Asian Journal of Chemistry; Vol. 27, No. 5 (2015), 1701-1703

ASIAN JOURNAL OF CHEMISTRY

http://dx.doi.org/10.14233/ajchem.2015.17552

Synthesis and Structure of Cadmium Complex $\{[Cd(adi)_{0.5}Cl(bimt)]\cdot H_2O\}_n$

JIAO-LIN ZHANG, BAO-LIAN HAO and HUAI-XIA YANG*

Pharmacy College, Henan College of Traditional Chinese Medicine, Zhengzhou 450008, P.R. China

*Corresponding author: E-mail: yanghuaixia886@163.com

Received: 4 March 2014; *Accepted*: 14 May 2014; *Published online*: 20 February 2015; AJC-16873

The cadmium complex $\{[Cd(adi)_{0.5}Cl(bimt)]\cdot H_2O\}_n$ (H_2adi = adipic acid, bimt = 2-((benzoimidazol-yl)methyl)-1*H*-tetrazole) was prepared by reaction of $CdCl_2\cdot 2.5H_2O$, bimt and H_2adip in methanol/water solution and its structure was determined by single crystal X-ray diffraction analysis. The crystals are triclinic, space group P-1 with a = 8.4863(17) Å, b = 8.5551(17) Å, c = 11.422(2) Å, α = 100.08(3)º, β = 106.33(3)º, γ = 98.37(3)°, V = 766.7(3) Å^3, Z = 2, F(000) = 434, Dc = 1.898 g/cm^3, μ = 1.623 cm^{-1}, the final R = 0.0252 and wR = 0.0566. A total of 8672 reflections were collected, of which 3584 were independent (Rint = 0.0216).

Keywords: Synthesis, Cadmium Complex, Crystal Structure.

INTRODUCTION

The related reports about Cd(II)-complexes gradually increase on an annual basis since Cd(II) can coordinate simultaneously to both oxygen-containing and nitrogen-containing ligands and the final products can exhibit novel structures and good photoluminescent properties[1]. In addition, the employment of mixed ligands of *N*-heterocyclic ligands and polycarboxylates is an effective approach for the construction of novel metal-organic frameworks (MOFs)[2]. To enrich the numbers of Cd(II)-complexes with *N*-heterocycles and polycarboxylic acids, in this article, we select multidentate unsymmetrical *N*-heterocycle 2-((benzoimidazol-yl)methyl)-1*H*-tetrazole (bimt) and flexible aliphatic adipic acid (H_2adi) as ligands to self-assemble with $CdCl_2\cdot 2.5H_2O$ and obtain the title complex $\{[Cd(adi)_{0.5}Cl(bimt)]\cdot H_2O\}_n$. The preparation and crystal structure of which is reported on herein.

EXPERIMENTAL

Synthesis: A methanolic solution (3 mL) of bimt (0.1 mmol) was added dropwise to an aqueous solution (2 mL) of $CdCl_2\cdot 2.5H_2O$ (0.1 mmol), then an aqueous solution (3 mL) of H_2adip (0.1 mmol) was added dropwise into the above mixture to give a clear solution at room temperature. Colourless block crystals suitable for X-ray analysis were obtained through slow crystallization in a closed container five weeks later.

Single-crystal structure determination: The crystal of $\{[Cd(adi)_{0.5}Cl(bimt)]\cdot H_2O\}_n$ with dimensions of 0.19 mm × 0.18 mm × 0.14 mm was mounted on a Rigaku Saturn CCD area-detector diffractometer with a graphite-monochromated MoK_α radiation (λ = 0.71073 Å) by using an ω scan mode at 293(2) K in the range of 1.91º ≤ θ ≤ 27.85º. The crystal belongs to triclinic system with space group P-1 and crystal parameters of a = 8.4863(17) Å, b = 8.5551(17) Å, c = 11.422(2) Å, α = 100.08(3)º, β = 106.33(3)º, γ = 98.37(3)°, V = 766.7(3) Å^3, Dc = 1.898 g/cm^3. The absorption coefficient μ = 1.623 mm^{-1} and Z = 2. The structure was solved by direct methods with SHELXS-97[3] and refined by the full-matrix least squares method on F^2 data using SHELXL-97[4]. The empirical absorption corrections were applied to all intensity data. H atom of O-H was initially located in a difference Fourier map and were refined with the restraint Uiso(H) = 1.2 Ueq(O). Other H atoms were positioned geometrically and refined using a riding model, with d(N---H) = 0.86 Å and Uiso(H) = 1.2 Ueq(N), d(C---H) = 0.93-0.97 Å and Uiso(H) = 1.2 Ueq(C). The final full-matrix least squares refinement gave R = 0.0252 and wR = 0.0566.

