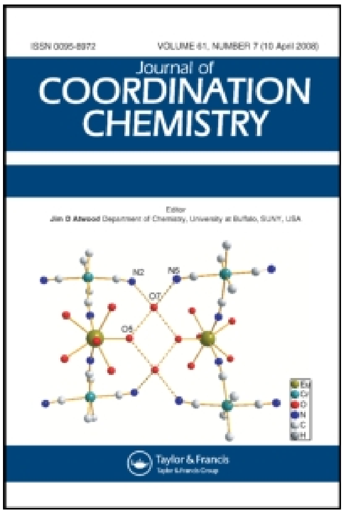

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Synthesis, crystal structure, and luminescence of a new coordination polymer, $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}$*_n*

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Synthesis, crystal structure, and luminescence of a new coordination polymer, $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}_n$

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A new cadmium coordination polymer based on imidazole-4,5-dicarboxylic acid (H_3IDC) and 4,4′-bipyridine (Bipy), $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}_n$, has been synthesized under solvothermal conditions and characterized by energy dispersive X-ray spectroscopy, elemental analysis, FT-IR spectroscopy, thermal analysis, and single crystal X-ray diffraction. It crystallizes in the orthorhombic system, space group *Pnnm* with $a = 20.530(2)$ Å, $b = 15.5957(14)$ Å, $c = 16.3846(15)$ Å, $\alpha = \beta = \gamma = 90^\circ$, $V = 5245.9(9)$ Å^3, and $Z = 2$. The complex exhibits a 3-D structure with channels along the *c*-axis, in which the free *N*,*N*-dimethylformamide and methyl-diethyl-amine molecules are located. The thermal behavior and luminescence of this complex have also been studied in the solid state.

Keywords: Cadmium; Carboxylate ligand; Coordination polymer; Solvothermal synthesis; Crystal structure

1. Introduction

Assembly of porous metal–organic frameworks (MOFs) has attracted much interest due to their structural diversity and promising applications for ion exchange, gas storage, separation, and catalysis. One of the most effective approaches to synthesize porous MOFs with unique structures and properties is the hydrothermal/solvothermal method by incorporating appropriate metal ions (connectors) with multifunctional bridging ligands (linkers). Imidazole-4,5-dicarboxylic acid (H_3IDC), a planar rigid ligand containing two nitrogens and four oxygens, has attracted much interest in coordination chemistry due to its different coordination modes. H_3IDC can be partially or fully deprotonated to generate H_2IDC^-, $HIDC^{2-}$, and IDC^{3-} at different pH values. Therefore, H_3IDC can potentially afford various coordination modes with metal ions to form a series of MOFs with different structures and useful properties [1–13]. MOFs containing polynuclear d^{10} metal ions exhibit intriguing photoluminescent

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properties [4, 11–15]. In this article, we report a new 3-D coordination polymer, $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}_n$, which is assembled from cadmium nitrate, imidazole-4,5-dicarboxylic acid, and 4,4′-bipyridine (Bipy) under solvothermal conditions.

2. Experimental

2.1. *Reagents and physical measurements*

All chemicals were obtained from commercial sources of analytical grade and used without purification. Elemental composition of the product was identified by energy dispersive X-ray spectroscopy (EDS) attached to a scanning electron microscope (Quanta 200, Philips-FEI). Elemental contents of carbon, hydrogen, and nitrogen were determined by a Vario EL III Analyzer (Analysensysteme GmbH). The IR spectrum of the complex was recorded on a Nicolet NEXUS 670 FT-IR spectrometer from 4000 to 400 $\mathrm{cm^{-1}}$ using a KBr pellet at room temperature. Thermogravimetric analysis (TGA) was performed on a SDT Q600 thermal analyzer under air with a heating rate of 10°C $\mathrm{min^{-1}}$. The fluorescence spectrum was measured with a PE LS55 fluorescence spectrophotometer at room temperature using a powdered crystal sample.

