bonds to form a polycatenated 3D framework. Complex 2 has dicadmium(II) di-μ-chloride units which are connected by bimb bridging ligands to form an infinite non-interpenetrating 2D network. The results provide a nice example of the solvent system exerting a great effect on the construction of supramolecular frameworks.

Keywords: Crystal structure; 2D Network; Imidazole-containing ligand; Cadmium(II) complex; Blue luminescence

INTRODUCTION

Recently, crystal engineering and design of novel solid-state materials have attracted great interest from chemists [1,2]. The control of structure and topology is one of the major goals in supramolecular chemistry [3,4]. Assembly of extended structures by propagating the chemical structure of multifunctional ligands and the coordination geometry of metal ions may yield a series of network architectures with various topologies. Much effort has been made in the rational design and preparation of new materials and the current focus is mainly on understanding the factors that determine the assembly process. The formation of supramolecular architectures depends on the combination of several factors, such as the coordination geometry of metal ions, the nature of ligands, the ratio between metal salt and ligand, and reaction conditions such as solvent system, templates or counter ions [5–8]. In the past several years, extensive studies have been carried out and many one- (1D), two- (2D) and three-dimensional (3D) frameworks with novel structures have been obtained by using bridging rigid ligands e.g. 4,4′-bipyridine, 2,4,6-tri(4-pyridyl)-1,3,5-triazine, etc. [9–11]. Recently Stang and his co-workers reported three different types of solid-state coordination species using the flexible bridging ligand 4,4′-trimethylenedipyridine [12]. In contrast to the rigid ligands, the flexible ligands can adopt different conformations according to the different geometric needs of metal ions and as a result can provide metal–organic frameworks with various structures and topologies. For example, it has been reported that the flexible ligand 1,4-bis(imidazol-1-ylmethyl)-benzene (bix) reacted with silver(I) nitrate [13] or zinc(II) nitrate hexahydrate [14] to give infinite polyrotaxane networks and with manganese(II) [15] to generate an infinite 1D chain. In our previous study, we designed and synthesized a flexible ligand 4,4′-bis(imidazol-1-ylmethyl)biphenyl (bimb), and have obtained a poly-metallocage-like complex

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$[Mn(bimb)_3][ClO_4]_2{\cdot}2H_2O$ by reaction of the bimb ligand with $Mn(ClO_4)_2{\cdot}6H_2O$ [16]. We report herein the syntheses, X-ray single crystal structures and luminescence properties of two 2D coordination polymers $[Cd(bimb)_2Cl_2]$ (**1**) and $[Cd(bimb)(DMF)Cl_2]{\cdot}DMF$ (**2**), obtained by reactions of cadmium(II) chloride with the bimb ligand in different solvent systems. The results show that the solvent has a significant effect on the formation of supramolecular complexes in this assembly system.

EXPERIMENTAL

Materials and Measurements

All commercially available chemicals were of reagent grade and used as received without further purification. Solvents were purified according to standard methods. Samples for C, H and N analyses were dried under vacuum and the analyses were determined on a Perkin-Elmer 240C elemental analyser at the analysis center of Nanjing University. ^1H NMR spectral measurements were recorded on a Bruker DRX-500 NMR spectrometer at room temperature. Luminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer at room temperature (25°C). 4,4′-Bis(imidazol-1-ylmethyl)biphenyl (bimb) was prepared according to the reported procedure [16,17].

Preparation of the Complexes

[Cd(bimb)$_2$Cl$_2$] 1

This complex was prepared by slow diffusion between two layers of an aqueous solution (10 ml) of $CdCl_2{\cdot}2.5H_2O$ (11.4 mg, 0.05 mmol) and bimb (15.7 mg, 0.05 mmol) in ethanol (10 ml) at room temperature. Several weeks later, colorless platelet crystals suitable for X-ray analysis were obtained in 65% yield. ^1H NMR (d_6-DMSO, 298 K): δ 7.86 (s, 2H), 7.64 (d, 4H), 7.34 (d, 4H), 7.26 (s, 2H), 6.95 (s, 2H), 5.26 (s, 4H). Anal. calcd. for $C_{40}H_{36}CdCl_2N_8$: C, 59.16; H, 4.47; N, 13.80%. Found: C, 59.07; H, 4.76; N, 13.64%.

