Synthesis and Single Crystal Investigation of Two-Dimensional Rectangular Network [M(4,4′-bpy) (Phth)(H₂O)]ₙ·2H₂O with Small Neutral Cavities

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Introduction

Recently, intense research activities have been directed toward the development of the designed construction of extended porous frameworks from soluble molecular building blocks. This includes the assembly of coordination complexes,[1] inorganic metal clusters,[2] and organic molecules,[3] which can create various supramolecular architectures sustained by strong covalent coordinate bonds or by weaker bonding forces, such as hydrogen bonding and $\pi\cdots\pi$ interactions. By the judicious choice of the building units and appropriate metal centers, it is possible to design anionic, cationic, and neutral porous frameworks having a wide range of compositions. Open framework structures in various coordination polymers are of great interest, not only because of their structural architectures, but because they are also useful solids in molecular adsorption/separation[4] and guest−host chemistry.[5]

We have initiated a synthetic approach for the preparation of noninterpenetrating neutral open networks with variable cavity/channel size in which 4,4′-bipyridyl (4,4′-bpy), 1,2 benzenedicarboxylate (phth), and related species are chosen as building blocks. By utilizing the octahedral or square planar geometry of the M⁺² ion (M = transition metal) and the appropriate choice of the bridging ligands, neutral or cationic rectangular grids are reported to be constructed in four different ways.[6] In an endeavor to construct a neutral cavity-containing porous networks with two different edge lengths by incorporating neutral and dianionic ligands, we synthesized two isostructural metal−organic rectangular grids [M(4,4′-bpy)(phth)(H₂O)]ₙ

Table 1. Summary of Crystallographic Data and Parameters for Complexes **1a** and **1b**

	complex **1a**	complex **1b**
chemical formula	C₁₈H₂₀N₂O₈Co₁	C₁₈H₂₀N₂O₈Cd₁
formula weight	451.29	504.76
space group	P 2/n (No. 13)	P 2/n (No. 13)
a/Å	7.596(3)	7.790(4)
b/Å	11.309(3)	11.647(2)
c/Å	10.770(2)	10.6990(10)
α/deg	90.00	90.00
β/deg	92.51(3)	92.59(2)
γ/deg	90.00	90.00
V/Å³	924.3(5)	969.7(5)
Z	2	2
λ (Å)	0.7107	0.7107
ρ_{calcd} (g cm⁻³)	1.622	1.729
T (°C)	23	23
μ (cm⁻¹)	9.80	11.18
final (R1) (on F_o^2)[a]	0.0541	0.0271
final (wR2) (on F_o^2)[b]	0.1383	0.0708

[a] R1 = $\Sigma||F_o| - |F_c||/\Sigma |F_o|$. [b] wR2 = $[\Sigma w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]^{1/2}$.

(where M = Co²⁺ **1a**, M = Cd²⁺ **1b**, 4, 4′-bpy = 4, 4′-bipyridyl, and phth = 1, 2 benzenedicarboxylate). The formation of **1a** and **1b** are confirmed by single crystal X-ray diffraction, IR, and analytical data. Although, a few reports are found in the literature regarding the synthesis and structural studies of cationic M⁺² rectangular grids,[7] to our knowledge, there are only two cases of neutral rectangular grids[6,8] reported so far.

Experimental Section

Materials and Methods. All of the chemicals for the synthesis were reagent grade and used as purchased. Elemental analyses (C, H, N) were performed on a model 2400 Perkin-Elmer elemental analyzer. Infrared spectra were recorded on a Perkin-Elmer Spectrum GX FT-IR spectrophotometer as KBr pellets.

Synthesis of Complex 1a and 1b. An ethanolic solution (15 cm³) of 4,4′-bpy (156 mg, 1 mmol) was added dropwise to a stirring aqueous solution of Co(NO₃)₂·6H₂O (240 mg, 1 mmol) kept on an oil bath at 50 °C for 10 min. Disodiumphthalate (210 mg, 1 mmol) in 10 mL of water−ethanol (1:1) was added slowly, and the temperature of the bath was raised to 80 °C. The solution was then refluxed for 3 h, filtered, and kept for crystallization after reducing the volume ca. 10 mL. The same procedure was adopted for complex **1b** also, except the metal CdSO₄·3H₂O (321 mg, 1 mmol) was used instead of the cobalt(II) salt. Dark orange red and colorless crystals suitable for diffraction studies appeared after 3 days in the case of **1a** and **1b,** respectively. Both of the crystal types were insoluble in water and common organic solvents.

