Inorg. Chem. **1998,** *37,* 2645−2650

Clathration of Two-Dimensional Coordination Polymers: Synthesis and Structures of $[M(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ and $[Cu(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_4\cdot(4,4'\text{-}H_2Bpy)$ ($M = Cd^{II}$, Zn^{II} and bpy = Bipyridine)

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Received November 12, 1997

In the presence of guest 2,4′-bpy molecules or under acidic conditions, three compounds, $[Cd(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (**1**), $[Zn(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (**2**), and $[Cu(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_4\cdot(4,4'\text{-}H_2bpy)$ (**3**), were obtained from the reactions of the metal salts and 4,4′-bpy in an $EtOH-H_2O$ mixture. **1** has a 2-D square-grid network structure, crystallizing in the monoclinic space group $P2/n$, with $a = 13.231(3)$ Å, $b = 11.669(2)$ Å, $c = 15.019(3)$ Å, $\beta = 112.82(3)°$, $Z = 2$; **2** is isomorphous with **1**, crystallizing in the monoclinic space group $P2/n$, with $a = 13.150(3)$ Å, $b = 11.368(2)$ Å, $c = 14.745(3)$ Å, $\beta = 110.60(3)°$, $Z = 2$. The square grids superpose on each other into a channel structure, in which each layer consists of two pairs of shared edges, perfectly square-planar with an M^{II} ion and a 4,4′-bpy at each corner and side, respectively. The square cavity has dimensions of $11.669(2) \times 11.788(2)$ and $11.368(2) \times 11.488(2)$ Å for **1** and **2**, respectively. Every two guest 2,4′-bpy molecules are clathrated in each hydrophobic host cavity and are further stabilized by $\pi-\pi$ stacking and hydrogen bonding interactions. The NMR spectra clearly confirm that both **1** and **2** contain 4,4′-bpy and 2,4′-bpy molecules in a 1:1 ratio, which have stacking interaction with each other in the solution. **3** crystallizes in the orthorhombic space group *Ibam*, with $a = 11.1283(5)$ Å, $b = 15.5927(8)$ Å, $c = 22.3178(11)$ Å, $Z = 4$. **3** is made up of two-dimensional square $[Cu_4(4,4'\text{-bpy})_4]$ grids, where the square cavity has dimensions of 11.13×11.16 Å. Each $[4,4'\text{-}H_2bpy]^{2+}$ cation is clathrated in a square cavity and stacks with one pair of opposite edges of the host square cavity in an offset fashion with the face-to-face distance of ca. 3.95 Å. Within each cavity, the $[4,4'\text{-}H_2bpy]^{2+}$ cation forms twin three-center hydrogen bonds with two pairs of ClO_4^- anions. The results suggest that the guest 2,4′-bpy molecules and protonated $[4,4'\text{-}H_2bpy]^{2+}$ cations present in the reaction systems serve as structure-directing templates in the formation of the crystal structures and exclude self-inclusion of the networks having larger square cavities.

Introduction

Recently, a new research realm in crystal engineering of supramolecular architectures assembled by means of coordinate covalent bonding,[1] hydrogen bonding,[2] or other weak intermolecular interactions[3] has been rapidly expanding in order to rationally develop new classes of functional materials with zeolite-like molecular-sized channels, cavities, and pores. The construction of such cavities surrounded mainly by aromatic edges is very attractive because the shape, size, and function of the cavity may be designable on the basis of the different oxidation states, the coordination preference of the metal ions, the types of ligands and solvents, and the molar ratio of the metal ions to the ligands. So far a number of boxes[4] and a wide range of infinite frameworks, including diamondoid,[5] honeycomb,[5a,6] grid,[7] T-shaped,[8] ladder,[9] brick wall,[7a,9a] and octahedral[10] frameworks, has already been generated with simple, linear spacers such as 4,4′-bipyridine and pyrazine.

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S0020-1669(97)01429-8 CCC: \$15.00

Table 1. Crystallographic and Experimental Data for **1**−**3**

	1	**2**	**3**
empirical formula	$C_{40}H_{38}CdCl_2N_8O_{11}$	$C_{40}H_{38}ZnCl_2N_8O_{11}$	$C_{30}H_{30}CuCl_4N_6O_{18}$
fw	990.08	943.05	967.94
cryst syst	monoclinic	monoclinic	orthorombic
space group	*P*2/*n* (No. 13)	*P*2/*n* (No. 13)	*Ibam* (No. 72)
a (Å)	13.231(3)	13.150(3)	11.1283(5)
b (Å)	11.669(2)	11.368(2)	15.5927(8)
c (Å)	15.019(3)	14.745(3)	22.3178(11)
β (deg)	112.82(3)	110.60(3)	90
V (Å^3)	2137.3(7)	2063.3(7)	3872.6(3)
Z	2	2	4
ρ_{calc} (g cm^{-3})	1.538	1.518	1.660
T (°C)	20(2)	20(2)	20(2)
λ (Mo Kα) (Å)	0.710 73	0.710 73	0.710 73
μ (Mo Kα) (cm^{-1})	7.05	7.96	9.25
R_1 ($I > 2\sigma(I)$)^a	0.0448	0.0576	0.0546
wR_2 (all data)^a	0.1167	0.1660	0.1546

^{a} $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$, w$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, $w = [\sigma^2(F_o)^2 + (0.1(\max(0,F_o^2) + 2F_c^2)/3)^2]^{-1}$.

