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CRYSTAL STRUCTURE AND LUMINESCENCE OF TWO CADMIUM 3,4,5-TRIMETHOXYLBENZOATE COMPLEXES

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Two novel cadmium complexes with TMB (HTMB = 3,4,5-trimethoxybenzoic acid) are synthesized by the solution evaporation method. The structure and luminescent property of the two complexes are characterized by single crystal and powder X-ray diffraction, FT-IR spectroscopy, and photoluminescence emission spectra. $Cd_2(TMB)_4(H_2O)_4 \cdot H_2O$ (**1**) is a binuclear complex containing two Cd ions at a distance of 4.091 Å, both coordinated in octahedral geometry. Along the [100] direction, a 1D chain linked by intermolecular hydrogen bonds is formed. $Cd(TMB)_2(IM)$ $(H_2O)_2$ (**2**) is a mononuclear complex in which the Cd ion coordination can be described as a distorted pentagonal bipyramid, and weak hydrogen bonding interactions are present in its molecule. The fluorescent measurement shows that both complexes exhibit strong emission in the solid state at room temperature. Powder X-ray diffraction confirmed their crystallinity and purity.

Keywords: 3,4,5-trimethoxylbenzoate, crystal structure, cadmium, spectral analysis, luminescence

INTRODUCTION

Coordination complexes containing transition metals have found a variety of applications in both field of materials science and chemical engineering, including gas storage, magnetic materials, luminescent probes, and catalysts [1—4]. One of the most important classes of complexes is carboxylates, among which benzoic acid derivates are the most important and simplest aromatic carboxylic acids. They always provide π electron systems and easily construct potential luminescence materials combining with proper metal ions as well as nitrogen heterocyclic ligands [5, 6]. On the other hand, because of its d^{10} electronic configuration, the cadmium ion is particularly suitable for the construction of photochemical important complexes with different coordination number and polyhedron geometries [7, 8].

Working on cadmium complexes with benzoic acid [9] and its derivates, a few ligands such as 4-hydroxybenzoic acid [10], 1,3,5-benzene-tricarboxylic acid [11], and benzene-1,4-dicarboxylic acid [12] have been reported in recent years. However, the cadmium complex combining with 3,4,5-trimethoxybenzoic acid has never been reported. In order to get an insight into the coordination geometry of cadmium and the luminescent property of 3,4,5-trimethoxybenzoic complexes, we investigated two cadmium complexes $Cd_2(TMB)_4(H_2O)_4 \cdot H_2O$ (**1**) and $Cd(TMB)_2(IM) \cdot (H_2O)_2$ (**2**) (HTMB = = 3,4,5-trimethoxybenzoic acid, IM = imidazole). Systematic characterizations of the two complexes have been performed by the elemental analysis, single crystal X-ray diffraction, Fourier transform infrared spectroscopy (FTIR), powder X-ray diffraction (XRD) and photoluminescence (PL) spectra.

EXPERIMENTAL

Materials and instrumentation. All the reagents and solvents purchased from commercial sources were used without further purification. Elemental analyses were performed on a Perkin-Elmer 240C automatic analyzer. FTIR spectra were recorded from KBr pellets in the range 4000—600 cm^{-1} on a Nicolet FTIR 3600 spectrometer. PL spectra were recorded at room temperature by an F-4500 FL spectrophotometer with a spectral resolution of 1 nm. Powder XRD measurements were performed using an X′Pert PRO diffractometer (Spectris Pte Ltd.) with monochromatized CuK_α radiation (λ = 1.5418 Å).

