Cooperative Guest Inclusion by a Zeolite Analogue Coordination Polymer. Sorption Behavior with Gases and Amine and Group 1 Metal Salts

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Abstract: Reaction of CuX_2 (X = NO_3, Cl, $(SO_4)_{1/2}$) salts and Hpymo·HX (Hpymo = 2-hydroxypyrimidine; X = Cl, NO_3) in aqueous amine solutions (amine = NH_3, CH_3NH_2) leads to formation of the poorly crystalline three-dimensional open-framework coordination polymer $[Cu(pymo\text{-}N1,N3)_2]_\infty$ (**1**). Under the same reaction conditions, but in the presence of amine and group 1 metal salts of single charged voluminous anions, highly crystalline clathrates of the type $\{[Cu(pymo\text{-}N1,N3)_2]\cdot(AX)_{1/3}\}_\infty$ (**1·AX** with A = NH_4, CH_3NH_3, Li, K, Rb; X = ClO_4, BF_4, PF_6) are obtained. The X-ray crystal structure of **1·NH$_4$ClO$_4$** reveals that the combination of square-planar Cu^{2+} ion with 120° bond angles provided by Hpymo generates a three-dimensional porous $[Cu(pymo\text{-}N1,N3)_2]_\infty$ framework with ammonium and perchlorate ions and water molecules included in the pores. **1** possesses a rich host−guest chemistry. Indeed, N_2 sorption at 77 K by empty host **1** reveals its microporous nature with a BET surface area of ca. 200 $m^2\ g^{-1}$. Hydrated **1** loses water upon heating and when exposed to moist air regenerates the original hydrated material. Likewise, **1·NH$_4$ClO$_4$** loses ammonia upon heating, giving the corresponding activated acidic material **1·HClO$_4$** which upon exposure to gaseous ammonia regenerates **1·NH$_4$ClO$_4$**. In addition, **1** reversibly and selectively sorbs $AClO_4$ salts (A = NH_4, Li, Na, K, Rb) when exposed to $AClO_4$ aqueous solutions giving highly crystalline **1·AClO$_4$** clathrates. Cl^-, NO_3^-, SiF_6^{2-}, and SO_4^{2-} salts are, however, not taken up. Salt sorption curves are of type V and possess hysteresis loops. This behavior agrees with the observed guest-induced structure phase change taking place in the **1** framework after guest inclusion.

Introduction

One of the goals of contemporary science is the molecular design of materials to achieve specific properties. Very successful approaches are molecular architecture and crystal engineering. Within these two fields a combination of metal ions with organic ligands has been shown to be very fruitful in building discrete molecular polygons and polyhedra[1,2] as well as highly defined one-, two-, and three-dimensional polymers.[3−7] A very interesting group of compounds are two- and three-dimensional porous coordination polymers which possess high potential as absorbents for gas storage, molecular sieving, chemical sensing, and catalysis.[3,7] Some of these open-framework solids are structurally and functionally related to zeolites and other inorganic microporous materials.[8] Zeolites and related inorganic materials generally combine microporosity with high thermal stability but are much more difficult to modify and derivatize in a systematic way than coordination polymers. In addition, the flexibility of coordination frameworks and the different electronic nature of pores confer novel properties on these new materials.[9] The development of selective anion sequestering agents, especially in polar solvents such as water,