On the other hand, the design of supramolecular architectures has attracted much attention in the field of host−guest chemistry.[7b] Although a number of the infinite frameworks are rigid and well meet the requirements that the host is relatively rigid and contains large cavities, and although the van der Waals surfaces and electrostatic potential surfaces of the host and guest may be complementary,[4a] it is somewhat surprising that very few frameworks have been reported to clathrate larger organic guest molecules.[1a,7b,c] We report herein the preparation and crystal structures of three square grids clathrating larger neutral or cationic organic guest molecules, namely $[M(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (M = Cd^{II} (**1**), Zn^{II} (**2**) and $[Cu(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_4\cdot(4,4'\text{-}H_2bpy)$ (**3**) (bpy = bipyridine).

Experimental Section

All reagents were commercially available and used as received. The C, H, and N microanalyses were carried out with a Perkin-Elmer 240 elemental analyzer. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker ARX-300 NMR spectrometer using CD_3OD solvent at room temperature; the CD_3OD signal was used to lock the field and all chemical shifts are given relative to TMS; ^{1}H NMR spectra were measured at 300.132 MHz, and ^{13}C NMR spectra were obtained at 75.475 MHz using CD_3OD as an internal standard with wide-band proton decoupling. The FT-IR spectra were recorded from KBr pellets in range 4000−400 cm^{-1} on a Nicolet 5DX spectrometer.

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 great care.*

Synthesis. $[Cd(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (1). To a solution of $Cd(NO_3)_2\cdot 4H_2O$ (0.308 g, 1.0 mmol) in 4:1 (*v*/*v*) EtOH/H_2O (10 mL) was added a solution of 4,4′-bpy (0.156 g, 1.0 mmol) in EtOH (5 mL) slowly with stirring for 15 min at 60 °C; a solution of 2,4′-bpy (0.156 g, 1.0 mmol) in EtOH (5 mL) was then slowly added. The resulting mixture was stirred for 15 min at 60 °C, and addition of $NaClO_4$ (2.0 mmol, 0.280 g) followed. Colorless block-crystals were deposited within 5 days (yield: 0.322 g, 0.325 mmol, 65% based on the ligands). Anal. Calcd for $C_{40}H_{38}N_8CdO_{11}Cl_2$: C, 48.52; H, 3.87; N, 11.32; Found: C, 48.34; H, 3.68; N, 11.22. IR data (ν/cm^{-1}): 3049 w, 1597 s, 1540 m, 1491 w, 1454 m, 1409 s, 1326 w, 1220 m, 1146 vs, 1105 vs, 1080 vs, 998 m, 826 w, 801 m, 777 s, 728 m, 629 vs, 564 w, 490 w. ^{1}H NMR data (ppm): 7.34−7.26 (8H, m), 6.75 (2H, br), 6.66 (1H, d, J = 7.9), 6.58 (1H, t), 6.49 (4H, d, J = 4.6). ^{13}C NMR data (ppm): 154.40, 150.62, 150.57, 150.25, 148.78, 147.00, 138.56, 125.26, 122.91, 122.41.

$[Zn(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (2). The reaction was carried out in the same way as for **1** except that $Zn(ClO_4)_2\cdot 6H_2O$ was used instead of $Cd(NO_3)_2\cdot 4H_2O$ and $NaClO_4\cdot H_2O$ (yield: 0.273 g, 0.258 mmol, 58% based on the ligands). Anal. Calcd for $C_{40}H_{38}N_8ZnO_{11}Cl_2$: C, 50.94; H, 4.06; N, 11.88. Found: C, 50.73; H, 4.02; N, 11.72. IR data (ν/cm^{-1}): 3050 w, 1679 w, 1609 s, 1539 m, 1489 w, 1461 m, 1412 s, 1321 w, 1222 m, 1145 vs, 1089 vs, 997 m, 807 m, 772 s, 730 m, 681 w, 625 s, 498 w. ^{1}H NMR data (ppm): 7.27−7.21 (8H, m), 6.66 (2H, d, J = 4.8), 6.62 (1H, d, J = 7.9), 6.54 (1H, t), 6.42 (4H, d, J = 4.7). ^{13}C NMR data (ppm): 154.59, 150.55, 150.13, 148.44, 146.90, 138.55, 125.16, 122.73, 122.44, 122.36.

