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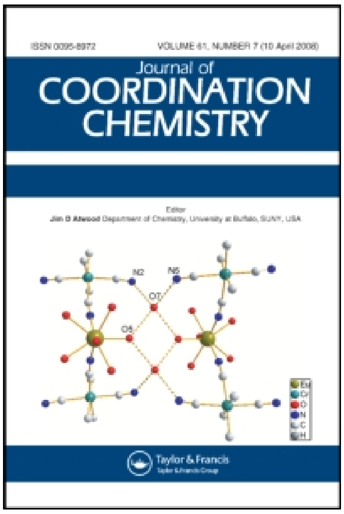

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Crystal structures and fluorescent properties of the first 2d and 3d cadmium(II) pyromellitate coordination polymers

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CRYSTAL STRUCTURES AND FLUORESCENT PROPERTIES OF THE FIRST 2D AND 3D CADMIUM(II) PYROMELLITATE COORDINATION POLYMERS

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Two novel cadmium polymeric complexes, $[Cd_2(btec)\cdot 6H_2O]_n$ (**1**), and $[Cd_2(btec)]_n$ (**2**) (H_4btec = 1,2,4,5-benzenetetracarboxylic acid), were obtained by assembly of $Cd(NO_3)_2\cdot 4H_2O$ and $Cd(OH)_2$ with H_4btec at different pH values and characterized by elemental analysis, IR spectra, X-ray single-crystal diffraction, TGA and fluorescent spectra. Complex **1** crystallizes in the triclinic system with space group $P\bar{1}$, $a = 5.595(1)$, $b = 7.770(2)$, $c = 9.685(2)$ Å, $\alpha = 111.93(2)$, $\beta = 101.78(2)$, $\gamma = 98.28(2)°$ and complex **2** crystallizes in the monoclinic system with space group $C2/m$, $a = 6.588(2)$, $b = 18.038(5)$, $c = 4.728(2)$ Å, $\beta = 116.49(1)°$. Complex **1** contains a novel step-like 2D layered network and complex **2** possesses a 3D pillared-layered structure. These two complexes exhibit strong fluorescent emission bands at 363.5 and 486.5 nm ($\lambda_{ex} = 215$ nm) for complex **1**, 386.5 nm ($\lambda_{ex} = 335$ nm) for complex **2** in the solid state at room temperature.

Keywords: Hydrothermal synthesis; Crystal structure; 1,2,4,5-Benzenetetracarboxylate; Cadmium complexes

INTRODUCTION

There has been an increasing interest in the coordination chemistry of cadmium in recent years due to the increased recognition of its role in biological organisms [1], as well as in molecular-based materials [2,3]. In the quest for molecular-based materials with interesting properties, much attention has been focused on one-, two- and three-dimensional coordination polymers of cadmium [4–6].

In preparing coordination polymers of cadmium, organic aromatic polycarboxylate ligands including 1,3,5-benzenetricarboxylic acid and 1,4-benzenedicarboxylic acid [7–10] have been frequently employed as multidentate O-donor ligands. In contrast, there have been few attempts to prepare metal–organic polymers of cadmium based on btec. To our knowledge, only two coordination polymers of cadmium and btec

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have been reported, $[Cd_4(btec)_2(phen)_4\text{-}(H_2O)_4]_n$ with an infinite 1D double-chain structure [11] and $[Cd_4(btec)_2\text{-}(piperazine)_3(H_2O)_2]_n$ with a 3D structure [12]. On the other hand, it is well known that the btec ligand contains multiple bridging moieties, which lead to a variety of connection modes with transition metal centers and provide abundant structural motifs. A series of interesting multi-dimensional polymers have been obtained by employing btec [13–20]. With the exception of a few reports [13–17], applications are largely unexplored. Our aim is to synthesize novel high-dimensional coordination polymers with cadmium and btec. We have been investigating coordination polymers introduced by different coordination architectures, and wish to prepare materials with excellent photoactivity. In this article, we report the first 2D and 3D cadmium pyromellitate coordination polymers, $[Cd_2(btec) \cdot 6H_2O]_n$ (**1**), and $[Cd_2(btec)]_n$ (**2**), which display strong fluorescent emissions and are based on different coordination architectures.

