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**CADMIUM(II) COMPLEX WITH (1'H-[2,2']BIIMIDAZOLY-1-YL)-ACETIC ACID:  
SYNTHESIS, CRYSTAL STRUCTURE, AND LUMINESCENCE****J. Wang, J.-Q. Tao, X.-J. Xu, C.-Y. Tan**

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A new cadmium(II) complex with (1'H-[2,2']biimidazoly-1-yl)-acetic acid (HBDAC)  $[\text{Cd}(\text{BDAC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  is synthesized and structurally characterized, which crystallizes in the monoclinic system, space group  $P2_1/c$ ,  $a = 8.465(3) \text{ \AA}$ ,  $b = 14.164(5) \text{ \AA}$ ,  $c = 11.294(3) \text{ \AA}$ ,  $\alpha = 90^\circ$ ,  $\beta = 127.405(17)^\circ$ ,  $\gamma = 90^\circ$ ,  $Z = 2$ . The  $[\text{Cd}(\text{BDAC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$  units are further bridged by O—H $\cdots$ O, N—H $\cdots$ O, C—H $\cdots$ O hydrogen bonds,  $\pi$ — $\pi$  stacking and C—O $\cdots$  $\pi$  interactions, generating a three-dimensional supramolecular structure. In addition, luminescence measurements reveal that complex **1** exhibits strong fluorescent emission in the solid state at room temperature.

**Keywords:** Cd(II) complex, crystal structure, hydrogen bonding, C—O $\cdots$  $\pi$  interaction, photoluminescence.

**INTRODUCTION**

Considerable interest has been devoted to the development of the design, synthesis, and characterization of metal organic framework materials with luminescent properties because of their potential applications in chemical sensors, photochemistry, and electroluminescent display [1–3]. In particular, the coordination complexes of cadmium(II) are being studied [4–6]. The most effective and facile approach to coordination polymers is to utilize multi-pyridine and dicarboxylate ligands to link metal ions [7–9]. Among them, all kinds of imidazole and their derivatives have been extensively used in the synthesis of a metal organic framework (MOF) because of their diversified coordination modes and flexibility [10–13]. However, relatively less attention has been paid to a new imidazole derivative ligand: (1'H-[2,2']biimidazoly-1-yl)-acetic acid. Here, we select (1'H-[2,2']biimidazoly-1-yl)-acetic acid (HBDAC), generating a new Cd(II) coordination complex  $[\text{Cd}(\text{BDAC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ .

**EXPERIMENTAL**

The HBDAC ligand was synthesized following the published procedure [14]. All other reagents and solvents were commercially available and used without further purification. The IR spectra were obtained within the 400–4000  $\text{cm}^{-1}$  as KBr disks on a VECTOR 22 spectrometer. Elemental analysis was performed on a Perkin Elmer 240C elemental analyzer. An emission spectrum was recorded on a Hitachi F-4500 fluorescence spectrophotometer, using a 5 nm slit width and excitation at room temperature for the solid samples.

**Synthesis of  $[\text{Cd}(\text{BDAC})_2(\text{H}_2\text{O})_2] \cdot \text{H}_2\text{O}$ .** A mixture of  $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  (0.0346 g, 0.1 mmol), HBDAC (0.0192 g, 0.1 mmol), NaOH (0.008 g, 0.2 mmol) in  $\text{H}_2\text{O}$  (10 ml) was sealed in a 16 ml Teflon-lined stainless steel container and heated at 90 °C for 72 h. After cooling to room temperature,