$[Cu(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_4\cdot(4,4'\text{-}H_2bpy)$ (3). An alcohol solution (10 cm^3) of 4,4′-bpy (0.312 g, 2.0 mmol) was added dropwise to a stirred aqueous solution (5 mL) of $Cu(NO_3)_2\cdot 6H_2O$ (0.296 g, 1.0 mmol) at 50 °C for 15 min. The solution was adjusted to pH ≈ 5 by addition of dilute $HClO_4$ solution, and to this was added an aqueous solution (5 cm^3) of $NaClO_4$ (0.280 g, 2.0 mmol). The clear solution precipitated deep-blue block-shaped crystals after several days, 56% yield based on 4,4′-bpy. The crystals are lilac when viewed in one direction and grayish-blue when viewed from a different direction. Anal. Calcd for $C_{30}H_{30}N_6CuO_{18}Cl_4$: C, 37.23; H, 3.12; N, 8.68. Found: C, 37.12; H, 3.07; N, 8.46. IR data (ν/cm^{-1}): 3444 s, 3381 s, 3219 m, 3163 m, 3098 m, 2924 w, 2853 w, 1637 m, 1609 vs, 1532 w, 1489 s, 1419 s, 1222 m, 1145 vs, 1110 vs, 1082 vs, 1011 m, 814 s, 786 m, 723 w, 632 vs, 533 w, 484 w.

X-ray Crystallography. Diffraction intensities for complexes **1**, **2**, and **3** were collected at 20 °C on an Enraf-Nonius CAD4 diffractometer using the ω-scan technique. Lp and absorption corrections were applied.[11] The structures were solved with direct methods of SHELXS-86[12] and refined with full-matrix least-squares technique using the SHELXL-93 program.[13] Non-hydrogen atoms were refined anisotropically. The alkyl hydrogen atoms were generated geometrically (C−H = 0.96 Å); the aqua hydrogen atoms were located from difference maps and refined with isotropic temperature factors. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated.[14] The crystallographic data for **1**−**3** are listed in Table 1. Atomic coordinates, equivalent isotropic displacement parameters, and selected interatomic distances and angles for **1**−**3** are given in Tables 2−5, respectively. Drawings were produced with ORTEP-3.[15]

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Table 2. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **1**

atom	*x*	*y*	*z*	U_{eq}[a]
Cd(1)	7500	218(1)	7500	31(1)
N(1)	7500	−1764(3)	7500	37(1)
C(11)	7691(3)	−2356(3)	8309(2)	42(1)
C(12)	7696(3)	−3529(3)	8338(2)	41(1)
C(13)	7500	−4151(4)	7500	33(1)
C(14)	7500	−5415(4)	7500	34(1)
C(15)	8116(3)	−6032(3)	8321(2)	41(1)
C(16)	8094(3)	−7211(3)	8288(2)	41(1)
N(2)	7500	−7805(3)	7500	35(1)
N(3)	6557(2)	144(2)	8539(2)	41(1)
O(1w)	9203(2)	188(2)	8838(2)	48(1)
C(21)	6838(3)	729(3)	9363(2)	50(1)
C(22)	6253(3)	713(3)	9939(3)	53(1)
C(23)	5319(3)	30(3)	9692(2)	38(1)
C(24)	5035(3)	−577(4)	8843(3)	55(1)
C(25)	5659(3)	−497(4)	8292(3)	54(1)
N(4)	14393(3)	2973(4)	8759(4)	91(1)
N(5)	10847(3)	1697(4)	8901(3)	70(1)
C(30)	15234(5)	3548(6)	8681(6)	116(2)
C(31)	15286(5)	4700(5)	8616(6)	104(2)
C(32)	14437(5)	5313(5)	8634(5)	93(2)
C(33)	13554(4)	4774(4)	8712(4)	72(1)
C(34)	13564(3)	3601(4)	8774(3)	59(1)
C(35)	12622(3)	2950(3)	8831(3)	54(1)
C(36)	11798(3)	3461(4)	9036(3)	60(1)
C(37)	10939(3)	2812(4)	9073(3)	66(1)
C(38)	11644(4)	1195(4)	8696(4)	75(1)
C(39)	12535(3)	1778(4)	8673(3)	68(1)
Cl(1)	10754(1)	−2957(1)	8887(1)	58(1)
O(1)	10498(3)	−2002(3)	9345(2)	89(1)
O(2)	10416(4)	−3966(3)	9252(3)	111(1)
O(3)	11872(3)	−3043(5)	9140(5)	142(2)
O(4)	10117(4)	−2916(4)	7891(2)	113(1)
O(2w)	7500	1850(6)	2500	121(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **2**

