Asian Journal of Chemistry; Vol. 23, No. 8 (2011), 3647-3650

ASIAN JOURNAL OF CHEMISTRY

www.asianjournalofchemistry.co.in

Synthesis and Crystal Structure of 2,2'-(1,4-Butanediyl)*bis*-(1*H*-benzoimidazole) Cd(II) Complex

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(*Received*: 24 November 2010; *Accepted*: 27 April 2011) AJC-9867

A novel Cd(II)complex (**1**) with 2,2'-(1,4-butanediyl)*bis*(1*H*-benzimidazole)(H_2C_4BIm) has been synthesized and characterized by X-ray single-crystal diffraction analysis. The complex crystallizes in monoclinic, space group P21/C with a = 7.003(5) Å, b = 18.111(5) Å, c = 16.566(5) Å, V = 2099.4(17) Å^3, Z = 4, $C_{21}H_{24}N_4O_6Cd$, Mr = 540.84, Dc = 1.711 g cm^{-3}, F(000) = 1096, μ = 1.088 mm^{-1}, the final R = 0.0367 and wR = 0.0622 for 3367 observed reflections with I > 2σ(I). The coordination geometry of Cd(II) atom is 5-coordinated to form trigonal bipyramidal geometry. The crystal structure is represented by continuous zigzag chains of $C_{21}H_{24}N_4O_6Cd$ molecules, these continuous zigzag chains are further linked by intermolecular hydrogen bondings and C-H···π interaction into a 3-dimensional framework.

Key Words: Hydrothermal synthesis, Crystal structure, Synthesis.

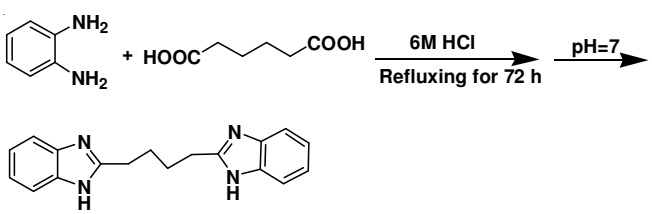
INTRODUCTION

Recently, coordination polymers and supramolecular architectures formed through the deliberate selection of metals and multifunctional ligands have received much attention for their fascinating structural diversity and specific functionality, which have made them highly promising in various application in microelectronics[1,2], non-linear optical and fluorescence properties[3,4], porous materials and catalysis and molecular magnetization[5,6]. Rational design and synthesis of crystalline materials by selecting certain geometric metal ions and special organic ligands has achieved much progress. Most organic ligands containing oxygen, nitrogen or sulfur donors are selected to coordinate to metal centers[7] to form polymers. *Bis*(2-benzimidazoles) and some substituted *bis*(2-benzimidazolyl) alkanes are attractive choices for their multifunctional linking groups because of their free-multivariate configuration. In recent years, more and more scientists give more attention to the research on *bis*(2-benzimidazoles) and their metal complexes. Many new metal complexes possessing novelty structure and excellent functional peculiarity based on them have been reported[8,9]. In this paper, we report the syntheses and crystal structure of the interesting coordination polymer $[Cd(HC_4BIm)(C_3H_2O_4)(H_2O)_2]_n$.

EXPERIMENTAL

All chemicals and solvents obtained from commercial sources were of reagent grade and used without further purification. Crystal structure data were collected by a Bruker Smart ApexII diffractometer.

Synthesis of 2,2'-(1,4-butanediyl)*bis*(1*H*-benzoimidazole) ligand (H_2C_4BIm): The solution of 1,2-diaminobenzene (5.405 g, 100 mmo1) in HCl solution (6 M) and hexanedioic acid (7.30 g, 50 mmol) was refluxing for 72 h. The reaction mixture was slowly cooled down to room temperature and the blue prismatic crystals were collected. The product was dissolved in hot water and disposed with ammonia, after the mixture was cooled down and the white products were obtained. Finally, the white products were recrystallizated with methnol and water, the 2,2'-(1,4-butanediyl)*bis*(1*H*-benzoimidazole) ligand was synthesized. Calcd. (%) For $C_{18}H_{18}N_4$: C, 74.48; H, 6.21, N, 19.31. Found (%): C, 74.52; H, 6.03; N, 19.39.