2.2. *Synthesis of the complex*

A mixture (pH = 6) of $Cd(NO_3)_2 \cdot 4H_2O$ (0.3085 g, 1.0 mmol), H_3IDC (0.4681 g, 3.0 mmol), Bipy (0.3604 g, 2.0 mmol), DMF (5.0 mL), and glacial acetic acid (2.5 mL, 99.95%) was sealed in a Teflon-lined (25 mL) stainless steel vessel and heated at 165°C for 6 days and then cooled to room temperature at a rate of 5°C $\mathrm{h^{-1}}$. Block-shaped crystals were collected, washed with distilled water, and dried in air. Anal. Calcd (%): C, 36.17; H, 2.72; N, 12.30. Found (%): C, 36.08; H, 2.79; N, 12.11.

2.3. *Single crystal X-ray diffraction analysis*

Single crystal X-ray diffraction analysis of the complex was carried out on a Bruker SMART APEX II CCD diffractometer with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) by using the φ/ω scan technique at room temperature. The structure was refined on F^2 by full-matrix least-squares using the SHELXL-97 program package [16]. Crystallographic data and selected bond lengths and angles for this complex are listed in tables 1 and 2.

3. Results and discussion

3.1. *Energy dispersive X-ray spectroscopy*

The EDS analysis (figure 1) indicates the presence of C, N, O, and Cd in the complex.

Table 1. Crystal data and structure refinement for the complex.

Empirical formula	$C_{96}H_{86}Cd_9N_{28}O_{34}$
Formula weight	3187.53
Temperature (K)	298(2)
Wavelength (Å)	0.71073
Crystal system, space group	Orthorhombic, *Pnnm*
Unit cell dimensions (Å, °)	
a	20.530(2)
b	15.5957(14)°
c	16.3846(15)
α	90
β	90
γ	90
Volume (Å^3), Z	5245.9(9), 2
Calculated density (g cm^{-3})	2.018
Absorption coefficient (mm^{-1})	1.885
$F(000)$	3124
Crystal size (mm^3)	$0.28 \times 0.15 \times 0.12$
θ range for data collection	1.59–25.01
Limiting indices	$-24 \le h \le 24$; $-18 \le k \le 13$; $-18 \le l \le 19$
Reflections collected/unique	21285/4798 [R(int) = 0.0425]
Completeness to $\theta = 25.01$ (%)	99.7
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.8054 and 0.6205
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4798/0/423
Goodness-of-fit on F^2	1.133
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0452$, $wR_2 = 0.1099$
R indices (all data)	$R_1 = 0.0724$, $wR_2 = 0.1365$
Largest difference peak and hole (e Å^{-3})	1.560 and −2.153

3.2. *FT-IR spectroscopy*

The FT-IR spectrum (Supplementary material) exhibits absorption bands assigned, referring to the literature [17, 18]. A strong and broad band at 3442 cm^{-1} is assigned to the stretching of O–H and N–H. The absence of the characteristic band at 1630 cm^{-1} for H–O–H bending shows that the complex does not contain water in its lattice. The band at 2875 cm^{-1} is due to stretching of $-CH_2-$. Peaks at 1575 and 1350 cm^{-1} correspond to the asymmetric and symmetric vibrations of carboxylate (COO^-), respectively. The difference between them being more than 200 cm^{-1} indicates that carboxylate is monodentate [18]. The peak at 1470 cm^{-1} is the stretching band of C–C. The peaks at 1120 and 1020 cm^{-1} are C–N stretches. The bands at 803 and 625 cm^{-1} are assigned to bending of Cd–O.

3.3. *Description of crystal structure*

The crystal structure of $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}_n$ consists of nine Cd(II) ions, four kinds of ligands ($HIDC^{2-}$, IDC^{3-}, monodentate Bipy, and bidentate Bipy), two free DMFs, and two $N(CH_3)(CH_2CH_3)_2$.

The nine Cd(II) ions have three different coordination modes as shown in figure 2. Cd(1) is six-coordinate with two oxygens (O3, O5) and two nitrogens (N1, N3) from individual chelating $HIDC^{2-}$ and IDC^{3-}, and two carboxyl oxygens (O3, O7) from individual monodentate $HIDC^{2-}$ and IDC^{3-}. Cd(2) is six-coordinate with one nitrogen

