Construction of Nano-Channels Based on Zinc(II) Pyrazine-2-carboxylate Complexes

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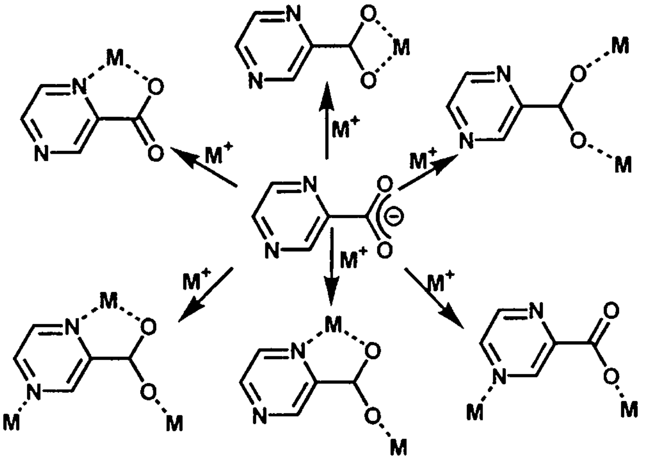
The reaction of pyrazine-2-carboxylate (pca) and bis(pyridine) derivatives, such as 4,4′-bipyridine (bipy), 1,2-bis(4-pyridyl)ethylene (bpen), 1,2-bis(4-pyridyl)ethane (bpea), 1,3-bis(4-pyridyl)propane (bpp), and 4,4′-azopyridine (azp), with zinc perchlorate gives supramolecules with grid and/or channel structures. The new complexes reported here are *trans*-$[Zn(bipy)(pca)(H_2O)]ClO_4{\cdot}(EtOH)_{0.5}{\cdot}(H_2O)_{0.5}$ (**1**), $[Zn(\mu\text{-}bpen)(bpen)(pca)(H_2O)]{\cdot}ClO_4{\cdot}2H_2O$ (**2**), $[Zn(bpea)(pca)]ClO_4{\cdot}(EtOH)_{0.5}$ (**3**), and $[Zn(bpp)(pca)(MeOH)]ClO_4$ (**4**). Their structures have been established by single-crystal X-ray diffraction. Some of these complexes contain voids with nanometer dimensions. Small molecules such as H_2O, MeOH, and EtOH contained in these voids can be removed without destruction of the parental suprastructure.

Introduction

The basic concepts for constructing supramolecules by self-assembly techniques have been well developed over the past two decades, especially by Lehn's group.[1−4] The entries to this new field are classified from the structural viewpoint into sphere-like molecules, infinite one-dimensional molecules (molecular wires), multi-dimensional molecules, including interwoven coordination polymers and grid and/or channel-like molecules, and dendrimers; we have used the term "molecular dot" for globular molecules.[5] There has been a plethora of reports on grids and/or channel-like networks composed from metal−ligand components, especially with Mn, Co, Ni, Cu, and Zn as metal ions and 4,4′-bipy, aromatic carboxylates, pyrazine, and pyridylporphyrins as organic linkers.[1−4,6−15] These molecules can also be divided into the following categories with regards to their possible applications to nanotechnologies: chemical sensors, microreactors, molecular devices, optoelectronic devices, drug-delivery systems, thin-film technologies, etc.[16−21] One of our current interests in supramolecules has been directed to the trapping of small environmental gaseous molecules such as CO_2, NO_2, and SO_2 into channel-like structures and their possible conversion into more useful chemicals. Since there have been several reports of the trapping of CO_2 by mononuclear Zn complexes and its subsequent reduction into organic species,[22,23] the design of a microreactor prepared from Zn^{II} supramolecules is especially intriguing for the activation of CO_2 molecules and their conversion into organic derivatives, a process that is the key step in C_1 chemistry. As the first step to achieve this goal, we decided to construct new channel-like and/or cage-like nanostructures containing Zn^{II} and a pyrazine-2-carboxylate linker. The reason for the choice of the pyrazine-2-carboxylate (pca) ligand is its potential multidentate coordination ability, depicted in Scheme 1, where several possible new bridging modes are shown. Such multidentate ex-



Scheme 1

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amples of pca have not been reported to the best of our knowledge. Here we report on the synthesis of new zinc(II) pyrazine-2-carboxylate complexes with various bis(pyridine) ligands and a structural study of their interlaced supramolecular structures by single-crystal X-ray diffraction.

Results and Discussion

Synthetic Reactions

As described in the Exp. Sect., simply mixing the three components [pcn, the bis(pyridine) ligand, and zinc(II) perchlorate] in EtOH/H_2O at room temperature yielded new cage-type supramolecules. It seems worthy to mention why pcn is employed to build such supramolecules in most reactions instead of simply using pyrazine-2-carboxylic acid (Hpca). At first Hpca was indeed used for such attempts, because several recent reports have shown the versatile nature of pyridine-2-carboxylates and pca was expected to exhibit a similar behavior.[24] However, only limited results were obtained, as described below. Lin et al. have demonstrated that 4-cyanopyridine is susceptible to hydrolysis under hydro(solvo)thermal conditions to yield isonicotinic acid.[24b] With this in mind, zinc perchlorate, 2-cyanopyrazine, and bipy were mixed in EtOH/H_2O in a 1:1:1 molar ratio. After standing at room temperature for several days, pale-yellow crystals of $[Zn(pca)(bipy)(H_2O)]ClO_4$ (**1**) were obtained. An X-ray diffraction study revealed a grid-like structure in the solid state. A more detailed discussion of this nano-grid can be found below. Thus, we have verified that pcn undergoes hydrolysis under ambient conditions to give pca.