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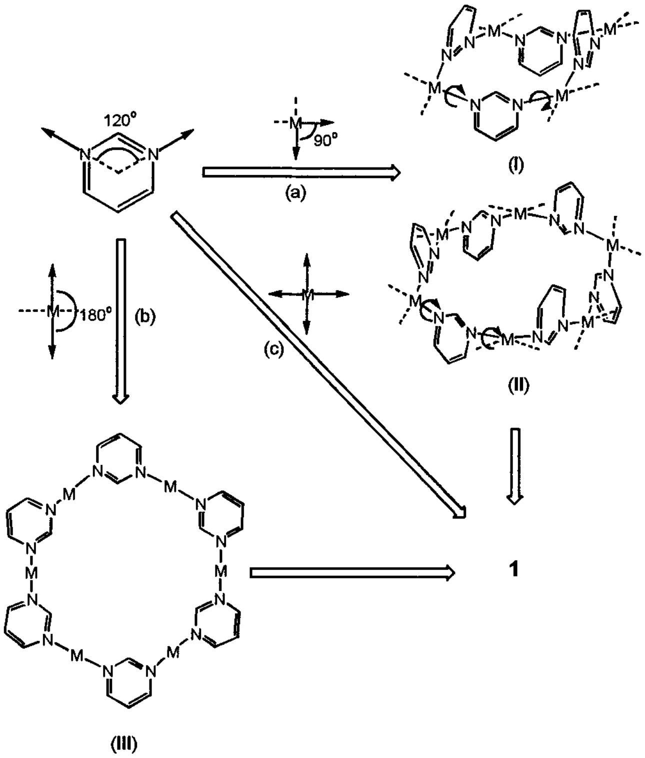
10.1021/ja002624a CCC: \$20.00

Scheme 1. Assemblies Generated by Combination of 120° Bond Angles Provided by a Pyrimidine Derivative with Metal Entities Possessing 90° (a) and 180° (b) Bond Angles or Square-Planar Geometry (c)[a]



[a] Metallacalix[*n*]arene ($n = 4$, **I**; 6, **II**); molecular hexagon (**III**).

is particularly interesting due to their possible use in ameliorating the environmental impact of anions.[10] This task has not yet been achieved with any degree of success, especially if we compare the supramolecular chemistry of cations.[11,12]

We have previously applied the principles of molecular architecture to build metallamacrocycles analogues to calix[4]-arenes[1d,13] by combining a metal entity with 90° bond angles and simple pyrimidine derivatives. In the same way, we have also obtained molecular hexagons[14] by using linearly coordinated metal ions (Scheme 1). In the present work, we extend these principles to crystal engineering by simultaneously combining the above-mentioned geometries, using highly coordinating "naked" Cu^{2+} ions and a symmetric pyrimidine derivative (Scheme 1). In this way, tetranuclear and hexanuclear structural motifs are generated which interlock with each other to build a three-dimensional porous framework. The noncharged open-framework generated in this way possesses an unprecedented affinity for salts of ClO_4^-, BF_4^-, and PF_6^- anions.

Results and Discussion

The reaction of CuX_2 salts (X = Cl, NO_3, $(SO_4)_{1/2}$) with Hpymo·HX (Hpymo = 2-hydroxypyrimidine, X = Cl, NO_3) in a 1:2 ratio in aqueous amine solutions (amine = NH_3, CH_3NH_2) produced a purple poorly crystalline solid of composition $[Cu(pymo)_2]\cdot 2.25H_2O$ (**1**). Its low solubility in common solvents and its spectroscopic properties pointed to a polymeric material (see Supporting Information). Applying the same synthetic procedure but in the presence of amine and group 1 metal salts of singly charged voluminous anions (ClO_4^-, BF_4^-, PF_6^-), highly crystalline materials of the type $[Cu(pymo)_2]\cdot(AX)_{1/3}\cdot(H_2O)_{4/3}$ (**1·AX** with A = Li, K, Rb, CH_3NH_3, NH_4; X = ClO_4, BF_4, PF_6) were obtained. X-ray powder diffractograms proved that this set of compounds is isomorphous.