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

Cd(1)–O(7)	2.254(6)	Cd(1)–N(3)	2.257(7)
Cd(1)–N(1)	2.266(6)	Cd(1)–O(3)#1	2.278(5)
Cd(1)–O(5)	2.396(6)	Cd(1)–O(3)	2.510(6)
Cd(2)–O(5)#2	2.216(6)	Cd(2)–N(2)	2.248(7)
Cd(2)–N(4)	2.290(7)	Cd(2)–N(5)	2.348(7)
Cd(2)–O(7)#2	2.354(6)	Cd(2)–O(1)	2.479(6)
Cd(3)–O(8)#3	2.226(6)	Cd(3)–O(8)#1	2.226(6)
Cd(3)–O(8)	2.226(6)	Cd(3)–O(8)#4	2.226(6)
Cd(3)–N(6)#4	2.326(14)	Cd(3)–N(6)	2.326(14)
O(7)–Cd(1)–N(3)	138.2(2)		
O(7)–Cd(1)–N(1)	94.6(2)	N(3)–Cd(1)–N(1)	100.5(3)
O(7)–Cd(1)–O(3)#1	99.6(2)	N(3)–Cd(1)–O(3)#1	96.0(2)
N(1)–Cd(1)–O(3)#1	136.0(2)	O(7)–Cd(1)–O(5)	68.5(2)
N(3)–Cd(1)–O(5)	69.7(2)	N(1)–Cd(1)–O(5)	110.9(2)
O(3)#1–Cd(1)–O(5)	113.1(2)	O(7)–Cd(1)–O(3)	118.8(2)
N(3)–Cd(1)–O(3)	102.9(2)	N(1)–Cd(1)–O(3)	69.4(2)
O(3)#1–Cd(1)–O(3)	67.2(2)	O(5)–Cd(1)–O(3)	172.6(2)
O(5)#2–Cd(2)–N(2)	114.9(2)	O(5)#2–Cd(2)–N(4)	139.3(2)
N(2)–Cd(2)–N(4)	104.3(3)	O(5)#2–Cd(2)–N(5)	95.1(3)
N(2)–Cd(2)–N(5)	94.5(3)	N(4)–Cd(2)–N(5)	92.0(3)
O(5)#2–Cd(2)–O(7)#2	69.9(2)	N(2)–Cd(2)–O(7)#2	165.6(2)
N(4)–Cd(2)–O(7)#2	69.4(2)	N(5)–Cd(2)–O(7)#2	98.6(3)
O(5)#2–Cd(2)–O(1)	90.5(2)	N(2)–Cd(2)–O(1)	71.0(2)
N(4)–Cd(2)–O(1)	92.4(2)	N(5)–Cd(2)–O(1)	165.5(2)
O(7)#2–Cd(2)–O(1)	95.9(2)	O(8)#3–Cd(3)–O(8)#1	180.000
O(8)#3–Cd(3)–O(8)	85.3(3)	O(8)#1–Cd(3)–O(8)	94.7(3)
O(8)#3–Cd(3)–O(8)#4	94.7(3)	O(8)#1–Cd(3)–O(8)#4	85.3(3)
O(8)–Cd(3)–O(8)#4	180.000	O(8)#3–Cd(3)–N(6)#4	93.8(3)
O(8)#1–Cd(3)–N(6)#4	86.2(3)	O(8)–Cd(3)–N(6)#4	93.8(3)
O(8)#4–Cd(3)–N(6)#4	86.2(3)	O(8)#3–Cd(3)–N(6)	86.2(3)
O(8)#1–Cd(3)–N(6)	93.8(3)	O(8)–Cd(3)–N(6)	86.2(3)
O(8)#4–Cd(3)–N(6)	93.8(3)	N(6)#4–Cd(3)–N(6)	180.000

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

(N5) from Bipy, two oxygens (O1, O7) and two nitrogens (N2, N4) from chelating $HIDC^{2-}$ and IDC^{3-}, and one carboxyl oxygen (O5) from one monodentate IDC^{3-}. Cd(3) is coordinated with four oxygens (O8) from four carboxyl groups in two chelating IDC^{3-} and two nitrogens (N6) from two Bipy; the four oxygens are located in the equatorial plane and two nitrogens are axial. The Cd–O bond lengths are in the range 2.216–2.510 Å and Cd–N bond lengths are in the range 2.248–2.348 Å.

As shown in figure 3, the imidazole-4,5-dicarboxylic acid shows three different coordination modes, namely μ-4 IDC^{3-}, μ-3 $HIDC^{2-}$, and μ-5 IDC^{3-}, in which both μ-4 IDC^{3-} and μ-5 IDC^{3-} connect to Cd(II) in symmetrical coordinate modes, while the μ-3 $HIDC^{2-}$ links to Cd(II) in asymmetrical mode.

