

SYNTHESIS AND STRUCTURE OF A CLATHRATED TWO-DIMENSIONAL METAL-ORGANIC FRAMEWORK:



(L = BIS(1-PYRAZINYLETHYLIDENE)HYDRAZINE)

Dayu WU^{a1,*}, Genhua WU^{a2}, Wei HUANG^b and Zhuqing WANG^{a3}

^a School of Chemistry and Chemical Engineering, Anqing Normal College,
Anqing, 246011, P.R. China; e-mail: ¹ wudayu_nju@yahoo.com.cn, ² wugenh@aqtc.edu.cn,
³ wangzhq@aqtc.edu.cn

^b State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering,
Nanjing University, Nanjing, 210093, P.R. China; e-mail: weihuang0525@yahoo.com.cn

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The compound $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{L})_2$ was obtained by the reaction of $\text{Cd}(\text{ClO}_4)_2$, bis(1-pyrazinylethylidene)hydrazine (L) and 4,4'-bipyridine in aqueous MeOH. Single-crystal X-ray diffraction has revealed its two-dimensional metal-organic framework. The 2-D layers superpose on each other, giving a channel structure. The square planar grids consist of two pairs of shared edges with Cd(II) ion and a 4,4'-bipyridine molecule each vertex and side, respectively. The square cavity has a dimension of $11.817 \times 11.781 \text{ \AA}$. Two guest molecules of bis(1-pyrazinylethylidene)hydrazine are clathrated in every hydrophobic host cavity, being further stabilized by π - π stacking and hydrogen bonding. The results suggest that the hydrazine molecules present in the network serve as structure-directing templates in the formation of crystal structures.

Keywords: Cadmium; Bipyridine ligands; Coordination complexes; Crystal structure; X-ray diffraction; Clathration; Metal-organic framework.

Construction of metal-organic frameworks (MOFs) based on metal-ligand coordination is an active research area, mostly motivated by their intriguing structural features and enormous range of applications in catalysis, as adsorbent and in molecular recognition¹. MOFs can be designed and constructed to generate cavities or channels of various size and shape by controlling the architecture and functionalization of organic linkers². So far, simple linear spacers, such as 4,4'-bipyridine and pyrazine, have proved to be efficient in generating of a wide range of infinite frameworks, including diamondoid³, honeycomb⁴, grid⁵, T-shaped⁶, ladder⁷, brick-wall⁸, and octahedral⁹ frameworks.

On the other hand, the design of supramolecular architecture with pore or channel structure has attracted much attention in the field of host-guest chemistry, as hollow host molecules possess the potential to bind guests, to stabilize reactive intermediates or to promote chemical reactions in their interior¹⁰. Although the high-dimensional metal-organic framework can often absorb some solvent molecules and guest counterions, it is somewhat surprising that only very few frameworks have been reported to clathrate larger organic guest molecules¹¹. We report here the preparation and crystal structure of a 2-D metal-organic framework with a square grid clathrating larger neutral organic guest molecule, namely $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{L})_2 \cdot \text{H}_2\text{O}$ (L = bis(1-pyrazinylethylidene)hydrazine; Chart 1).

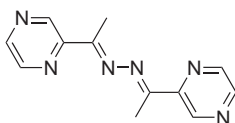


CHART 1
The guest molecule (L)

RESULTS AND DISCUSSION

The title complex has been characterized by single-crystal X-ray crystallography. The complex crystallized in the orthorhombic space group $C222(1)$. The structural analysis has unambiguously revealed that the asymmetric unit consists of one 4,4'-bpy ligand, half a Cd(II) ion, a neutral guest molecule, bis(1-pyrazinylethylidene)hydrazine (Chart 1), and a disordered perchlorate anion. X-ray crystallography shows that the title complex is made up of two-dimensional square grids (Figs 1 and 2). The bond distances and bond angles are within the normal range (Table I). The superposition of such square grids creates large square channels, as shown in Fig. 3. Every layer consists of two pairs of shared edges to perfectly form a square plane with the Cd(II) ion and the 4,4'-bpy ligand at each vertex and side, respectively; although, each square is slightly distorted ($\text{cis-N-Cd-N} = 89.07(14)$ and $91.08(14)^\circ$, see Table I). The square cavity has a dimension of $11.817 \times 11.781 \text{ \AA}$, which is comparable with those in related compounds^{11b}. In the title complex, the metal ion is located at a two-fold crystallographic axis. Its coordination sphere is a slightly distorted octahedral geometry, with four pyridyl groups (the average distance $\text{Cd-N} = 2.358 \text{ \AA}$) in the equatorial positions and two aqua ligands ($\text{Cd-O} = 2.375(3)$ and $2.451(3) \text{ \AA}$, respectively)

