

**Infinite Three-Dimensional Coordination Polymers: Synthesis and Structures of  $[\text{Cd} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]_n (\text{pic})_{2n}$ ,  $[\text{Zn} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]_n (\text{pic})_{2n} (\text{H}_2\text{O})_{2n}$ , and  $[\text{Zn} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]_n (4,4'\text{-bpy})_n (\text{H}_2\text{O})_n (\text{pic})_{2n}$**

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**Abstract:** Three Complexes of the formula  $[\text{Cd} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]_n (\text{pic})_{2n}$  (**1**),  $[\text{Zn} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]_n (\text{pic})_{2n} (\text{H}_2\text{O})_{2n}$  (**2**) and  $[\text{Zn} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]_n (4,4'\text{-bpy})_n (\text{pic})_{2n} (\text{H}_2\text{O})_n$  (**3**) (4,4'-bpy = 4,4'-bipyridine; pic = picric anion) have been synthesized and characterized by elemental analysis and single-crystal x-ray diffraction. They all have infinite three-dimensional network structure, crystallizing in the monoclinic space group C2/c (**1**) and Cc (**2,3**).

**Keywords:** Clathration, 4, 4' - bipyridine, picric anion, three - dimensional network.

Recently, a new research realm in crystal engineering of supramolecular architectures assembled by means of coordinate covalent bonding<sup>1</sup>, hydrogen bonding<sup>1</sup>, or other weak intermolecular interactions<sup>2</sup> has been rapidly expanding in order to rationally develop new classes of functional materials with cavities or pores. These types of compounds may exhibit interesting topological structures and the clathrations of the cavity structures may have many potential properties such as catalysis<sup>3</sup>, electrical conductivity<sup>4</sup>, magnetism<sup>5</sup> and host-guest chemistry<sup>6</sup>.

The simple bis (monodentate) ligand 4,4'-bipyridine affords a variety of two<sup>7</sup>- and three<sup>8</sup>-dimensional frameworks when coordinated to various metal ions in different conditions. Here we describe the crystal structures of complexes formed by the interaction of 4,4'-bpy molecule with  $\text{M}^{2+}$  ( $\text{M}^{2+} = \text{Zn}^{2+}, \text{Cd}^{2+}$ ) ion accompanied by picric anion, an anion having big volume and poor coordination ability.

The divalent transition metal picrate was treated with 4,4'-bipyridine at 1:2 mole ratio in  $\text{H}_2\text{O}-\text{CH}_3\text{CN}$  (**2, 3**) or  $\text{H}_2\text{O}-\text{CH}_3\text{COCH}_3$  (**1**) at different temperature. Initially formed precipitate was filtered. The yellow crystals suitable for x-ray diffraction study were obtained from the filtrate by slowly evaporating in the air for several weeks.

The crystallographic data for complexes **1-3** are listed in **Table 1**. Selected interatomic distances and angles for complexes **1-3** are given in **Table 2**, respectively.

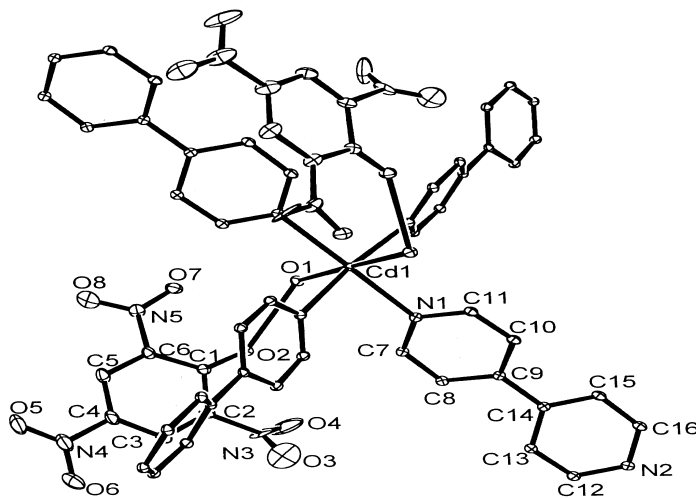
X-ray crystallography shows that complexes **1, 2** and **3** have similar coordination units of  $[\text{M} (4,4'\text{-bpy})_2 (\text{H}_2\text{O})_2]^{2+}$ , in which the metal ion has quasi-octahedral

geometry with four pyridine groups at the equatorial positions and two water molecules