Synthesis of $[Cd(HC_4BIm)(C_3H_2O_4)(H_2O)_2]_n$ (1): A mixture of $Cd(CH_3COO)_2·2H_2O$ (0.5 mmol), H_2C_4BIm (0.084 g, 0.5 mmol) and H_2O (16 mL) was heated at 165 ºC for 3 days in a 25-mL Teflon-lined stainless steel vessel under autogenous pressure. After the reaction mixture was

slowly cooled down to room temperature, colourless prismatic crystals were produced (yield *ca.* 78 %).

X-Ray crystallographic determination: A transparent colourless prism-like single crystal was used for the single crystal X-ray diffraction analysis. The complete single crystal X-ray analysis was performed using a Bruker Smart ApexII diffractometer. The data were collected and the unit cell parameters were refined using the programs[10]. The structure was solved by the direct method followed by the refinement of positional and thermal parameters in the anisotropic approximation for all non-hydrogen atoms using the programs[11]. The hydrogen atoms attached to carbon atoms were fixed at their ideal positions.

The main crystallographic parameters of the studied sample, the characteristics of the single crystal X-ray diffraction experiment and the details of the structure model refinement using the least square method are shown in Table-1, while the main interatomic distances and bond angles are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA, SINGLE CRYSTAL X-RAY DIFFRACTION EXPERIMENT CHARACTERISTICS AND REFINEMENT DETAILS FOR THE STRUCTURE OF **1**

Formula	$C_{21}H_{24}N_4O_6Cd$
Molecular weight	540.84
Temperature (K)	293(2)
Wavelength (Å)	0.71069
Crystal system, space group	Monoclinic, P21/C
a, b, c (Å)	7.003(5), 18.111(5), 16.566(5)
β (°)	92.295(5)
V (Å^3)	2099.4(17)
Z	4
ρ_x (g/cm^3)	1.711
μ (mm^{-1})	1.088
F(000)	1096
Crystal size, mm	0.4 × 0.3 × 0.2
θ range of data collection	1.67≤ θ ≤ 28.32
Limiting indices	-9 ≤ h ≤ 8, -23 ≤ k ≤ 22, -21 ≤ l ≤ 19
Number of reflections meas./indep.	12552/4868 [R_{int} = 0.0481]
Reflections with I > 2σ(I)	3367
Absorption correction	Semi-empirical from equivalents
Refinement method	Full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.016
Final R indices [I > 2σ(I)]	R1 = 0.0367, wR2 = 0.0622
R indices (all data)	R1 = 0.0727, wR2 = 0.0712
Largest diff. peak and hole (e/Å^3)	0.535/-0.7

RESULTS AND DISCUSSION

X-Ray diffraction analysis of $[Cd(HC_4BIm)(C_3H_2O_4)(H_2O)_2]_n$ (**1**) shows that Cd(II) atom is located at the core of an unusual distorted trigonal bipyramidal geometry with two coordinated nitrogen atoms N2 and N4(x-1, -y + 1/2, z + 1/2) from two different H_2C_4BIm ligands (Cd(1)-N(2) = 2.252(3) Å, Cd(1)-N(4A) = 2.322(3) Å, which are consistent with the corresponding values reported0[9]), oxygen atoms O1 and O(4A) (x + 1, y, z) from two carboxyls of two malonic acids (Cd(1)-O(1) = 2.157 (3) Å, Cd(1)-O(4) = 2.208(3) Å) and O5 from a water molecule (Cd(1)-O(5) = 2.536(3) Å, which is slightly longer than that of Cd(1)-O(1) and Cd(1)-O(4), indicating the weaker coordination ability of water than H_2C_4BIm ligand). The coordination environment of Cd(II) atom in **1** is showed (Fig. 1). In crystal structure, the atomic structure of its crystals is represented by continuous chains of $Cd(HC_4BIm)(C_3H_2O_4)$ molecules, each end of the HC_4Bim^- ligand acts as a monodentate bridging ligand binding to Cd(II) atoms using nitrogen atoms of deprotonated benzimidazole part, which make the Cd(II) atoms are connected to form 1D *zig-zag* chains (Fig. 2). The Cd···Cd distance in the chain is 11.137 Å. In addition, the HC_4Bim^- ligand is nearly a planar fragment composed of aromatic rings (non-hydrogen atoms are out of the plane not more than by 0.0464 Å) with the dihedral angle being 2.55(2)°.