[Cd(bimb)(DMF)Cl$_2$]·DMF 2

A white powder was obtained after mixing an ethanol solution (2.5 ml) of $Cd(Cl)_2{\cdot}2.5H_2O$ (11.4 mg, 0.05 mmol) and bimb (15.7 mg, 0.05 mmol) in ethanol (2.5 ml) at room temperature. The powder was dissolved in *N,N′*-dimethylformamide (DMF) (10 ml) and colorless crystals were obtained in 70% yield by slow diffusion of diethyl ether into the DMF solution over several days at room temperature. ^1H NMR (d_6-DMSO, 298 K): δ 7.96 (s, 2H), 7.92 (s, 2H), 7.64 (d, 4H), 7.35 (d, 4H), 7.30 (s, 2H), 6.98 (s, 2H), 5.28 (s, 4H), 2.89 (s, 6H), 2.74 (s, 6H). Anal. calcd. for $C_{26}H_{32}CdCl_2N_6O_2$: C, 48.50; H, 5.01; N, 13.05%. Found: C, 48.63; H, 5.10; N, 13.19%.

TABLE I Crystallographic data for complexes **1** and **2**

Complex	1	2
Empirical formula	$C_{40}H_{36}CdCl_2N_8$	$C_{26}H_{32}CdCl_2N_6O_2$
Formula weight	812.07	643.88
Crystal system	Monoclinic	Monoclinic
Space group	$C2/c$	$P2_1/c$
a (Å)	26.170(3)	13.7368(2)
b (Å)	7.4351(6)	16.5809(5)
c (Å)	18.3972(13)	13.8723(2)
β (°)	92.263(5)	114.4042(18)
V (Å^3)	3576.9(5)	2877.37(10)
Z	4	4
T (K)	200	200
μ (mm^{-1})	0.802	0.978
Measured reflections	16653	25642
Independent reflections	4114	6568
Observed reflections	2719	4387
R_{int}	0.0727	0.0802
$R1$ [$I > 2\sigma(I)$]	0.0428	0.0481
$wR2$ [$I > 2\sigma(I)$]	0.0640^a	0.0922^b

[a] $w = 1/[\sigma^2(F_o)^2 + (0.0304P)^2]$, $P = (F_o^2 + 2F_c^2)/3$. [b] $w = 1/[\sigma^2(F_o)^2 + (0.0503P)^2]$, $P = (F_o^2 + 2F_c^2)/3$.

Crystallography

The collections of crystallographic data for the complexes **1** and **2** were carried out on a Rigaku RAXIS-RAPID imaging plate diffractometer at 200 K, using graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The structures were solved by direct methods with SIR92 [18] and expanded using the Fourier technique [19]. All data were refined anisotropically by the full-matrix least-squares method for non-hydrogen atoms. The hydrogen atoms were generated geometrically. All calculations were carried out on an SGI workstation using the teXsan crystallographic software package from the Molecular Structure Corporation [20]. Details of the crystal parameters, data collection and refinement are summarized in Table I, and selected bond lengths and angles with their estimated standard deviations are listed in Table II. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication No. CCDC-191731 (**1**) and CCDC-191732 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk].

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TABLE II Selected bond distances (Å) and angles (°) for **1** and **2**

