

SHORT COMMUNICATION

SYNTHESIS AND CRYSTAL STRUCTURE OF A TRIHYDRATE OF DINUCLEAR BENZIMIDAZOLE-2-PYRIDINECARBOXYLATE-CADMIUM(II)

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ABSTRACT. A new compound, $[\text{Cd}_2(\text{C}_7\text{H}_6\text{N}_2)_3(\text{C}_6\text{H}_4\text{O}_2\text{N})_4]\cdot 3\text{H}_2\text{O}$ (**1**), has been prepared under mild hydrothermal conditions and structurally characterized by single crystal X-ray diffraction. The two cadmium(II) ions are bridged by a carboxyl group from one 2-pyridinecarboxylate ligand. The thermal gravimetry (TG) data indicate three steps of decomposition, and the final thermal decomposition product is CdO.

KEY WORDS: Cadmium, Crystal structure, 2-Pyridinecarboxylic acid, Benzimidazole

INTRODUCTION

Cadmium(II), being a d^{10} ion, provides few spectroscopic signatures for structure monitoring, however, the structure of the cadmium complex could be elucidated by X-ray crystallography. In recent years, extensively attention has been focused on the design and synthesis of cadmium(II) carboxylate coordination complex for their intriguing structural motifs, photoluminescent properties and other potential applications in molecular-based materials [1-4]. In this paper, we report the synthesis and crystal structure of the title complex **1**. Its elemental analysis and thermal analysis have also been investigated.

EXPERIMENTAL

$\text{Cd}(\text{OAc})_2\cdot 2\text{H}_2\text{O}$ (0.266 g, 1 mmol), 2-pyridinecarboxylic acid (0.246 g, 2 mmol), benzimidazole (0.18 g, 1.5 mmol), and water (17 mL) were mixed with stirring, adjusted the pH value to 7.0, then the mixture was sealed in a 25 mL stainless-steel reactor equipped with a Teflon liner and heated at 120 °C for 72 h to give pale yellow crystals of the title complex, yield 31% based on Cd. Upon cooling, The C, H, O and N contents were determined by elemental analysis: calcd. (%) for $\text{Cd}_2\text{C}_{45}\text{H}_{34}\text{N}_{10}\text{O}_{11}$: C 48.45; H 3.05, O 15.78; N 12.55. Found (%) C 48.23; H 2.82; O 15.53; N 12.31.

RESULTS AND DISCUSSION

Single crystal structure determination by X-ray diffraction was performed on a Bruker Apex II diffractometer, X-ray source (MoK α radiation, $\lambda = 0.71073$ Å). A total of 20836 reflections were collected with 6694 ($R_{\text{int}} = 0.0507$) independent reflections with $I > 2\sigma(I)$ ($2.22 < \theta < 26.10$). $-13 \leq h \leq 13$, $-19 \leq k \leq 19$, $-16 \leq l \leq 16$. The title complex is monoclinic, P2(1) space group (No. 11) with $a = 11.192(7)$ Å, $b = 16.085(10)$ Å, $c = 13.423(9)$ Å, $\beta = 93.981(9)^\circ$, $V = 2410(3)$ Å³, $Z = 2$, $R_1 = 0.0442$, $wR_2 = 0.0596$ [5]. Crystal data, collection and refinement of **1** are given in Table 1. Empirical absorption correction was applied. The structure was solved by the direct method and refined by full-matrix least squares on F^2 using the SHELXL-97 software [6]. All of the non-hydrogen atoms were refined anisotropically.

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Table 1. Crystal data, collection and refinement of **1**.

Crystal data		Data collection		Refinement	
C ₄₅ H ₃₄ Cd ₂ N ₁₀ O ₁₁	V = 2410 (3) Å ³	Bruker Apex II CCD diffractometer	9251 independent reflections	R [F ² > 2σ(F ²)] = 0.044	H atoms treated by a mixture of independent and constrained refinement
M _r = 1115.62	Z = 2	Absorption correction: multi-scan SADABS (Bruker, 2001)	6694 reflections with I > 2σ(I)	ωR(F ²) = 0.067	Δρ _{max} = 0.68 e.Å ⁻³
Monoclinic, P21	Mo Kα	T _{min} = 0.781, T _{max} = 0.827	R _{int} = 0.051	S = 0.99	Δρ _{min} = -0.51 e.Å ⁻³
a = 11.192 (7) Å	μ = 0.95 mm ⁻¹	20836 measured reflections		9251 reflections	Absolute structure: Flack H D (1983), Acta Cryst. A39, 876-881
b = 16.085 (10) Å	T = 292 K			637 parameters	Flack parameter: 0.007 (17)
c = 13.423 (9) Å	0.26 × 0.23 × 0.20 mm			1 restraint	
β = 93.981 (9)°					