Crystal Structure of 1·NH₄ClO₄. The crystal structure of **1·NH₄ClO₄** has been solved by X-ray crystallography. This compound crystallizes in a highly symmetric space group of the cubic system, namely $Pn\bar{3}m$. Its structure consists of a three-dimensional porous coordination $[Cu(pymo\text{-}N1,N3)_2]_\infty$ network with ammonium and perchlorate ions and water molecules included in the pores. The Cu^{2+} centers are located in the intersection of three crystallographic binary axes, whereas a symmetry plane intersects the pymo entities through O2, C2, and C5 atoms. The $[Cu(pymo\text{-}N1,N3)_2]_\infty$ framework is generated by distorted square-planar Cu^{2+} ions coordinated to four nitrogen donor atoms of four different pymo moieties, each one symmetrically bridging two copper centers (Figure 1a). In this way, tetranuclear and hexanuclear molecular boxes analogous to calix[*n*]arenes ($n = 4$, 6) along with planar hexanuclear molecular hexagons are generated (Figure 1b,c). The three structural motifs interlock to give a highly symmetric three-dimensional framework that acts as a host for NH_4ClO_4 (Figure 2). This result confirms that simple pyrimidine derivatives are ideally suited for applying the principles of molecular architecture and crystal engineering to build complex structures.[1d,13,14]

The $[Cu(pymo)_2]_\infty$ framework in **1·NH₄ClO₄** can be considered an open structure. It accounts only for approximately 80% of the total volume of the unit cell, the remaining 20% being intracrystalline pore volume that is filled with ammonium and perchlorate ions and water molecules. The pores form a diamondoid network. The pores of ~8.1 Å diameter are defined by planar $[Cu_6(pymo)_6]$ molecular hexagons and contain an ammonium cation and two water molecules. Each of these pores connects two cavities of ~14 Å diameter in which two perchlorate anions are included (see Figures 1 and 2). The anions play a very important role in the structure stabilization (see below).[15] It seems that anion guests have to fulfill some prerequisites with respect to charge and size. They have to possess three H-bonding acceptor groups in a suitable configuration to interact with two water molecules and an ammonium cation in the $[Cu_6(pymo)_6]$ hexagon plane (Figure 1b). Neither Cl^- nor NO_3^- fulfill this requirement. In the case of SO_4^{2-} and SiF_6^{2-}, which possess suitable geometries, it seems that their higher charge with the consequent higher hydration energy[16] precludes incorporation. ClO_4^-, BF_4^-, and PF_6^- display the proper geometry and lower polarity that favor inclusion. The structural role played by protonated amines is also very important and puts **1** in a close relation to zeolites for which size and form of organic amines determine the resulting porous structure.[8,17]

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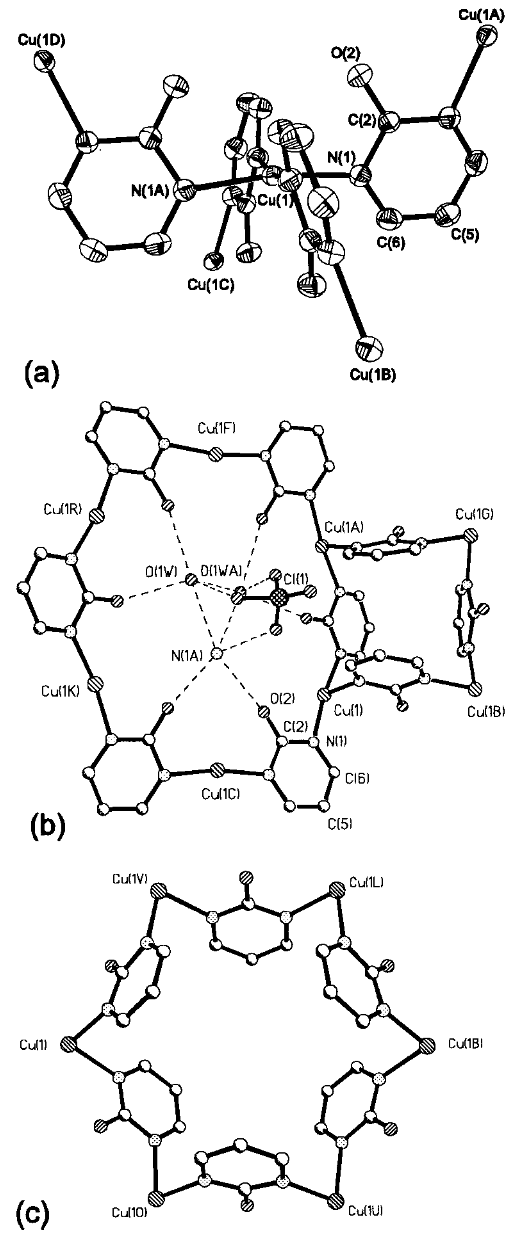