C, H, N analysis and IR data for Complex **1a**; Calcd: C, 47.9; H, 4.52; N, 6.30%. Found: C, 47.69; H, 4.62; N, 6.30%. IR (KBr, cm⁻¹): 3488 m, 3373 w, 3150 mbr, 1608 s, 1555 vs, 1486 m, 1405 s, 1213 m, 1082 m, 1012 m, 950 w, 836 w, 764 s, 696 vw, 364 m, 566 m, 527 m, 421 vw.

C, H, N analysis and IR data for Complex **1b**; Calcd: C, 42.80; H, 3.86; N, 5.03%. Found: C, 42.83; H, 4.00; N, 5.26%. IR (KBr, cm⁻¹): 3430 mbr, 1608 s, 1559 vs, 1488 m, 1407 vs, 1219 m, 1076 m, 1008 m, 807 s, 762 s, 729 w, 696 w, 636 s, 522 w, 491 vw.

X-ray Crystallographic Analysis. Data for both of the crystal types were collected on an Enraf-Nonius CAD-4 diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.7107). Cell constants and the orientation matrix for data collection were obtained from least-squares refinement using 25 high angle reflections in the θ range 8−12°.

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Table 2. Selected Bond Lengths [Å] and Angles [Deg] for Complexes **1a** and **1b**

Complex **1a**[a]			
Co(1)−O(1W)#1	2.116(3)	Co(1)−O(1W)	2.116(3)
Co(1)−N(1)	2.111(4)	Co(1)−N(2)	2.137(5)
Co(1)−O(1)#1	2.136(3)	Co(1)−O(1)	2.136(3)
C(7)−O(2)	1.237(5)	C(7)−O(1)	1.263(5)
C(7)−C(8)	1.503(5)		
O(1W)#1−Co(1)−O(1W)	178.73(16)	O(1W)#1−Co(1)−N(1)	90.64(8)
O(1W)−Co(1)−N(1)	90.64(8)	O(1W)#1−Co(1)−N(2)	89.36(8)
O(1W)−Co(1)−N(2)	89.36(8)	N(1)−Co(1)−N(2)	180.000(1)
O(1W)#1−Co(1)−O(1)#1	86.73(12)	O(1W)−Co(1)−O(1)#1	93.19(12)
N(1)−Co(1)−O(1)#1	93.45(8)	N(2)−Co(1)−O(1)#1	86.55(8)
O(1W)#1−Co(1)−O(1)	93.19(12)	O(1W)−Co(1)−O(1)	86.73(12)
N(1)−Co(1)−O(1)	93.45(8)	N(2)−Co(1)−O(1)	86.55(8)
O(1)#1−Co(1)−O(1)	173.10(15)	O(2)−C(7)−O(1)	124.4(4)
O(2)−C(7)-C(8)	118.1(3)	O(1)−C(7)−C(8)	117.5(3)
Complex **1b**[b]			
Cd(1)−N(1)	2.281(3)	Cd(1)−N(2)	2.299(3)
Cd(1)−O(1W)	2.321(2)	Cd(1)−O(1W)#1	2.321(2)
Cd(1)−O(1)#1	2.342(2)	Cd(1)−O(1)	2.342(2)
O(1)−C(7)	1.251(4)	O(2)−C(7)	1.248(3)
C(8)−C(7)	1.513(4)		
N(1)−Cd(1)−N(2)	180.0	N(1)−Cd(1)−O(1W)	90.29(4)
N(2)−Cd(1)−O(1W)	89.71(4)	N(1)−Cd(1)−O(1W)#1	90.29(4)
N(2)−Cd(1)−O(1W)#1	89.71(4)	O(1W)-Cd(1)−O(1W)#1	179.42(8)
N(1)−Cd(1)−O(1)#1	95.19(5)	N(2)−Cd(1)−O(1)#1	84.81(5)
O(1W)−Cd(1)−O(1)#1	86.07(8)	O(1W)#1−Cd(1)−O(1)#1	93.88(8)
N(1)−Cd(1)−O(1)	95.19(5)	N(2)−Cd(1)−O(1)	84.81(5)
O(1W)−Cd(1)−O(1)	93.88(8)	O(1W)#1−Cd(1)−O(1)	86.07(8)
O(1)#1−Cd(1)−O(1)	169.61(10)	O(2)−C(7)−O(1)	124.2(2)
O(2)−C(7)−C(8)	117.9(2)	O(1)−C(7)−C(8)	117.9(2)