In this work, we found a monodentate benzimidazole binuclear Cd(II). To the best of our knowledge, this structure has not been reported so far. In the asymmetry unit of **1**, it contains two cadmium(II) center, each cadmium is six coordinated (as shown in Figure 1), however, the coordination environment of the two centers are different. Around Cd1(II) ion there are two O atoms of two different 2-pyridinecarboxylic and four N atoms, two of the four are from two different benzimidazoles, the other two are from 2-pyridinecarboxylic. These six atoms around the Cd1, formed a tetragonal pyramid geometry configuration, N1 and N2 are occupied two axial sites and N4, N6, O1, O3 are all located at the equatorial positions. For the second Cd2, there are three bridged O atoms of three 2-pyridinecarboxylate, two N atoms of two 2-pyridinecarboxylate and a N atom from a benzimidazole around it. Similar to the Cd1 center, the N7 and N8 are sited at the axial sites, O4, O5, O7, N10 are located at equatorial positions. The Cd-O distances (Table 2) range from 2.286(4) to 2.333(4) Å. These Cd-O distances are slightly shorter than the normal Cd-O distance [7], these distances are also shorter than the related material [Cd(2-pyridinecarboxylate)(μ-Cl)]_n [8]. The Cd-N distances are between 2.246(5) and 2.445(5) Å. These distances are similar to our previous work (2.319(3) -2.334(3)) Å [9], these Cd-N_{imidazole} distances (2.246-2.268 Å) are also in accord with the literature [10, 11], the Cd-N_{pyridine} distances (2.333-2.445 Å) are longer than [Cd(2-pyridine- carboxylate)(μ-Cl)]_n 2.302 Å [8]. The O2, O6, O8 are the deprotonized O atoms for the sake of the charge balance. It is worth noting that carboxyl O₃C₂₁O₄ connect Cd1 and Cd2 in the bridged manner of Cd₁-O₃C₂₁O₄-Cd₂, which makes the asymmetry unit a dinuclear structure. The mean plane containing C27-C29-C31 are nearly vertical to another plane which containing C40-C42-C44 (the dihedral angles is 82.25 °). While the plane which containing C40-C42-C44 and plane which containing C22-C242-C26 are almost coincide (the dihedral angle is 1.65°). The dihedral angle is 13.45 which reveals that the C27-C29-C31 plane is also coincide with C35-C37-C39 plane. C40-C42-C44 plane is also nearly vertical to the other two plane (plane C1-C3-C5, dihedral 86.48°; plane C8-C10-C12, dihedral 82.71°), while C40-C42-C44 plane is lean to plane C15-C18-C20 (dihedral 24.91°). Furthermore, there are three free water molecules in **1**. There exist strong hydrogen bonds in complex **1**, these hydrogen bonds belong to three types: N_{imidazole}-H...O_{carboxyl}, N_{imidazole}-H...O_w and O_w-H...O_{carboxyl}. The distances between the donor and acceptor are in the range from

2.704(8) to 2.852(8) Å, these angles between donors, H atoms and acceptors are in the range from 151(6) to 174.8° shown in Table 3. The hydrogen bonds connected **1** to a three dimensional structure. It is clear the strong hydrogen bonds stabilized the structure of **1**.