EXPERIMENTAL

Synthesis

Preparation of $[Cd_2(btec) \cdot 6H_2O]_n$ *(1)*

$Cd(NO_3)_2 \cdot 4H_2O$ (0.308 g, 1 mmol), 1,2,4,5-benzenetetracarboxylic dianhydride (0.218 g, 1 mmol), $NH_3 \cdot H_2O$ ($0.02\,cm^3$) and H_2O ($15\,cm^3$) were sealed in a Teflon-lined stainless-steel reactor (solution $pH = 3.5$). The mixture was heated at 160°C for six days and white plate-like crystals were obtained after the mixture was cooled to room temperature.

Yield 57%. Anal. Calcd. for $C_{10}H_{14}Cd_2O_{14}$(%): C, 20.6; H, 2.4. Found: C, 20.3; H, 2.2.

IR: ν_{as} (COO) 1558, ν_s (COO) 1439, (C–C, phenyl ring) 1385.

Preparation of $[Cd_2(btec)]_n$ *(2)*

A mixture of $Cd(OH)_2$ (0.146 g, 1 mmol), 1,2,4,5-benzenetetracarboxylic dianhydride (0.218 g, 1 mmol), $NH_3 \cdot H_2O$ ($0.1\,cm^3$) and H_2O ($15\,cm^3$) was heated in a Teflon-lined stainless-steel reactor (solution $pH = 8.5$) at 160°C for six days and yellow prism-like crystals were formed after the mixture was cooled to room temperature.

Yield 64%. Anal. Calcd. for $C_{10}H_2Cd_2O_8$(%): C, 25.3; H, 0.4. Found: C, 24.9; H, 0.52.

IR: ν_{as} (COO) 1560, ν_s (COO) 1488, (C–C, phenyl ring) 1390.

Physical Measurements

The elementary analyses were performed on a Vario EL III CHNOS elemental analyzer. IR spectra were measured as KBr pellets on an ABB Bomen MB-Series spectrophotometer in the range $400\text{–}4000\,cm^{-1}$. Thermogravimetric data were collected on a Mettler Toledo TGA/SDTA 851^e analyzer in flowing nitrogen at a heating rate of 10°C/min. Fluorescence measurements were made with an Edinburgh Instrument FL-FS920 TCSPC luminescence spectrometer on powdered crystalline material of **1** and **2**.

X-ray Data Collection and Structure Refinement

A white plate-like crystal ($0.18 \times 0.14 \times 0.12$ mm) of complex **1** and a yellow prism crystal ($0.30 \times 0.20 \times 0.04$ mm) of complex **2** were mounted on a Siemens Smart CCD diffractometer and used for data collection. Diffraction data were collected at room temperature using graphite-monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) in the range $4.72 < 2\theta < 50.16°$ for **1** and $4.52 < 2\theta < 50.04°$ for **2** with the ω and φ scan method. A total of 1304 and 465 reflections were measured for compounds **1** and **2**, of which 1173 and 423 reflections with $I > 2\sigma(I)$, were used to refine the structures, respectively. Lorentz-polarization and Ψ-scan absorption corrections were applied to the intensity data. The structures were solved by direct methods and refined by the full-matrix least-squares method on F^2 using the SHELXTL-97 program package [24]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located in a difference Fourier map and their positions and isotropic displacement parameters were refined. The atomic coordinates and equivalent thermal parameters of all non-hydrogen atoms are given in Tables I and II. Selected bond lengths and bond angles are listed in Table III.

Crystal Data

For compound **1**, $C_{10}H_{14}Cd_2O_{14}$, $M = 583.01$, triclinic, space group $P\bar{1}$, $a = 5.595(1)$, $b = 7.770(2)$, $c = 9.685(2)$ Å, $\alpha = 111.93(2)$, $\beta = 101.78(2)$, $\gamma = 98.28(2)°$, $V = 370.9(1)$ Å^3,

