A Novel Zinc(II) Supramolecular Complex with Open 2D Channels

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In recent years, the construction of metal-organic frameworks with open channels or cavities has been focused on because of their intriguing variety of architectures and potentially interesting properties.[1-5] In general, we can select the appropriate organic molecules and metal-ion building blocks to assemble multidimensional networks containing channels or cavities of various sizes and shapes.[6-11,5] However, the complexes, especially to the low dimensional complexes with channels or cavities in two different directions have rarely been reported.[12,13] In this paper, we synthesized the title complex, $[Zn(PZDC)(4,4'\text{-bpy})_{0.5}(H_2O)_2]\cdot(4,4'\text{-bpy})_{0.5}\cdot H_2O$ (**I**) with pyrazine-2,6-dicarboxylic (H_2PZDC) and auxiliary ligand 4,4'-bpy, which has the novel 3D supramolecular network with open 2D channels. Such structural feature, to the best of our knowledge, has never been described before in the system of metal-PZDC complexes.[14-23] In the complex, free 4,4'-bpy molecule may serve as a structure directing (or 'templating') agent thus resulting in the formation of the structure.

Single crystal X-ray structural analysis reveals that the title complex (**I**) crystallizes in orthorhombic I222 space group and exhibits a unique 3D supramolecular network containing open 2D channels along the a- and b-axis. In the asymmetric unit, there is only one crystallographically independent Zn(II) ion, one PZDC ligand, half of coordinated 4,4'-bpy as well as half of free 4,4'-bpy molecule, and two coordinated water molecules together with one free water molecule. The Zn(II) ion is six-coordinated, by two nitrogen atoms and one oxygen atom from one PZDC ligand, one nitrogen atom from one 4,4'-bpy molecule and two oxygen atoms from two water molecules. Therefore, the local coordination geometry of Zn(II) ion is in a distorted octahedron with a N2O4 donor net and is shown in Figure 1.

In the title complex, the coordinated 4,4'-bpy molecule bridges two Zn(II) ions to generate a binuclear unit. Such binuclear units as the building blocks are linked by rich hydrogen bonds and π-π stacking interactions into 3D supramolecular network, which has open 2D channels and the channels volume is 37.8% of the total crystal volume as estimated by PLATON. Interestingly, in the complex the shape and size of the two channels are different. Along the a-axis, these 1D supramolecular chains are arranged alternatively by hydrogen bonds between the coordinated water molecule and the uncoordinated carboxylate oxygen atoms into 3D supramolecular network containing the 1D rectangular channels with the dimension of approximate 10.131×10.652 Å^2, which are occupied by the free 4,4'-bpy molecules (see Figure 2a).

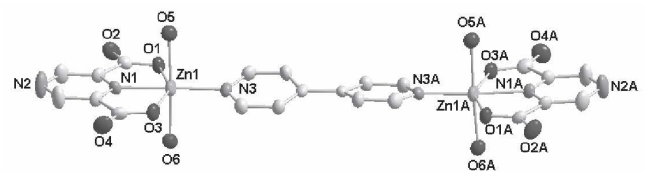

Figure 1. The coordination environment of Zn(II) ions in the title complex with 30% probability thermal ellipsoids. Lattice water molecule and free 4,4'-bpy molecule and all hydrogen atoms are omitted for clarity.

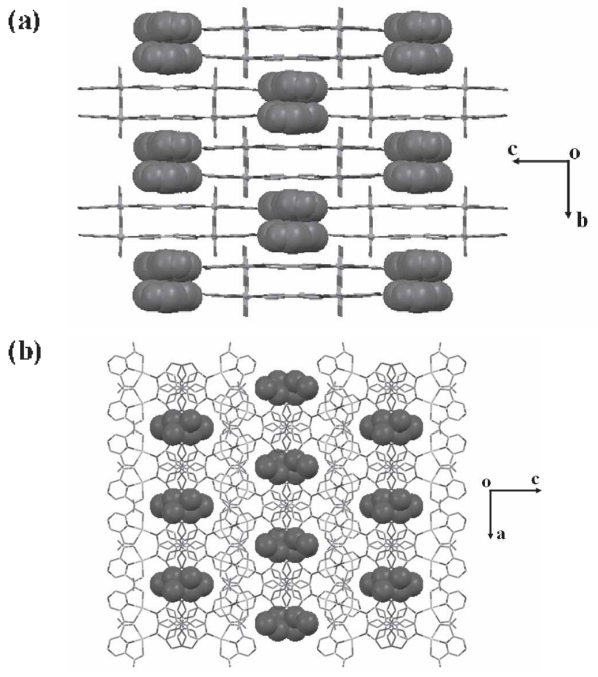

Figure 2. (a) 3D packing diagram viewed along the a-axis (the space filling models represent free 4,4'-bpy molecules. (b) 3D packing diagram viewed along the b-axis (the space filling models represent guest water molecules).