Synthesis of $Cd_2(TMB)_4(H_2O)_4 \cdot H_2O$ (1). 3,4,5-trimethoxybenzoic acid (1.0 mmol, 0.212 g) and cadmium acetate (0.5 mmol, 0.133 g) were added to 15 ml of the ethanol-water (1:2 (*v*/*v*)) solution under stirring at room temperature. After 0.5 h, the pH value of the mixture was adjusted to about 5.5 by adding a NaOH solution (6 mol/l), and the cloudy solution was continuously stirred for 1 h. After the insoluble solid was filtered off, the colorless filtrate was kept at room temperature and colorless single crystals of 1 were harvested in 10 days. Yield: 72 % (based on cadmium acetate). Anal. Calcd. (%) for $C_{40}H_{56}Cd_2O_{26}$: C, 40.80; H, 4.79. Found (%): C, 40.72; H, 4.74.

Synthesis of $Cd(TMB)_2(IM)(H_2O)_2$ (2). To 15 ml of the ethanol-water (1:2 (*v*/*v*)) solution, 3,4,5-trimethoxylbenzoic acid (1.0 mmol, 0.212 g), imidazole (1.0 mmol, 0.67 g), and cadmium acetate (0.5 mmol, 0.133 g) were added under stirring at room temperature. In half an hour later, the pH value of the mixture was adjusted to about 6.5 with a NaOH solution (6 mol/l), and the cloudy solution was continuously stirred for 1 h. After the insoluble solid was filtered off, the colorless filtrate was kept at room temperature and colorless single crystals of 2 were harvested in 5 days. Yield: 56 % (based on cadmium acetate). Anal. Calcd. (%) for $C_{23}H_{30}CdN_2O_{12}$: C, 43.24; H, 4.73; N, 4.38. Found (%): C, 43.19; H, 4.71; N, 4.42.

Single crystal X-ray diffraction analysis. Diffraction intensities for the crystals were collected at 298 K on a Bruker SMART 1000 CCD diffractometer employing graphite monochromatized MoK_α radiation (λ = 0.71073 Å) in ω and φ scan modes. The structures were solved by direct methods [13] and refined by the full matrix least squares method on F^2 using SHELXS-97 and SHELXL-97 programs respectively [14, 15]. Non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in geometrically calculated positions. Some disorder was noted for two methyl groups in complex **1**, with two nearby site having occupancies constrained to sum to 100 %. C9 was found with a 63 % occupancy, while C9′ had a 37 % occupancy. As for C10, it was found with a 59 % occupancy, while C10′ had a 41 % occupancy. For complex **2**, the imidazole ring was found to be symmetrically disordered with occupancy of 50 % in two different positions. The crystallographic data and experimental refinement parameters of the two complexes are given in Table 1. Selected bond lengths and angles are listed in Table 2. Crystallographic data for the complexes have been deposited at the Cambridge Crystallographic Data Center (CCDC) as Supplementary Publication CCDC Nos. 784699 and 784700. Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or http://www.ccdc.cam.ac.uk).

RESULTS AND DISCUSSIONS

Crystal structure of complex 1. As shown in Fig. 1, complex **1** exhibits a binuclear unit with two symmetric Cd ions bridged by two carboxylate groups with a distance of 4.091 Å. Each Cd ion is six-coordinated to four oxygen atoms from three TMB ligands and two oxygen atoms from two water molecules to give octahedron geometries, as illustrated in Fig. 2, *a*. The Cd—O average distance from coordinated water is 2.2825 Å, which is shorter than that of the Cd—O bond length of 2.3329 Å from the carboxylate group. The two kinds of crystallographically independent TMB ligands are both bidentate. However, one acts in a bridging-bidentate mode linking two Cd ions and another acts in a chelating-bidentate mode.

In complex **1**, the crystal water molecule plays a very important role for the assembly of the structure. There are plenty of intermolecular hydrogen bonds, as listed in Table 3. Along the [100] direc-