Cd(bimb)$_2$Cl$_2$ (**1**)			
Cd(1)–N(12)	2.339(2)	Cd(1)–N(32)	2.364(2)
Cd(1)–Cl(1)	2.6359(7)		
Cl(1)–Cd(1)–Cl(1)^{i}	180.0	N(12)–Cd(1)–N(12)^{i}	180.0
N(12)–Cd(1)–N(32)^{i}	86.71(8)	N(12)–Cd(1)–N(32)	93.29(8)
N(32)–Cd(1)–N(32)^{i}	180.0	N(12)–Cd(1)–Cl(1)	90.95(6)
N(12)–Cd(1)–Cl(1)^{i}	89.06(6)	N(32)–Cd(1)–Cl(1)	89.83(6)
N(32)–Cd(1)–Cl(1)	90.17(6)		
[Cd(bimb)(DMF)Cl$_2$]·DMF (**2**)			
Cd(1)–N(22)	2.298(3)	Cd(1)–N(12)	2.334(3)
Cd(1)–Cl(2)	2.5601(11)	Cd(1)–Cl(1)	2.6588(9)
Cd(1)–O(1)	2.375(3)	Cd(1)–Cl(1)^{i}	2.6750(9)
Cd(1)–Cl(1)–Cd(1)^{i}	99.62(3)	N(12)–Cd(1)–O(1)	79.57(11)
Cl(1)–Cd(1)^{i}	2.6750(9)	C(1)–O(1)–Cd(1)	126.1(3)
N(12)–Cd(1)–O(1)	79.57(11)	N(22)–Cd(1)–O(1)	80.85(11)
N(22)–Cd(1)–N(12)	97.36(11)	O(1)–Cd(1)–Cl(1)	89.96(7)
O(1)–Cd(1)–Cl(2)	166.37(7)	N(12)–Cd(1)–Cl(2)	89.89(9)
N(22)–Cd(1)–Cl(2)	92.08(8)	N(12)–Cd(1)–Cl(1)	91.31(8)
N(22)–Cd(1)–Cl(1)	165.97(8)	Cl(1)–Cd(1)–Cl(1)^{i}	80.38(3)
N(12)–Cd(1)–Cl(1)^{I}	166.03(8)	N(22)–Cd(1)–Cl(1)^{i}	88.86(8)
Cl(2)–Cd(1)–Cl(1)	98.97(3)	Cl(2)–Cd(1)–Cl(1)^{i}	102.43(3)
O(1)–Cd(1)–Cl(1)^{i}	89.14(7)	Cd(1)–Cl(1)–Cd(1)^{i}	99.62(3)

Symmetry code for **1**: $^{i}0.5 - x, 1.5 - y, -z$ and for **2**: $^{i}1 - x, -y, -z$.

RESULTS AND DISCUSSION

The complexes **1** and **2** are almost insoluble in water and organic solvents such as methanol, ethanol and acetonitrile, but have moderate solubility in DMF and DMSO. From ^{1}H NMR spectral measurement of samples in d_6-DMSO at 298 K, six signals at δ 7.78 (s, 2H), 7.63 (d, 4H), 7.33 (d, 4H), 7.21 (s, 2H), 6.91 (s, 2H), 5.23 (s, 4H) were observed for the bimb ligand. On comparison of the ^{1}H NMR data of **1** and **2** (see the Experimental section) with those of the bimb ligand, down-field shifts were observed for the signals of imidazole protons while the signals of biphenyl protons were almost unchanged. The ^{1}H NMR results suggest that the bimb ligand is coordinated to the metal atoms through the imidazole nitrogen atoms in DMSO solution.

Crystal Structure of Complex 1

The polymeric structure of Cd(bimb)$_2$Cl$_2$ **1** was confirmed by X-ray single crystal structure determination. The complex crystallizes in the monoclinic space group $C2/c$ and Fig. 1a shows the coordination environment of the Cd(II) atom in **1** with the atom numbering scheme. The cadmium(II) atom sits on the inversion center and is coordinated by four imidazole nitrogen atoms from four different bimb ligands with N–Cd–N bond angles varying from 86.71(8) to 180.0° and Cd–N bond distances of 2.339(2) and 2.364(2) Å (Table II). Two additional positions are occupied by chloride ions in a *trans* arrangement with a Cl–Cd–Cl bond angle of 180.0° and Cd–Cl bond distance of 2.6359(7) Å (Table II). Therefore the coordination environment of the cadmium(II) atom can be described as a distorted octahedron with an N$_4$Cl$_2$ donor set. Each bimb ligand in turn connects two Cd(II) atoms to give a corrugated 2D network structure of **1** as illustrated in Fig. 1b. Each Cd(II) center is linked to four different Cd(II) atoms via the four different bimb ligands to form a 2D, approximately rhombohedral grid with (4,4) topology. Figure 1c shows the simplified 2D network where only the Cd(II) atoms are presented. In each Cd$_4$ parallelogram, the Cd–Cd edge distances through the bimb ligand are 15.70 Å (e.g. Cd1A–Cd1D and Cd1B–Cd1C), and 16.29 Å (e.g. Cd1A–Cd1C and Cd1B–Cd1D), respectively. The Cd1C–Cd1D and Cd1A–Cd1B diagonals of the Cd$_4$ parallelogram are 18.40 and 26.17 Å and the internal angles of the parallelogram are 70.2 and 109.8°, respectively. Even though such large grids are present in each 2D sheet, there are no large open channels in the complex **1** due to the interleaved stacking of the 2D sheets as exhibited in Fig. 2. The Cd(II) atom in one layer is located at the center of the grid of adjacent layers. It can be seen from the Fig. 2a that the 2D layers in the complex **1** repeat in an –ABAB– stacking sequence. It is noteworthy that the 2D sheets were further linked by C–H···Cl hydrogen bonds between the alternate layers, i.e. between A–A layers and between B–B layers, to form a polycatenated 3D framework (Fig. 2a). A schematic drawing is shown in Fig. 2b. The data of the hydrogen bonds are summarized in Table III.