TABLE I Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) of compound **1**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cd(1)	4623(1)	9267(1)	1585(1)	17(1)
C(1)	2892(14)	12265(10)	3730(8)	15(2)
C(2)	1399(14)	13706(10)	4372(9)	16(2)
C(3)	1932(14)	14712(10)	5974(8)	15(2)
C(4)	−558(13)	13984(10)	3395(8)	12(1)
C(5)	−1313(14)	12996(10)	1637(8)	14(2)
O(1)	4177(10)	11725(8)	4636(6)	23(1)
O(2)	2748(10)	11695(8)	2311(6)	22(1)
O(3)	−624(10)	13926(7)	922(6)	21(1)
O(4)	−2713(9)	11302(7)	959(6)	15(1)
O(2W)	8032(12)	9432(9)	3430(7)	27(1)
O(1W)	6337(14)	6800(12)	77(11)	40(2)
O(3W)	2200(13)	7592(9)	2592(8)	26(1)

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters (Å $\times 10^3$) of compound **2**

Atom	*x/a*	*y/b*	*z/c*	U_{eq}
Cd(1)	0	7086(1)	5000	14(1)
C(1)	−2930(12)	6350(4)	8380(18)	10(2)
C(2)	−4099(13)	5674(4)	6532(18)	12(2)
C(3)	−3252(19)	5000	7970(30)	14(2)
O(1)	−2651(10)	6927(3)	7000(14)	16(1)
O(2)	−2142(10)	6301(4)	1347(13)	20(1)

TABLE III Selected bond lengths (Å) and angles (°) for compounds **1** and **2**

Compound **1**[a]			
Cd(1)–O(2)	2.244(5)	Cd(1)–O(3)$_{W}$	2.337(6)
Cd(1)–O(2)$_{W}$	2.283(6)	Cd(1)–O(4b)	2.345(5)
Cd(1)–O(4a)	2.320(5)	Cd(1)–O(1)$_{W}$	2.395(7)
O(2)–Cd(1)–O(2)$_{W}$	115.2(2)	O(2W)–Cd(1)–O(4b)	88.2(2)
O(2)–Cd(1)–(4a)	87.18(18)	O(4a)–Cd(1)–O(4b)	73.84(19)
O(2)–Cd(1)–O(3)$_{W}$	91.3(2)	O(2)$_{W}$–Cd(1)–O(1)$_{W}$	78.9(3)
O(2)$_{W}$–Cd(1)–(3)$_{W}$	86.7(2)	O(4a)–Cd(1)–O(1)$_{W}$	76.0(3)
O(4a)–Cd(1)–(3)$_{W}$	113.6(2)	O(3)$_{W}$–Cd(1)–O(1)$_{W}$	100.6(3)
O(2)–Cd(1)–O(4b)	84.57(19)	O(4b)–Cd(1)–O(1)$_{W}$	85.2(3)
Compound **2**[b]			
Cd(1)–O(2a)	2.192(6)	Cd(1)–O(1)	2.345(6)
Cd(1)–O(1c)	2.271(6)		
O(2a)–Cd(1)–O(2b)	99.5(3)	O(1c)–Cd(1)–O(1)	114.8(2)
O(2a)–Cd(1)–O(1d)	95.7(2)	O(1d)–Cd(1)–O(1)	76.8(2)
O(1d)–Cd(1)–O(1c)	76.7(3)	O(2b)–Cd(1)–O(1e)	84.6(2)
O(2b)–Cd(1)–O(1)	86.4(2)		

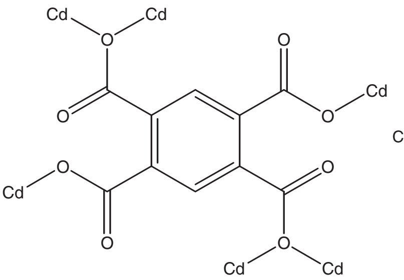
[a] Symmetry code for **1**: (a) $= -x, -y+2, -z$; (b) $= x+1, y, z$.

[b] Symmetry code for **2**: (a) $= x, y, z-1$; (b) $= -x, y, -z+2$; (c) $= x+1/2, -y+3/2, z$; (d) $= -x-1/2, -y+3/2, -z+1$; (e) $= -x, y, -z+1$.