Table 1

## Crystal data and structure refinement for complex 1

	1		1
Empirical formula	C <sub>16</sub> H <sub>20</sub> CdN <sub>8</sub> O <sub>7</sub>	$\rho_{\text{calcd}}$ , g/cm <sup>3</sup>	1.694
Formula weight	548.80	$\mu(\text{MoK}\alpha)$ , mm <sup>-1</sup>	1.071
Crystal system	Monoclinic	Crystal size, mm	0.28×0.24×0.22
Space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	$\theta$ range, deg.	2.69—25.99
<i>a</i> , <i>b</i> , <i>c</i> , Å	8.465(3), 14.164(5), 11.294(3)	<i>F</i> (000)	552
$\beta$ , deg.	127.405(17)	$R_1^a$ [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0422
<i>V</i> , Å <sup>3</sup>	1075.7(6)	$wR_2^b$ [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.1021
<i>Z</i>	2	GOOF	1.084

white block crystals were collected by filtration and washed by water and ethanol several times. (yield 42.9 %, based on HBDAC). Elemental analysis for C<sub>16</sub>H<sub>20</sub>CdN<sub>8</sub>O<sub>7</sub> (*M*<sub>w</sub> = 548.80): C, 35.02; H, 3.67; N, 20.42; found: C, 35.10; H, 3.69; N, 20.48 %. Selected IR peaks (cm<sup>-1</sup>): 3412 (m), 1643 (s), 1481 (s), 1275 (s), 849 (w), 788 (w), 733 (w).

**X-ray crystallography.** The crystal structure was determined on a Siemens (Bruker) SMART CCD diffractometer using monochromated MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 291 K. All absorption correction was performed using the SADABS program [15]. The structure was solved by a direct method using the SHELXL-97 program [16] and refined by the full-matrix least-squares technique on *F*<sup>2</sup> with SHELXL-97. All non-hydrogen atoms were located in difference Fourier maps and refined anisotropically. All H atoms were refined isotropically, with the isotropic vibration parameters related to the non-H atom to which they are bonded. Crystal data collection and refinement parameters are given in Table 1.

## RESULTS AND DISCUSSION

Single crystal X-ray diffraction revealed that complex 1 crystallized in the monoclinic space group *P*2<sub>1</sub>/*c* with an asymmetric unit consisting of a cadmium atom on the crystallographic inversion center, one singly deprotonated HBDAC ligand, one aqua ligand, and a half-occupied crystallization water molecule. As shown in Fig. 1, the cadmium atom Cd1 possesses a distorted {CdN<sub>4</sub>O<sub>2</sub>} octahedron, with the equatorial positions taken by chelating nitrogen atoms from two different BDAC<sup>-</sup> ligands. Axial positions are filled by two aqua ligands. The Cd—N bond lengths (2.285(3)—2.306(4) Å) and Cd—O bond lengths (2.399(3) Å) are comparable with the corresponding values found in other Cd(II) complexes [17, 18]. The key bond lengths and bond angles are listed in Table 2.

As to the BDAC<sup>-</sup> anion, the dihedral angle between two imidazole rings is 11.3°, and the pendant carboxylate group has the dihedral angles of 106.1° relative to the plane of their linking aromatic ring.

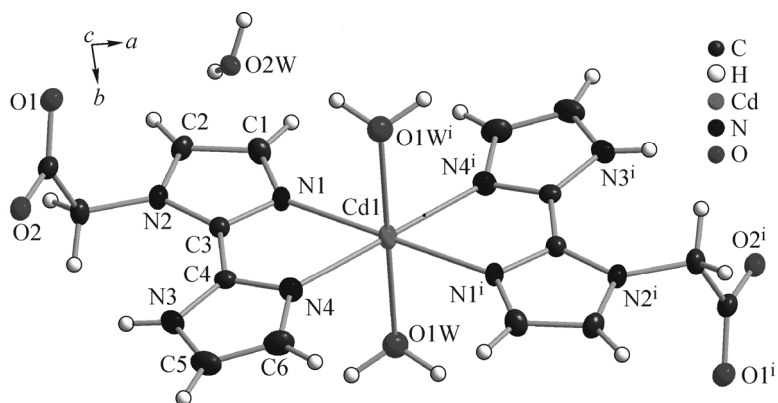


Fig. 1. ORTEP view of asymmetric unit for complex 1, displacement ellipsoids are drawn at the 30 % probability level