Table 1

Crystal data and structure refinement parameters for complexes **1** *and* **2**

	Complex **1**	Complex **2**
Empirical formula	$C_{40}H_{56}Cd_2O_{26}$	$C_{23}H_{30}CdN_2O_{12}$
Formula weight	1177.65	638.89
Temperature, K	298(2)	298(2)
Wavelength, Å	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	$P\overline{1}$	$C2/c$
a, *b*, *c*, Å	7.7946(6), 9.8336(7), 15.8970(11)	17.1679(13), 8.6128(6), 18.0427(13)
α, β, γ, deg.	94.1100(10), 92.7890(10), 103.7180(10)	90, 102.5350(10), 90
Volume, $Å^3$	1177.97(15)	2604.3(3)
Z	1	4
Density (calculated), Mg/m^3	1.66	1.629
Absorption coefficient, mm^{-1}	0.993	0.905
$F(000)$	600	1304
Crystal size, mm	0.40×0.30×0.20	0.36×0.20×0.20
θ range for data collection, deg.	2.57 to 25.01	2.43 to 28.24
Index ranges	$-9 \le h \le 7, -11 \le k \le 11, -18 \le l \le 18$	$-21 \le h \le 21, -10 \le k \le 8, -23 \le l \le 19$
Reflections collected	6260	8746
Independent reflections	3944	2820
Completeness to max θ, %	98.30	99.40
Absorption correction	None	None
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data / restraints / parameters	3944 / 37 / 342	2820 / 3 / 191
Goodness-of-fit on F^2	1.083	1.148
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0297$, $wR_2 = 0.0769$	$R_1 = 0.0337$, $wR_2 = 0.0938$
R indices (all data)	$R_1 = 0.0306$, $wR_2 = 0.0777$	$R_1 = 0.0345$, $wR_2 = 0.0945$
Largest diff. peak and hole, $e/Å^{-3}$	0.865 and –1.013	0.849 and –0.661

Table 2

Selected bond lengths (Å) *and angles* (deg.) *for complexes* **1** *and* **2**

Complex **1**				Complex **2**	
Cd1—O1	2.4743(18)	Cd1—O7a$^{\#1}$	2.2619(17)	Cd1—N1	2.197(2)
Cd1—O2	2.3125(19)	Cd1—O11	2.281(2)	Cd1—O1	2.510(2)
Cd1—O6	2.2758(19)	Cd1—O12	2.284(2)	Cd1—O2	2.313(2)
				Cd1—O6	2.381(2)
O1—Cd1—O2	54.53(6)	O2—Cd1—O12	91.03(8)	N1—Cd1—O2	139.37(13)
O1—Cd1—O6	148.10(7)	O6—Cd1—O7a$^{\#1}$	123.49(7)	N1—Cd1—O6	86.86(12)
O1—Cd1—O7a$^{\#1}$	88.25(6)	O6—Cd1—O11	94.27(8)	N1—Cd1—O1	85.64(13)
O1—Cd1—O11	89.18(7)	O6—Cd1—O12	87.57(7)	O2—Cd1—O1	53.77(8)
O1—Cd1—O12	91.72(8)	O11—Cd1—O7a$^{\#1}$	88.63(7)	O2—Cd1—O6	92.47(9)
O2—Cd1—O6	93.61(7)	O11—Cd1—O12	176.06(7)	O6—Cd1—O1	87.23(8)
O2—Cd1—O7a$^{\#1}$	142.71(7)	O12—Cd1—O7a$^{\#1}$	87.57(7)		
O2—Cd1—O11	92.61(7)				

Symmetry operation: $^{\#1}$ $-1+x$, $-1+y$, z.