In the crystal, three Cd1 ions, three Cd2 ions, four imidazole-4,5-dicarboxylic acid ligands, and one Bipy ligand connect forming a 3-D structure with channels along the *c*-axis (figure 4). Moreover, the connectivity of Cd3 ions with imidazole-4,5-dicarboxylic acid ligands play an important role in the vertical development of the channel. The free *N*,*N*-dimethylformamide and methyl-diethyl-amine molecules are located in the channels.

$N(CH_3)(CH_2CH_3)_2$ was not added as source material and used materials did not contain this impurity either. On the basis that DMF can decompose at b.p. 153°C and

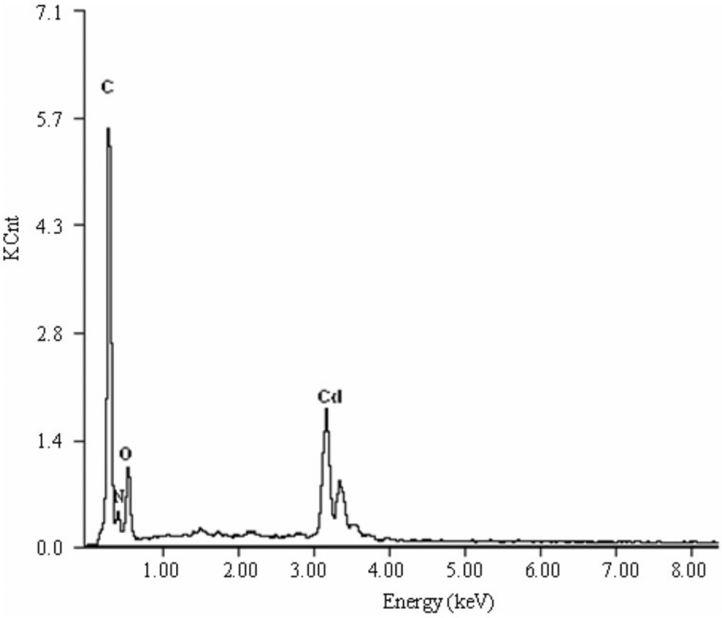

Figure 1. EDS of the complex.

acetic acid can react with amine forming ethylamine in the presence of a reductant [19], we propose the formation of $N(CH_3)(CH_2CH_3)_2$ under the present conditions as follows. First, DMF decomposes at the reaction temperature producing CO and $NH(CH_3)_2$. Then, the $NH(CH_3)_2$ might be oxidized by the existing little oxygen in the autoclave, forming nitrogen oxide, followed by the elimination of one methyl and oxygen as methanol, forming $NH_2(CH_3)$. Finally, acetic acid reacted with $NH_2(CH_3)$, forming $(CH_3CH_2)_2N(CH_3)$ in the presence of CO as a reductant.

Both the composition and structural features in the present complex are different from those in reported Cd(II) coordination polymers, imidazole-4,5-dicarboxylate complexes, and its analogues [1–13, 20–23]. For example, $\{[Cd(2\text{-}mBIM)_3](ClO_4)_2\}_n$ and $[Cd(BIM)_2(NO_3)_2]_n$ were prepared from the reaction of *bis*(2-methylimidazol-1-yl)methane(2-mBIM) with $Cd(ClO_4)_2$ and *bis*(imidazol-1-yl)methane (BIM) with $Cd(NO_3)_2$ in ethanol and water, respectively. Their structures featured a 32-membered M_4L_4 and 16-membered M_2L_2 macrometallacycle, respectively [20]. $[Cd(L_{-H})_2]_\infty$ and $[Cd(L_{-H})(NO_3)]_\infty$ ($L = C_{10}H_8N_2O_2$) were synthesized by the hydrothermal reactions of 4-(imidazole-1-yl)-benzoic acid and CdX_2. Their structures featured an infinite rhombic grid and an infinite zigzag chain, respectively [21]. $[Cd_2Cl_2(1,3\text{-}BDC)(TTBT)(H_2O)]$ and $[CdCl(1,4\text{-}HBDC)(TTBT)]$ (1,3-BDC = 1,3-benzenedicarboxylate, 1,4-BDC = 1,4-benzenedicarboxylate and TTBT = 10,11,12,13-tetrahydro-4,5,9,14-tetraaza-benzo[b]triphenylene) possessed helical chain structures [22]. $[M(HIMDC)(4,4'\text{-}bipyO)_{0.5}(H_2O)]_n$ [H_3IMDC = 4,5-imidazoledicarboxylate, 4,4′-bipyO = 4,4′-bipyridine-*N*,*N*′-dioxide, M = Co and Zn] had infinite 2-D herringbone architectures [23]. The title compound exhibits a 3-D structure with channels along the *c*-axis. The main feature of this complex is that there are five kinds of species, μ-4 IDC^{3-}, μ-3 $HIDC^{2-}$, μ-5 IDC^{3-}, monodentate Bipy, and bidentate Bipy, coexisting in one compound.