RESULTS AND DISCUSSION

Slow evaporation of the mixture of $CdCl_2\cdot 2.5H_2O$, bimt and H_2adip in methanol/water solution gave colourless crystals suitable for X-ray analysis.

Structure of the title complex: The title complex was confirmed by single crystal X-ray diffraction analysis. Crystallographic and refinement parameters are given in Table-1. The selected bond lengths, bond angles and hydrogen bonds are listed in Tables 2 and 3, respectively. The structure was solved by direct methods. Anisotropic displacement parameters were applied to all nonhydrogen atoms in full-matrix least-

TABLE-1
CRYSTAL DATA AND STRUCTURAL REFINEMENT OF THE TITLE COMPLEX

Items	Values
Empirical formula	$C_{12}H_{14}N_6O_3CdCl$
Formula weight	438.14
Temperature (K)	293(2)
Crystal system	Triclinic
Space group	P-1
a (Å)	8.4863(17)
b (Å)	8.5551(17)
c (Å)	11.422(2)
α(deg)	100.08(3)
β(deg)	106.33(3)
γ(deg)	98.37(3)
Volume (Å^3)	766.7(3)
Z	2
Calculated density (Mg m^{-3})	1.898
Absorption coefficient (mm^{-1})	1.623
F(000)	434
Crystal sizes (mm)	0.19 × 0.18 × 0.14
R(int)	0.0216
Data/restraints/parameters	3584 / 0 / 208
Goodness-of-fit on F^2	1.046
Final R indices [I > 2σ(I)]	R_1 = 0.0252, wR_2 = 0.0566
Final wR_2 indices (all data)	R_1 = 0.0276, wR_2 = 0.0580
$\Delta\rho_{fin}$ (max/min), e.Å^{-3}	0.359/-0.503

square refinements based on F^2. The hydrogen atoms were set in calculated positions with a common fixed isotropic thermal parameter.

The molecular structure and the packing view of the title complex are shown in Figs. 1, 2 and 3, respectively.

The title complex crystallizes in triclinic space group P-1. The unit cell contains one Cd(II) ion, a half of adi^{2-} anion, one chloride anion, one bimt ligand and one uncoordinated water molecule. As can be seen in Fig. 1, each Cd(II) ion is hexa-coordinated by two oxygen atoms from one chelating carboxylate group of the adipate anion, two nitrogen atoms from two symmetry-related bimt ligands and two chloride anions, featuring an irregular $CdO_2N_2Cl_2$ coordination geometry. As shown in Table-2, most of the bond angles around the central Cd(II) ion deviate dramatically from the ideal angles of 90° or 180° expected for an octahedral geometry, as exemplified by the angles of O1-Cd1-O2, N6$^{\#1}$-Cd1-Cl1, O2-Cd1-Cl1 and N6$^{\#1}$-Cd1-O1 (55.15(6)°, 114.25(5)°, 148.95(5)° and 149.88(7)°, respectively; symmetry codes:$^{\#1}$ x, y + 1, z). The Cd-O bond lengths of 2.3288(18) and 2.4067(18) Å, Cd-N

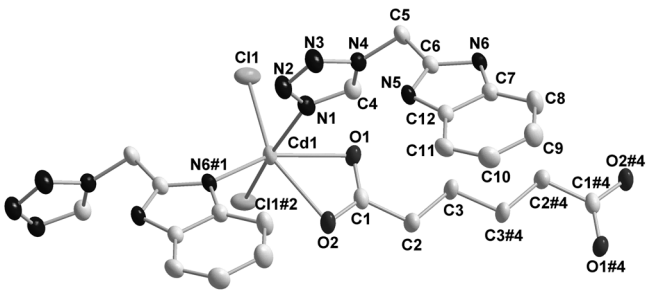

Fig. 1. Coordination environment of the Cd(II) ion in the title complex with atom numbering scheme, hydrogen atoms and uncoordinated water molecules are omitted for clarity (#1 x, y + 1, z; #2 -x + 1, -y + 2, -z + 2; #4 -x + 2, -y + 1, -z + 2)