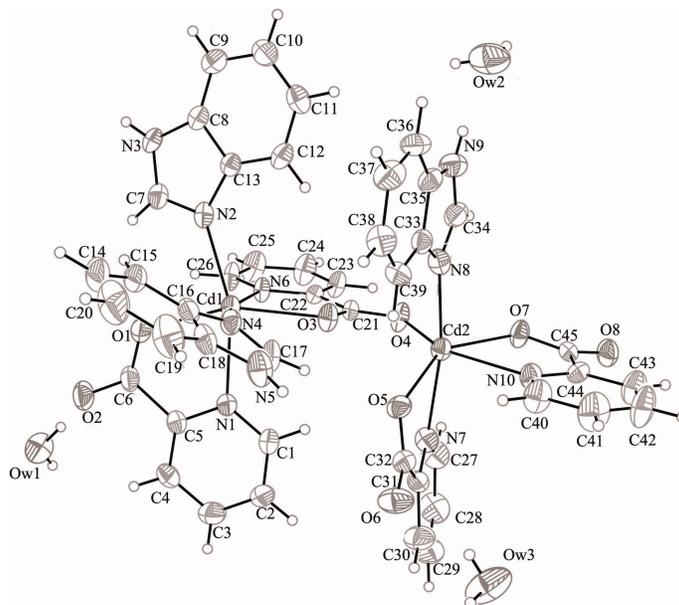


Figure 1. The content of asymmetric unit of the title compound (**1**) showing the atomic numbering and 30% probability displacement ellipsoids.

Table 2. Selected geometric parameters of complex **1**.

Length	(Å)	Length	(Å)	Angle	(°)	Angle	(°)
Cd(1)-N(4)	2.251(5)	Cd(2)-N(7)	2.333(5)	O(1)-Cd(1)-N(1)	70.95(15)	O(4)-Cd(2)-N(7)	87.66(16)
Cd(1)-N(2)	2.268(5)	Cd(2)-N(10)	2.445(5)	O(3)-Cd(1)-N(1)	85.99(16)	N(8)-Cd(2)-N(10)	91.75(17)
Cd(1)-O(1)	2.286(4)	Angle	(°)	N(6)-Cd(1)-N(1)	89.92(16)	O(5)-Cd(2)-N(10)	81.73(15)
Cd(1)-O(3)	2.323(4)	N(4)-Cd(1)-N(2)	95.57(17)	N(8)-Cd(2)-O(5)	100.43(16)	O(7)-Cd(2)-N(10)	68.53(14)
Cd(1)-N(6)	2.376(5)	N(4)-Cd(1)-O(1)	95.57(17)	N(8)-Cd(2)-O(7)	97.33(16)	O(4)-Cd(2)-N(10)	148.24(15)
Cd(1)-N(1)	2.389(5)	N(2)-Cd(1)-O(1)	89.01(15)	O(5)-Cd(2)-O(7)	145.67(13)	N(7)-Cd(2)-N(10)	92.90(17)
Cd(2)-N(8)	2.246(5)	N(4)-Cd(1)-O(3)	90.62(16)	N(8)-Cd(2)-O(4)	93.90(17)	O(3)-Cd(1)-N(6)	70.79(14)
Cd(2)-O(5)	2.308(4)	N(2)-Cd(1)-O(3)	112.39(15)	O(5)-Cd(2)-O(4)	127.58(14)	N(4)-Cd(1)-N(1)	93.23(16)
Cd(2)-O(7)	2.321(4)	O(1)-Cd(1)-O(3)	153.86(14)	O(7)-Cd(2)-O(4)	79.75(13)	N(2)-Cd(1)-N(1)	159.46(16)
Cd(2)-O(4)	2.333(4)	N(4)-Cd(1)-N(6)	160.89(16)	O(1)-Cd(1)-N(6)	96.36(16)	N(2)-Cd(1)-N(6)	87.81(16)

Table 3. Hydrogen bonds for **1** [Å and °].

D-H...A	d (D-H)	d (H...A)	d (D...A)	<(DHA)
N(3)-H(3B)...O(7)#1	0.86	1.90	2.735(6)	161.6
N(9)-H(9B)...OW2	0.86	1.86	2.720(9)	174.8
N(5)-H(5A)...OW1#2	0.86	1.92	2.749(8)	162.7
OW1-HW1B...O(6)#3	0.76(6)	2.11(6)	2.852(8)	164(7)
OW1-HW1A...O(2)	0.96(6)	1.79(7)	2.704(8)	159(6)
OW3-HW3A...O(6)	0.79(6)	2.10(6)	2.817(8)	151(6)
OW2-HW2B...O(2)#4	0.95(9)	1.80(10)	2.744(8)	174(9)
OW3-HW3B...O(8)#5	0.80(11)	2.02(11)	2.767(8)	155(11)

Symmetry transformations used to generate equivalent atoms:

#1 $-x, y-1/2, -z+1$ #2 $x-1, y, z$ #3 $x+1, y, z$ #4 $-x, y+1/2, -z+1$ #5 $-x-1, y-1/2, -z+2$.