[a] Symmetry transformations used to generate equivalent atoms: #1 −x + 3/2, y, −z + 3/2. [b] Symmetry transformations used to generate equivalent atoms: #1 −x + 1/2, y, −z + 1/2.

The $\omega - 2\theta$ scan mode, with maximum θ value being 24.99°, was used to collect the intensity data for both complexes. The data were corrected for Lorentz and Polarization effects; an empirical absorption correction was applied for complex **1a**, using the program NRCVAX,[9] but not for **1b**. Structure solutions were carried out using the patterson method, with full-matrix least-squares refinement on F^2 using SHEL-EXL-97.[10] Hydrogen atoms were located either from a difference Fourier map or kept fixed using the riding model. Crystallographic data and refinement for the compounds are presented in Table 1and selected bond distances and angles in Table 2, respectively.

Results and Discussion

An *ORTEP*[11] view depicting the coordination sphere and atom numbering scheme for **1b** is shown in Figure 1. The metal centers coordinated to two trans μ-4,4′bpy ligands and two trans water molecules, forming the square base; two trans μ-phth ions at the apical position, with slightly longer M−O bond (Co1−O1 = 2.136(3) Å, Cd1−O1 = 2.342(2)Å), complete the slightly distorted octahedral coordination environment both in **1a** and **1b**, which are isostructural (Table 2). The presence of a carboxylate group in **1a** and **1b** was confirmed by the very strong peaks at 1555, 1405 and 1559, 1407 cm^{-1}, respectively, in the IR spectra; the low Δ_{oco} values (150 and 152 cm^{-1}) may be attributed to the strong H-bonding interaction of the carboxylate oxygens[12] with water molecules, as observed from crystallographic studies. The cavity-containing rectangular grids runs parallel to the crystallographic *ab* plane. The intra grid M···M separation, where the metal center resides at the corners

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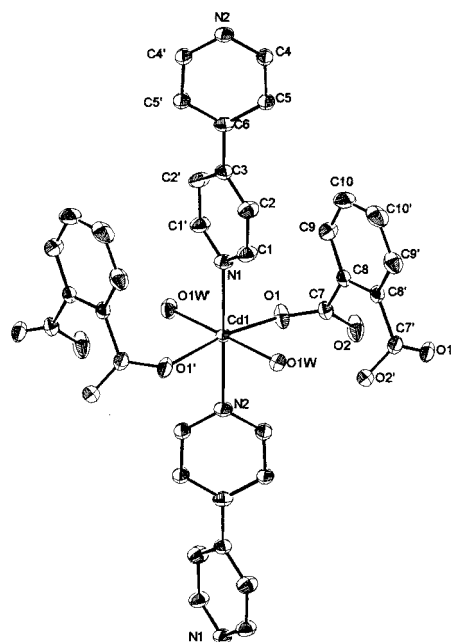

Figure 1. ORTEP (40% probability for the thermal ellipsoids) view of the coorination sphere in complex **1b** with atom numbering scheme. The same atom numbering scheme is adopted for the isostructural complex **1a**.
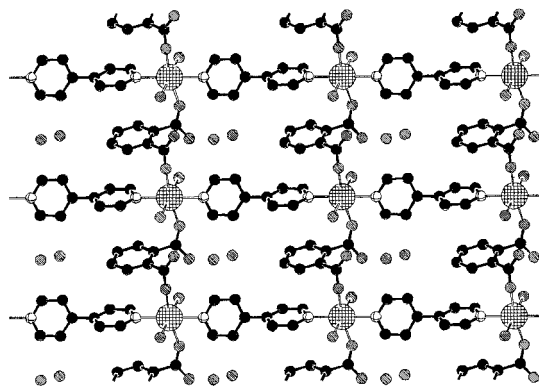