Similar reactions were attempted for various combinations of other ligands; these results are also described below for **2**−**4**. The crux of our synthesis is that the CN group of pcn is oxidized to CO_2^- during the reaction and/or upon exposure to air for several days, thus creating a potentially multidentate linker ligand. The essential contribution of the CO_2^- group in the pca ligand becomes clear when the cage structure of **1** is compared with a similar cage architecture with pyrazine as bridging ligand reported previously by Bourne's group.[25] Their network structures are significantly different from ours: the carboxylate group in pca induces a more sophisticated multidimensional structure which is dependent on the coexistence of bridging ligands, as described in the crystal structure section below. The most common function of pca in **1**−**4** is as a chelating bridging ligand, as depicted in the bottom center of Scheme 1. However, the bridging mode of the O atom of pca in **2** is highly unusual, as described in the following section. Another interesting finding from the present synthesis merits a comment; pcn and/or pca are not incorporated into the final products when pyrazine, 4,4′-bipyridine *N*,*N*′-dioxide (bpy-O), and/or azp are used as co-ligands. It is possible that the pcn ligand, which is initially coordinated to the Zn ion by an N atom of the pyrazine skeleton, is affected by the steric and/or electronic influence of the co-ligand and is expelled from the coordination sphere during the hydrolysis of the CN group; the hydrolysis mechanism of the CN group is still unclear. These results strongly suggest that the combination of pca with other potentially bidentate ligands and suitable hydrolysis conditions should allow the synthesis of more sophisticated channel-like structures with multifunctional binding modes of pca different from those in Scheme 1. The next challenge should be to realize other coordination modes such as those of the left and right at the bottom of Scheme 1, where pca functions as a longer grid than those of **1**−**4**.

Molecular and Cage Structures

The minimum units needed to delineate the molecular structure of each product are shown below. Complexes **1**, **4**, and **5** exhibit distorted octahedral skeletons around the Zn ions, whereas **2** has a distorted edge-shared dinuclear octahedral skeleton and **3** exhibits a distorted five-coordinate square-pyramidal one. In **1** (Figure 1a), pca functions as a tridentate bridging ligand as shown in Scheme 1. The sixth coordination site is occupied by the O atom (O1) of a water molecule.

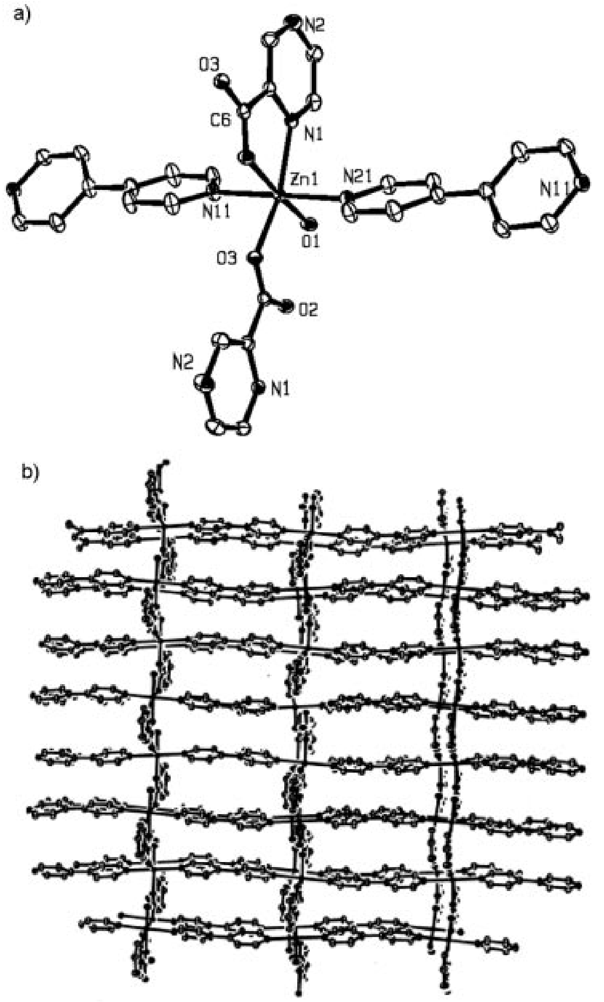

Figure 1. (a) ORTEP drawing of *trans*-$[Zn(bipy)(pca)(H_2O)]ClO_4$ (**1**); (b) view of the crystal structure of **1** along the *a* axis

The coordination mode of pca in **2** is rather complicated. It binds as a chelating ligand to a single Zn ion through N and O atoms, and the same O atom also bridges two Zn ions, as shown in Figure 2a. This type of coordination mode was not expected and is not shown in Scheme 1. The O atom (O3) from a water molecule occupies the sixth coordination site.

The coordination mode of pca in **3** is the same as in **1**, although the fundamental structure of the Zn ion is square-pyramidal (Figure 3a). The function of pca in **4** (Figure 4a) is also the same as in **1**, with a molecule of methanol loosely bound in the sixth coordination site. Although the bridging O atom appears to be free in Figures 1a, 3a, and 4a, which show only the independent part of each molecule, it actually straddles the neighboring Zn ions, thereby forming a multidimensional array by linking the Zn ions.

The two pyrazine rings in **5** (Figure 5a) connect two Zn sites; four water molecules occupy the equatorial *trans* positions, and thus form *trans*-linear infinite chains. The mononuclear Zn complex **6** does not merit special comments.