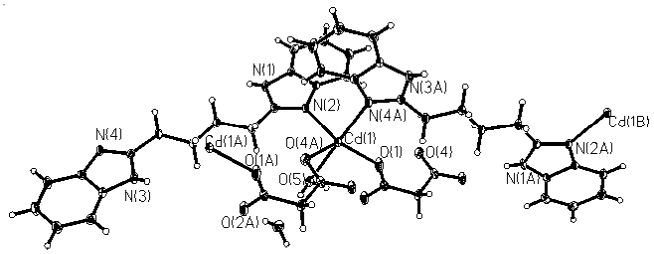


Fig. 1. Coordination environment of Cd(II)atom in **1** (30 % thermal ellipsoids)

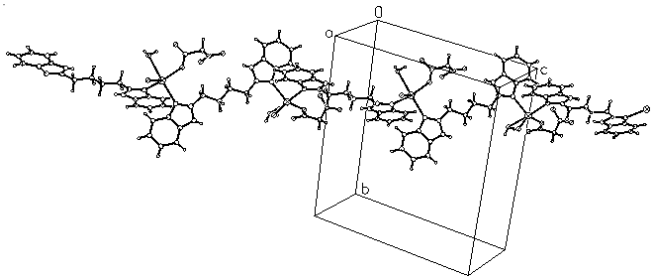


Fig. 2. *Zig-zag* chain of **1** in crystal structure

Owing to the abundant nitrogen atoms in the H_2C_4BIm ligand and abundant oxygen atoms in water or carboxylic acid molecules, the extensive hydrogen-bonding interactions are formed. The intermolecular hydrogen bonds between the oxygen atoms from the malonic acid ligands and the lattice water molecules [O(1W)···O(3) = 2.795(4) Å, O(1W)-H(112)···O(3) = 169.7(3)º, symmetry code: -x - 1, -y + 1, -z + 2], extend the 1D *zig-zag* chains to a 2D layer paralleling along the *bc* plane, shown in Fig. 3. Then the 2D planes are further linked to form a 3D supramolecular structure (Fig. 4) through intermolecular hydrogen bonds (O(1w)···O(2) = 2.866(4) Å, O(1w)-H(111)···O(2) = 163.1º, symmetry code: x + 1, y, z; N(3)···O(5) = 2.948(1) Å, N(3)- H(223)···O(5) = 168.3(2)º, symmetry code: symmetry code: x + 1, y, z) and C-H···π interaction between the benzimidazole part (N1, N2, C1-C7) and H9B of neighbouring molecules of about 3.699 Å, which indicates the interaction of π-election systerm. Another, there are some intramolecular hydrogen bonds (O(5)···O(2) = 2.650(5) Å, O(5)-H(333)···O(2) = 173.9º; O(5)···O(1) = 3.083(4) Å, O(5)-H(333)···O(1) = 118.5; O(5)···O(1w) = 2.735(5) Å, O(5)-H(334)···O(1w) = 177.1°) exit in molecular crystal structure. Details of the hydrogen bonds are given in Table-3. These intramolecular and intermolecular hydrogen bondings, C-H···π interaction and coordination bonds and play important roles in the formation, stability and crystallization of **1**, which assemble the molecules into a three-dimensional network.