**Table 1** Crystallographic and Experimental Data for complexes 1-3

	complex 1	complex 2	complex 3
Empirical formula	[ Cd ( 4, 4' - bpy ) <sub>2</sub> - ( H <sub>2</sub> O ) <sub>2</sub> ] <sub>n</sub> ( pic ) <sub>2n</sub>	[ Zn ( 4, 4' - bpy ) <sub>2</sub> - ( H <sub>2</sub> O ) <sub>2</sub> ] <sub>n</sub> ( H <sub>2</sub> O ) <sub>2n</sub> - ( pic ) <sub>2n</sub>	[ Zn ( 4, 4' - bpy ) <sub>2</sub> - ( H <sub>2</sub> O ) <sub>2</sub> ] <sub>n</sub> ( 4, 4' - bpy ) <sub>n</sub> - ( H <sub>2</sub> O ) <sub>n</sub> ( pic ) <sub>2n</sub>
Fw	917.02	906.01	1044.18
Cryst. Syst.	monoclinic	monoclinic	monoclinic
Space group	C2/c	Cc	Cc
a ( Å )	16.551(2)	14.390	22.716(2)
b ( Å )	16.782(2)	11.418(1)	16.191(3)
c ( Å )	14.689(2)	22.908(3)	16.166(2)
β (deg)	118.47(1)	95.08(1)	131.085(7)
v ( Å <sup>3</sup> )	3587(2)	3749(1)	4481(2)
Z	4	4	4
ρ <sub>calc.</sub> ( g·cm <sup>-3</sup> )	1.698	1.605	1.548
T (K)	297	297	297
λ ( MoKα ) ( Å )	0.71073	0.71073	0.71073
μ	6.917	7.588	6.452
R <sub>1</sub>	0.0476	0.0872	0.0488
R <sub>w</sub>	0.0590	0.0851	0.0528
F(000) (e)	1848	1856	2144
Crystal size (mm)	0.25 × 0.25 ×	0.12 × 0.15 ×	0.15 × 0.15 × 0.18
No. of reflection measured	0.15	0.18	4654
No. of observed data	3646	4036	3332
Criterion for observed data	3172	2584	I > 3σ(I)
Largest diff. Peak and hole (e/Å <sup>3</sup> )	I > 3σ(I)	I > 1σ(I)	0.497 and -0.058

**Figure 1** Crystal Structure of [ Cd ( 4, 4' - bpy )<sub>2</sub> ( H<sub>2</sub>O )<sub>2</sub> ]<sub>n</sub> ( pic )<sub>2n</sub>



**Table 2** Selected Bond Distance ( Å ) and Angles ( deg ) for **1-3**

complex 1		complex 2		complex 3	
Cd(1)-O(1)	2.327(3)	Zn(1)-O(W1)	2.083(9)	Zn(1)-O(1)	2.181(4)
Cd(1)-N(1)	2.361(4)	Zn(1)-O(W2)	2.19(1)	Zn(1)-O(2)	2.108(4)
Cd(1)-N(2)	2.381(4)	Zn(1)-N(1)	2.172(9)	Zn(1)-N(1)	2.150(7)
		Zn(1)-N(2)	2.164(9)	Zn(1)-N(2)	2.207(6)
		Zn(1)-N(3)	2.15(2)	Zn(1)-N(3)	2.160(7)
		Zn(1)-N(4)	2.22(2)	Zn(1)-N(4)	2.198(6)
O(1)-Cd(1)-O(1)	177.3(1)	O(W1)-Zn(1)-O(W2)	176.9(4)	O(1)-Zn(1)-O(2)	178.3(2)
O(1)-Cd(1)-N(1)	86.9(1)	O(W1)-Zn(1)-N(1)	91.7(7)	O(1)-Zn(1)-N(1)	89.2(2)
O(1)-Cd(1)-N(1)	91.0(1)	O(W1)-Zn(1)-N(2)	93.5(5)	O(1)-Zn(1)-N(2)	89.8(2)
O(1)-Cd(1)-N(2)	85.2(1)	O(W1)-Zn(1)-N(3)	91.7(4)	O(1)-Zn(1)-N(3)	90.0(2)
O(1)-Cd(1)-N(2)	96.7(1)	O(w1)-Zn(1)-N(4)	90.3(4)	O(1)-Zn(1)-N(4)	89.9(2)
N(1)-Cd(1)-N(1)	83.4(1)	O(W2)-Zn(1)-N(1)	86.5(7)	O(2)-Zn(1)-N(1)	92.6(2)
N(1)-Cd(1)-N(2)	171.3(1)	O(W2)-Zn(1)-N(2)	88.3(5)	O(2)-Zn(1)-N(2)	90.3(2)
N(1)-Cd(1)-N(2)	93.0(1)	O(W2)-Zn(1)-N(3)	90.7(4)	O(2)-Zn(1)-N(3)	88.2(2)
N(2)-Cd(1)-N(2)	91.6(1)	O(W2)-Zn(1)-N(4)	87.2(4)	O(2)-Zn(1)-N(4)	90.1(2)
		N(1)-Zn(1)-N(2)	174.8(8)	N(1)-Zn(1)-N(2)	89.5(2)
		N(1)-Zn(1)-N(3)	88.0(7)	N(1)-Zn(1)-N(3)	179.0(1)
		N(1)-Zn(1)-N(4)	91.8(7)	N(1)-Zn(1)-N(4)	89.4(2)
		N(2)-Zn(1)-N(3)	92.4(6)	N(2)-Zn(1)-N(3)	89.9(2)
		N(2)-Zn(1)-N(4)	87.7(6)	N(2)-Zn(1)-N(4)	178.9(2)
		N(3)-Zn(1)-N(4)	178.0(5)	N(3)-Zn(1)-N(4)	91.2(2)