Figure 1. We show (a) the basic building block that generates the three-dimensional framework in **1·NH_4ClO_4**; (b) the molecular hexagon interlocking with a tetranuclear molecular box (in addition, extensive H-bonding interactions between two water molecules, an ammonium cation, a perchlorate anion, and six O-pymo are also shown); and (c) a view of the structural motif analogous to a calix[6]arene. Such a motif is placed in the confluence of 6 planar molecular hexagons related by $-3m$ symmetry operations. Cu−N1 1.988(5) Å, N1−Cu1−N1A 170.7(3)°, N1−Cu1−N1B 89.8(3)°.

It should be noted that there are only very few examples of three-dimensional structures generated by reaction of simple pyrimidine derivatives with naked metal ions. One of these rare examples is the acentric $\{[Cu(pyrimidine\text{-}N^1,N^3)_2]^+\}_\infty$ (**16**) framework,[6b] which resembles feldspar aluminosilicate minerals[18] and possesses large voids filled with BF_4^- anions. In addition, it is also interesting to note the uncharged nature of the **1** framework which contrasts with most polymeric networks build by nitrogen donor organic ligands[3] and, surprisingly, is still able to enclathrate polar guests such as NH_4ClO_4.

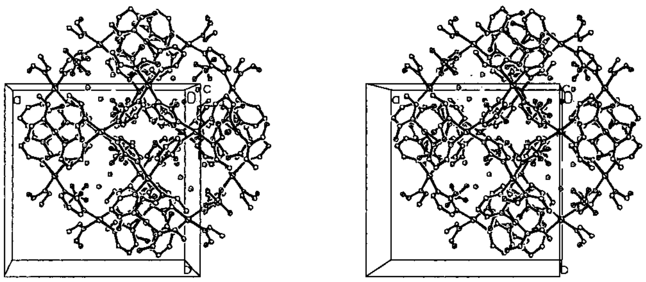

Figure 2. Stereoscopic view of the three-dimensional $[Cu(pymo)_2]_\infty$ framework including perchlorate, ammonium, and water guests.

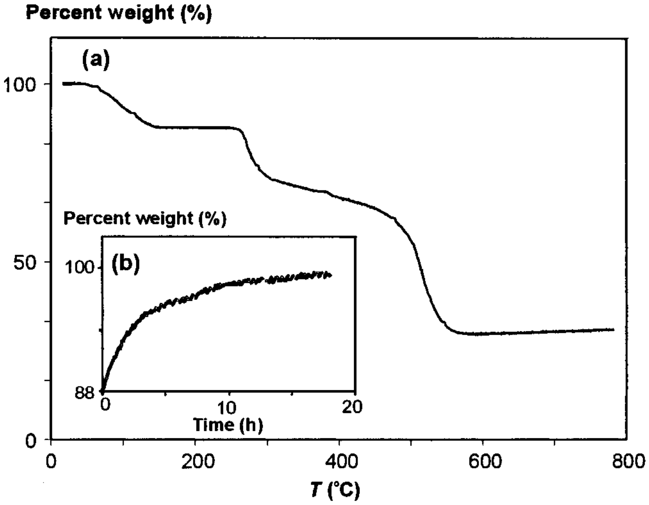

Figure 3. Thermal behavior of the hydrated **1** framework (a) and water sorption at 25 °C by anhydrous **1** when exposed to moist air (b).