atom	*x*	*y*	*z*	U_{eq}[a]
Zn(1)	7500	231(1)	7500	22(1)
N(1)	7500	−1643(3)	7500	21(1)
C(11)	7669(3)	−2272(3)	8315(2)	27(1)
C(12)	7684(3)	−3477(3)	8350(2)	28(1)
C(13)	7500	−4103(4)	7500	22(1)
C(14)	7500	−5426(4)	7500	22(1)
C(15)	8100(3)	−6053(3)	8319(2)	29(1)
C(16)	8078(3)	−7268(3)	8289(2)	27(1)
N(2)	7500	−7896(3)	7500	20(1)
N(3)	6582(2)	174(2)	8489(2)	26(1)
O(1w)	9025(2)	197(2)	8741(2)	32(1)
C(21)	6879(3)	721(3)	9349(3)	34(1)
C(22)[b]	6280(3)	686(4)	9947(3)	39(1)
C(23)	5324(3)	37(3)	9683(3)	27(1)
C(24)	5032(3)	−533(4)	8798(3)	40(1)
C(25)	5663(3)	−442(4)	8232(3)	38(1)
N(4)	14351(3)	2925(4)	8741(4)	73(1)
N(5)	10768(3)	1644(4)	8874(3)	51(1)
C(30)	15195(5)	3504(6)	8663(6)	92(2)
C(31)	15264(5)	4680(6)	8616(5)	81(2)
C(32)	14415(5)	5322(5)	8648(5)	75(2)
C(33)	13530(4)	4770(4)	8722(4)	56(1)
C(34)	13519(3)	3571(4)	8763(3)	42(1)
C(35)	12566(3)	2901(4)	8818(3)	39(1)
C(36)	11734(3)	3448(4)	9019(3)	45(1)
C(37)	10864(3)	2786(4)	9045(3)	49(1)
C(38)	11568(4)	1115(4)	8671(4)	56(1)
C(39)	12484(3)	1702(4)	8662(4)	50(1)
Cl(1)	10708(1)	−2941(1)	8887(1)	44(1)
O(1)	10446(3)	−1928(3)	9328(3)	68(1)
O(2)	10365(4)	−3961(3)	9262(3)	88(1)
O(3)	11825(3)	−3021(5)	9127(5)	121(2)
O(4)	10098(5)	−2914(4)	7884(3)	95(2)
O(2w)	7500	1778(6)	2500	94(2)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 4. Atomic Coordinates (×10^4) and Equivalent Isotropic Displacement Parameters (Å^2 × 10^3) for **3**

atom	*x*	*y*	*z*	U_{eq}[a]
Cu(1)	0	0	2500	35(1)
O(1w)	0	1614(2)	2500	60(1)
N(1)	1831(2)	0	2500	34(1)
N(2)	0	0	3412(1)	37(1)
N(3)	2848(3)	1596(2)	5000	71(1)
C(1)	2450(2)	663(2)	2716(1)	44(1)
C(2)	3687(2)	690(2)	2719(1)	43(1)
C(3)	4333(2)	0	2500	35(1)
C(4)	−673(2)	547(2)	3725(1)	54(1)
C(5)	−697(2)	564(2)	4338(1)	56(1)
C(6)	0	0	4669(1)	39(1)
C(7)	3233(5)	1288(3)	4509(2)	140(2)
C(8)	4084(4)	653(3)	4496(2)	138(2)
C(9)	4529(3)	334(2)	5000	45(1)
Cl(1)	1350(1)	2946(1)	3771(1)	89(1)
O(1)[b]	240(4)	2788(3)	3486(2)	129(2)
O(2)[b]	1476(5)	3851(2)	3732(3)	143(2)
O(3)[b]	2244(5)	2525(3)	3453(2)	157(2)
O(4)[b]	1260(5)	2694(4)	4362(2)	198(2)
O(1′)[c]	820(12)	2177(7)	3804(7)	168(7)
O(2′)[c]	770(12)	3615(7)	3568(6)	135(5)
O(3′)[c]	2385(8)	2774(8)	3359(6)	112(6)
O(4′)[c]	2015(8)	3109(6)	4292(5)	73(3)

[a] U_{eq} is defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor. [b] sof = 0.8. [c] sof = 0.2.

Results and Discussion

Crystal Structures. X-ray crystallography shows that complexes **1** and **2** are isomorphous, made up of two-dimensional square grids of solvate 2,4′-bpy and lattice water molecules (see Figures 1 and 2 for **1**). The superposition of such square grids creates large square channels as shown in Figure 3. Each layer consists of two pairs of shared edges, perfectly square planar with an M(II) ion and a 4,4′-bpy at each corner and side, respectively, though each square is distorted slightly (*cis*N−Cd−N = 87.90(6), 92.10(6); *cis*N−Zn−N = 88.29(7), 91.71(7)°). The square cavity has dimensions of 11.669(2) × 11.788(2) and 11.368(2) × 11.488(2) Å for **1** and **2**, respectively, which are comparable to those of the related compounds.[1a,7b,c,f] In **1** and **2**, the metal ion, being located at a 2-fold crystallographic axis, has slightly distorted octahedral geometry with four pyridyl groups (Cd−N = 2.307(3)−2.347(3) Å, Zn−N = 2.129(3)−2.196(3) Å) at the equatorial positions and two aqua (Cd−O = 2.367(3) Å, Zn−O = 2.189(3) Å) at the apical positions. It is noteworthy that every two guest 2,4′-bpy molecules are clathrated in each hydrophobic host cavity (Figure 1) and further stabilized by $\pi-\pi$ stacking and hydrogen bonding interactions. The relatively hydrophobic end, i.e. the 2-pyridyl moiety, inserts into the hydrophobic square cavity, whereas the 4-pyridyl end forms a receptor hydrogen bond with an aqua ligand of adjacent upper or lower layer (O···N = 2.771(4) Å for **1** and **2**). The aqua ligand also forms a donor hydrogen bond with a perchlorate anion (O···O = 3.006(4) Å for **1**, 2.989(4) Å for **2**).