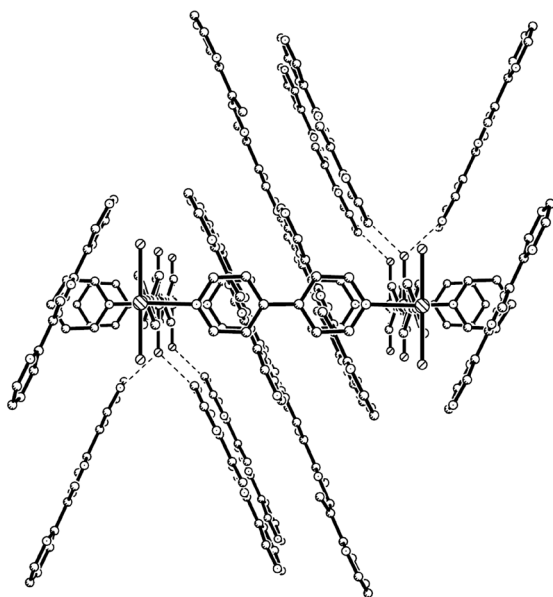


FIG. 1

View of the square units in the title compound along [100]; perchlorate anions and hydrogen bonds are not shown for clarity

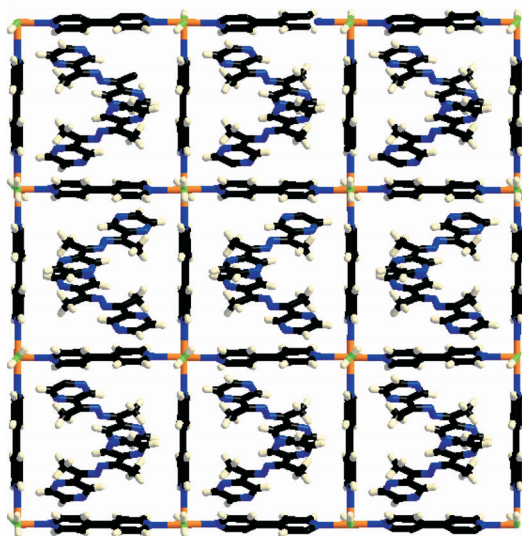


FIG. 2

View of one layer of the square grids in the structure of the title compound along [010]

TABLE I
Selected bond length (in Å) and bond angles (in °) in $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{L})_2 \cdot \text{H}_2\text{O}$

Bond length		Bond angle	
Cd1–N7	2.357(3)	N7–Cd1–N8	89.07(14)
Cd1–N8	2.358(3)	N7–Cd1–N8#	91.08(14)
Cd1–O2	2.446(4)	N7–Cd1–N7#	174.68(17)
C5–N4	1.273(8)	N8–Cd1–N8	176.79(17)
C7–N3	1.282(9)	N7–Cd1–O1	92.66(8)
N3–N4	1.411(6)	N8–Cd1–O1	88.40(9)
O1...N6##	2.873(6)	N7–Cd1–O2	87.34(8)
		N8–Cd1–O2	91.60(9)
		O1–Cd1–O2	180.00(1)

Symmetry code to yield the equivalent atom #: 1 - x , y , $-z + 1/2$; ##: $-x$, $-y + 1$, $1.5 + z$.

