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A 1-D Cd(II) Complex Based on 2-(1*H*-imidazole-1-ylmethyl)-1*H*-benzimidazole and 1,3,5-Benzenetricarboxylate

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In this paper, a new complex, {[CdCl(H₂btc⁻)(imb)]·H₂O}_n (1) has been synthesized through the reaction of CdCl₂·2.5H₂O with ligands 2-(1*H*-imidazole-1-ylmethyl)-1*H*benzimidazole (imb) and 1,3,5-benzenetricarboxylic acid (H₃btc) in water at 80 °C. Single X-ray diffraction analysis shows that complex 1 exhibits 1-D double-stranded chain in which two Cd(II) ions are bridged by two carboxyl groups from two benzenetricarboxylates. These 1-D double-stranded chains are further stacked via hydrogen bonds and the π - π interactions leading to 3-D structure. A thermogravimetric analysis was carried out and the fluorescent property of the complex was investigated.

[Supplementary materials are available for this article. Go to the publisher's online edition of Synthesis and Reactivity in Inorganic, Metal-Organic, and Nano-Metal ChemistrySynthesis and Reactivity in Inorganic, Metal-Organic for the following free supplemental resources(s): Figures of the Spectrum Complex].

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Key words Cd(II)-complex, crystal structure, fluorescent property, thermogravimetric analysis

INTRODUCTION

Investigation on the design, syntheses, structures and properties of the complexes is becoming popular due to their potential applications as electronic, optic, magnetic and catalytic materials.^{[1-} ^{5]} However, it is often difficult to control the structures of the final metal-organic assemblies and to predict the exact nature of the complexes^[6,7] owning to the influence of many factors, like solvent, template, temperature, pH value of the solution, geometric requirements of the metal ions, counter ions, the nature of the ligands.^[8-10] Among the factors mentioned above, the skillful selection of organic ligands possessing appropriate coordination sites is crucial for designing novel complexes.^[11,12] Multifunctional N-heterocyclic ligands such as imidazole, triazole, tetrazole, benzimidazole, benzotriazole, pyridine, pyrazine, hexahydropyridine, piperazine and their derivatives^[13-17] possess strong coordinating capability and display diverse conformations and different coordination modes when coordinate to metal ions. Meanwhile, aromatic polycarboxylic acids like 1,2-benzenedicarboxylic acid (o-H₂bdc), 1,3-benzenedicarboxylic acid (*m*-H₂bdc), 1,4-benzenedicarboxylic acid (*p*-H₂bdc), 1,3,5-benzenetricarboxylic acid (H₃btc), 1,2,4,5-benzenetetracarboxylate (H₄btec) and so forth^[18-20] can exhibit versatile coordination modes, for instance monodentate mode, symmetric bidentate mode, asymmetric bidentate mode, bridging mode, mix-bridging mode.^[21-24] In addition, Cd(II) ion is able to coordinate

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simultaneously to both oxygen-containing and nitrogen-containing ligands and the final products can exhibit promising luminescent properties.^[18,25]

Herein, we select 2-(1*H*-imidazole-1-ylmethyl)-1*H*-benzimidazole (imb) in which the methylene group can freely rotate to meet the requirement of coordination geometries of metal ions in the assembly process and 1,3,5-benzenetricarboxylic acid (H₃btc) as ligands to react with $CdCl_2\cdot2.5H_2O$ and have obtained complex {[$CdCl(H_2btc^-)(imb)$]·H₂O}_n (1). The results indicate O atoms from H₃btc and N atoms from imb can coordinate to Cd(II) ion simultaneously. The IR spectrum, the fluorescent property and thermogravimetric feathures have also been investigated.

EXPERIMENTAL SECTION

General Details

The ligand 2-(1*H*-imidazole-1-ylmethyl)-1*H*-benzimidazole (imb) was synthesized according to the literature method.^[26,27] All chemicals were of AR Grade from commercial sources and were used without further purification. IR data were recorded on a BRUKER TENSOR 27 spectrophotometer with KBr pellets in the 400-4000 cm⁻¹ region. Elemental analyses (C, H, and N) were carried out on a FLASH EA 1112 elemental analyzer. PXRD pattern was recorded using Cu- Kα radiation on a PANalytical X'Pert PRO diffractometer. TG measurement was performed by heating the sample from 30 °C to 700 °C at 10 °C min⁻¹ in air on a NETZSCH STA 409 PC/PG differential thermal analyzer. Steady state fluorescence measurements were performed using a Fluoro Max-P spectrofluorimeter at room temperature in the solid state.