In the complex **1**, the bimb ligand has an extended conformation with "C" shape as shown in Fig. 2a, which is to say that the two terminal imidazole groups are in the *cis* conformation with reference to the average plane of biphenyl group. The dihedral angles between the imidazole ring plane and the average plane of biphenyl group are 96.9 and 83.1°

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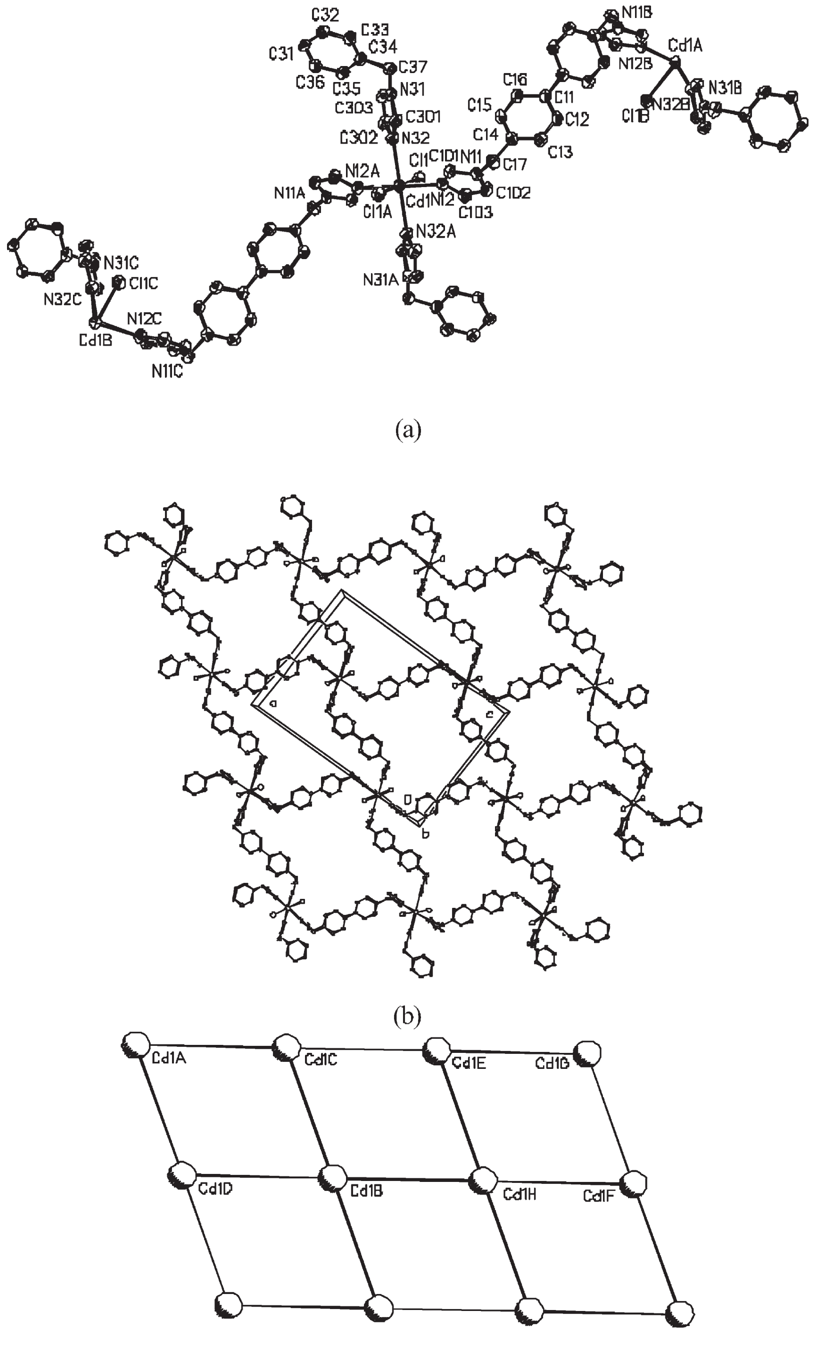