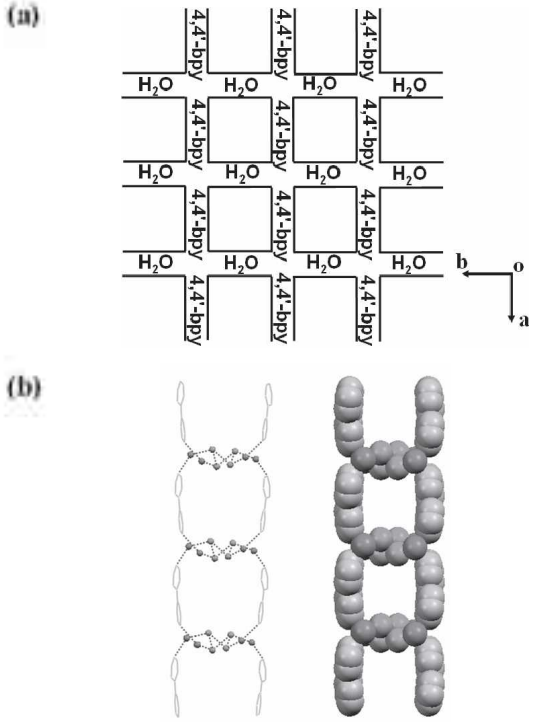

Figure 3. (a) The schematic diagram of the open 2D channels of the title complex which contains the guest water and 4,4'-bpy molecules; (b) The ladder-like hydrogen-bonded chain composed of the free water and 4,4'-bpy molecules in the title complex.

Along the b-axis, these 1D supramolecular chains are assembled into 3D network structure with 1D rhombic channels in which the guest water molecules reside, as shown in Figure 2b. In such packing fashion, the coordinated 4,4'-bpy and uncoordinated 4,4'-bpy molecules crisscross in different directions to form beautiful flower-like structure with the 4,4'-bpy molecules overlapping and showing weak π-π interactions (with the distance of 3.358 Å). Guest water molecules reside in these channels, which take part in extensive hydrogen bonds.

Figure 3a shows the schematic diagram of the open 2D channels of the title complex which contains the guest water and 4,4'-bpy molecules. The most interesting feature of the complex is that the guest water molecules and free 4,4'-bpy molecules in the two channels form the ladder-like hydrogen-bonded chains. The water-4,4'-bpy chain consists of water molecule bridge which is disordered and the 4,4'-bpy rod. Four water molecules (with the occupancy of 65%) lie in the apexes of tetrahedron with the average O_{water}-O_{water} separation is 2.798 Å, and another four pendent water molecules (with the occupancy of 35%) connect with the four water molecules, respectively. On the other hand, the four pendent water molecules link with free 4,4'-bpy molecules *via* hydrogen bonds (O-H···N) to form the infinite ladder-like chains, as shown in Figure 3b. In the complex, free 4,4'-bpy may play a template role in the construction of the supramolecular structure.

Experimental Section

General methods and materials. Pyrazine-2,6-dicarboxylic acid dihydrate was synthesized according to the literature.[24-26] All the other reagents were used as received without further purification. The C, H, N analyses were carried out with a Vario EL elemental analyzer. The IR spectrum was recorded with a Nicolet Avatar 360 FT-IR spectrometer using the KBr pellet technique.

Synthesis of $[Zn(PZDC)(4,4'\text{-bpy})_{0.5}(H_2O)_2]\cdot(4,4'\text{-bpy})_{0.5}\cdot H_2O$ (I). The complex was prepared by the reaction of $Zn(NO_3)_2\cdot 6H_2O$ (0.0297 g, 0.1 mmol), H_2PZDC (0.0204 g, 0.1 mmol), 4,4'-bpy (0.0192 g, 0.1 mmol), NaOH (0.3 mL, 0.65 mol·L^{-1}) and H_2O (3 mL) in a Teflon-lined stainless steel vessel (25 mL) and heated at 160°C for 4 days under autogeneous pressure and then cooled slowly to room temperature. The solution was filtered and allowed to stand at room temperature for a few months. Light-yellow block crystals were obtained. Elemental analysis for $C_{16}H_{16}ZnN_4O_7$ calcd: C, 39.07; H, 3.63; N, 11.91%. Found: C, 39.30; H, 3.61; N, 11.36%. IR (KBr pellet, cm^{-1}): 3440 br, 1650 s, 1612 s, 1565 w, 1535 m,

Table 1. Crystal data and structure refinement parameters for the title complex.