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Synthesis of $\{[CdCl(H_2btc)(imb)] \cdot H_2O\}_n$ (1)

A mixture of imb (0.1 mmol), CdCl₂·2.5H₂O (0.1 mmol), H₃btc (0.1 mmol) and water (10 mL) was sealed into a 25 mL Teflon-lined stainless autoclave and heated at 80 °C for 72h. The reaction mixture was then allowed to cool to room temperature at rate of 10 °C/h. Colorless crystal of {[CdCl(H₂btc⁻)(imb)]·H₂O}_n was collected with a yield of 54% (based on Cd). Anal. Calcd for C₂₀H₁₇CdClN₄O₇(573.225): C, 41.90; H, 2.99; N, 9.77%. Found: C, 42.08; H, 3.02; N, 9.53%. IR(KBr, cm⁻¹): 3449(w), 3131(w), 1674(s), 1618(s), 1555(s), 1431(w), 1367(s), 1280(w), 1240(m), 1090(m), 1028(w), 753(s), 726(w), 698(w), 654(w), 619(w).

Single-Crystal Structure Determination

A suitable single crystal of complex **1** was carefully selected and glued to a thin glass fiber. Crystal structure determinations by X-ray diffraction were performed on a Rigaku Saturn 724 CCD area detector with graphite monochromator for the X-ray source (Mo-K α radiation, $\lambda =$ 0.710 73 Å) operating at 50 kV and 40 mA. The data were collected in ω scan mode at temperature of 293(2) K, and the crystal-to-detector distance was 45 mm. An empirical absorption correction was applied. The data were corrected for Lorentz-polarization effects. The structures were solved by direct methods and completed by difference Fourier syntheses and refined by full-matrix least-squares using the SHELXS-97 program package.^[28] All nonhydrogen atoms were refined anisotropically. The hydrogen atoms of the ligands were positioned geometrically and refined using a riding model. The hydrogen atoms of the water molecules were found at reasonable positions in the differential Fourier map and located there. All the

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hydrogen atoms were included in the final refinement. Crystallographic crystal data and structure processing parameters for complex **1** are summarized in detail in Table 1. Selected bond lengths and bond angles are listed in Table 2. Hydrogen bonds are given in Table 3.

RESULTS AND DISCUSSION

IR Spectroscopy

As shown in FIG. S1, the IR spectra of complex **1** exhibits that the absorption band at 3449 cm⁻¹ could be associated with the stretching vibrations of O-H. The absorption band at 3131 cm⁻¹ originates from the stretching vibrations of Ar-H. The absorption bands at 1618 cm⁻¹, 1555 cm⁻¹, 1431 cm⁻¹, and 1367 cm⁻¹ originate from the C=C and C=N stretching vibrations. The absorption band at 753 cm⁻¹ is corresponding to characteristic stretching vibrations of \bigcirc or \bigcirc . The absorption band at 698 cm⁻¹ can be attributed to the stretching vibrations of \bigcirc . In addition, the separations (\varDelta) between v_a (COO) and v_s (COO) are different for the unidentate, chelating (bidentate) and bridging complexes. In complex **1**, H₂btc⁻ group exhibits the v_a (COO) and v_s (COO) at 1555 cm⁻¹ and 1431 cm⁻¹(\varDelta = 124 cm⁻¹). This \varDelta is comparable to those of bridging complex and H₂btc⁻ group can be assigned to bridging mode.^[29] Furthermore, the very strong absorption band observed at 1674 cm⁻¹ can be attributed to the presence of COOH unit. These analyses are consistent with the results of the X-ray diffraction.