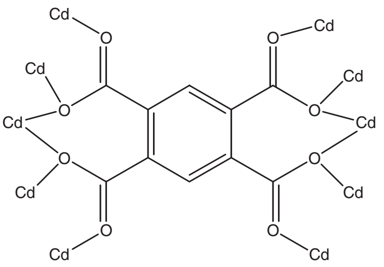
$Z = 1$, $F(000) = 282$, $D_x = 2.61\,\mathrm{Mg\,m^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 29.29\,\mathrm{mm^{-1}}$, the final $R_1 = 0.0412$, $wR_2 = 0.0945$ with 147 parameters, $S = 1.082$, $(\Delta/\sigma)_{\max} = 0.000$, largest difference peak and hole: 1.128 and $-1.168\,\mathrm{e\,Å^3}$. For compound **2**, $C_{10}H_2Cd_2O_8$, $M = 474.92$, monoclinic, space group $C2/m$, $a = 6.588(2)$, $b = 18.038(5)$, $c = 4.728(2)$ Å, $\beta = 116.49(1)°$, $V = 502.9(3)$ Å^3, $Z = 2$, $F(000) = 444$, $D_x = 3.14\,\mathrm{Mg\,m^{-3}}$, $\mu(\mathrm{Mo\,K\alpha}) = 42.70\,\mathrm{mm^{-1}}$, final $R_1 = 0.0450$, $wR_2 = 0.1097$, $S = 1.089$, $(\Delta/\sigma)_{\max} = 0.001$, largest difference peak and hole: 1.304 and $-1.624\,\mathrm{e\,Å^3}$.

RESULTS AND DISCUSSION

Structure 1



A



B

Complex **1** exhibits an interesting 2D layered network. The central cadmium ion is coordinated by three oxygen atoms from three different btec ligands and three coordinated water molecules with an average Cd–O$_{\mathrm{btec}}$ distance of 2.303(5) Å and

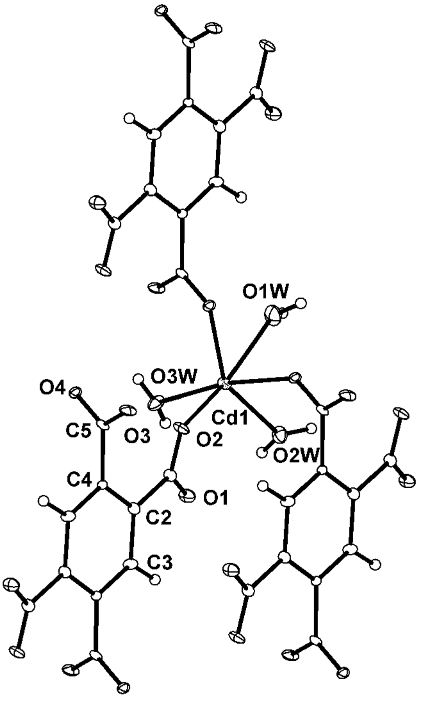


FIGURE 1 ORTEP plot with atom numbering scheme of complex **1**, showing the local coordination environment of Cd(II).

Cd–O_w of 2.338(9) Å in a distorted octahedral geometry. The coordination environment of the central cadmium ion is shown in Fig. 1. The bond angles O–Cd–O range from 73.84(19) to 91.3(2)°. Four carboxylate groups of the btec ligand exhibit two kinds of coordination modes as shown in Scheme A. Each of two *para*-carboxylate groups adopts a monodentate mode, coordinating to one cadmium atom whereas each of the other two *para*-carboxylate groups exhibits a chelating-bridging mode linking two cadmium atoms. Thus, btec acts as μ_6-bridge linking six cadmium atoms. Two bridging hydroxyl oxygen atoms from two btec ligands bridge two Cd^{2+} ions to form a binuclear unit that can be viewed as the basic structural building block. The binuclear Cd(II) units are linked by the carboxylate groups in btec, producing a step-like 2D layered structure along the *b* axis (Fig. 2).

The layer grids consist of two kinds of holes (Fig. 2, **I** and **II**): one is a 14-atom-ring hole containing two metal atoms and two btec units whose *ortho*-carboxylate groups are coordinated to the two metal atoms (**I**), and the other is a 16-atom-ring hole, around which are two Cd^{2+} centers and two btec units whose *meta*-carboxylate groups chelate the two Cd^{2+} centers (**II**). In the packing arrangement of **1**, the adjacent 2D step-like layers are parallel with each other and construct a 3D framework via O_w–H···O hydrogen bonds between the free carboxylate of the btec and water molecules.