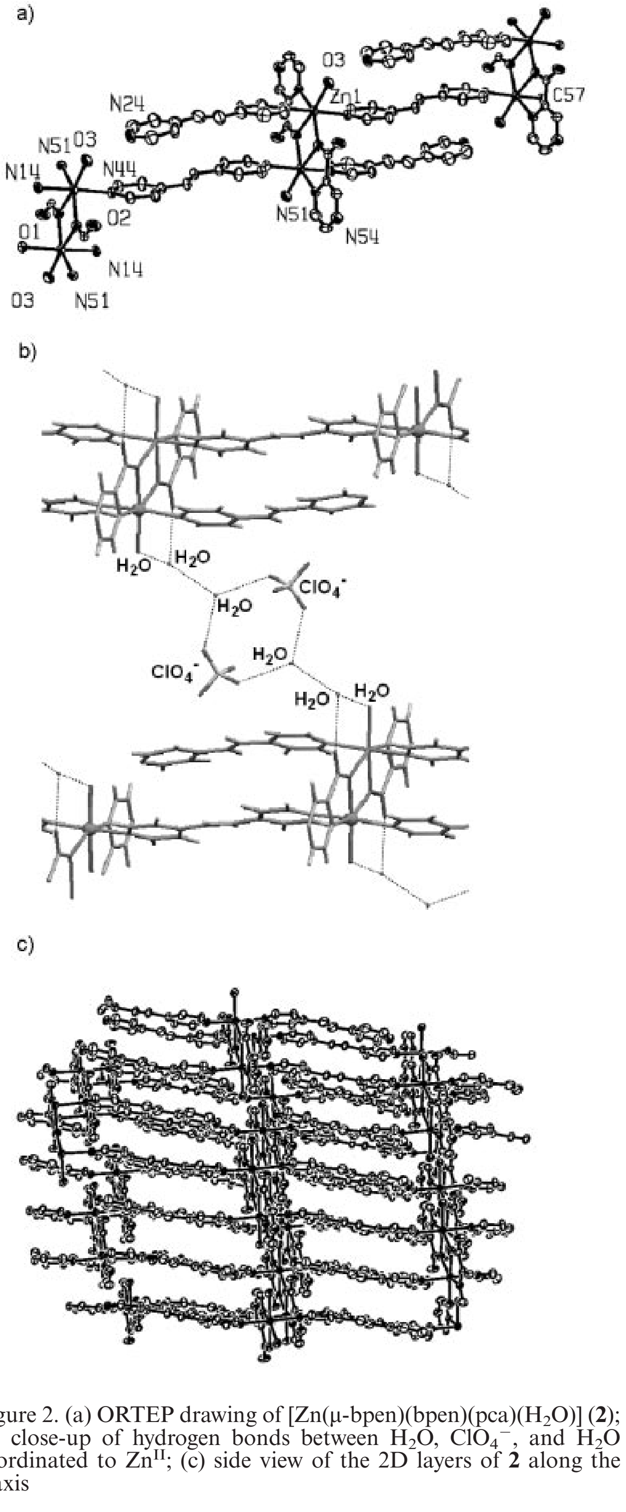

Figure 2. (a) ORTEP drawing of [Zn(μ-bpen)(bpen)(pca)(H_2O)] (**2**); (b) close-up of hydrogen bonds between H_2O, ClO_4^-, and H_2O coordinated to Zn^{II}; (c) side view of the 2D layers of **2** along the *b* axis

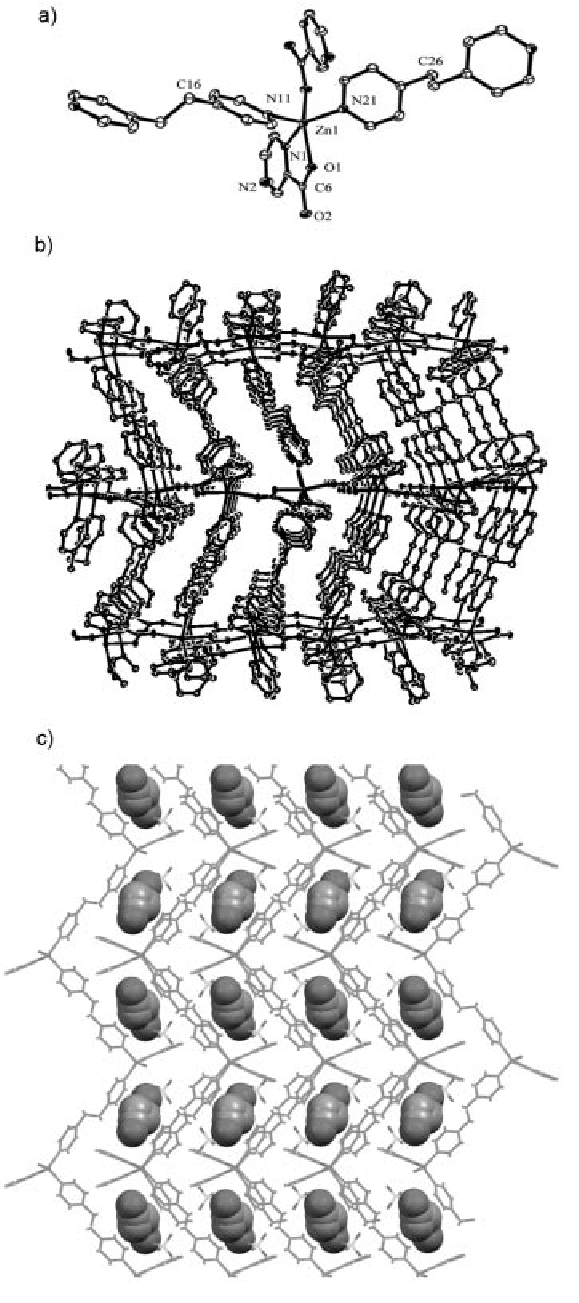

Figure 3. (a) ORTEP drawing of *trans*-[Zn(bpea)(pca)$_2$] (**3**); (b) two-dimensional sheet of **3** along the *a* axis; (c) guest ethanol molecules in the channels