(a)

(b)

(c)

FIGURE 1 (a) Crystal structure of $[Cd(bimb)_2Cl_2]$ **1** with atom numbering scheme and hydrogen atoms omitted for clarity. The thermal ellipsoids were drawn at 50% probability. (b) Infinite 2D network of **1** on the *ac* plane. (c) The 2D sheet consisting of rhombohedral grids where only the cadmium(II) atoms are presented.

for the bimb ligand. The bimb ligand is especially flexible and the bimb in **1** is distorted to suit the geometric requirements dictated by coordination of the metal ion. The dihedral angle between two benzene ring planes of each biphenyl group is 32.3°, which is very different from that in the free bimb ligand and in the reported complex of $[Mn(bimb)_3][ClO_4]_2{\cdot}2H_2O$, in which the two benzene ring planes of the biphenyl group are almost co-planar [16].

Crystal Structure of Complex 2

To compare the structures of complexes obtained from different solvents, we also carried out an X-ray crystallographic analysis for complex **2**, which

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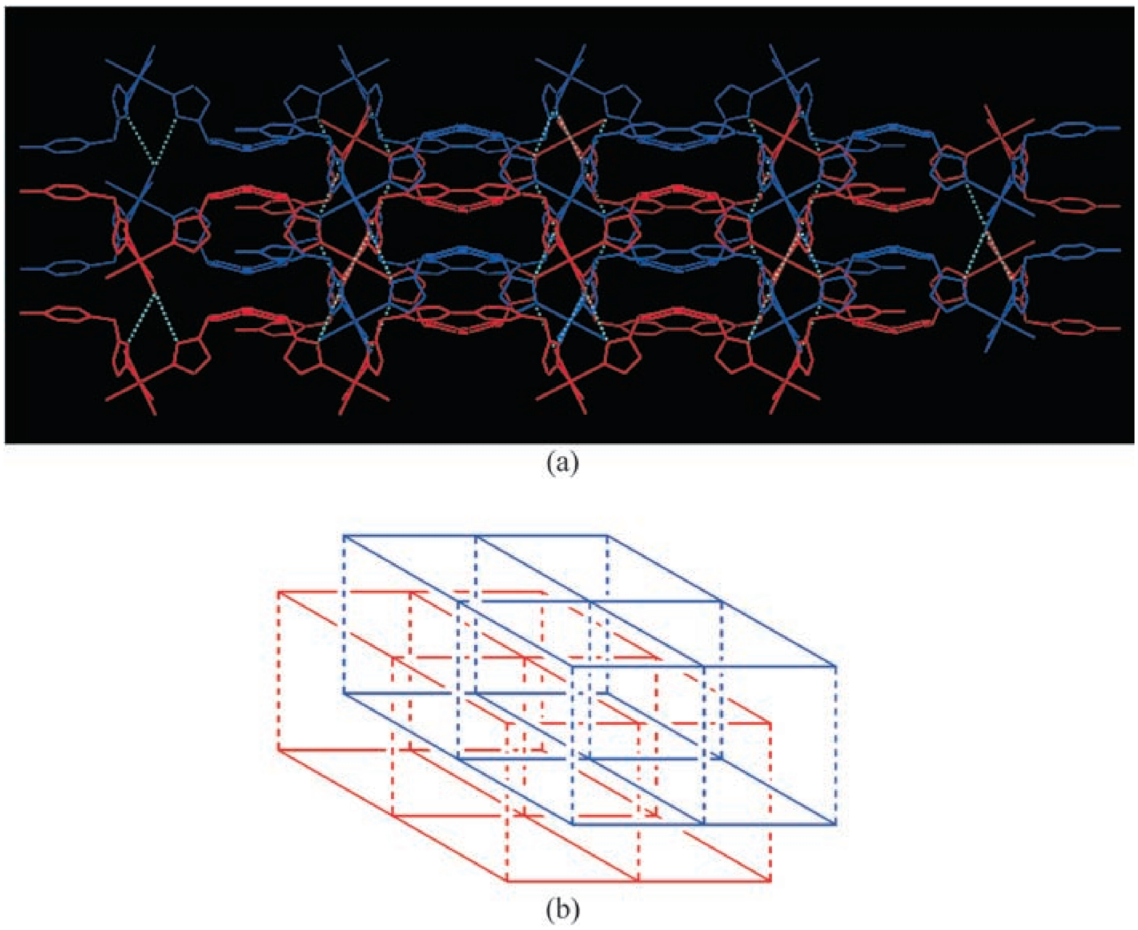