at the apical positions, as shown in **Figure 1**. In these complexes, each pair of adjacent metal ions are bridged by a  $\mu_2$ -4,4'-bpy ligand to form infinite three-dimensional network structures. The three-dimensional cavity of the network has dimensions of  $8.2097(3) \times 8.2097(3) \times 9.3158(3)$  Å,  $9.185(1) \times 11.418(2) \times 11.418(2)$  Å and  $11.4420(9) \times 11.4377(9) \times 8.5833(9)$  Å for complexes **1**, **2** and **3**, respectively, which are different from those of the reported two-dimensional cavities<sup>8,9,10,11</sup> formed by divalent metal and the ligand of 4,4'-bipyridine. The size of the cavity corresponds to the number of the guest molecules that are clathrated in each host cavity of the complex and are further stabilized by hydrogen bonding interactions. Here the guests clathrated in each cavity represent two picric anions for complex **1**, two water molecules and two picric anions for complex **2**, one water molecule, one 4,4'-bipyridine molecule and two picric anions for complex **3**. Actually, in complex **1**, the coordinated water molecule exists interaction with both the oxygen of the deprotonated hydroxyl and the oxygen of the nitro-group in the picric anion *via* inter-molecular hydrogen bonding ( O(1)···O(2): 2.644(4) Å, O(1)···O(7): 2.941(6) Å ). In complex **2**, the picric anion and uncoordinated water molecule, which interact with each other through hydrogen bonds ( O(W<sub>3</sub>)···O(6):2.80(2), O(W<sub>4</sub>)···O(12):2.92(2) Å ), are inlaid in the cavity of the network by hydrogen bonds with coordinated water molecule ( O(W1)···O(W3): 2.79(2), O(W2)···O(W4): 2.71(2) Å for uncoordinated water molecule with coordinated water molecule; O(W1)···O(10): 2.61(2), O(W2)···O(3): 2.72(1) Å for coordinated water molecule with the oxygen of the hydroxyl in picric anion ). Unlike complex **1** and **2**, there is no really hydrogen bonding between the picric anion and the coordinated water

molecule in complex **3**. Only a very weak interaction exists between the picric anion and the coordinated water molecule by forming double hydrogen-bonding of the type  $N-O\cdots H-O-H\cdots O-Zn$ . The most interesting feature that differs from complex **1** and **2** is that the uncoordinated 4,4'-bipyridine is clathrated in the cavity only in the form of free molecule by forming hydrogen bonding with the coordinated water molecule (  $O(1)\cdots N(11)$ : 2.715(8),  $O(2)\cdots N(12)$ : 2.743(8) ).

It is noteworthy that the pair of pyridyl rings are twisted a certain angle (  $32.3(2)^\circ$  for complex **1**,  $39.5(4)^\circ$  and  $14(1)^\circ$  for complex **2**,  $34.2(3)^\circ$ ,  $150.00(4)^\circ$  and  $17.6(6)^\circ$  for complex **3** ). Perhaps it can be ascribed to the big volume and poor coordinating ability of the counter-anion of picric.

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