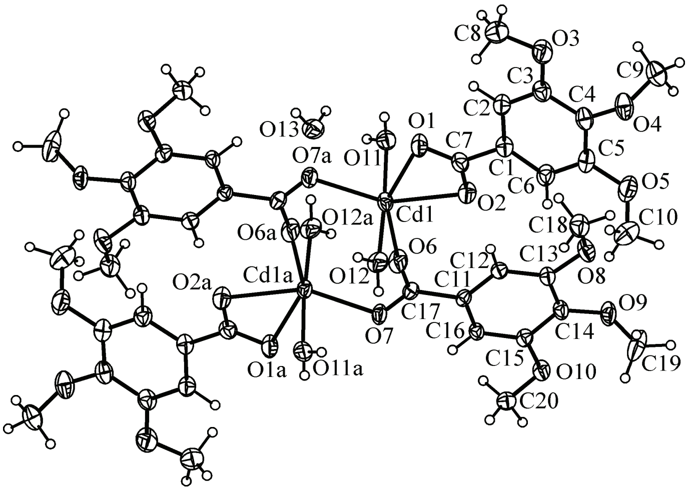

Fig. 1. Molecular structure of complex **1**

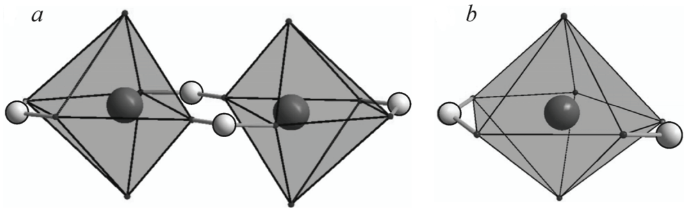

Fig. 2. Coordination environment of complexes **1** (*a*) and **2** (*b*)

tion, a 1D chain linked by two types of hydrogen bonds between O13 atoms from crystal water and O11 and O12 atoms from coordination water were formed. Still there are O1 atoms from the carboxyl group acting as an acceptor linked with crystal water as a donor through strong hydrogen bond interactions.

Crystal structure of complex 2. The coordination environment of Cd ion in complex **2** is given in Fig. 2, *b*. The geometry of $CdNO_6$ composed of four oxygen atoms from two TMB ligands, two oxygen atoms from two coordination water molecules, and one nitrogen atom from one imidazole ligand can be described as a distorted pentagonal bipyramid. The Cd—N bond length is 2.197 Å, which is shorter than the average Cd—O length (2.405 Å).

Table 3

Hydrogen bonds for complex **1** (Å *and* deg.)

D—H…A	*d*(D—H)	*d*(H…A)	*d*(D…A)	∠DHA
O11—H11A…O7$^{\#1}$	0.809(17)	1.995(15)	2.791(2)	168(4)
O11—H11B…O13	0.816(16)	1.976(15)	2.780(3)	168(4)
O12—H12A…O13$^{\#2}$	0.814(18)	1.988(18)	2.798(3)	174(3)
O12—H12B…O9$^{\#3}$	0.0806(19)	2.400(3)	3.0383(3)	137(3)
O12—H12B…O10$^{\#3}$	0.0806(19)	2.17(2)	2.906(3)	153(3)
O13—H13A…O1$^{\#4}$	0.820(3)	1.91(3)	2.702(3)	163(5)
O13—H13B…O8$^{\#5}$	0.82(2)	2.13(2)	2.928(3)	166(4)

Symmetry operation: $^{\#1}$ 1+x, y, z; $^{\#2}$ 1–x, 2–y, 1–z; $^{\#3}$ 1+x, y, z; $^{\#4}$ 2–x, 2–y, 1–z; $^{\#5}$ 1–x, 1–y, 1–z.