Structural Description

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Single X-ray diffraction analysis reveals complex 1 crystallizes in the triclinic space P-1. All of the Cd(II) ion is equivalent and five-coordinated. FIG. 1 depicts the coordination environment of the Cd(II) center. It can be clearly seen that each Cd(II) ion is in a distorted trigonal biyramid coordination geometry. The apical positions are occupied by one O atom (Cd-O: 2.203(3) and 2.380(4) Å) from the carboxyl of H₂btc⁻ group and one terminal Cl atom (Cd-Cl: 2.376(4) Å). The equatorial plane is completed by two N atoms (Cd-N: 2.246(4) and 2.265(4) Å) from the benzimidazole ring and imidazole ring of two imb ligands and one O atom from the carboxyl of H_2 btc⁻ group. In addition, as shown in FIG. 2, only one carboxyl of each 1,3,5benzenetricarboxylate coordinates to the Cd(II) ion and bridges two Cd(II) ions in pairs leading to a dinuclear structure $[Cd_2Cl_2(H_2bt_2)_2]$, in which the distance of Cd1...Cd1#1 (Symmetry code #1: -x+2, -y+2, -z+2) is 4.341 Å. The dimers are further linked to give a 1-D double-stranded chain through bridging imb ligands (FIG. 3). The intrachain Cd…Cd distance separated by the ligand imb is 9.398 Å. Furthermore, it is necessary to analyze the conformation of ligand imb since the flexible can adopt different conformations in the process of obtaining complexes. Values in the ranges $0-(\pm)90^{\circ}$ can be indicative of *cis* or *syn* conformation, while values in the range $(\pm)90-180^{\circ}$ can be indicative of *trans* or *anti* conformation.^[30-32] In the crystal structure of complex 1, all of the imb ligands are equivalent and the torsion angle of N1-N2-C4-C5 is - 117.2° . Thus, ligand imb adopts *trans* conformation in complex **1**. Additionally, there are five kinds of hydrogen bonds in complex 1 (FIG. 4), N-H…O hydrogen bonds between benzimidazole groups and uncoordinated water molecules, O-H--O hydrogen bonds between carboxyl/carboxyl groups, and between uncoordinated water molecules and carboxyl groups, O-H…Cl hydrogen bonds between carboxyl groups and Cl atoms, and between uncoordinated water molecules and

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Cl atoms. Meanwhile, as illustrated in FIG. 3, on the same side of the 1-D chain the separation between benzene rings from H₂btc⁻ groups and benzimidazole rings from imb ligands is 3.35 Å, so there are π - π interactions. These 1-D double-stranded chains are stacked via hydrogen bonds and the π - π interactions leading to 3-D structure (FIG. 5).

XRD Pattern and Thermogravimetric Analysis

To confirm the phase purity of these complexes, PXRD pattern was recorded for **1**, and it is comparable to the corresponding simulated one calculated from the single-crystal diffraction data (FIG. S2 in the Supplementary material), indicating a pure phase of the bulk sample. Thermogravimetric analysis (TGA) of **1** was performed by heating the complex from 30 °C to 700 °C at 10 °C min⁻¹ in air. As shown in FIG. S3 in the Supplementary material, the first mass loss of 3.23% occurs between 50 °C to 189 °C, corresponding to the release of the crystal water molecules (Calcd 3.14%). Then the solid continues to lose mass from 295 °C to 555 °C corresponding to the release of Cl atoms and the decomposition of imb ligands and 1,3,5-benzenetricarboxylates. Finally, a plateau occurs from 555 °C to 700 °C. The residue equals 22.67%, which is attributed to CdO (Calcd 22.40%).

Fluorescence Spectrum

It is well-known that a number of d¹⁰ transition metal complexes exhibit interesting fluorescent properties. For instance, Cd(II) complexes have been investigated for fluorescent properties and potential applications as fluorescent materials, such as light-emitting diodes.^[33] So the fluorescent property of complex **1** was determined in the solid state at room temperature. As

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shown in FIG. 6 it exhibits an emission band at about 327 nm when excited at 295 nm. The fluorescent properties of uncoordinated ligand imb and H₃btc were also measured in the solid state at room temperature to understand the nature of the emission band. The free ligand imb displays an emission band at 303 nm ($\lambda_{ex} = 290$ nm) and H₃btc gives an emission band at 318 nm ($\lambda_{ex} = 290$ nm), respectively. The result reveals that the emission band of complex **1** may be involved with contributions from imb ligands and H₂btc⁻ groups.^[34-36] Compared to the bands for uncoordinated ligand imb and H₃btc, the emission spectrum of complex **1** appears bathochromic shift.

CONCLUSION

In summary, we have successfully obtained a new complex through reacting 1,3,5benzenetricarboxylic acid with Cd(II) ions in the presence of a flexible *N*-heterocyclic ligand 2-(1*H*-imidazole-1-ylmethyl)-1*H*-benzimidazole (imb) in water. In **1**, imb ligands coordinate to Cd(II) ions with *trans* conformation and every partially deprotonated 1,3,5benzenetricarboxylate bridges two Cd(II) ions. The result illustrates the flexible imb has the ability to adjust its configuration to meet the coordination requirements of metal centers, and 1,3,5-benzenetricarboxylate could adopt different coordination modes according to the pH values to connect metal centers. It is predicted that more metal-organic complexes containing neutral ligands and carboxylate anions with interesting structures as well as physical properties will be synthesized.