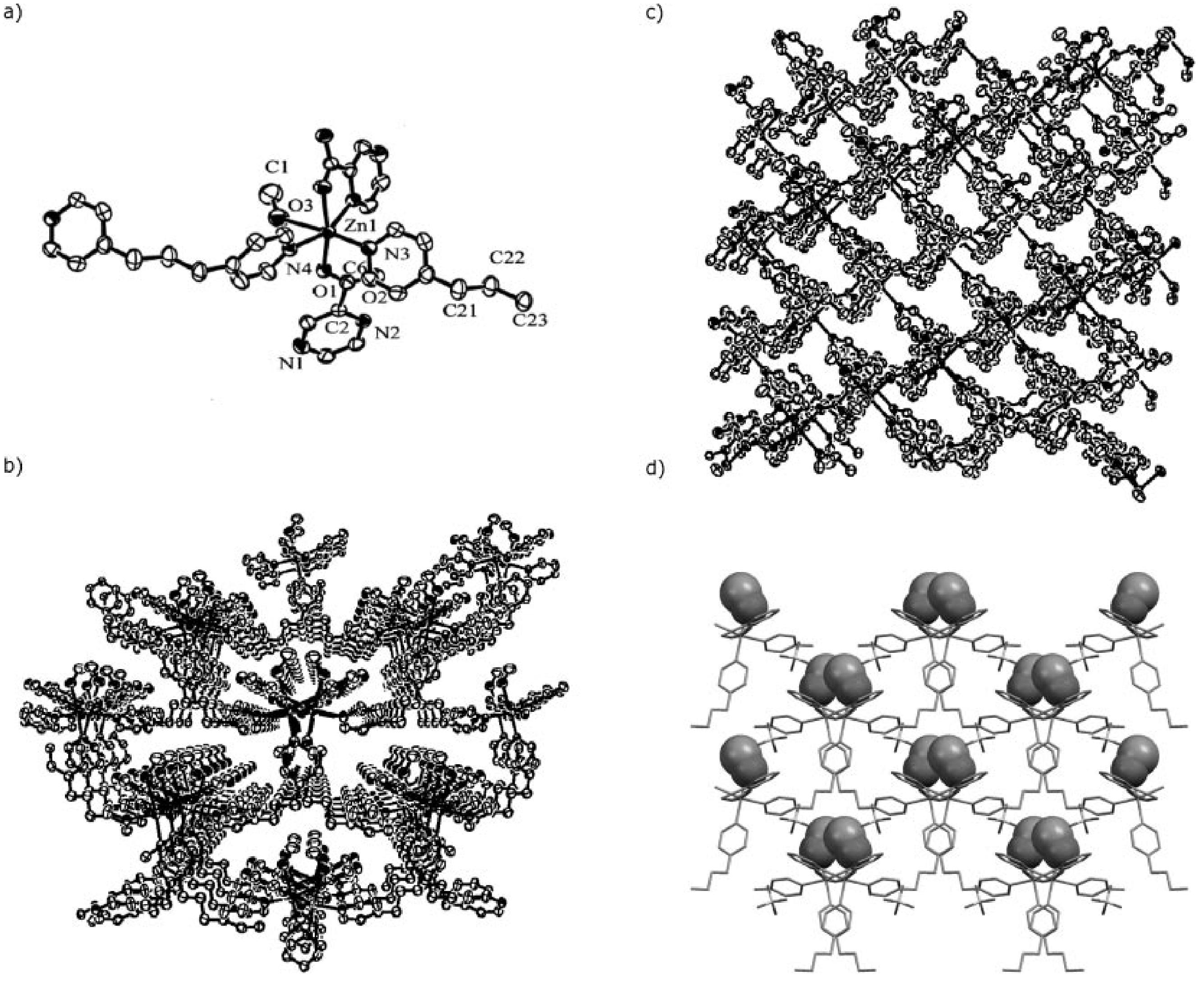

Figure 4. (a) ORTEP drawing of [Zn(bpp)(pca)(MeOH)] (**4**); (b) top view of the multidimensional structure of **4** along the *c* axis; (c) side view of the 3D layers of **4** along the *a* axis; (d) view of the weakly bound methanol molecules in the channels

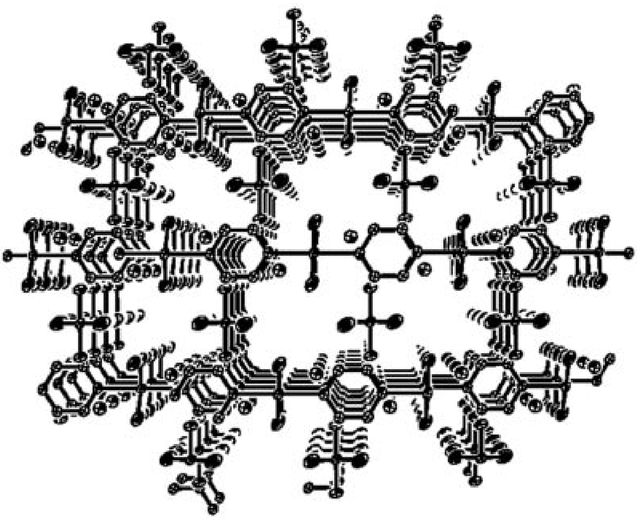

Figure 5. 2D grids built up by hydrogen-bonded networks between 1D chains of **5** and SiF_6^{2-}

The Zn−N and Zn−O bond lengths of pca are 2.082−2.190 and 2.028−2.166 Å, respectively, which are in the normal range for these compounds.[12,13,15,25] One methanol molecule is loosely coordinated to Zn [Zn−O = 2.431(4) Å] in **4**. The $Zn-OH_2$ distances in **2** and **5** are normal.

The grid architecture of **1** is shown in Figure 1b. It is constructed by pca and bipy linkers with Zn^{II} corners. The approximate size of the cages is 5.9 Å × 11.4 Å; hereafter, the size of the cage is defined by the N·· N distances unless stated otherwise. One H_2O molecule, one EtOH molecule, and a ClO_4 anion are contained in each channel and the ClO_4^- anion tethers solvate molecules through hydrogen bonds.