Figure 2. Pluto diagram of the rectangular grids with the included lattice water molecules.

of the rectangle, bridged via 4,4′-bpy and phathlate dianion is 11.309(3) × 7.596(3) Å in **1a** and 11.647(2) × 7.790(4)Å in **1b**, respectively (Figure 2). The different metal ions (Co^{2+}, Cd^{2+}) impact very little change in the effective grid size of isostructural complexes **1a** and **1b**; interestingly, almost similar intra grid M···M separation is achieved in the cavity containing the rectangular grid complex [Co(pyz)(terph)(H$_2$O)]$_n$ to include an aromatic guest molecule.[6]

Packing diagrams viewed down the *a* and *c* axes are shown in Figure 3 and Figure 4 , respectively. The adjacent sheets are staggered in such a way that the metal ion of the first approximately corresponds to the center of the grid of the second, and vice versa (Figure 4). The layers stack along crystallographic *c* axis, and the distance between the neighboring layer is 5.394 and 5.349 Å, corresponding to **1a** and **1b**. The distance between the edge-sharing metal ions of the first rectangular grid and the central metal of the staggered neighboring sheet (which is almost at the center of the first rectangular grid) is Co···Co = 8.164, 9.047 Å in **1a** and Cd···Cd = 9.139, 9.343 Å in **1b**, respectively. The relative displacement of the adjacent layers reduces the

(12) Mehrotra, R. C.; Bhora, R. *Metal Carboxylates*; Academic Press: New York, 1983.

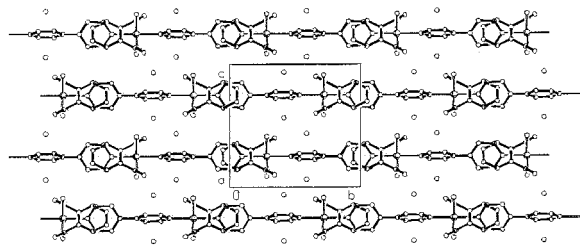**Figure 3.** Packing diagram viewed down the *a* axis for **1a** showing alternate layers of the rectangular sheets and the included water molecules.
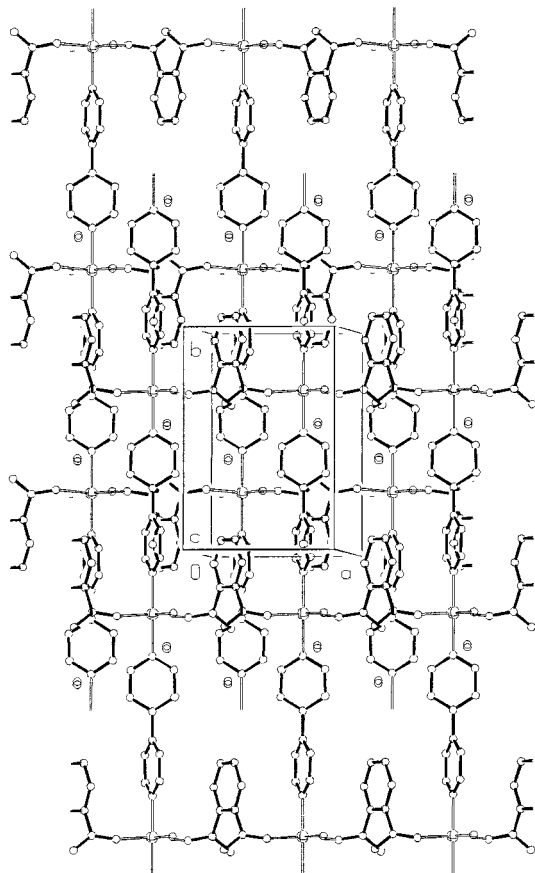

Figure 4. Packing diagram viewed down the *c* axis for **1a** showing the staggering of the adjacent layers.

effective cavity size (Figure 5), which in turn accommodates only two water molecules as solvent of crystallization.