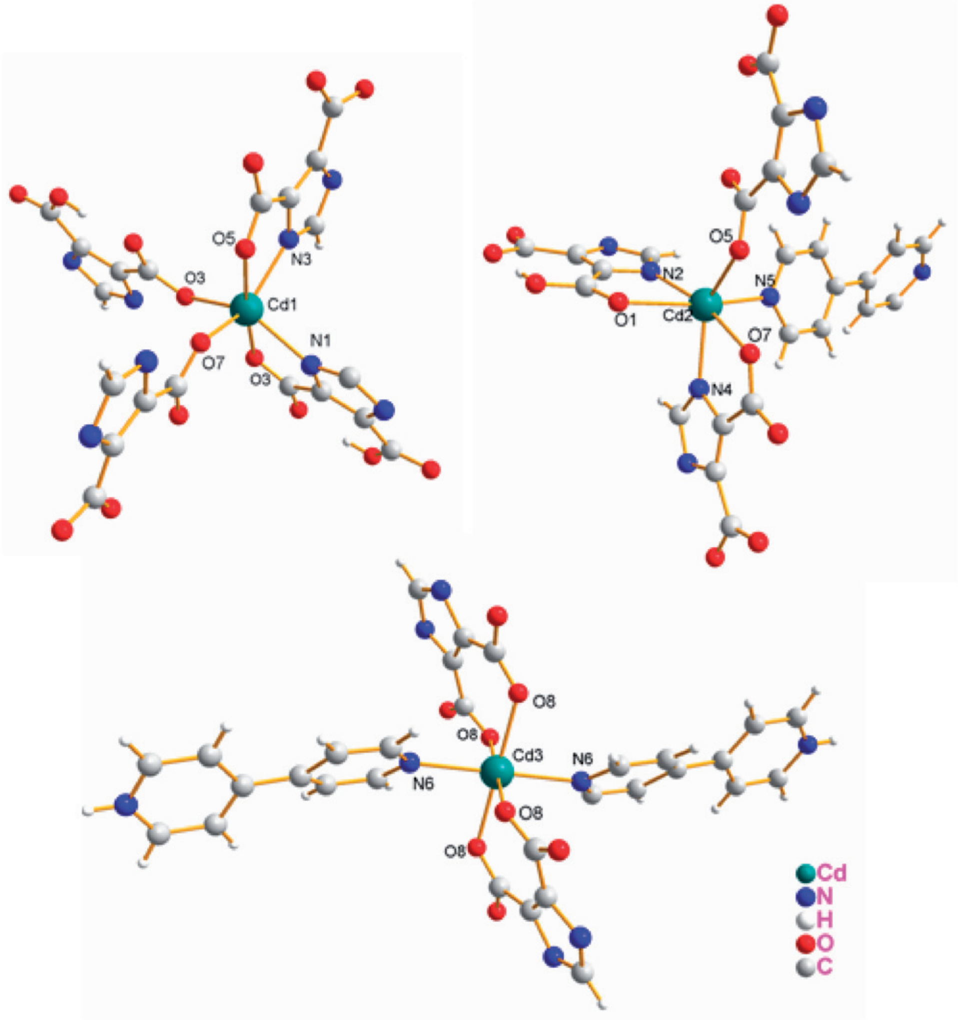

Figure 2. The various coordination modes of Cd(II).

The structural differences can be attributed to the different ligands used and different synthetic conditions.