The function of bpen in **2** is twofold: one bpen ligand connects the neighboring Zn ions directly through two N atoms (two strong interactions) to form a quasi one-dimensional chain, while, at first glance, the other bpen acts as a monodentate ligand through one N atom. However, a closer inspection of the packing diagram reveals that the remaining N atom is connected to the O atom in H_2O, which is coordinated to another Zn ion by a hydrogen bond (weak interactions; Figure 2b). Thus, the fundamental unit of the grid is composed from the dimer $[Zn(bpen)(pca)(H_2O)]_2$. In addition, layers composed from these dimers are connected by other hydrogen bonds among O atoms in ClO_4^- and coordinated H_2O and free H_2O, and thus three-dimensional cages are formed by hydrogen bonds (Figures 2b and c). The ClO_4^- anion is essential for the formation of these three-dimensional architectures. The approximate size of the cages is 3.4 Å × 13.6 Å.

Substituting the $-CH_2-CH_2-$ unit (bpea) in **3** for the $-CH=CH-$ unit (bpen) in **2** causes significant changes in the crystal structure. First, the six-coordination around the Zn ion in **2** is reduced to five in **3**. The basic skeleton around the Zn ion is regarded as a square pyramid. The basal square is constructed from N, O (chelating pca), O (bridging pca), and N (bpea) atoms, and the apex is occupied by the N atom from another bpea ligand (Figure 3a). Next, the main motif (the longer grid) of the supramolecule of **3** contains polymeric, pleated (Z-shaped) chains around the corner zinc ions, which are then interlaced by pca by coordination of O atoms to Zn ions (the shorter grids) yielding a two-dimensional sheet (Figure 3b). The size of the grids is approximately 13.3 Å × 5.7 Å, and the distance between the sheets is 8.96 Å. The ClO_4^- anion and EtOH molecule are situated between the sheets and are not connected to the cages by hydrogen bonds. The incorporated EtOH molecules are depicted in Figure 3c. The cage structure is maintained after the loss of EtOH upon heating, as described below and thus **3′**, which is complex **3** without EtOH, exhibits quite similar lattice constants and the same space group. This phenomenon is important for the construction of a microreactor from these coordination polymers. The thermal behavior is described below.

The polymeric structure of **4** is topologically more complicated (Figure 4b, projected almost along the *c* axis). The skeletal motif looks like an atoll. The other crystal-packing diagram has been shown to emphasize how the organic scaffolds are used to bridge the Zn ions and/or how the motif of the atoll is built up (Figure 4c, projected almost along the *a* axis); the minimum numbers of atoms are employed in this diagram to represent the organic linkers. The side view (Figure 4c) demonstrates clearly that the horizontal layer (which is the vertical column in Figure 4b) is composed of bridging pca ligands thus giving rise to a shorter period. The perpendicular grids in Figure 4b are then constructed by tethering the horizontal layers to different Zn ions by another bpp linker (Figure 4b) and thus these two-dimensional grids are built up to form the three-dimensional framework. One methanol molecule coordinates loosely to each zinc ion to complete the six-coordination (Figure 4d). The whole architecture is best described as an oblate honeycomb; one ClO_4^- anion per Zn ion is positioned in each lacuna. The methanol ligand is easily removed upon heating. The approximate size of the cages is 12.4 Å × 5.3 Å when the methanol is neglected.

Figure 5 shows the almost square grids of **5**, the main component of which is an infinite one-dimensional chain of (pyrazine)Zn units. The chains are "glued" to each other by hydrogen bonds between the F atoms in SiF_6^{2-} and the aromatic protons. Two-dimensional sheets are thus formed in the solid state. The approximate size of the cages is 9.9 Å × 9.3 Å.

We suggested in our previous paper that the length of the linker determines the type and the structure of the polymer formed, and that the dimensionality of the polymer is reduced from two to one if a longer linker is used; these complexes were Mn derivatives containing pyridin-2-ylmethanol and another bridging bis(pyridine) ligand.[26] However, the present exploration suggests that the grid structure becomes highly undulated with the elongation of the distance between two pyridine rings used in this study. For **1**−**4**, pca is an indispensable lattice constituent, although the lattice length made by pca is rather short. An appropriate combination of short and long lattice constituents [pca and bis(pyridine) ligand], together with the multiple coordination modes of pca, will be required to form sophisticated structures containing nano-channels, especially the three-dimensional channels of **4**.

Thermogravimetric Measurements

Our stated aim is the construction of cage-like cavities and/or grid structures which contain enough lacuna to accommodate small gaseous molecules. As was described above, the supramolecules **2**, **3**, and **4** are good candidates for this purpose because their caged structures are maintained after the removal of the solvent molecules. In this section, the process of the loss of H_2O, EtOH, and/or MeOH is explored by the use of thermogravimetric analysis. The samples were exposed to air for 1 h before analyzing them. The results of the thermogravimetric measurements are shown in Figures 6a and b for **2** and **4**, respectively. The TG-DTA plot for **2** (Figure 6a) exhibits two steps of H_2O loss. The first step is assigned to the loss of included H_2O and the latter step to loss of coordinated H_2O. The residual cage is stable up to 280 °C. The TG-DTA plot for **3** (not shown), however, exhibits only a small step corresponding to the loss of ethanol. This indicates that the weakly trapped ethanol molecules are easily lost upon exposure to air during the pre-treatment of the sample; the cage structure is stable up to 300 °C. The TG-DTA plot for **4** (Figure 6b) indicates that the weakly coordinated methanol is easily lost upon heating in the range from 60 to 110 °C. The remaining cage is stable up to 270 °C. These thermogravimetric analyses strongly suggest that the nano-channels in **2**−**4** after the loss of ethanol and/or methanol are good candidates for porous materials to trap small molecules. Therefore, gas-absorption measurements were performed for the residual porous-channel-containing supramolecules **2′**−**4′** {**2′** = $[Zn(\mu\text{-}bpen)(bpen)(pca)]ClO_4$; **4′** = $[Zn(pca)(bpp)]ClO_4$} with N_2. However, our preliminary gas-absorption measurements are not indicative of a decent absorption ability, especially at low N_2 pressure. Therefore,