TABLE-2
MAIN BOND LENGTHS (Å) AND BOND ANGLES (º) OF **1**

Bond	Dist.	Bond	Dist.	Bond	Dist.
N(4)-Cd(1)[1]	2.322(3)	O(1)-Cd(1)	2.157(3)	O(4)-Cd(1)[2]	2.208(3)
O(5)-Cd(1)	2.536(3)	Cd(1)-O(4)[3]	2.208(3)	Cd(1)-N(4)[4]	2.322(3)
N(2)-Cd(1)	2.252(3)	N(1)-H(222)	0.71(3)	C(22)-O(3)	1.255(4)
C(22)-O(4)	1.245(4)	C(20)-O(1)	1.248(4)	C(18)-N(3)	1.385(4)
C(17)-C(18)	1.387(5)	C(14)-C(15)	1.375(5)	C(13)-N(4)	1.397(4)
C(12)-N(3)	1.341(4)	C(12)-N(4)	1.326(4)	C(8)-C(9)	1.519(4)
C(7)-N(1)	1.347(4)	C(7)-N(2)	1.329(4)	C(6)-N(1)	1.378(4)
O(1W)-H(111)	0.818(18)	O(1W)-H(112)	0.825(18)	O(5)-H(333)	0.816(17)
Angle	**ω**	**Angle**	**ω**	**Angle**	**ω**
N(4)[4]-Cd(1)-O(5)	172.08(9)	N(2)-Cd(1)-O(5)	82.03(9)	O(4)[3]-Cd(1)-O(5)	86.09(9)
O(1)-Cd(1)-O(5)	81.71(9)	N(2)-Cd(1)-N(4)[4]	95.23(10)	O(4)[3]-Cd(1)-N(4)[4]	101.72(9)
O(1)-Cd(1)-N(4)[4]	94.14(9)	O(4)[3]-Cd(1)-N(2)	100.19(9)	O(1)-Cd(1)-N(2)	128.85(11)
C(22)-O(4)-Cd(1)[2]	106.4(2)	C(20)-O(1)-Cd(1)	138.4(2)	C(13)-N(4)-Cd(1)[1]	121.3(2)
C(12)-N(4)-Cd(1)[1]	131.1(2)	C(7)-N(2)-C(5)	106.0(3)	C(7)-N(1)-C(6)	109.1(3)
C(5)-N(2)-Cd(1)	123.61(19)	O(2)-C(20)-O(1)	125.6(3)	O(2)-C(20)-C(21)	119.0(3)
O(4)-C(22)-O(3)	123.5(3)	N(3)-C(18)-C(13)	105.0(3)	N(4)-C(12)-N(3)	112.1(3)
N(2)-C(7)-N(1)	110.8(3)	N(4)-C(12)-C(11)	124.1(3)	N(1)-C(7)-C(8)	124.3(3)
N(2)-C(5)-C(6)	109.4(3)	C(1)-C(6)-C(5)	122.8(3)	N(1)-C(6)-C(5)	104.6(3)

Symmetry code: 1: x + 1, -y + 1/2, z-1/2; 2: x-1, y, z; 3: x + 1, y, z; 4: x-1, -y + 1/2, z + 1/2.

TABLE-3
PARAMETERS OF HYDROGEN BONDS AND C-H···π INTERACTION OF HC_4Bim^- IN COMPLEX CRYSTAL

D-H···A	d(D-H)	d(H···A)	d(D···A)	∠ (DHA)	Symmetry operations
O(5)-H(333)···O(2)	0.816	1.837	2.948	173.87	–
O(5)-H(333)···O(1)	0.816	2.609	2.650	118.53	–
O(5)-H(334)···O(1W)	0.809	1.927	3.083	177.14	–
O(1W)-H(112)···O(3)	0.824	1.980	2.795	169.68	-x-1, -y + 1, -z + 2
O(1W)-H(111)···O(2)	0.818	2.073	2.866	163.11	x + 1, y, z
N(3)-H(223)···O(5)	0.706	2.254	2.948	168.34	x + 1, y, z
C(9)-H(9B)···Cg	0.970	2.922	3.699	134.60	x - 1, y, z

Note: Cg is center of the plane of the C1C2C3C4C5C6 ring.