It is noteworthy that a pair of opposite edges are each non-coplanar, with the pair of pyridyl rings being twisted by 27.68-

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(15) Farrugia, L. J. *ORTEP-3 for Windows*, Version 1.02 Beta; University of Glasgow: Glasgow G12 8QQ, Scotland, U.K., 1997.

Table 5. Selected Bond Distances (Å) and Angles (deg) for **1**−**3**[a]

$[Cd(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (**1**)			
Cd(1)−N(1)	2.313(3)	Cd(1)−O(1w)	2.367(3)
Cd(1c)−N(2)	2.307(3)	O(1w)···N(5)	2.771(4)
Cd(1)−N(2*a*)	2.307(3)	O(1w)···O(1)	3.006(4)
Cd(1)−N(3)	2.347(3)		
Cd(1)−O(1w)−N(5)	119.73(12)	O(1w*b*)−Cd(1)−O(1w)	178.31(11)
Cd(1)−O(1w)−O(1)	119.27(11)	C(11)−N(1)−Cd(1)	121.2(2)
N(1)−Cd(1)−N(3)	87.90(6)	C(16)−N(2)−Cd(1c)	121.3(2)
N(1)−Cd(1)−O(1w)	89.16(5)	C(21)−N(3)−Cd(1)	124.7(2)
N(3*b*)−Cd(1)−N(3)	175.79(13)	C(25)−N(3)−Cd(1)	118.9(2)
N(3*b*)−Cd(1)−O(1w*b*)	90.66(10)	C(37)−N(5)−O(1w)	130.0(3)
N(3*b*)−Cd(1)−O(1w)	89.27(10)	C(38)−N(5)−O(1w)	113.0(3)
N(2*a*)−Cd(1)−O(1w)	91.02(6)	N(5)−O(1w)−O(1)	99.71(14)
O(1w)−Cd(1)−N(3)	90.02(10)	Cl(1)−O(1)−O(1w)	139.9(2)
O(1w)−Cd(1)−N(3*b*)	89.27(10)		
$[Cd(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_2\cdot(2,4'\text{-bpy})_2\cdot H_2O$ (**2**)			
Zn(1)−N(1)	2.130(4)	Zn(1)−O(1w)	2.189(3)
Zn(1*c*)−N(2)	2.129(3)	O(1w)···N(5)	2.771(4)
Zn(1)−N(2*a*)	2.129(3)	O(1w)···O(1)	2.989(4)
Zn(1)−N(3)	2.196(3)		
Zn(1)−O(1w)−N(5)	122.69(13)	O(1w*b*)−Zn(1)−O(1w)	177.97(12)
Zn(1)−O(1w)−O(1)	123.49(12)	C(11)−N(1)−Zn(1)	122.1(2)
N(1)−Zn(1)−N(3)	88.29(7)	C(16)−N(2)−Zn(1c)	122.0(2)
N(1)−Zn(1)−O(1w)	88.98(6)	C(21)−N(3)−Zn(1)	124.6(2)
N(2*a*)−Zn(1)−O(1w)	91.02(6)	C(25)−N(3)−Zn(1)	118.9(2)
N(3*b*)−Zn(1)−O(1w*b*)	90.02(10)	C(37)−N(5)−O(1w)	128.2(3)
N(3*b*)−Zn(1)−N(3)	176.58(14)	C(38)−N(5)−O(1w)	114.5(3)
N(3*b*)−Zn(1)−O(1w)	89.92(10)	N(5)−O(1w)−O(1)	92.42(14)
O(1w)−Zn(1)−N(3)	90.02(10)	Cl(1)−O(1)−O(1w)	138.5(2)
O(1w)−Zn(1)−N(3*b*)	89.92(10)		
$[Cu(4,4'\text{-bpy})_2(H_2O)_2](ClO_4)_4\cdot(4,4'\text{-}H_2bpy)$ (**3**)			
Cu(1)−N(2)	2.036(3)	O(1w)···O(1)	2.875(5)
Cu(1)−N(1)	2.038(2)	N(3)···O(4)	2.842(6)
Cu(1)−O(1w)	2.517(3)	O(4)···O(4*c)*	2.847(9)
N(2)−Cu(1)−O(1w*c)*	12.709(14)	C(7*c)*−N(3)−O(4)	150.3(3)
N(2*a)*−Cu(1)−O(1w*c)*	167.291(14)	C(7)−N(3)−O(4)	90.3(2)
O(1w)−Cu(1)−O(1w*c)*	77.291(14)	Cl(1)−O(1)−O(1w)	122.5(2)
Cu(1)−O(1w)−O(1)	129.55(10)	Cl(1)−O(4)−N(3)	127.3(3)
C(1)−N(1)−Cu(1)	121.12(13)	Cl(1)−O(4)−O(4*c)*	162.9(3)
C(4)−N(2)−Cu(1)	121.61(14)	N(3)−O(4)−O(4*c)*	59.94(11)

[a] Symmetry codes: (*a*) *x*, *y*+1, *z*; (*b*) −*x* + $^3/_2$, *y*, −*z* + $^3/_2$; (*c*) *x*, *y* − 1, *z* for **1** and **2**; (*a*) −*x*, *y*, −*z* + $^1/_2$; (*b*) −*x*, −*y*, z; (*c*) *x*, *y*, −*z* + 1 for **3**.