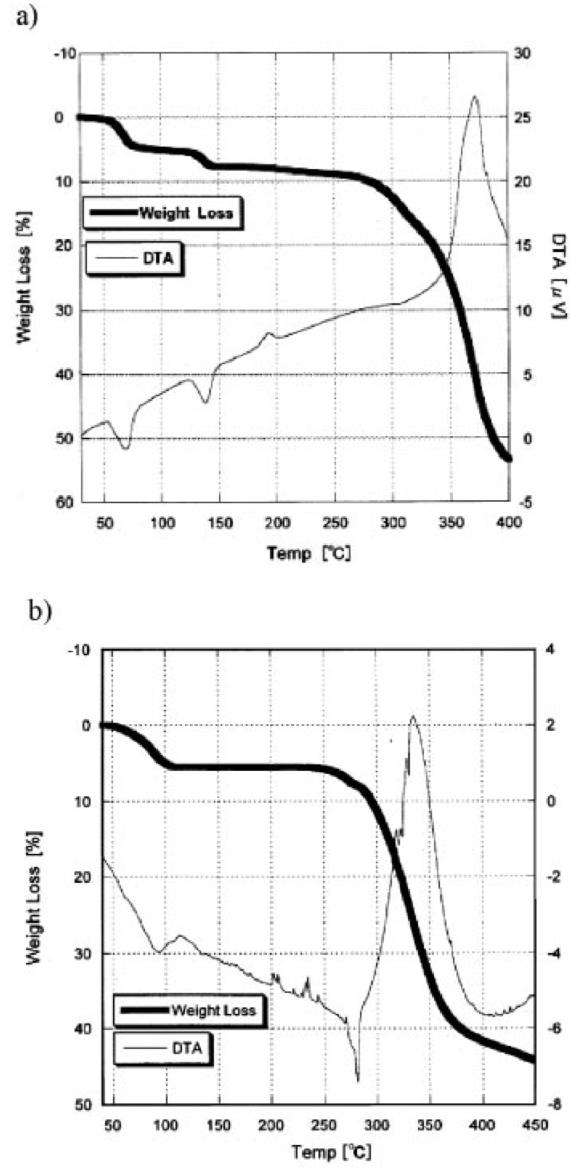

Figure 6. TG-DTA plots for **2** (a) and **4** (b) vs. temperature

our efforts to determine the ability of these porous molecules for this purpose are continuing with other gases.

Conclusion

New caged and/or porous supramolecules have been synthesized from pyrazine-2-carbonitrile, bis(pyridine) ligands, and zinc perchlorate. Hydrolysis of the CN group to CO_2^- during the crystallization process is essential for the success of the synthesis. The channel architectures of the complexes survive after removal of solvent molecules for the three supramolecules chosen as new examples of coordination polymers.

Experimental Section

Materials and General Procedures: Syntheses and manipulations were generally performed in the open air unless otherwise described. Pyrazine-2-carboxylic acid, pyrazine-2-carbonitrile, and pyrazine were purchased from Tokyo Kasei Kogyo Co., Ltd. 4,4′-Bipyridine (bipy) and the other pyridines NC_5H_4-R-C_5NH_4 (R = CH=CH, CH_2-CH_2, $CH_2-CH_2-CH_2$) were purchased from Wako Pure Chemical Ind., Ltd. or Aldrich. The following abbreviations are used for pyrazine derivatives and bis(pyridine) ligands: pcn (pyrazine-2-carbonitrile), Hpca (pyrazine-2-carboxylic acid), bpen [1,2-bis(4-pyridyl)ethylene], bpea [1,2-bis(4-pyridyl)ethane], bpp [1,3-bis(4-pyridyl)propane]. 4,4′-Azopyridine (azp) was synthesized according to a literature method.[27] $Zn(ClO_4)_2{\cdot}6H_2O$, other ligands, and solvents were also purchased from Wako Pure Chemical Ind., Ltd. or Aldrich. Thermogravimetric measurements were carried out with a Rigaku TAS-300 and TG8101D thermoflex. Gas-absorption measurements were performed with a Yuasa-ionics Autosorb1. ***Caution:*** *Organic perchlorate salts are potentially explosive; all perchlorates salts should be handled with care!*

Synthesis of *trans*-[Zn(bipy)(pca)(H_2O)]ClO_4·(EtOH)$_{0.5}$(H_2O)$_{0.5}$ (1): A 1:1 mixture of pyrazine-2-carbonitrile (pcn; 105 mg, 1 mmol) and bipyridine (bipy; 155 mg, 1 mmol) was dissolved in 15 mL of EtOH/H_2O (2:1) and the mixture was stirred at room temperature for 2 h. An aqueous solution (5 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (380 mg, 1 mmol) was then added and the mixture stirred for 7 h. The mixture was left standing at room temperature for several days to yield a pale-yellow precipitate. Yield: 240 mg (46%). $C_{17}H_{19}ClN_4O_9Zn$ (524.2): calcd. C 38.89, H 3.47, N 11.34; found C 38.23, H 3.47, N 11.14.