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SUPPLEMENTARY MATERIAL

Crystallographic data reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication. CCD number is 854253. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving. htm (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033).

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FIG. 1. Coordination environment of the Cd(II) center in complex **1** with the atom numbering scheme. Uncoordinated water molecules and part of hydrogen atoms are omitted for clarity (Symmetry code #1: -x+2, -y+2, -z+2; #2: x+1, y, z).

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FIG. 2. View of dinuclear structure in complex 1 connected by carboxyl groups (Symmetry code #1: -x+2, -y+2, -z+2).

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FIG. 3. View of the 1-D double-stranded chain of complex 1 connected by imb ligands. Uncoordinated carboxyl of H_2btc^- groups and uncoordinated water molecules are omitted for clarity.

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FIG. 4. View of hydrogen bonds in **1**.

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FIG. 5. 3-D structure of complex **1** in the solid state supported by hydrogen bonds and π - π interactions.

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FIG. 6. Emission spectra of uncoordinated ligand imb, H_3 btc and complex **1** in the solid state at room temperature.

Table 1 Ca	rystallographic	data and structure	e processing param	eters of complex 1

Empirical formula	$C_{20}H_{17}CdClN_4O_7$	Volume (Å ³)	983.2(3)
Formula weight	573.23	Ζ	2
Temperature (K)	293(2)	<i>F</i> (000)	572
Crystal system	Triclinic	Crystal sizes (mm)	$0.23 \times 0.20 \times 0.19$
Space group	<i>P</i> -1	<i>R</i> (int)	0.0194
<i>a</i> (Å)	9.3981(19)	Data/restraints/parameters	3841 / 0 / 309
<i>b</i> (Å)	9.835(2)	Goodness-of-fit on F^2	1.024
<i>c</i> (Å)	11.985(2)	Final R^a indices $[I > 2\sigma(I)]$	$R_1 = 0.0439$
a(deg)	98.01(3)		$wR_2 = 0.1327$

β(deg)	107.62(3)	R indices (all data)	$R_1 = 0.0469$
γ(deg)	106.19(3)		$wR_2 = 0.1398$

Table 2 Selected bond distances (Å) and angles (deg) of complex 1

Cd(1)-O(2)#1	2.203(3)	Cd(1)-N(3)#2	2.246(4)	Cd(1)-N(1)	2.265(4)
Cd(1)-Cl(1)	2.376(4)	Cd(1)-O(1)	2.380(4)	N(1)-Cd(1)-O(1)	83.99(14)
Cl(1)-Cd(1)-	176.28(11)	O(2)#1-Cd(1)-	139.54(14)	O(2)#1-Cd(1)-	96.99(15)
O(1)		N(3)#2		N(1)	
N(3)#2-Cd(1)-	123.45(15)	O(2)#1-Cd(1)-	89.60(14)	N(3)#2-Cd(1)-	86.58(14)
N(1)		Cl(1)		Cl(1)	
N(1)-Cd(1)-	94.63(15)	O(2)#1-Cd(1)-	93.99(13)	N(3)#2-Cd(1)-	91.30(13)
Cl(1)		O (1)		O(1)	

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

D-H···A	d(D-H) (Å)	d(H…A) (Å)	d(D…A) (Å)	<(D-
				H····A)(deg)
N(4)-H(4C)····O(7)	0.86	1.97	2.798(6)	160.5
O(7)-H(1W)···O(6)	0.73(9)	2.23(9)	2.941(7)	165(9)
	0.00		0.0000	
O(3)-H(3)···O(6)#2	0.82	1.75	2.526(5)	157.2
Q(5)-H(5)····Cl(1)#4	0.82	1.87	2.617(5)	151.7
	0.02	1107	21017(0)	10111
O(7)-H(2W)…Cl(1)#5	0.78(8)	2.26(8)	3.036(7)	177(8)

Table 3 Hydrogen bonds of complex 1

Symmetry transformations used to generate equivalent atoms: #2 x+1, *y*, *z*; #4 x, *y*+1, *z*; #5 -x+1, -y+2, -z+1.

²¹ ACCEPTED MANUSCRIPT

²² ACCEPTED MANUSCRIPT