3.4. *Thermal behavior*

To evaluate the thermal stability of this complex, its TGA has been performed (Supplementary material). There is no significant mass loss up to 275°C, and then one step of rapid mass loss between 275 and 610°C corresponding to the decomposition of the complex. The total mass loss is 68.54%, which might correspond to the loss of all the organic components and can be compared with the calculated value of 68.26%. The resulting residue should be CdO because the TGA was performed under air. The higher

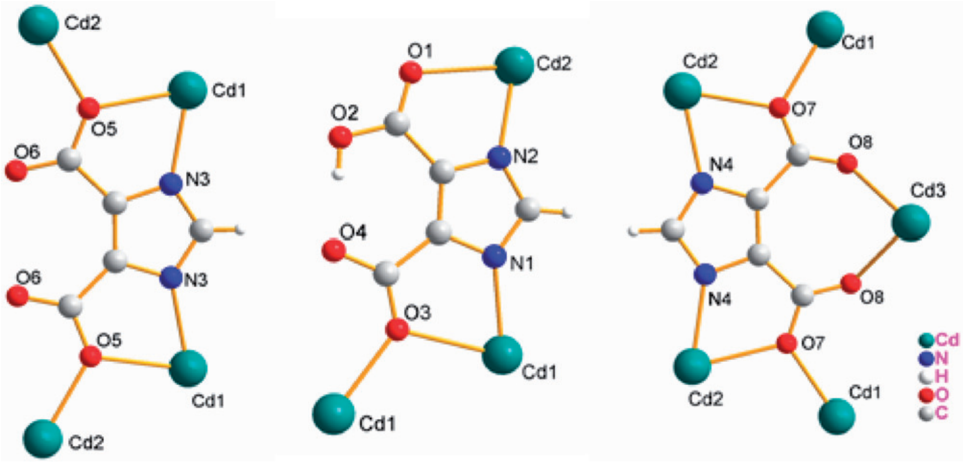

Figure 3. The various coordination modes of $HIDC^{2-}$ and IDC^{3-} in the complex.

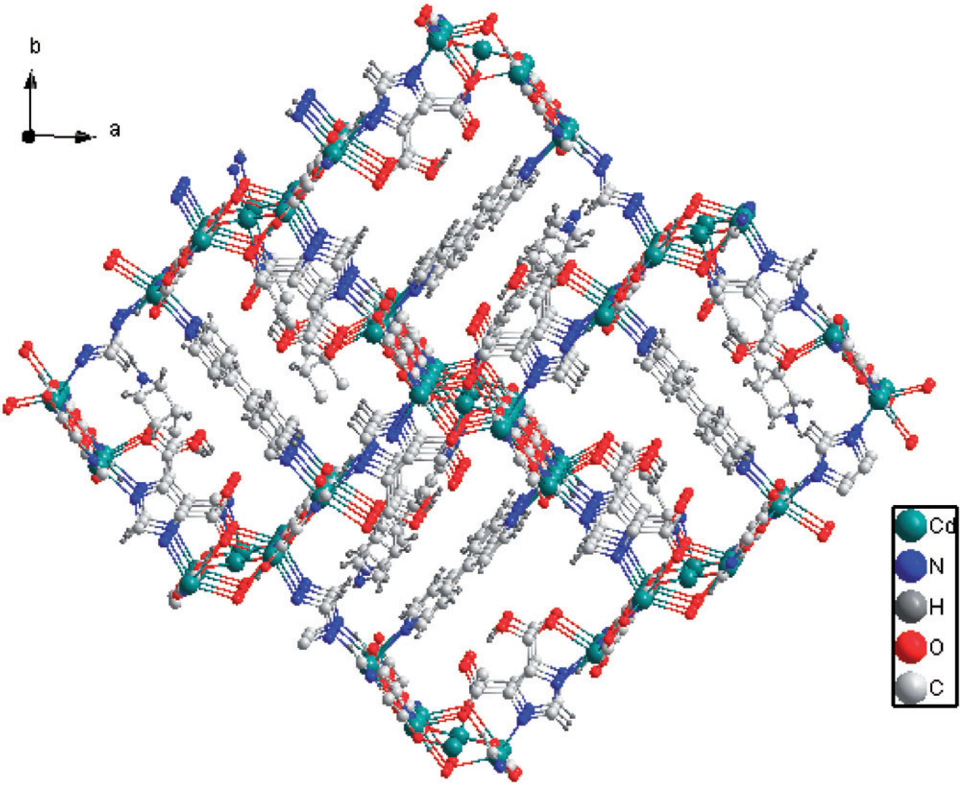

Figure 4. A view of the 3-D structure of the complex along the *c*-axis. Free DMF and $N(CH_3)(CH_2CH_3)_2$ molecules are omitted for clarity.