Selected bond distances (Å) and angles (deg.) for complex 1

Cd(1)—N(1)	2.285(3)	N(1)—Cd(1)—N(4)	74.08(13)	N(1)—Cd(1)—N(4)#1	105.92(13)
Cd(1)—N(4)	2.306(4)	N(1)#1—Cd(1)—N(4)	105.92(13)	N(1)#1—Cd(1)—N(4)#1	74.08(13)
Cd(1)—O(1W)	2.399(3)	N(1)#1—Cd(1)—N(1)	180.0(2)	N(4)—Cd(1)—N(4)#1	180.00(19)
C(8)—O(1)	1.232(5)	N(1)—Cd(1)—O(1W)	91.15(12)	N(1)#1—Cd(1)—O(1W)	88.85(12)
Cd(1)—N(1)#1	2.285(3)	N(1)—Cd(1)—O(1W)#1	88.85(12)	N(1)#1—Cd(1)—O(1W)#1	91.15(12)
Cd(1)—N(4)#1	2.306(4)	N(4)—Cd(1)—O(1W)	90.29(13)	N(4)—Cd(1)—O(1W)#1	89.71(13)
Cd(1)—O(1W)#1	2.399(3)	N(4)#1—Cd(1)—O(1W)	89.71(13)	N(4)#1—Cd(1)—O(1W)#1	90.29(13)
C(8)—O(2)	1.267(5)				

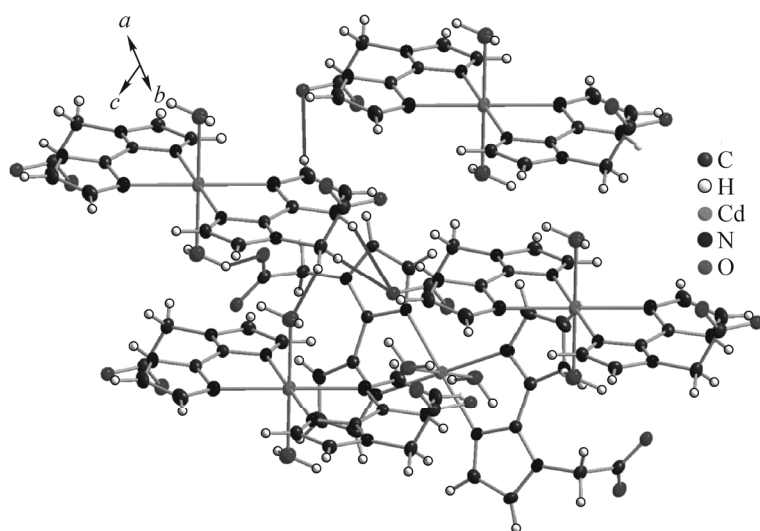
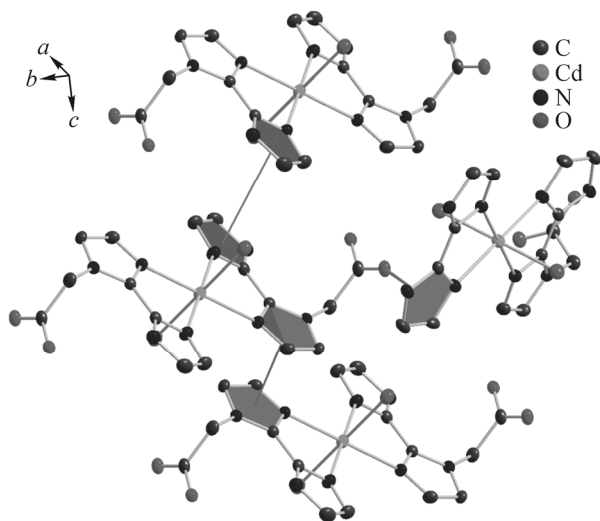
#1  $-x, -y, -z$ .