(9)°, whereas another pair of edges are each coplanar. This difference is most likely attributed to host−guest interaction. There is close edge-to-face interaction with carbon (or nitrogen) to carbon contacts[16] at ca. 3.6 Å between both pyridyl rings of each guest molecule and those of one coplanar edge. The guest molecule stacks with adjacent guest molecules in an offset fashion with the distance of 3.485(7)−3.990(9) Å, indicating significant π−π stacking interaction.[17]

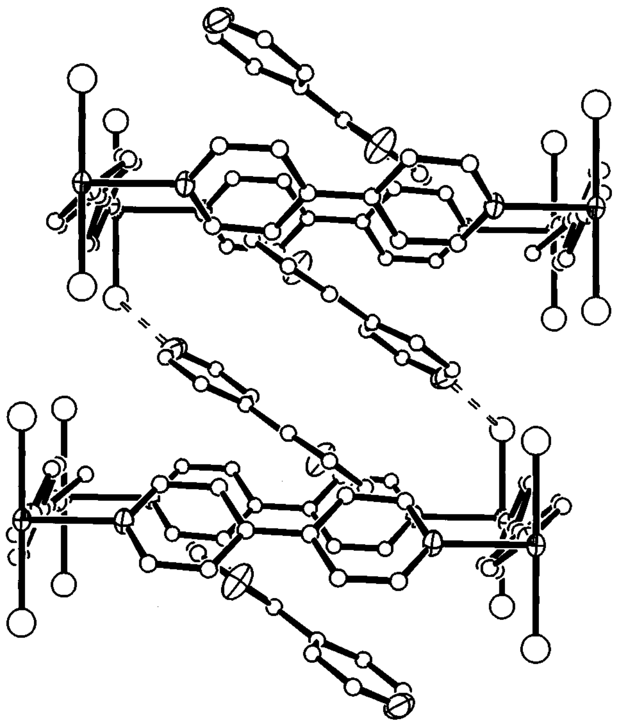

Figure 1. View of the square units of **1** along [010]; perchlorate anions are not shown. Hydrogen bonds are represented by broken lines. C = small circle, O = large circle, N = unshaded ellipsoid, and Cd = shaded ellipsoid.

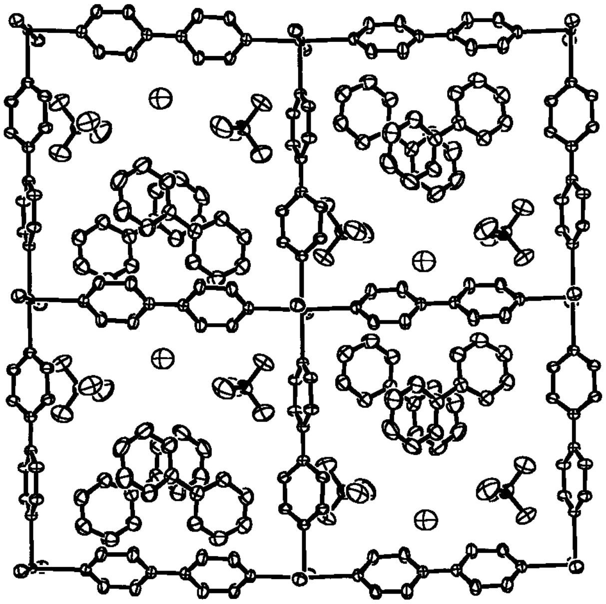

Figure 2. View of one layer of the square grids of **1** along [101].

Complex **3** is made up of two-dimensional square $[Cu_4(4,4'\text{-bpy})_4]$ grids, $[4,4'\text{-}H_2bpy]^{2+}$ cations and ClO_4^- anions. The grids consist of squares, which are slightly distorted as the sides (11.13 × 11.16 Å) are marginally different, with the Cu^{II} ions at the corners and the 4,4′-bpy molecules on the sides. The dimensions of the cavity are similar to those of **1** and **2**. The metal ion displays elongated octahedral coordination with four pyridyl groups (Cu−N = 2.036(3)−2.038(2) Å) at the equatorial positions and two aqua (Cu−O = 2.517(3) Å) at the axial positions (Figure 4). Each $[4,4'\text{-}H_2bpy]^{2+}$ cation is clathrated in a square cavity and is stabilized by hydrogen bonds and π−π stacking interactions. Within each cavity, the $[4,4'\text{-}H_2bpy]^{2+}$ cation forms twin three-center hydrogen bonds with two pairs of ClO_4^- anions (N···O = 2.842(6) Å). The ClO_4^- anions are also hydrogen bonded to the aqua ligands (O···O = 2.847(9) Å). A pair of opposite edges are each non-coplanar with the pair of pyridyl rings being twisted by 49.5°, whereas another pair of edges are each coplanar. The pyridyl rings of the $[4,4'\text{-}H_2bpy]^{2+}$ cation are also coplanar, a feature that has been observed in $\{[Cu(4,4'\text{-bpy})(H_2O)_2(ClO_4)_2](4,4'\text{-bpy})\}_n$.[7c] The guest stacks with one pair of opposite edges of the host square cavity in an offset fashion with the face-to-face distance of ca. 3.95 Å, which is indicative of π−π stacking interaction.[17,18] It is also noteworthy that the guest $[4,4'\text{-}H_2bpy]^{2+}$ cation is

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(16) Burley, S. K.; Petsko, G. A. *Science* **1985**, *229*, 23.