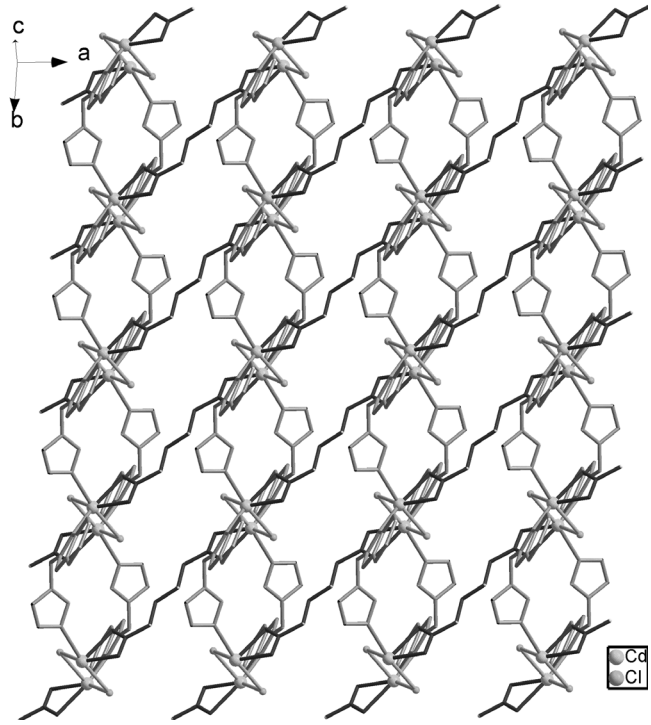

Fig. 2. View of the 2D network structure of the title complex

bond lengths of 2.2583(19) and 2.442(2) Å and Cd-Cl bond lengths of 2.5375(9) and 2.6617(14) are close to those in the reported Cd(II) complexes[5].

As depicted in Fig. 2, two Cd(II) ions are linked together two μ_2-bridging chlorine anions, leading to the $[Cd_2Cl_2]$ binuclear unit. The binuclear units are bridged by adi^{2-} anions

TABLE-2
SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR THE TITLE COMPLEX

Cd(1)-N(6)#1	2.2583(19)	Cd(1)-O(1)	2.3288(18)
Cd(1)-O(2)	2.4067(18)	Cd(1)-N(1)	2.442(2)
Cd(1)-Cl(1)	2.5375(9)	Cd(1)-Cl(1)#2	2.6617(14)
N(6)#1-Cd(1)-O(1)	149.88(7)	N(6)#1-Cd(1)-O(2)	96.68(7)
O(1)-Cd(1)-O(2)	55.15(6)	N(6)#1-Cd(1)-N(1)	90.63(8)
O(1)-Cd(1)-N(1)	80.53(7)	O(2)-Cd(1)-N(1)	91.07(7)
N(6)#1-Cd(1)-Cl(1)	114.25(5)	O(1)-Cd(1)-Cl(1)	94.79(5)
O(2)-Cd(1)-Cl(1)	148.95(5)	N(1)-Cd(1)-Cl(1)	91.16(6)
N(6)#1-Cd(1)-Cl(1)#2	100.21(6)	O(1)-Cd(1)-Cl(1)#2	90.13(6)
O(2)-Cd(1)-Cl(1)#2	88.06(6)	N(1)-Cd(1)-Cl(1)#2	169.16(5)
Cl(1)-Cd(1)-Cl(1)#2	84.09(3)	-	-

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

TABLE-3
HYDROGEN BONDS OF THE TITLE COMPLEX

D-H···A	d(D-H) (Å)	d(H···A) (Å)	d(D···A) (Å)	(D-H···A) (°)
N(5)-H(5C)...O(3)	0.86	1.95	2.736(3)	151.7
O(3)-H(1W)...N(2)#5	0.85	2.42	3.244(3)	164.3
O(3)-H(2W)...O(2)#6	0.85	2.04	2.858(3)	162.4

Symmetry transformations used to generate equivalent atoms: #5 -x, -y + 1, -z + 1; #6 -x + 1, -y + 1, -z + 1

and bimt ligands leading to 2-D layer structure with Schlafli symbol $(4^4\cdot6^2)$, in which both carboxylates of each adipate coordinate to Cd(II) ions in chelating mode and bimt ligands coordinate to Cd(II) ions with bridging fashion. As can be seen in Fig. 3 and Table-3, these 2-D layers are further piled up into 3-D framework by hydrogen bonding interactions.