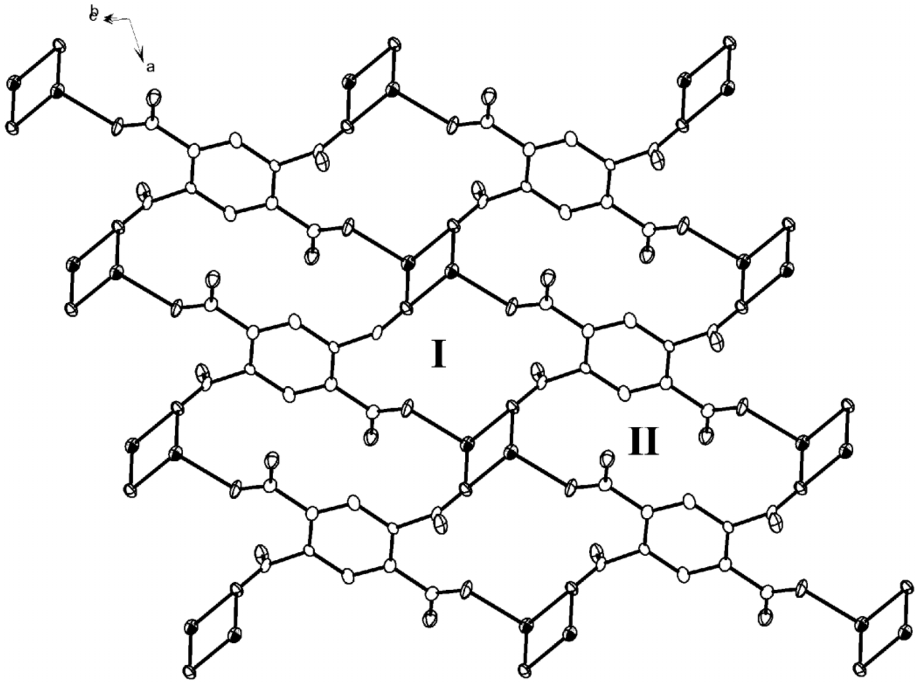


FIGURE 2 The 2D layer of **1** along the *b* axis. Water molecules are omitted for clarity.

Structure 2

Complex **2** possesses a 3D framework structure. All carboxylate groups of the organic ligand are deprotonated; four carboxylate groups of btec are engaged in coordination to metals (Scheme B). This coordination mode is rare in 1,2,4,5-benzenetetracarboxylic-based coordination polymeric complexes for steric reasons [15]. Each carboxylate group adopts the same chelating mode, and the whole ligand connects ten cadmium atoms by 12 coordinate bonds. The cadmium is located on a twofold axis. Three pairs of O atoms from five btec ligands are related by the twofold axis (Fig. 3). The octahedron around Cd^{2+} is slightly distorted, with Cd–O bond lengths in the range 2.192(6)–2.345(6) Å and O–Cd–O bond angles between 76.7(3) and 114.8(2)°. The btec anions are also located in special positions, with two non-substituted ring C atoms [C(3) and C(3d), $(d) = -1 - x, y, 1 - z$] in the mirror plane, and the C(2)–C(2d) bond bisected by the twofold axis. As a consequence, the benzene ring is perfectly planar.

The 3D structure of **2** is made up of 2D Cd–O layers cross-linked by the btec ligands (Fig. 4a). In the structure of **2**, two Cd–O octahedra related by an inversion center are joined through their edges, forming a repeating Cd_2O_{10} binuclear Cd(II) building unit. These edge-sharing binuclear Cd_2O_{10} units further connect to form 1D zigzag chains (Fig. 4b). The adjacent zigzag chains are linked by O–C–O bridges to form a 2D layered structure parallel to the *ac* plane (Fig. 4b). The 2D layers are connected by the benzene rings of 1,2,4,5-benzenetetracarboxylates to give rise to the 3D framework structure (Fig. 4a).