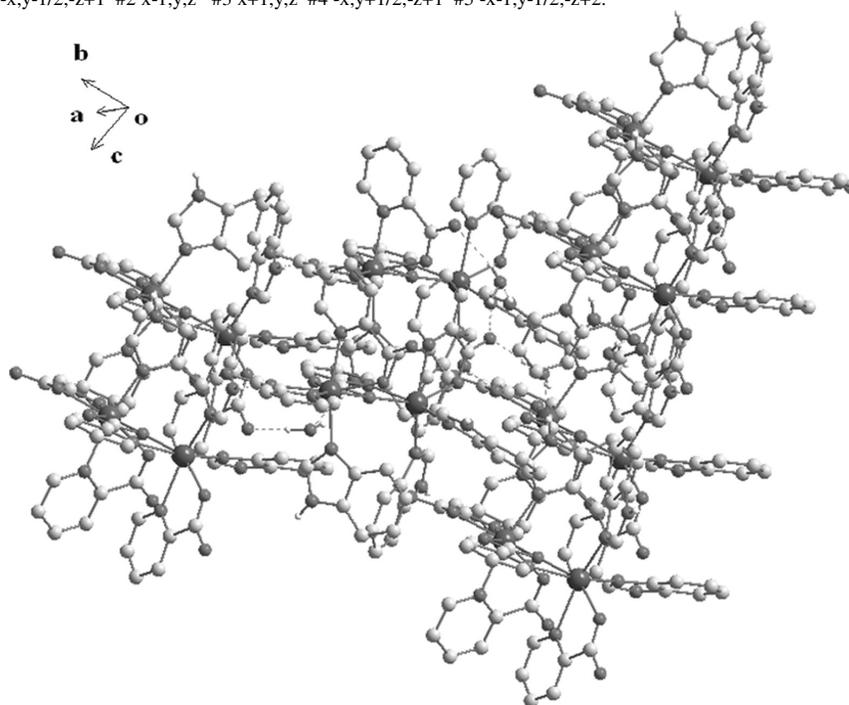


Figure 2. Three dimensional structure and hydrogen bonds of **1** (dotted line indicating the hydrogen bonds, the hydrogen atoms are omitted for clarify except for the Ow-H and N-H).

TG curve of the title complex **1** $[\text{Cd}_2(\text{C}_7\text{H}_6\text{N}_2)_3(\text{C}_6\text{H}_4\text{O}_2\text{N})_4] \cdot 3\text{H}_2\text{O}$ is presented in Figure 3 where three weight loss steps exist and the decomposition mainly takes place at around 200, 350 and 460 °C. The first weight loss stage may be related to the removal of three water molecules (found: 4.6%; calcd.: 4.8%); the second weight loss step corresponds to the release of three benzimidazoles (found: 30.5%, calcd.: 31.8%); the third weight loss step corresponds to the release of three 2-pyridinecarboxylics (found: 41.2%, calcd.: 43.8%). After 620 °C, nearly no weight loss is observed and the residue weight of 22.7% suggests it to be CdO (calcd.: 23.0%).

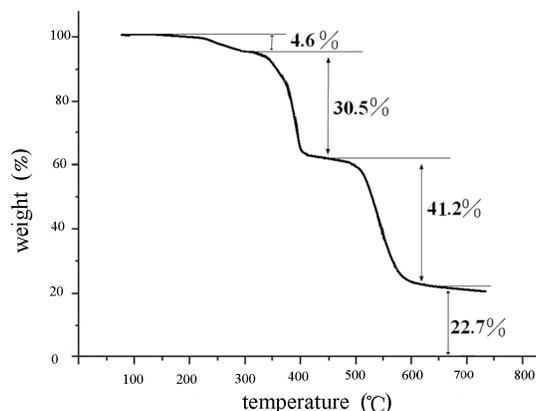


Figure 3. TG curve of the complex 1.

CONCLUSIONS

We synthesized the title complex **1**, determined its crystal structure by X-ray diffraction then investigated its thermal analysis.

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