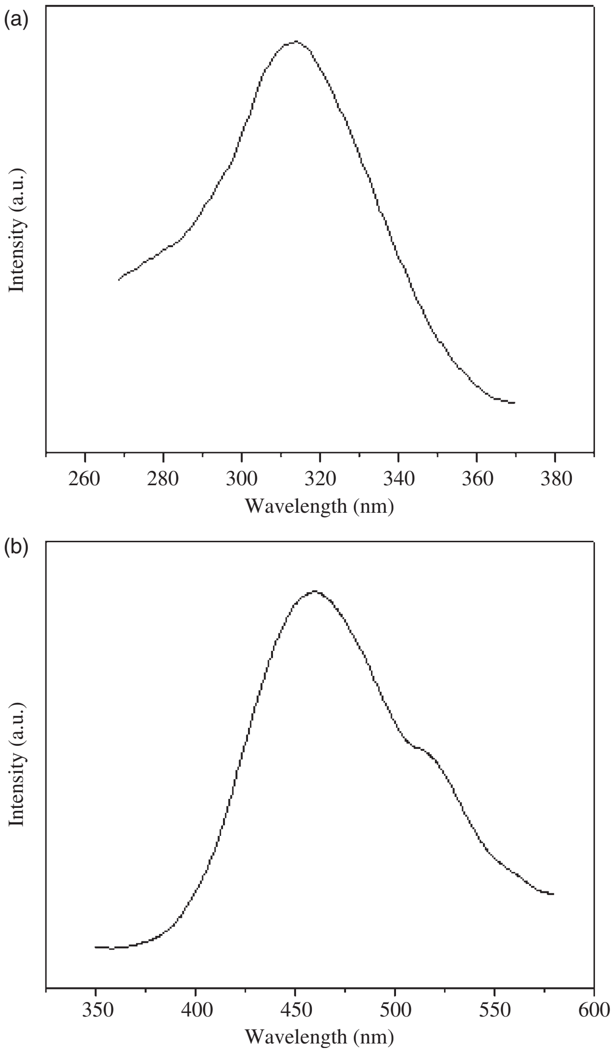

Figure 5. Solid-state excitation (a) and emission (b) spectra.

decomposition temperature indicates that the framework of this complex possesses good thermal stability.

3.5. *Luminescent property*

Previous studies have shown that coordination polymers containing zinc and cadmium ions exhibit photoluminescence [4, 11–15]. Herein, we investigated the luminescence of this complex in the solid state at room temperature. As shown in figure 5, upon excitation of the solid sample at 318 nm, it exhibited a strong fluorescent emission band at 461 nm. For excitation wavelengths between 280 and 480 nm, there is no obvious emission observed for free H_3IDC under the same experimental conditions, while free Bipy presents weak photoluminescence emission at 486 nm [4]. The fluorescence emission of this complex may arise from the coordination of $HIDC^{2-}$, IDC^{3-} to the Cd(II), namely, the ligand to metal charge transfer (LMCT) [24, 25].

4. Conclusions

A new cadmium coordination polymer, $\{[Cd_9(IDC)_2(HIDC)_6(Bipy)_4] \cdot 2N(CH_3)(CH_2CH_3)_2 \cdot 2DMF\}_n$, has been solvothermally synthesized by the reaction of cadmium nitrate with imidazole-4,5-dicarboxylic acid and 4,4′-bipyridine. It exhibits a 3-D structure with channels along the *c*-axis, in which DMF and the formed $N(CH_3)(CH_2CH_3)_2$ by *in situ* reactions are located. This complex is stable up to 275°C and presents intense fluorescence emission.

Supplementary material

CCDC-702337 contains the supplementary crystallographic data for this article. These data can be obtained free of charge at www.ccdc.cam.ac.uk [or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; Fax: +44(0)1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

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