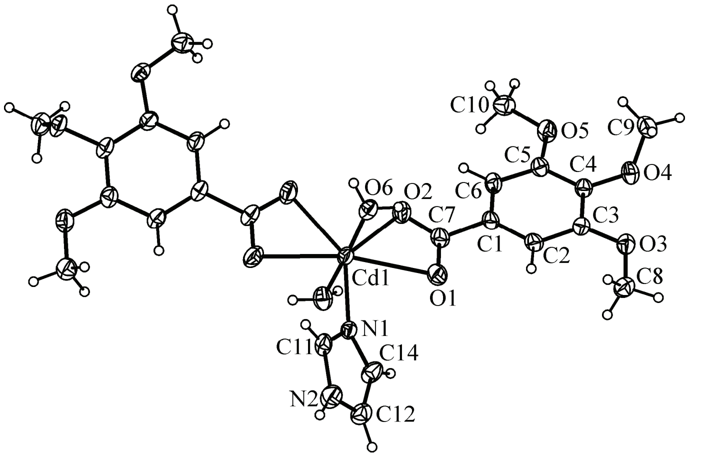

Fig. 3. Molecular structure of complex **2**

In Fig. 3, the molecular structure indicates that both TMB ligands adopt a chelating-bidentate mode linking to the only one crystallographically independent Cd ion. Weak hydrogen bonding interactions are present between different molecules. In the first case, it is the N—H...O interactions ($d_{N2—O2}$ = = 2.787(3) Å, and ∠N2—H2A...O2$^{\#1}$ = 164°, $^{\#1}$ x, 1+y, z), whereas in the second case, it is O—H...O interactions ($d_{O6—O3}$ = 2.9243 Å, ∠O6—H6A...O3$^{\#2}$ = 161(3)°; $d_{O6—O4}$ = 3.1833 Å, ∠O6—H6B...O4$^{\#3}$ = = 144(3)°; $d_{O6—O5}$ = 2.9833 Å, ∠O6—H6B...O5$^{\#3}$ = 146(3)°; $^{\#2}$ 1.5–x, 0.5–y, 1–z; $^{\#3}$ x, –y, 0.5+z).

FTIR and solid state fluorescent spectrum. Fig. 4 shows the FTIR spectra of complex **1** and **2**. The experimental results show that the characteristic asymmetric and symmetric C=O stretching modes of the TMB moieties are observed at 1550 cm^{-1} and 1394 cm^{-1} for complex **1**, while in complex **2** they are at 1561 cm^{-1} and 1391 cm^{-1}. The separation between ν_{as} and ν_s for the two complexes are 156 cm^{-1} and 170 cm^{-1} respectively. Compared with the value observed in pure 3,4,5-trimethoxylbenzoic acid ($\Delta\nu = 266$ cm^{-1}), both separations are smaller due to the bidentate coordination from O atoms to cadmium atoms [16]. In addition, smaller $\Delta\nu$ in complex **1** contrasted to complex **2** indicates a stronger rigidity, which is consistent with the X-ray analysis results. The characteristic bands of C=C stretching modes of TMB were observed at 1507 cm^{-1} for complex **1** and 1503 cm^{-1} for complex **2**. Broad absorption bands from 1480 cm^{-1} to 1430 cm^{-1} in complex **2** are assigned to the C=N stretching vibration of imidazole, while the bands at 1071 cm^{-1} can be assigned to the C-N stretching vibration. Besides, the N—H stretching and bending frequencies of the imidazole ligand are observed at 3139 cm^{-1} and 819 cm^{-1} respectively. Also, there are broad bands at 3546 cm^{-1} in complex **1** and 3537 cm^{-1}, 3474 cm^{-1} in complex **2**, which are contributed by the hydrogen bonding interactions from the OH or NH group in imidazole and coordinated or lattice water [17].