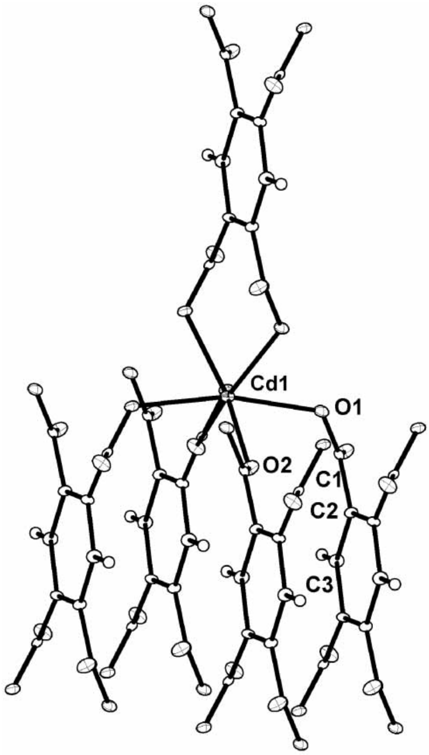


FIGURE 3 ORTEP plot with atom numbering scheme of complex **2**, showing the local coordination environment of Cd(II).

Thermal Properties of 1 and 2

TGA analyses have been performed on the two complexes. For **1**, there is three-step mass loss between 40 and 700°C. The first loss of 7.52% between 80 and 120°C corresponds to the loss of *ca.* 2.5 water molecules per formula (calc. 7.72%). Above 120°C, the compound shows no mass loss until it reaches 220°C, and the second loss of 11.24% in the range 220–300°C corresponds to the residual 3.5 coordinated water molecules per formula unit (calc. 10.81%). Above 300°C, complex **1** starts to decompose and the decomposition ends at 550°C, the third loss of 56.56% being due to the loss of the organic species (calc. 37.39%) and the slow evaporation of *ca.* 0.87 CdO per formula (calc. 19.16%) [22].

Complex **2** has high thermal stability, being stable up to 340°C because it contains no free or coordinated water molecules. It begins to decompose at 340°C and from 340 to 800°C a large mass loss of 87.45% corresponds to the removal of the organic species (calc. 45.9%) and the slow evaporation of *ca.* 0.77 CdO per formula (calc. 41.55%) [22].

Fluorescent Properties

The emission spectra of complexes **1** and **2** in the solid state at room temperature are shown in Fig. 5. Of particular interest is the fluorescence spectrum of powdered **1**, which shows a strong emission peak at 363.5 nm (λ_{ex} = 215 nm) that can be assigned