FIGURE 2 (a) Stacking of infinite 2D network of **1** with C–H···Cl hydrogen bonds indicated by dashed lines. (b) Schematic drawing of a polycatenated 3D framework linked by C–H···Cl hydrogen bonds indicated by dashed lines.

provides direct evidence for its structure. The complex **2** is also monoclinic but crystallizes in a different space group, $P2_1/c$, from **1**, which has space group $C2/c$. Figure 3a shows the crystal structure of **2** with the atom numbering scheme. It is clear from the crystal structure of **2** that two cadmium(II) atoms are bridged by a pair of chloride ions leading to the formation of a Cd_2Cl_2 diamond core. The two cadmium(II) atoms are equivalent since the complex has a C_2 symmetry axis passing through the Cd_2Cl_2 core. Each Cd(II) atom in complex **2** is coordinated by two, rather than the four as in **1**, imidazole nitrogen atoms from two different bimb ligands in a *cis* arrangement with an N–Cd–N bond angle of 97.36(11)° and Cd–N distances of 2.298(3) and 2.334(3) Å, respectively (Table II). In addition, another chloride ion and an oxygen atom from a DMF molecule are also coordinated to the Cd(II) atom with a Cd–Cl distance of 2.5601(11) Å and the Cd–O distance of 2.375(3) Å (Table II). Therefore the coordination environment of each cadmium(II) atom can be regarded as a distorted octahedron with an N_2Cl_3O binding set. It is interesting that three chloride ions coordinated to one Cd(II) atom have different coordination mode, two of them acting as μ-bridges between the two Cd(II) atoms and the other one as a terminal coordination group, while the two chloride ions in complex **1** are both terminal coordination groups. Owing to the presence of the symmetry axis, the Cd_2Cl_2 core is strictly planar and the Cd–Cd distance of 4.08 Å indicates that there is no obvious interaction between the two metal atoms. The two Cd–Cl bridging bond lengths are slightly different [2.6588(9) and 2.6750(9) Å] and longer than the terminal Cd–Cl bond length [2.5601(11) Å].

However, the bimb ligand in complex **2** has an extended geometry of "Z" shape, i.e. the two terminal imidazole groups are in the *trans* conformation with reference to the average plane of biphenyl group. The dihedral angles between the imidazole ring plane and the average plane of biphenyl group are 74.2 and 72.6°. In addition, the dihedral angle between two terminal imidazole ring planes is 8.2°, while the dihedral angle between the two benzene ring planes of the biphenyl group is 31.7°, these angles being similar to those observed in complex **1**. The dihedral angle between the two imidazole groups, which are coordinated to the same metal atom, is 58.6°.

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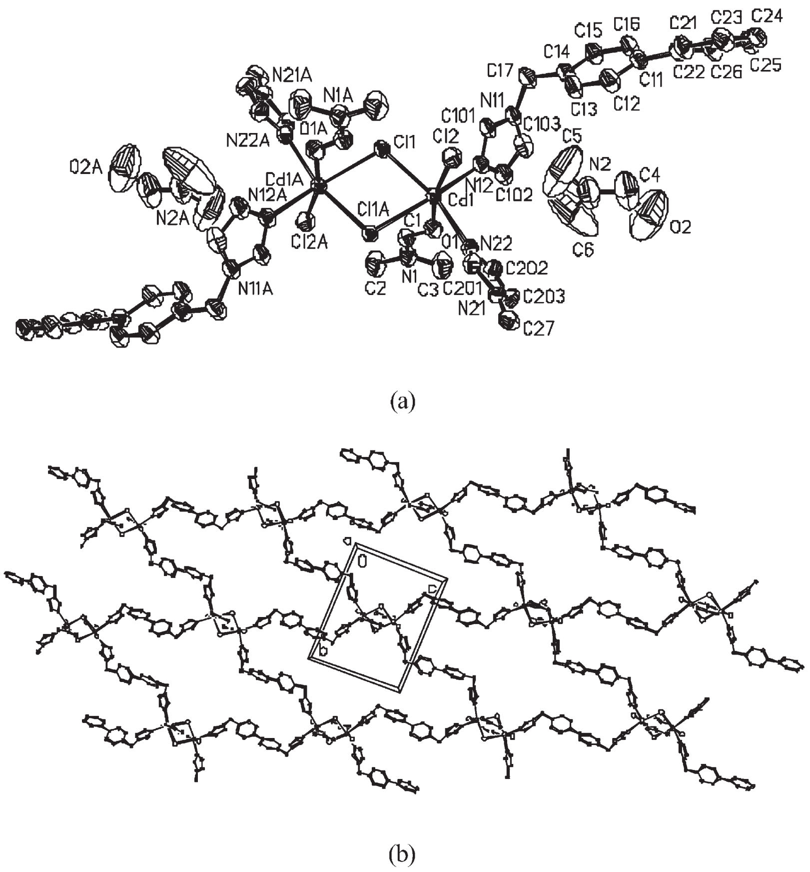