Sorption Behavior of 1. Single-crystal X-ray analysis on **1·NH_4ClO_4** (see above) revealed that a well-structured network of pores (occupied by ammonium perchlorate guests) accounts for about 20% of the volume of the crystal. X-ray powder diffraction shows that all **1·AX** adducts are highly crystalline and isomorphous whereas empty **1** displays a much lower crystallinity and a slightly different structure. These facts prompted us to test the microporous nature of **1** and the possible interconversion processes to the corresponding **1·AX** adducts.

(a) Gas sorption: The porous nature of **1** has been investigated by means of N_2 sorption at 77 K (see Supporting Information). The sorption isotherm is of type I agreeing with a microporous material since all pores are filled even at the lowest pressure value studied ($P/P_o = 0.1$). Applying the BET method[19] we obtain a surface area of ca. 200 $m^2\ g^{-1}$. Another proof of the microporous nature of **1** is the reversible loss of water. Thus, thermal analysis of hydrated **1** shows a dehydration process taking place in the 50−140 °C temperature range (Figure 3a). The material is stable up to 250 °C. Upon exposure of anhydrous **1** at 25 °C to moist air, original hydrated **1** is regenerated (Figure 3b). XRPD shows that the water exchange process is not responsible for any structural change in **1**. Similarly, **1·NH_4ClO_4**,[20] upon heating at 100 °C for 24 h, loses ammonia to give an activated **1·$HClO_4$** acidic material (Figure 4). This process is also reversible, and when **1·$HClO_4$** is exposed to gaseous NH_3, it regenerates **1·NH_4ClO_4**. This behavior gives **1** a close analogy to zeolites for which removal of protonated

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[20] N_2 sorption studies at 77 K prove that **1·NH_4ClO_4** does not behave as a porous material as a consequence of presence of the NH_4ClO_4 guest in **1** pores.