Chemical formula	C16H16ZnN4O7
Formula weight	441.70
Temperature [K]	294(2)
Crystal system	orthorhombic
Space group	I222
a (Å)	10.354(16)
b (Å)	13.136(2)
c (Å)	27.737(5)
α (°)	90
β (°)	90
γ (°)	90
V (Å^3)	3772.3(10)
Z	8
F(000)	1808
ρ [mg m^{-3}]	1.555
μ [mm^{-1}]	1.349
θ range (deg)	1.72-25.01
Reflections collected	7774
Crystal size (mm)	0.24◈0.22◈0.20
Flack	0.00(3)
Total independent, R_{int}	3341(0.0344)
Goodness-of-fit on F^2	1.141
R indices [I>2σ(I)]	R1 = 0.0389 wR2 = 0.1182

Table 2. Select bond lengths (Å) and angles (°) for the title complex.

Zn(1)-O(1)	2.169(3)	Zn(1)-O(5)	2.153(3)
Zn(1)-O(3)	2.242(3)	Zn(1)-O(6)	2.168(3)
Zn(1)-N(1)	2.054(3)	Zn(1)-N(3)	2.039(3)
O(1)-Zn(1)-O(3)	151.03(12)	O(6)-Zn(1)-O(3)	92.07(15)
O(5)-Zn(1)-O(1)	88.76(16)	N(3)-Zn(1)-O(1)	108.99(13)
O(5)-Zn(1)-O(3)	176.33(11)	N(1)-Zn(1)-O(1)	76.51(14)
O(5)-Zn(1)-O(6)	88.21(15)	N(1)-Zn(1)-O(3)	74.54(13)
O(6)-Zn(1)-O(1)	89.58(15)	N(1)-Zn(1)-O(5)	88.85(19)
N(1)-Zn(1)-O(6)	88.43(19)	N(3)-Zn(1)-O(3)	99.97(13)
N(3)-Zn(1)-O(5)	92.12(16)	N(3)-Zn(1)-O(6)	90.82(16)
N(3)-Zn(1)-N(1)	174.42(15)		

Table 3. Hydrogen bonds geometries (Å, °) for the title complex.

D-H···A	D(D-H)	d(H···A)	d(D···A)	∠DHA	Symmetry code
O5-H5A···O2	0.847	1.897	2.718	163.10	[1/2+x, 1/2-y, 1/2-z]
O5-H5B···O4	0.847	1.896	2.686	154.65	[-1/2+x, 1/2-y, 1/2-z]
O6-H6A···O2	0.847	1.955	2.773	161.84	[-x, 1-y, z]
O6-H6B···O3	0.873	2.053	2.779	140.01	[-x+2, -y+2, z]
O7-H7A'_a···N4	0.829	2.145	2.967	171.66	[1-x, 1-y, z]
O7-H7B'_a···O1	0.837	2.231	3.058	170.01	
O7'-H7'A···O7'_b	0.850	2.194	2.906	141.31	
O7'-H7'B···O7'_b	0.850	2.402	3.155	147.81	
C3-H3···O5	0.930	2.470	3.255	142.07	[-1/2+x,1/2-y, 1/2-z]
C4-H4···O7	0.930	2.581	3.245	129.10	[1/2-x, -1/2+y, 1/2-z]
C7-H7···O6	0.930	2.552	3.275	135.13	[-x+2, -y+2, z]
C12-H12···O5	0.930	2.601	3.423	148.02	

1489 w, 1415 m, 1361 s, 1215 m, 1198 w, 1135 m, 1071 s, 1023 m, 924 w, 808 s, 743 m.

X-ray crystallographic study. The single-crystal X-ray data collection for the title complex was performed with a Bruker SMART 1000 CCD diffractmeter, using graphite-monochromatized Mo-K_α radiation (λ = 0.71073Å). Semi-empirical absorption corrections were applied using the SADABS program.[27] The structure was solved by direct methods [28] and refined by full-matrix least squares on F^2 using the SHELXL-97 program.[29] All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were generated geometrically and treated by a mixture of independent and constrained refinement. The crystallographic data for the complex are listed in Table 1, selected bond lengths (Å) and angles (°) are listed in Table 2, the details of the hydrogen bonds for the complex are listed in Table 3.

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Supplementary Material. Crystallographic data for the structure reported in this paper has been deposited at the Cambridge Crystallographic Data Center as supplementary publication: CCDC No 693304 for the title complex. Copies of the data can be obtained free of charge on application to 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).

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