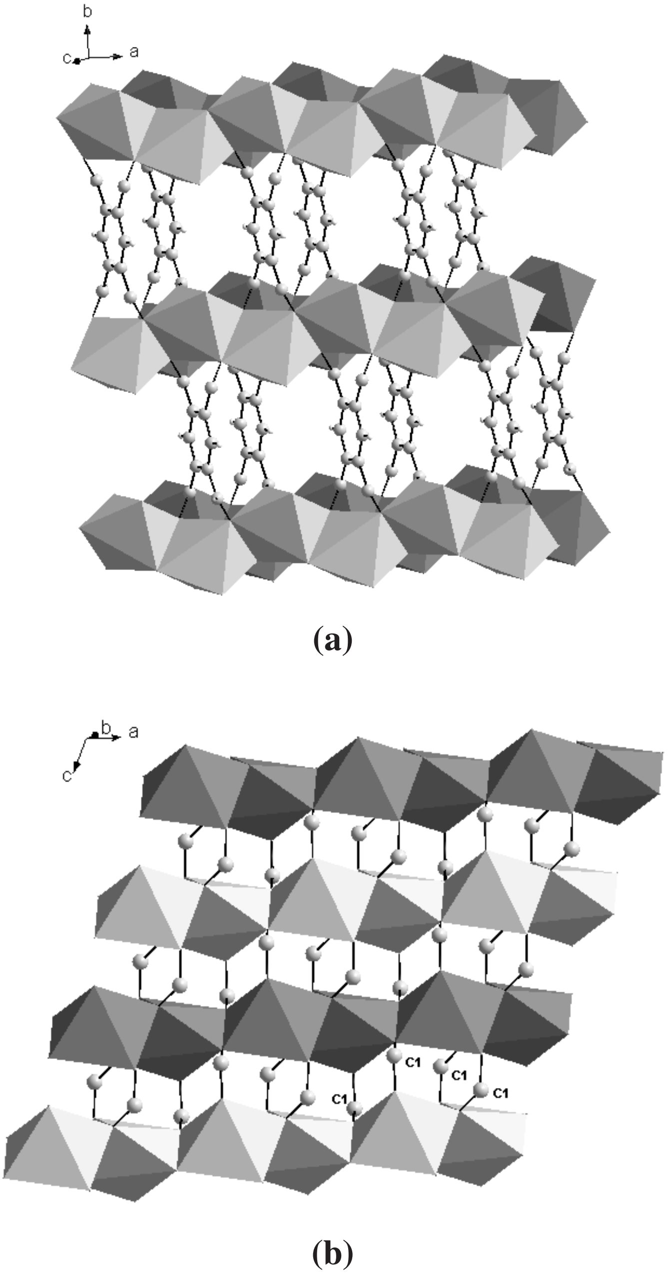
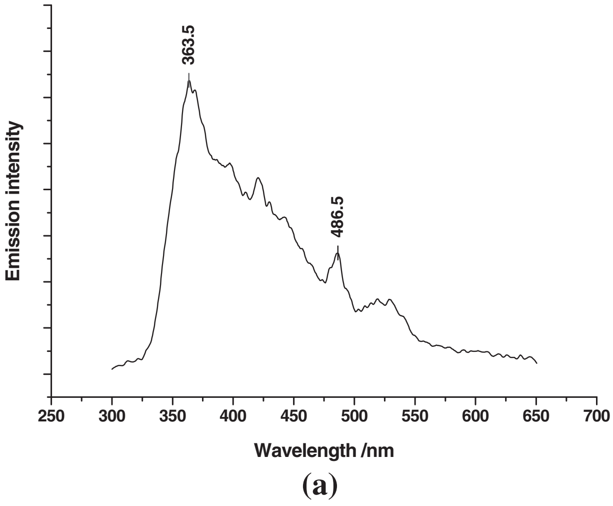


FIGURE 4 Polyhedral representations: (a) the 3D pillared-layered structure of **2**; (b) the 2D layer structure for **2**.

to the ligand-to-metal charge-transfer (LMCT) band. A relatively weak peak at 486.5 nm is also observed for **1**. Similar luminescence spectra were observed previously and the weak peak has been tentatively assigned to phosphorescence in a Cd(II) coordination polymer [23]. Complex **2** has an intense emission at 386.5 nm ($\lambda_{ex} = 335$ nm)



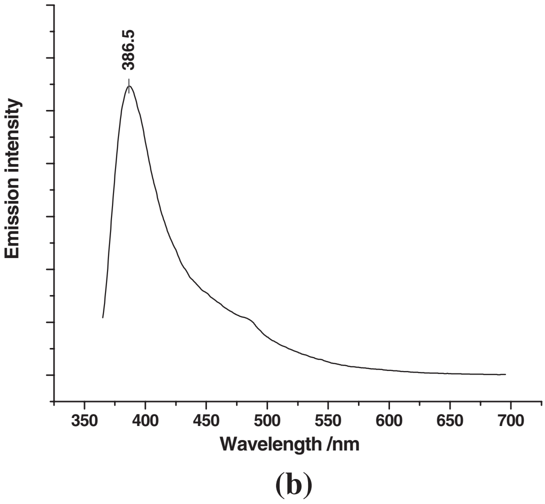


FIGURE 5 Solid-state emission spectra of complexes **1** (a) and **2** (b) at room temperature.

assigned to the LMCT band (Fig. 5). Complex **2** may be found applications in blue-light-emitting devices, since it is thermally stable (up to 340°C) and insoluble in common polar and non-polar solvents.

Acknowledgments

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Supplementary data

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC-214511 (**1**) and -214512 (**2**). Copies may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or via http://www.ccdc.cam.ac.uk).

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