Fig. 2. View of 3D network constructed by H bonds of complex 1

Fig. 3. View of C—O... $\pi$  and  $\pi$ ... $\pi$  interaction of complex 1

There are extensive intermolecular hydrogen bonds of O—H...O, N—H...O and C—H...O types in complex 1. The molecules of complex 1 are linked with each other through O(1W)—H(1Y)...O(1)<sup>i</sup>, N(3)—H(3)...O(2)<sup>ii</sup>, C(6)—H(6)...O(2)<sup>iii</sup>, C(7)—H(7A)...O(2)<sup>ii</sup>, and C(7)—H(7B)...O(1W)<sup>iv</sup> ( $i = -x-1, -y, -z-1$ ;  $ii = -x-2, y+0.5, -z-0.5$ ;  $iii = -x-1, y+0.5, -0.5-z$ ;  $iv = -x-1, y+0.5, -z+0.5$ ) hydrogen bonding interactions to construct a 3D supramolecular architecture (Fig. 2). In addition, the C—O... $\pi$  interaction (Fig. 3) are observed between C8—O1 and the centroid (Cg) of the C4—C5—C6—N3—N4 imidazole ring, with C8...Cg = 4.726(5) Å, O1...Cg = 3.583(4) Å and C8—O1...Cg = 154.6(3)°. Meanwhile, the 3D supramolecular structure is stabilized by  $\pi$ — $\pi$  interactions between the adjacent imidazole rings in an offset fashion with the centroid—centroid distances in the range of 3.472—3.693 Å (Fig. 3).

The IR spectra of complex 1 show that strong vibrations appear around 1643  $\text{cm}^{-1}$  and 1481  $\text{cm}^{-1}$  corresponding to the asymmetric and symmetric stretching vibrations of the carboxylate group respectively. The  $\Delta\nu$  ( $\nu(\text{OCO})_{\text{asym}} - \nu(\text{OCO})_{\text{sym}}$ ) is 162  $\text{cm}^{-1}$ , indica-

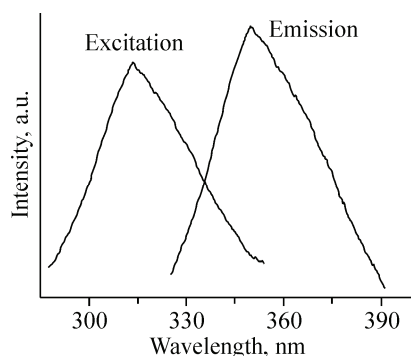


Fig. 4. Solid state emission spectrum of complex **1** at room temperature

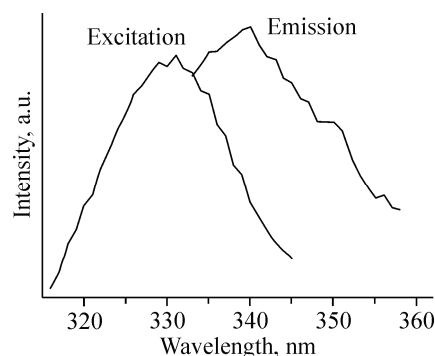


Fig. 5. Solid state emission spectrum of the HBDAC ligand at room temperature

ting that the carboxylate oxygen atoms do not bind Cd atoms. In addition, the absence of strong absorption bands around  $1700\text{ cm}^{-1}$  indicates that the ligands are deprotonated, which is in agreement with the X-ray single structure [ 19 ].

The fluorescent property of complex **1** was studied in the solid state at room temperature. Irradiation of crystalline samples of complex **1** with ultraviolet light ( $\lambda_{\text{ex}} = 314\text{ nm}$ ) caused intense emission with  $\lambda_{\text{max}}$  value of  $350\text{ nm}$  (Fig. 4), which is slightly red-shifted (by  $10\text{ nm}$ ) compared to that of the HBDAC ligand ( $\lambda_{\text{ex}} = 331\text{ nm}$ ,  $\lambda_{\text{em}} = 340\text{ nm}$ ) (Fig. 5). According to a recent review of  $d^{10}$  metal coordination polymer luminescence [ 20 ], the emissive behavior of **1** can be ascribed to ligand-centered electronic transitions.

**Supplementary material.** Crystallographic data for the structural analysis of complex **1** has been deposited at the Cambridge Crystallographic Data Centre, CCDC No.848083. Copy of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EQ, UK (fax: +44 1223 336 033; e-mail: deposit@ccdc.cam.ac.uk).

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