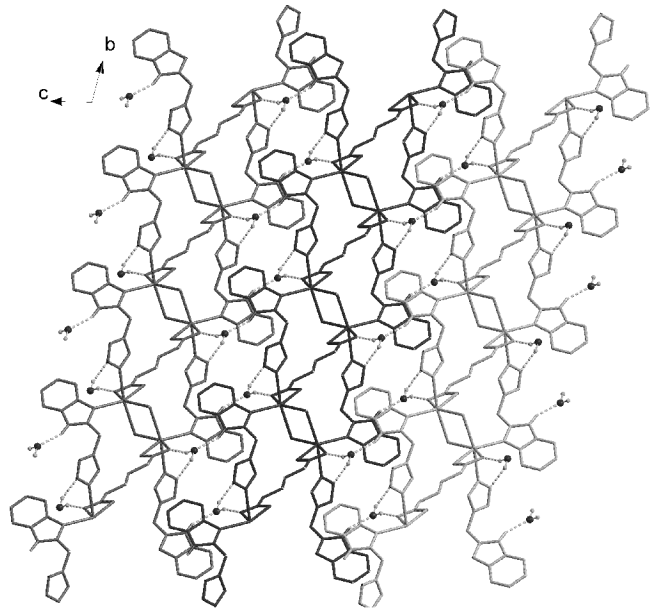

Fig. 3. 3D structure of the title complex linked by hydrogen bonds indicated by dashed lines

Conclusion

Self-assembly of $CdCl_2\cdot2.5H_2O$ with 2-((benzoimidazol-yl)methyl)-1*H*-tetrazole (bimt) and adipic acid (H_2adi) give rise to the title complex $\{[Cd(adi)_{0.5}Cl(bimt)]\cdot H_2O\}_n$. Single crystal X-ray diffraction determination reveals that it possesses a 2-D network with Schlafli symbol $(4^4\cdot6^2)$, which is further extended into the 3-D supramolecular architecture *via* hydrogen bonds.

Supplementary material

CCDC 989489 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/ retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44 1223 336033; email: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

ACKNOWLEDGEMENTS

The authors gratefully acknowledged the financial support from the Program for Innovative Research Team (in Science and Technology) in Henan College of Traditional Chinese Medicine.

REFERENCES

1. (a) B.T. Liu, R. Wang, G.H. Jin and X.R. Meng, *J. Coord. Chem*., **66**, 1784 (2013); (b) L. Cheng, J.B. Lin, J.Z. Gong, A.P. Sun, B.H. Ye and X.M. Chen, *Cryst. Growth Des.*, **6**, 2739 (2006); (c) A. Banisafar, D.P. Martin, J.S. Lucas and R.L. LaDuca, *Cryst. Growth Des*., **11**, 1651 (2011).
2. (a) S.S. Chen, R. Qiao, L.Q. Sheng, Y. Zhao, S. Yang, M.M. Chen, Z.D. Liu and D.H. Wang, *CrystEngComm*, **15**, 5713 (2013); (b) D.P. Martin, M.R. Montney, R.M. Supkowski and R.L. LaDuca, *Cryst. Growth Des*., **8**, 3091 (2008); (c) X.J. Wang, Y.H. Liu, C.Y. Xu, Q.Q. Guo, H.W. Hou and Y.T. Fan, *Cryst. Growth Des*., **12**, 2435 (2012); (d) T. Duangthongyou, C. Phakawatchai and S. Siripaisarnpipat, *J. Mol. Struct*., **987**, 101 (2011).
3. G.M. Sheldrick, SHELXS97, A Program for Crystal Structure Solution; University of Göttingen: Germany (1997).
4. G.M. Sheldrick, SHELXL97, A Program for Crystal Structure Refinement; University of Göttingen: Germany (1997).
5. (a) X. Su, T. Li, Y. Xiu and X.R. Meng, *Z. Naturforsch*., **67b**, 678 (2012); (b) X.X. Wang, X. Han, Y. Yang and X.R. Meng, *Synth. React. Inorg. Met-Org. Nano-Met. Chem.*, **44**, 462 (2014).