(17) Hunter, C. A.; Sanders, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

(18) Dance, I.; Scudder, M. *J. Chem. Soc., Chem. Commun.* **1995**, 1039.

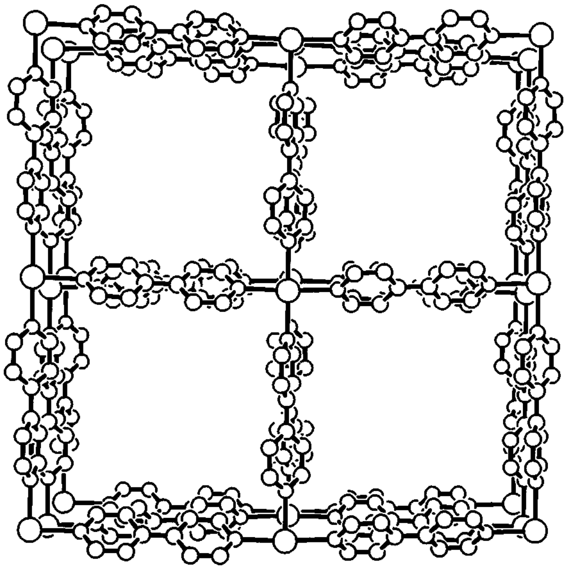


Figure 3. View of one layer of the square channels of **1** along [101]; aqua ligands and 2,4′-bpy molecules are not shown.

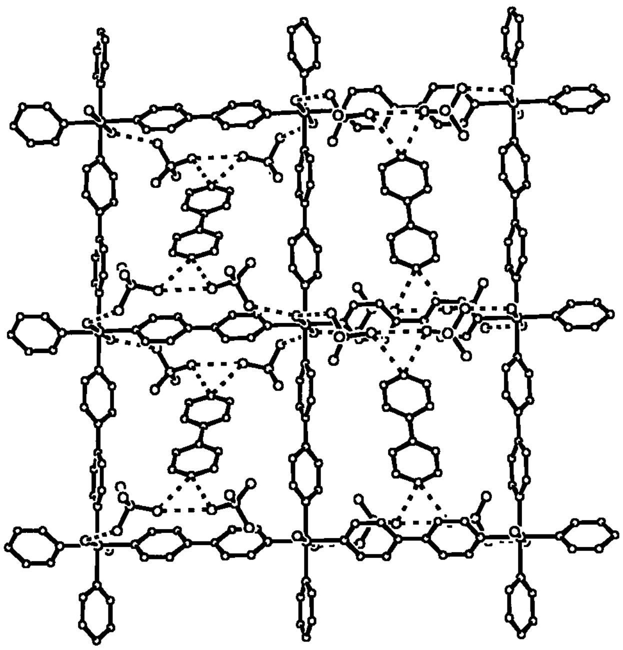
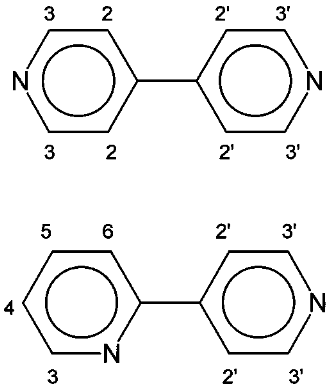


Figure 4. View of the square grids of **3** along [010]. Hydrogen bonds are represented by broken lines.

crystallographically centrosymmetric and located at the center of the cavity, which is significantly different from the 2,4′-bpy guests in complexes **1** and **2**. The 2-pyridyl end of the guest 2,4′-bpy in **1** and **2** inserts slightly into the hydrophobic square cavity, whereas the 4′-pyridyl end forms receptor hydrogen bonds with an aqua ligand that belongs to the adjacent upper or lower layer. Therefore, the host−guest interaction in complex **3** is best described as being an intralayer interaction, and complex **3** constitutes the first example that clathrates a large organic guest entity at the center of the void.

Preparation. Generally, with a 1:1 molar ratio of metal/4,4′-bpy, one-dimensional polymeric products should be expected in absence of suitable guest molecules.[7c,9c,19] However, only the two-dimensional square-grid complexes **1** and **2** were isolated when the reactions were conducted with equivalents of the metal salts, 4,4′-bpy and 2,4′-bpy, in an EtOH−H_2O mixture. Therefore, the presence of guest 2,4′-bpy molecules in the reaction system may be very important in the formation of the two-dimensional polymeric structures. It has been noted that the tetrahedral, trigonal, and octahedral metal templates are highly likely to form interpenetration or self-inclusion compounds, if the cavity generated in this way is more than 50% of the crystal by volume,[9b] and that the crystallization medium (i.e., solvent and/or template) can influence the nucleation process and architecture of the coordination polymers.[9c] Presumably, the guest 2,4′-bpy molecules may serve as templates to exclude self-inclusion.