Synthesis of [Zn(μ-bpen)(bpen)(pca)(H_2O)]ClO_4·2H_2O (2): pcn (105 mg, 1 mmol) and bpen (182 mg, 1 mmol) were dissolved in 10 mL of EtOH/H_2O (3:2) and the mixture was stirred at room temperature for 1 h. An aqueous solution (5 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (380 mg, 1 mmol) was then added. The resulting yellow solution immediately became a white suspension upon stirring. After 2 h of stirring, the precipitates were removed by filtration. The filtrate was then left standing at room temperature for several days to yield pale-yellow, plate-like single crystals. X-ray quality single crystals were grown from MeOH/H_2O. Yield: 210 mg (33%). $C_{23}H_{22}ClN_5O_9Zn{\cdot}2H_2O$ (613.3):calcd. C 44.90, H 3.93, N 11.38; found C 44.70, H 3.90, N 11.35. Upon heating, three H_2O (one coordinated and two free) molecules were lost. Judging from the color and the appearance of the thermally treated compound, the structure of the compound seems unchanged after loss of H_2O, as described in the thermogravimetric section.

Synthesis of [Zn(bpea)(pca)]ClO_4·(EtOH)$_{0.5}$ (3): pcn (105 mg, 1 mmol) and bpea (185 mg, 1 mmol) were dissolved in 15 mL of EtOH/H_2O (2:3) and the mixture was stirred at room temperature for 1 h. An aqueous solution (5 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (380 mg, 1 mmol) was then added. The solution became a white suspension and the mixture was stirred for 10 h. The colorless precipitates were removed by filtration and the filtrate was left standing at room temperature for several days to yield colorless, needle-shaped crystals. The cycle of precipitation and filtration was repeated several times and finally pale-yellow block single crystals were obtained. The yield of combined colorless crystals of **3** was 240 mg (46%) after recrystallization from MeOH/H_2O. $C_{19}H_{21}ClN_4O_7Zn$ (519.6): calcd. C 43.66, H 3.66, N 11.31; found C 43.41, H 3.63, N 11.28. The yellow crystals were determined to be [Zn(bpea)$_2$(H_2O)$_2$](ClO_4)$_2$(H_2O)$_2$ by single-crystal X-ray diffraction.[28] [Zn(bpea)(pca-

)](ClO4) (**3′**) was obtained upon heating **3**, as demonstrated by a single-crystal X-ray diffraction study. The structural details of **3** and **3′** are described in the text.

Synthesis of [Zn(bpp)(pca)(MeOH)]ClO_4 (4): pcn (60 mg, 0.5 mmol) and bpp (100 mg, 0.5 mmol) were dissolved in 15 mL of $EtOH/H_2O$ (1:2). After stirring of the solution for 1 h, an aqueous solution (5 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (190 mg, 0.5 mmol) was added to this mixture with stirring. After stirring at room temperature for 10 h, the solution was left standing at room temperature for several days to give a white, flocculent precipitate. The product was collected on a frit and was recrystallized from $MeOH/H_2O$ to give pale-yellow, pillar-like single crystals of **4**. Yield 190 mg (75%). $C_{19}H_{21}ClN_4O_7Zn$ (518.2): calcd. C 44.03, H 4.08, N 10.81; found C 43.84, H 4.02, N 10.78. Compound **4** was also obtained from the reaction of pca, bpp, and $Zn(ClO_4)_2{\cdot}6H_2O$ in a similar yield.

$[Zn(pyz)(H_2O)_4](SiF_6)(H_2O)$ (5): pcn (210 mg, 2 mmol) and pyrazine (pyz; 170 mg, 2 mmol) were dissolved in 4 mL of $EtOH/H_2O$ (3:1). An $EtOH/H_2O$ (1:1) solution (4 mL) of $Zn(SiF_6){\cdot}xH_2O$ (420 mg, 2 mmol) was then added with stirring. The mixture was left standing at room temperature for several days to give colorless crystals of **5**, whose structure was confirmed by a single-crystal X-ray diffraction study. Yield 270 mg (36%).

$[Zn(pca)_2(H_2O)_2]$ (6): pca (130 mg, 1 mmol) was dissolved in 10 mL of $EtOH/H_2O$ (1:1) and then 1 mmol of pyrazine (85 mg) was added. An aqueous solution (5 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (380 mg, 1 mmol) was added with stirring. After 10 h of stirring, the reaction mixture was left standing at room temperature for several days to yield colorless cubic crystals of **6**, whose structure was confirmed by a single-crystal X-ray diffraction study.[29]

$[Zn(bpy\text{-}O)(H_2O)_4](ClO_4){\cdot}(bpy\text{-}O)_2$(7): An ethanol solution (5 mL) of pcn (110 mg, 1 mmol) was mixed with an aqueous solution (10 mL) of bpy-O (185 mg, 1 mmol) with stirring. After 1 h, an $EtOH/H_2O$ solution (2:5; 7 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (380 mg, 1 mmol) was added and the mixture stirred for 19 h. The solution was left standing at room temperature to afford colorless plates. A single-crystal X-ray diffraction study showed that the product is $[Zn(bpy\text{-}O)(H_2O)_4](ClO_4){\cdot}(bpy\text{-}O)_2$ (**7**).[27] When pca was employed instead of pcn, **6** was isolated. Yield 190 mg (59%).

$[Zn(azp)_2(H_2O)_2](ClO_4)(MeOH)$ (8), $[Zn(azp)_2(H_2O)_4](ClO_4)_2$-$(azp)_{2.5}$ (9) and $[Zn_2(\mu\text{-}azp)_2(azp)_4(H_2O)_6](ClO_4)_2$ (10): azp (190 mg, 1 mmol) and pcn (110 mg, 1 mmol) were mixed in 6 mL of $EtOH/H_2O$ (1:1) with stirring. An aqueous solution (6 mL) of $Zn(ClO_4)_2{\cdot}6H_2O$ (380 mg, 1 mmol) was then added. After 4 h of stirring, the resulting orange-red precipitate was collected on a frit and recrystallized from MeOH to give red rectangular crystals of **8**; a single-crystal X-ray diffraction study supported the identification.[30] Two kinds of red single crystals (**9** and **10**) were also isolated from the original filtrate. Identification of these crystals was performed by a single-crystal X-ray diffraction study.[30] When pca was employed instead of pcn, **5** was obtained.