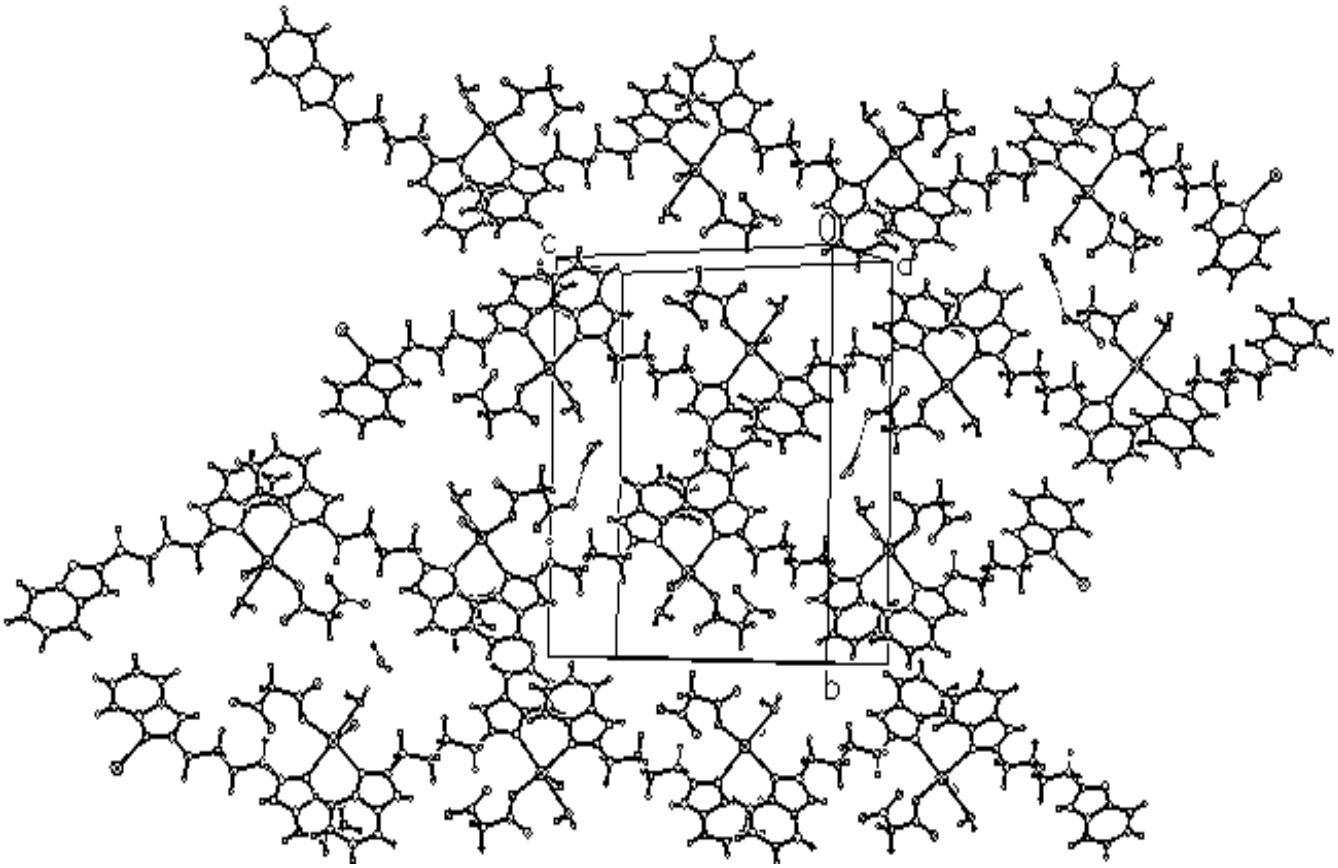


Fig. 3. 2D packing diagram of compound **1** in the crystal cell (intermolecular hydrogen bonds indicated by dashed lines)