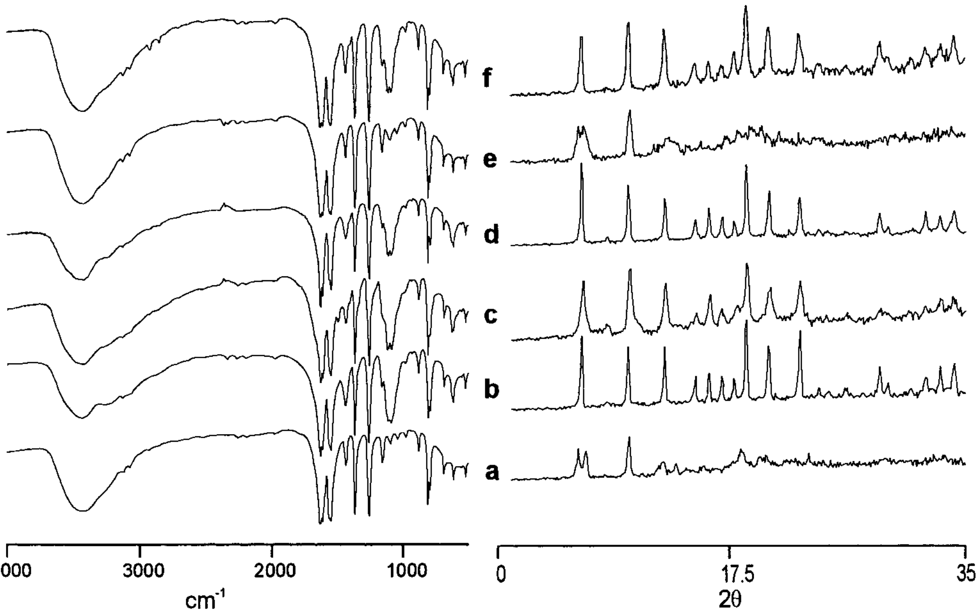

Figure 4. Host−guest chemistry of **1** toward NH_4ClO_4. Freshly prepared empty **1** (a) and **1·NH$_4$ClO$_4$** (b). **1·NH$_4$ClO$_4$** loses NH_3 upon heating at 100 °C to give **1·HClO$_4$** (c): we observe a slight lose of crystallinity but no phase change (line broadening in powder diffractogram) and slight changes in IR (broadening of some bands and apparition of a new band at 1490 cm^{-1}). **1·HClO$_4$** upon exposure to NH_3 vapors regenerates **1·NH$_4$ClO$_4$** (d). **1·NH$_4$ClO$_4$** when exposed to deionized water loses NH_4ClO_4 guests with a concomitant phase change to give **1** (e). Finally, when **1** is exposed for 48 h to a 0.1 M NH_4ClO_4 solution it gives **1·NH$_4$ClO$_4$**.

organic amines results in the formation of the corresponding activated acidic material along with formation of large voids.[8,17]

(b) Amine and group 1 metal salts sorption: We have found that formation of the **1** framework in aqueous ammonia solutions in the presence of group 1 metal perchlorate salts yields either pure **1·MClO$_4$** or mixed **1·M$_x$(NH$_4$)$_{1-x}$ClO$_4$** clathrates. **1·LiClO$_4$** is obtained as a pure material with all its voids being occupied by $LiClO_4$. With M = Na^+, K^+, and Rb^+, we obtain mixed enclathration of $MClO_4$ and NH_4ClO_4 salts with approximately 50% occupancy for K^+ and Rb^+ whereas Na^+ occupancy is only ∼10%. Under the same conditions Cs^+ is not taken up and the same happens with group 2 metals and lanthanide perchlorates.

We have also studied the sorption properties of previously isolated **1** with amine and group 1 metal perchlorate salts and found that the empty **1** framework when exposed to $AClO_4$ aqueous solutions for ca. 48 h gives the corresponding **1·AClO$_4$** clathrate with a concomitant structure phase change (Figure 4). NH_4^+, Li^+, Na^+, K^+, and Rb^+ salts are taken up, yet Cs^+ is not. Salt inclusion by **1** follows a type V sorption isotherm with a hysteresis loop[21] (Figure 5). This type of behavior is typical of a sorption process for which a guest induced transition phase takes place (Supporting Information).[22] The dynamic structure exhibited by **1** is typical behavior of a third-generation porous solid following the Kitagawa classification.[3c] The affinity of **1** for group 1 metal salts does not follow the expected ionic radii trend but $Li^+ > K^+ > Rb^+ > Na^+ \gg Cs^+$. We think this result should be related to their differences in hydration energies.[23] Thus, while hydrated Li^+ and Na^+ might diffuse through the pores, K^+ and Rb^+ ions which possess a lower hydration energy might diffuse unhydrated. Nevertheless, we presume that alkali cations will not directly bind to exocyclic pymo O-donor atoms but they will interact through multiple H-bonding interactions through the metal second sphere of coordination (Scheme 2). In addtion, we have performed additional studies of competitive salt sorption and found that 50 mM $LiClO_4$, $KClO_4$, and $RbClO_4$ facilitate $NaClO_4$ incorporation. We presume that the guest induced phase change found in **1** makes the sorption process cooperative.

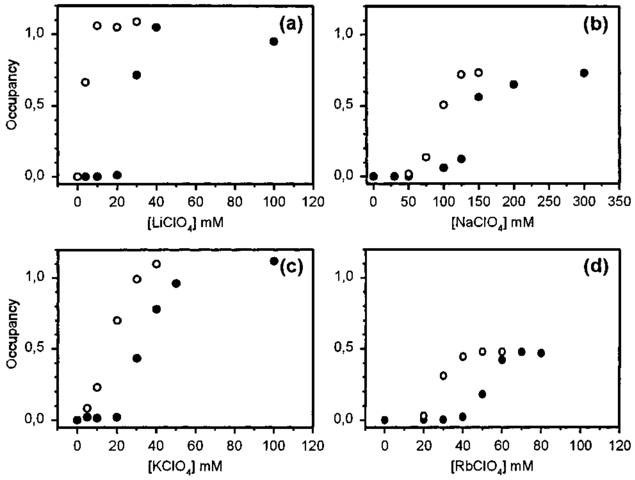

Figure 5. Sorption isotherms data at 298 K for **1** with group 1 metal perchlorate salts: $LiClO_4$ (a); $NaClO_4$ (b); $KClO_4$ (c); and $RbClO_4$ (d). Open symbols indicate desorption. It should be noted that in the case of $RbClO_4$ only partial occupancy is achieved, which may be due to the greater size of Rb^+.