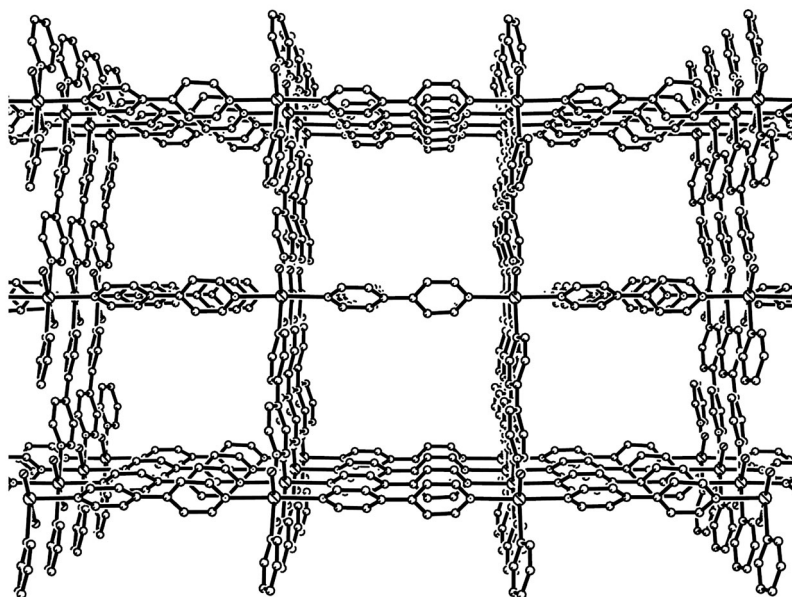


FIG. 3

View of the square channels in the title compound along $[110]$; hydrogen atoms, perchlorate anions and guest organic molecules are not shown for clarity

in the apical positions. It is noteworthy that two guest molecules of bis(1-pyrazinylethylidene)hydrazine are clathrated in every hydrophobic host cavity, being further stabilized by π - π stacking and hydrogen bonding (Fig. 1). The hydrophobic guest molecule, bis(1-pyrazinylethylidene)hydrazine, is in the square hydrophobic cavity and the 4-N terminal forms an acceptor hydrogen bond with an aqua ligand of the adjacent upper or lower layer ($O1 \cdots N6A = 2.873(6)$ Å, symmetry code A: $-x, -y + 1, 1.5 + z$). The perchlorate anions also form an acceptor of a weak hydrogen bond with pyrazine C-H ($O \cdots C = 3.452(9)$ Å). The guest molecules adopt nearly coplanar arrangement, in which all the carbon atoms are in the same plane. Each guest molecule is parallel to each other. In the individual hydrophobic host cavity, two guest molecules are interlaced to form 'x'-shaped configuration, which is possibly favored by the minimum potential energy and stability of the metal-organic frameworks. Furthermore, the guest molecule stacks with the adjacent guest molecules in an offset fashion, with the distance ca. 3.5 Å between the pyrazine rings. This indicates a significant π - π stacking interaction in the system, which further stabilizes the clathrated 2-D metal-organic framework. Thus, in the self-assembled structure of the clathrated MOFs, the main driving force can be attributed to the hydrophobic interactions between the cavity of MOF and aromatic rings of the guest molecules, and to the hydrogen bonds between the aqua ligands and the pyrazine nitrogen atom.

Comparison with a similar clathrated compound based on a two-dimensional square network composed of cadmium(II) and 4,4'-bipyridine published by Fujita et al.^{5a} reveals that the crystal structure of the title compound is characterized by several distinct features. (i) Using ClO_4^- instead of NO_3^- avoids coordination of the anion to the Cd(II) center; hence, it is expected to create a counteranion-balanced charged host 2-D network rather than a neutral host-guest complex. (ii) Here, a much larger guest molecule, bis(1-pyrazinylethylidene)hydrazine, was adopted for the clathration in the host 2-D framework compared to $o-C_6H_4X_2$ ($X = Cl, Br$). (iii) The terminal pyrazine-nitrogen atom as the acceptor of hydrogen bonding permits interaction with the coordinated water molecules. (iv) In addition to the host-guest interaction, weak interaromatic π - π interaction does also exist between the guest molecules in the host-guest framework. Two guest molecules of bis(1-pyrazinylethylidene)hydrazine are therefore clathrated in every hydrophobic host cavity. In conclusion, a 2-D square grid with a channel structure clathrating large neutral conjugated organic molecules has been prepared and structurally characterized, pointing to further oppor-

tunities in clathrating sterically demanding substrates in organic synthesis and catalysis.