FIGURE 3 (a) Coordination environment of the dicadmium(II) μ-chloride unit in complex [Cd(bimb)(DMF)Cl_2]·DMF **2** with atom numbering scheme and hydrogen atoms omitted for clarity. The thermal ellipsoids were drawn at 50% probability. (b) Infinite 2D network of **2** on the *bc* plane; uncoordinated DMF molecules are omitted.

Four Cd_2Cl_2 units and four molecules of bimb ligand are connected via Cd–N coordination bonds to form a 72-membered ring and further extend into a non-interpenetrating 2D network in the *bc* plane as shown in Fig. 3b. Unlike the complex **1** in which the 2D layers repeated in an –ABAB– stacking sequence, the fourth layer repeats the first layer in complex **2**, that is to say the 2D sheets of complex **2** are stacked in an –ABCABC– repeat sequence (Fig. 4a,b). There are C–H···Cl hydrogen bonds between two adjacent 2D sheets that further link the 2D networks to form a 3D framework. The uncoordinated DMF molecules are located at the vacancy of the framework and linked to the coordinated DMF molecule through C–H···O hydrogen bonds (Table III).

Luminescence Properties

An important feature of the complexes **1** and **2** is that, in the powdered solid state, they showed very similar photoluminescence with emission maxima at 420 nm and at 421 nm upon photoexcitation at 360 nm, respectively, which are almost the same as that (at 418 nm) observed in the reported complex [Mn$(bimb)_3$][ClO_4]$_2$·$2H_2O$ [16]. These emissions of **1** and **2** are neither metal-to-ligand charge transfer (MLCT) nor ligand-to-metal charge transfer (LMCT) in nature since the Cd(II) ion is difficult to oxidize or to reduce due to its d^{10} configuration. The observed emissions in **1** and **2** can probably be assigned to intraligand fluorescence since a very similar emission (at 423 nm) was also observed for the free bimb ligand. The enhancement of the intraligand photoluminescence in complexes **1** and **2** is probably caused by the increase in the ligand conformational rigidity due to its coordination to the Cd(II) atoms and thus a decrease in the non-radiative decay of the intraligand $^1(\pi-\pi^*)$ excited state [21].

In conclusion, the results of the present study show that the solvent systems play important roles in the formation of metal–organic frameworks (MOFs) and that assembly of flexible ligands with metal salts can form various MOFs with different conformations of the ligand. In the complex **1** without coordination of solvent molecules to the metal atom, 2D networks were further linked by C–H···Cl hydrogen bonds to give a polycatenated 3D framework, in which the bimb ligand has a *cis* conformation. In the case of non-interpenetrating 2D network complex **2** with coordination of DMF molecules to the metal atom, the bimb ligand has a *trans* conformation.