In the solid state, the molecules self-assemble via hydrogen bonds and $\pi\cdots\pi$ interactions. There is a reasonably good offset of $\pi\cdots\pi$ stacking between the coplanar edge-sharing 4,4′-bpy ring (N1−C3) and the phthalate ring (C8−C10) along *ab* plane. The corresponding C1g$\cdots$C2g distance is 3.91(4) Å in **1a** and 4.07(4) Å in **1b,** respectively, where C1g is the center of mass of the pyridyl ring (N1−C3) and C2g is the center of mass of the phthalate ring (C8−C10).[13] The pyridyl rings of the rigid 4,4′-bpy moiety are not coplanar. The pyridyl rings of the bridging 4, 4′-bpy ligand are twisted by 53.92(3)° and 52.98-(2)° in **1a** and **1b**, respectively, which minimizes the stereic effect and favors the $\pi\cdots\pi$ stacking with the aromatic phthalate ring. The coordinated water molecules form strong intra and intermolecular hydrogen bonds with the carboxylate oxygen of the phthalate and the lattice water molecules (O1w$\cdots$O2 = 2.681(4) Å, O1w$\cdots$O2w = 2.726(3) Å in **1a**; O1w$\cdots$O2 =

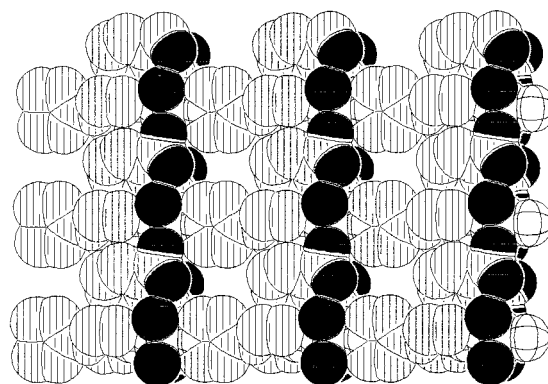(13) Hunter, C. A.; Sanders, J. K. *J. Am. Chem. Soc.* **1990**, *112*, 5525.

Figure 5. Space filling view of rectangular grid showing the micro channels (water molecules present in the channels are omitted for clarity).

2.703(3) Å, O1w$\cdots$O2w = 2.699(2) Å in **1b**). The water molecules present in the lattice are involved in a second set of O−H$\cdots$O interactions with the adjacent polymeric sheet via carboxylate oxygens of the phthalate dianion, giving rise to hydrogen bonded interconnected rectangular sheets (O2w$\cdots$O1= 2.802(3) Å, O2w$\cdots$O2 = 2.822(4) Å in **1a**; O2w$\cdots$O1= 2.806-(3) Å, O2w$\cdots$O2 = 2.829(4) Å in **1b**). The O−H$\cdots$O interactions which bridge the adjacent polymeric sheets may be the driving force for the offset packing of the successive sheets. The involvement of the strong hydrogen bonding interaction of the carboxylate oxygen is reflected in the rotation of the carboxylate group with respect to the aromatic ring (C8−C10), making an angle 59.63° in **1a** and 57.39° in **1b**, and the dihedral angle involving the carboxylate moiety of the phthalate ligand (C7, O1, and O2) with the MN_2O_2 (i.e., Co/Cd, O1w, O1w′, N1, and N2) plane is 60.69° and 57.60° in **1a** and **1b**, respectively. The utility of the cavity after the removal of the included water molecules for adsorption of a small molecule in both **1a** and **1b** is yet to be investigated.

Conclusion

In summary, we have been able to develop a synthetic approach for the construction of a neutral supramolecular architecture. By utilizing the appropriate multitopic ligands and exploiting the coordination ability of the metal center, rectangular grids involving the exobidnedate ligand 4,4′-bpy, and a carboxylate moiety, a cavity-containing neutral framework is designed, which are scantily reported. Considering the relatively small number of cavity-containing rectangular networks, much work is required to extend the knowledge of the relevant structural types and establish the right synthetic approaches leading toward the desired species. We are currently exploring the design of novel polymeric microporus coordination networks with tunable pore size by selecting mixed bridging ligands, and efforts are underway to investigate the inclusion properties and guest exchange phenomenon.

Supporting Information Available: Two X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.