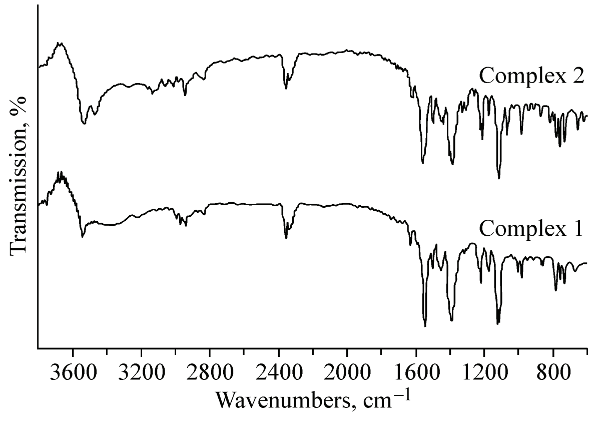

Fig. 4. FTIR spectrum of the two complexes

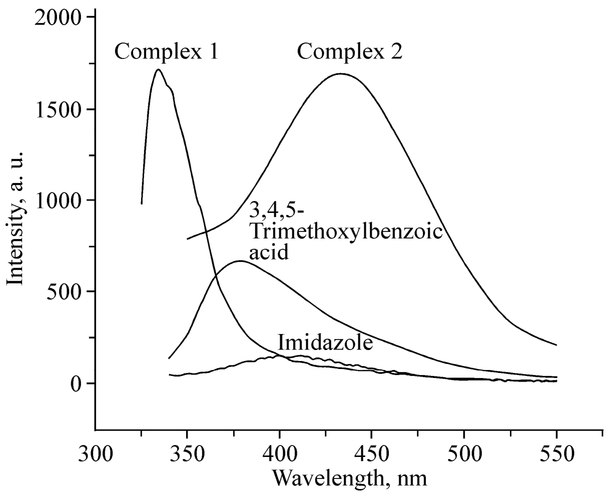

Fig. 5. Luminescence emission spectra for the ligands and complexes

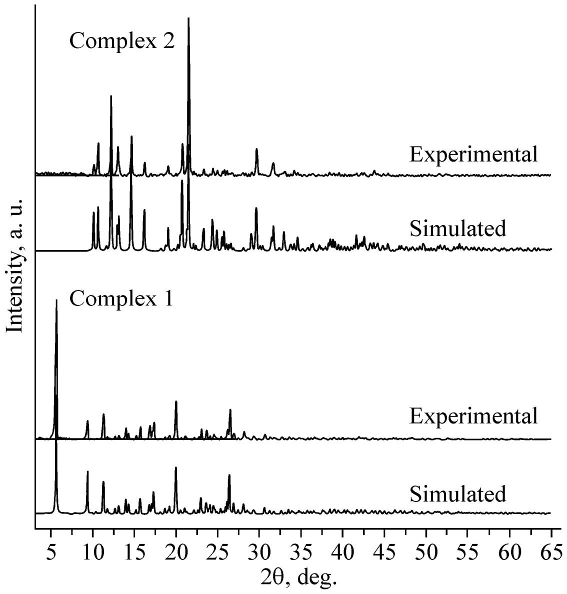

Fig. 6. Experimental and simulated powder X-ray diffraction patterns

The luminescent properties of cadmium complexes explored by other researchers indicate that the emission colors are remarkably affected by their incorporations into the organic π electron system containing coordination complexes. Both ligands used here contain the π electron system, herein PL of complex **1** and **2** in the solid state under room temperature was reported in Fig. 5. Complex **1** exhibits strong luminescence at 336 nm upon the excitation at 318 nm, while complex **2** shows broad luminescence at 432 nm excited at 329 nm. In order to determine more thoroughly the nature of these two emission bands, the free ligands of 3,4,5-trimethoxybenzoic acid and imidazole were also investigated. The emission maximum is at 377 nm (λ = 333 nm) for 3,4,5-trimethoxybenzoic acid and 412 nm (λ = = 322 nm) for imidazole. Even though the emission bands both in complexes **1** and **2** are significantly shifted and much more stronger compared with those of the free ligands, the luminescent behavior in these materials is most likely to be ascribed to the ligand-to-ligand π—π* or π—*n* charge transfer (LLCT) transition emission. The fluorescent enhancement may be due to the coordination interactions with Cd ions and crystal packing in the solid, which effectively increased the rigidity of the ligand and reduced the energy loss by the radiationless decay of the intraligand emission excited state [18]. The blue shift of complex **1** and the red shift of complex **2** may be attributed to the combination of different ligands and the increase or decrease in the intraligand HOMO-LUMO energy gap [19].

Powder X-ray diffraction analysis. The purity of the two complexes was confirmed by the powder XRD analysis (Fig. 6), in which both of the two experimental PXRD patterns were coincident with those simulated from the single crystal data at room temperature, indicating a single phase for each complex [20]. The small difference in intensity may be due to the preformed orientation of the powder samples.

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