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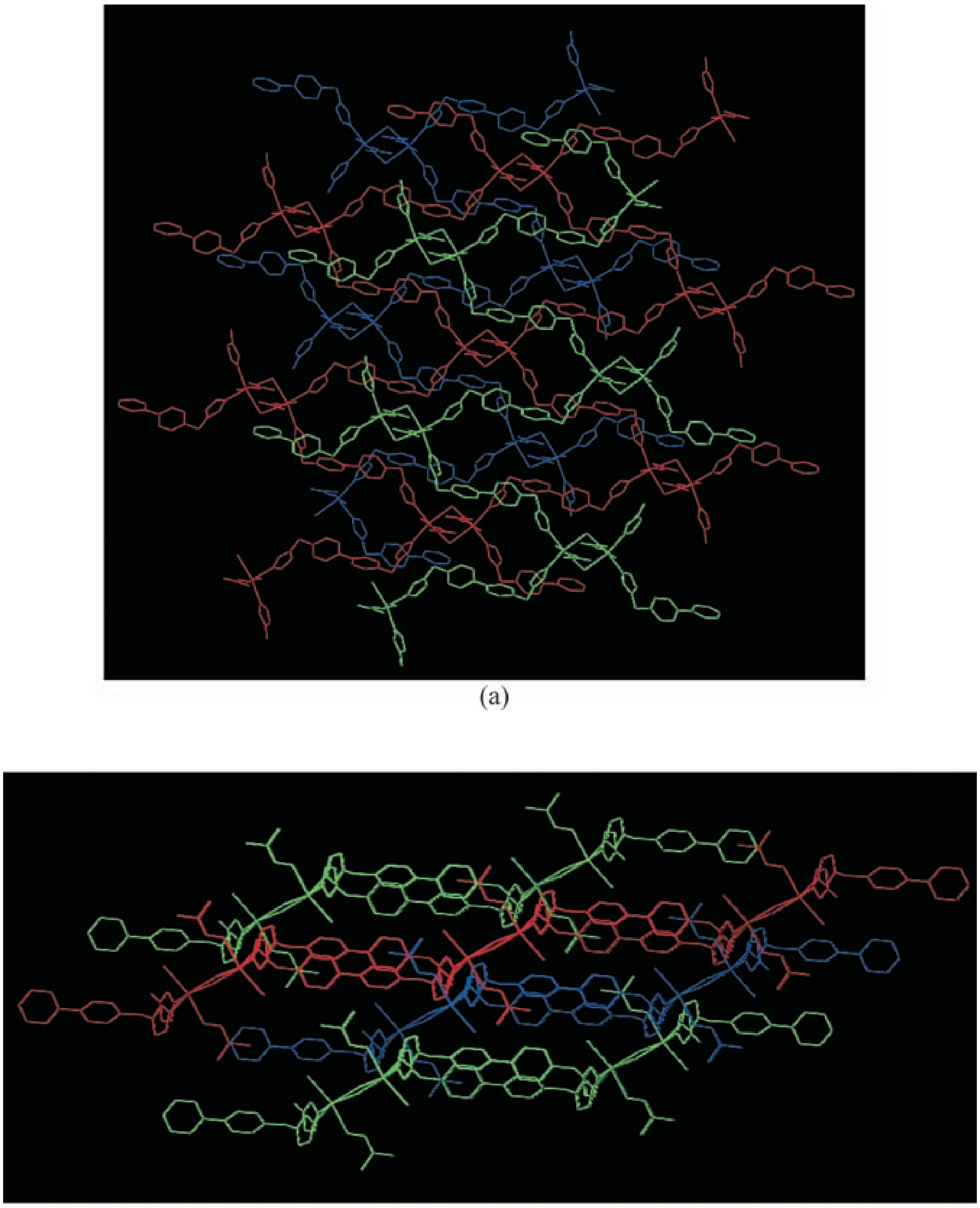
(a)

(b)

FIGURE 4 Perspective (a) and side (b) views of the stacking of the infinite 2D network of **2**; uncoordinated DMF molecules are omitted.

TABLE III Hydrogen bond data for the complexes **1** and **2**

D–H···A	D···A distance (Å)	D–H–A angle (°)
$Cd(bimb)_2Cl_2$ (**1**)		
C(101)–H(13)···Cl(1)^a	3.579(3)	144.6(3)
C(301)–H(16)···Cl(1)^a	3.657(3)	151.2(3)
$[Cd(bimb)(DMF)Cl_2]\cdot DMF$ (**2**)		
C(2)–H(2)···Cl(2)^b	3.701(6)	163.8(10)
C(3)–H(5)···O(2)^c	3.382(11)	159.0(11)
C(17)–H(20)···Cl(1)^d	3.776(5)	167.2(10)
C(27)–H(26)···O(2)^e	3.305(12)	152.4(11)
C(203)–H(32)···Cl(1)^f	3.510(5)	155.7(10)

Symmetry code for **1**: $^a x, 1+y, z$. Symmetry code for **2**: $^b 1-x, -y, -z$. $^c 1-x, -y, 1-z$. $^d x, -1/2-y, 1/2+z$. $^e x, 1/2-y, -1/2+z$. $^f 1-x, 1/2+y, 1/2-z$.

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