EXPERIMENTAL

General

All reagents were commercially available and were used as received. IR spectra were recorded on a Vector 22 Bruker spectrometer in the range 400–4000 cm^{-1} . Elemental analyses were performed with a Perkin–Elmer 240 analyzer. The guest molecule, bis(1-pyrazinylethylidene)hydrazine (L), was prepared according to the literature method¹² and identified with ^1H NMR and ESI-MS spectroscopy.

Safety note: Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and handled with care.

Synthesis of $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{L})_2 \cdot \text{H}_2\text{O}$

To 25 ml of a methanolic solution of $\text{Cd}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ (0.037 g, 0.1 mmol) a solution of 4,4'-bipyridine (0.0156 g, 0.1 mmol) in MeOH (5 ml) was slowly added during 30 min at re-

TABLE II

Crystallographic parameters for $[\text{Cd}(4,4'\text{-bpy})_2(\text{H}_2\text{O})_2](\text{ClO}_4)_2 \cdot (\text{L})_2 \cdot \text{H}_2\text{O}$ (L = bis(1-pyrazinylethylidene)hydrazine)

Chemical formula	$\text{C}_{44}\text{H}_{42}\text{CdN}_{16}\text{O}_{10}\text{Cl}_2$
Formula weight	1138.24
Crystal colour, habit	colourless, block
Crystal dimensions	$0.2 \times 0.2 \times 0.15$ mm
Crystal system	orthorhombic
Space group	$C222(1)$
Lattice parameters	$a = 11.7805(10)$ Å $b = 17.1957(15)$ Å $c = 23.633(2)$ Å
Volume	$4787.5(7)$ Å ³
Z	4
D_{calc}	1.579 g cm^{-3}
$F(000)$	2320
$\mu(\text{MoK}\alpha)$	0.644 mm^{-1}
Reflections/restraints/parameters	4225/27/344
Residuals: $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0383/0.0776
Goodness of fit, S	1.002

fluxing temperature on stirring. A solution of bis(1-pyrazinylethylidene)hydrazine (0.024 g, 0.1 mmol) in MeOH (5 ml) was slowly added in the next step. The resulting mixture was stirred for another 30 min at boiling temperature and cooled down. Colorless block crystals deposited within 5 days. Yield 0.04 g, 0.035 mmol; 70%). For $C_{44}H_{42}CdCl_2N_{16}O_{10}$ (1138.2) calculated: 46.43% C, 3.72% H, 19.69% N; found: 46.42% C, 3.65% H, 19.62% N. IR (KBr pellet, cm^{-1}): 3125.2 w, 1586.5 s, 1526.3 m, 1475.9 w, 1452.5 m, 1405.6 s, 1322.5 w, 1142.3 s, 1105.5 s, 1078.5 s, 997.5 m, 800.8 m, 768.8 s, 728.5 m, 625.5 s, 568.8 w.

X-ray Crystallography

Intensities were collected on a Siemens Smart-CCD diffractometer with graphite-monochromatized $MoK\alpha$ ($\lambda = 0.71073 \text{ \AA}$) using the SMART and SAINT programs¹³. Forty-five frames of data were collected at 298 K with an oscillation range of 1° /frame and an exposure time of 10 s/frame. Indexing and unit cell refinement were based on all the observed reflections from the 45 frames. The structure was solved by direct method and refined on F^2 by full-matrix least-squares methods with SHELXTL, version 5.1¹⁴. All the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. Hydrogen atoms were located geometrically, whereas those of solvent molecules were found on Fourier difference maps; all the hydrogen atoms were refined in a riding model. Crystallographic data for the title compound are listed in Table II.

CCDC 661340 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; fax: +44 1223 336033; or deposit@ccdc.cam.ac.uk).

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