Chart 1



In contrast to the isolation of complex **3**, we and others recently utilized Cu^{II} salts and 4,4′-bpy in the EtOH−H_2O or acetone−H_2O solvents under weakly basic conditions to synthesize some one-dimensional coordination polymers which are extended into two-dimensional networks by hydrogen bonds.[7c,e] Our current observations, therefore, may suggest that under acidic conditions, the protonated $[4,4'\text{-}H_2bpy]^{2+}$ cations serve as a structure-directing templates by virtue of the interplay of hydrophobic/hydrophilic interactions in the formation of infinite frameworks[20] and possibly also as templates to exclude self-inclusion of the networks having much larger square cavities.[9b]

Spectroscopic Properties

The NMR spectra can clearly confirm that both **1** and **2** comprise 4,4′-bpy and 2,4′-bpy molecules in a 1:1 ratio. In both complexes, although the ^1H NMR spectra display some overlap between the 4,4′-bpy and 2,4′-bpy molecules at ca. 7.34−7.26 ppm for **1** and 7.27−7.21 ppm for **2**, their high-field resonance peaks at 6.75 (2H), 6.66 (1H), and 6.58 ppm (1H) for **1** and at 6.66 (2H), 6.62 (1H), and 6.54 ppm (1H) for **2** can be assigned to $H_{2'}$, H_6, and H_4 of 2,4′-bpy, respectively; peaks at 6.49 ppm (4H) for **1** and 6.42 ppm (4H) for **2** can be assigned to H_2 of 4,4′-bpy, respectively, as compared with their free molecules. Their integral results display that the ratio of 4,4′-bpy to 2,4′-bpy is 1:1 in both **1** and **2**. The ^{13}C NMR resonance peaks at 150.62, 147.00, and 122.91 ppm of **1** and 150.55, 147.90, and 122.73 ppm of **2** can be unambiguously assigned to C_3, C_1, and C_2 of 4,4′-bpy, respectively (see Chart 1). The peaks at 154.40, 150.56, 150.25, 148.78, 138.56, 125.26, 122.91, and 122.41 ppm of **1** and 154.19, 150.55, 150.13, 148.85, 138.55, 125.16, 122.44, and 122.36 ppm of **2** are assigned to C_1, $C_{3'}$, C_3, $C_{1'}$, C_5, C_4, $C_{2'}$, and C_6 of 2,4′-bpy,

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(19) Li, M.-X.; Xie, G.-Y.; Gu, Y.-D.; Chen, J.; Zheng, P.-J. *Polyhedron* **1995**, *14*, 1235.

(20) (a) Haushalter R. C.; Mundi, L. *Chem. Mater.* **1992**, *4*, 31. (b) Zapf, P. J.; Haushalter R. C.; Zubieta, J. *J. Chem. Soc., Chem. Commun.* **1997**, 321.

respectively, as compared with the free molecule. The chemical shifts are significantly upshifted in comparison with those of the free molecules,[21] indicating some degree of $\pi-\pi$ stacking between oligomeric **1** (or **2**) and the 2,4′-bpy in solution.

Conclusions

Three two-dimensional square grids clathrating larger neutral or cationic organic molecules have been prepared and characterized. The square grids of **1** and **2** superpose on each other into a channel structure. Every two guest 2,4′-bpy molecules are clathrated in each hydrophobic host cavity and are further stabilized by $\pi-\pi$ stacking and hydrogen bonding interactions. In the two-dimensional square grid of **3**, each $[4,4'\text{-}H_2bpy]^{2+}$ cation is clathrated in a square cavity and stacks with one pair of opposite edges of the host square cavity in an offset fashion. Within each cavity, the $[4,4'\text{-}H_2bpy]^{2+}$ cation forms twin three-center hydrogen bonds with two pairs of ClO_4^- anions. The results suggest that the guest 2,4′-bpy molecules and protonated $[4,4'\text{-}H_2bpy]^{2+}$ cations present in the reaction systems may serve as structure-directing templates in the formation of the structures of **1**, **2**, and **3**, respectively, and exclude self-inclusion of the networks having larger square cavities.

Acknowledgment. This work was supported by the National Natural Science Foundation of China (No. 29625102) and the National Science Council for R & D, Malaysia (IRPA 09-02-03-0004).

Supporting Information Available: Three X-ray crystallographic files for **1**, **2**, and **3**, in CIF format, are available. Access information is given on any current masthead page.

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[21] Pouchert, C. J.; Behenke, J., Eds. *The Aldrich Library of ^{13}C and ^{1}H FT-NMR Spectra*, 1st ed.; Aldrich Chemical Company: Milwauke, WI, 1993; Vol. 3, p 240.