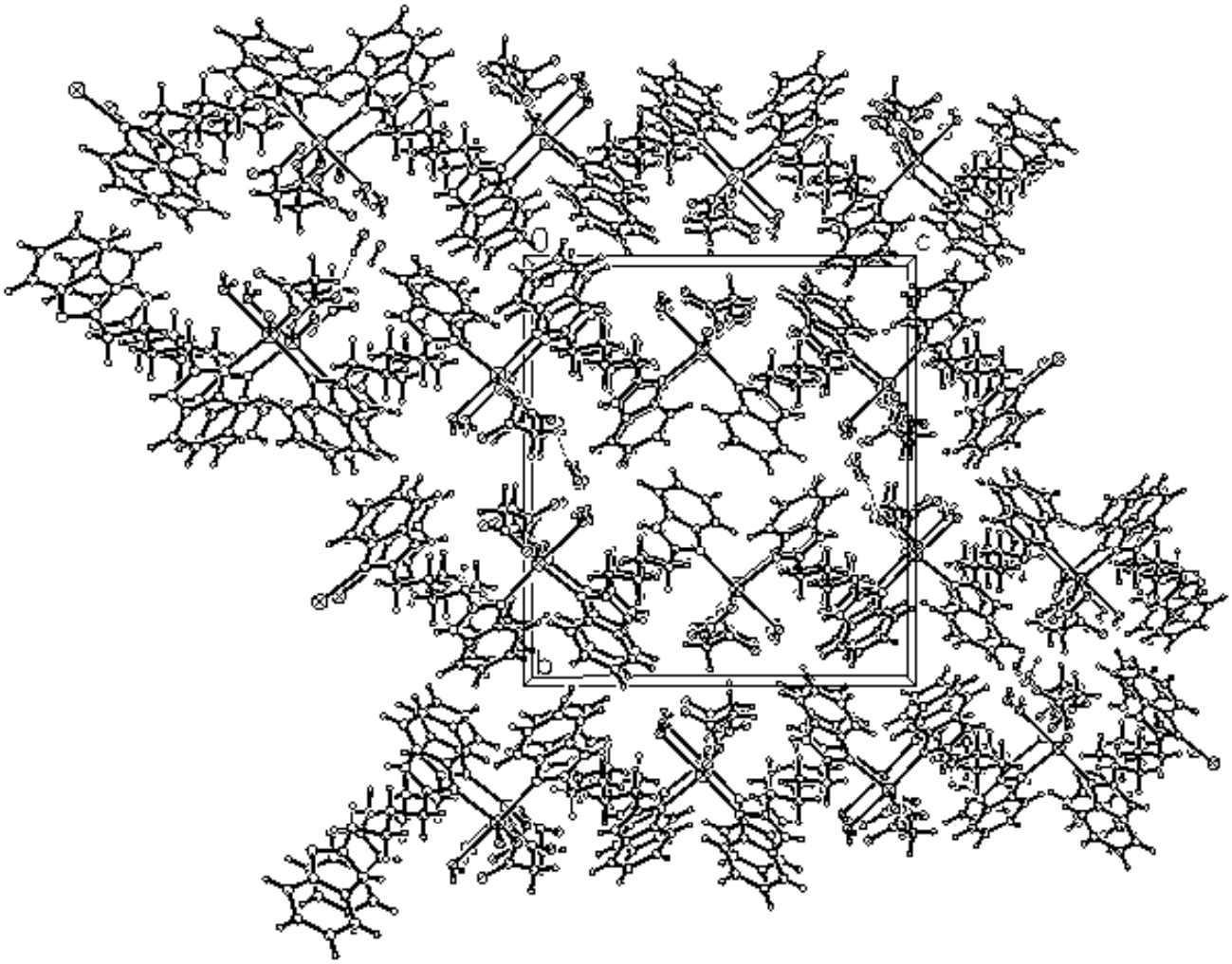


Fig. 4. 3-D network structure of the complex viewed down the a axis

Conclusion

In this work, a new three-dimensional supramolecular architecture of Cd(II) complex is successfully synthesized. The Cd(II) atom is 5-coordinated to form trigonal bipyramidal geometry, which is coordinated by two nitrogen atoms from two H_2C_4BIm ligands and three oxygen atoms from two malonic acid molecules and one coordinated water molecule. The crystal structure is represented by continuous *zigzag* chains of $C_{21}H_{24}CdN_4O_6$ molecules, these continuous *zigzag* chains are further linked by intermolecular hydrogen bondings and C-H···π interaction into a 3-dimensional framework.

ACKNOWLEDGEMENTS

The work was supported by the Special Scientific Research Project of Shaanxi Education Commission (Project No. 2010JS069 and No. 09JS067) and the Science Research Forndation of Baoji University of Arts and Sciences, China (project No. ZK0917).

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