X-ray Crystallography: Selected crystals of compounds **1**−**10** were attached on a nylon loop for low-temperature measurements. A Bruker SMART-APEX CCD diffractometer with graphite-monochromated Mo-K_a radiation (λ = 0.71073Å) was used for data collection on these crystals at 100 K. The structures were solved by direct methods using Sir-97 in a WinGx program package and refined with anisotropic thermal parameters by full-matrix least-squares techniques with SHELXS-97 in a WinGx program package.[31] The refinements were made on F^2 data; the final R and wR_2 values are given in Table 1 for **1**−**5**. Crystal data for **6**−**10** are not cited because these are known compounds. Selected bond lengths and angles are given in Table 2. The molecular structures of these compounds are given in the text. CCDC-232435 for (**1**), -232436 (**2**), -232437 (**3**), -232438 (**3′**), -232439 (**4**) and -232440 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Table 1. Crystal data

	1	**2**	**3**	**3′**	**4**	**5**
Empirical formula	$C_{17}H_{19}ClN_4O_9Zn$	$C_{23}H_{26}ClN_5O_{11}Zn$	$C_{19}H_{21}ClN_40_7Zn$	$C_{18}H_{18}ClN_40_{6.5}Zn$	$C_{19}H_{21}ClN_40_7Zn$	$C_4H_{14}N_2O_6F_6SiZn$
Formula mass	524.2	613.3	519.6	438.1	518.2	393.6
Crystal system	monoclinic	triclinic	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$	$P\bar{1}$	$P2_1/n$	$P2_1/n$	Cc	$P2/m$
Temperature [K]	100	293	100	293	100	293
a [Å]	10.492(6)	10.401(1)	10.1459(6)	10.282(4)	14.786(1)	7.0204(8)
b [Å]	9.410(5)	10.905(1)	20.402(1)	20.760(8)	16.528(1)	6.9920(8)
c [Å]	22.685(1)	13.543(2)	11.1216(6)	11.214(4)	10.2302(8)	7.1791(8)
α [°]	90	94.060(3)	90	90	90	90
β [°]	100.12(9)	106.279(3)	114.78(1)	115.25(7)	119.104(1)	104.324(2)
γ [°]	90	114.713(3)	90	90	90	90
V [Å^3]	2204.6(4)	1308.34(3)	2090.2(1)	2164.9(8)	2184.4(1)	341.44(2)
Z	4	2	4	4	4	4
$D_{calcd.}$ [g/cm^3]	1.58	1.56	1.72	1.45	1.58	1.90
μ [mm^{-1}]	1.291	1.101	1.362	1.296	1.296	1.982
θ range [°]	1.8−28.4	1.6−28.4	2.0−28.4	2.0−28.5	2.0−28.4	2.9−28.1
Reflections collected	12648	7903	11955	13038	6503	2097
Unique reflections	4984	5634	4754	5004	4472	834
No. of parameters	349	417	349	299	370	68
R_1	0.044	0.077	0.070	0.061	0.052	0.040
wR_2	0.116	0.151	0.189	0.186	0.145	0.111

Table 2. Selected bond lengths [Å] and angles [°] (bis-py = bipy, bpen, bpea, and bpp)

	1	2	3	3′	4	5
Zn–N(pca)	2.183(2)	2.189(5)	2.094(3)	2.041(4)	2.189(4)	
Zn–N(pyz)						2.199(3)
Zn–N(bis-py)	2.151(3)	2.137(5)	2.043(3)	2.024(4)	2.093(4)	
	2.139(3)	2.160(5)	2.046(3)	2.104(4)	2.116(4)	
Zn–O(pca)	2.107(2)	2.156(4)	2.124(3)	2.035(3)	2.048(3)	
	2.102(2)	2.203(5)	2.026(2)	2.131(3)	2.111(3)	
Zn–O(ROH)	2.111(2)	2.123(5)			2.431(5)	2.077(2)
N(pca)–Zn–N(bis-py)	91.40(8)	94.3(2)	109.1(1)	102.6(2)	101.2(2)	
	88.85(8)	95.5(2)	148.1(1)	148.1(2)	158.4(2)	
N(pyz)–Zn–N(pyz)						180.0
N(bis-py)–Zn–N(bis-py)	179.58(9)	169.1(2)	101.7(1)	108.2(2)	94.6(2)	
O(pca)–Zn–O(pca)	83.75(7)	75.7(2)	154.8(1)	155.1(2)	165.9(2)	
O(pca)–Zn–N(pca)	76.91(8)	149.5(2)	78.5(1)	91.3(1)	100.2(2)	
	160.63(8)	73.8(2)	85.7(1)	92.9(2)	75.8(1)	
O(pca)–Zn–N(bis-py)	90.86(8)	88.3(2)	94.8(1)	77.8(1)	97.2(2)	
	89.87(8)	94.7(2)	91.1(1)	96.2(2)	92.3(2)	
	89.52(8)	92.7(2)	108.9(1)	106.8(2)	96.9(2)	
	90.01(8)	85.7(2)	92.3(1)	85.9(1)	87.8(1)	
N(pca)–Zn–O(ROH)	97.06(9)	96.2(2)			83.0(2)	
N(bis-py)–Zn–O(ROH)	87.15(8)	87.6(2)			175.2(2)	91.70(8)
	92.48(8)	86.6(2)			82.0(2)	88.30(8)
O(pca)–Zn–O(ROH)	102.19(8)	114.3(2)			79.6(2)	
	173.19(7)				86.5(2)	
O(ROH)–Zn–O(ROH)						180.00(9)
						90.2(1)
						89.9(1)

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