Conclusions and Outlook

The framework of compound **1** possesses a close structural and functional analogy to zeolites and other open-framework inorganic materials. It should be noted that guest removal does not imply framework collapse but a structural change to a porous material. It is also interesting to note the uncharged character of the **1** framework, which differs considerably from previous examples of metallorganic frameworks containing nitrogen

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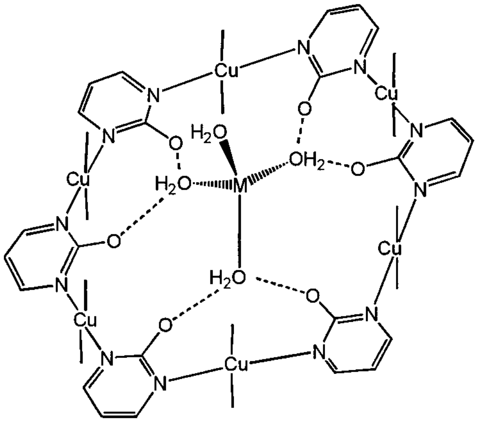
Scheme 2. Postulated Molecular Recognition of Hydrated Group 1 Metal Cations by Means of Extensive H-Bonding Interactions with the Planar Molecular Hexagon $Cu_6(pymo)_6$ Structural Motif



donor ligands, but nevertheless is still capable of selectively include highly polar guests. We think that the **1** framework exhibits high potential for perchlorate salt removal in polluted waters. We will continue using the simple combination of symmetric pyrimidine derivatives with metal ions of diverse stereochemistries to pursue new examples of polygons and three-dimensional porous materials, and study the effect of anions as template agents.

Experimental Section

Materials. 2-Hydroxypyrimidine·HCl was purchased from Aldrich and converted to the corresponding HNO_3 adduct by anion exchange. **Caution!** Perchlorate salts are potentially explosive and should be used in small quantities.

Preparation of $[Cu(pymo)_2]\cdot 2.25H_2O$ (1). An aqueous amine solution (30 mL of RNH_2:H_2O 2:8; R = H, CH_3) containing CuX_2 (1 mmol) and 2-Hydroxypyrimidine·HX (2 mmol, X = Cl, NO_3) gives a dark purple solid, after leaving the solution in open air for 1 day (pH 9.5). Yield 95%. Anal. Calcd for $CuC_8H_{10.5}N_4O_{4.25}$: C, 32.65; H, 3.60; N, 19.04; Cu, 21.59. Found: C, 32.5; H, 3.3; N, 19.1; Cu, 22.3. UV−vis (cm^{-1}): 18900. EPR: $g_{iso} = 2.05$.

Preparation of $[Cu(pymo)_2]\cdot(RNH_3X)_{0.333}\cdot(H_2O)_{1.333}$ (1·RNH_3X). Following the same procedure used for the synthesis of **1** but with the addition of CuX_2 (X = ClO_4, BF_4, PF_6) or $(NMe_4)BF_4$ salts (1 mmol) dark purple crystals of **1·RNH_3X** (RNH_2 = NH_3, CH_3NH_2) are obtained within 1 day. **1·NH_4ClO_4**: Yield 73%. Anal. Calcd for $CuCl_{0.333}C_8H_{10}N_{4.333}O_{4.666}$: C, 30.32; H, 3.18; N, 19.15; Cu, 20.05. Found: C, 30.4; H, 3.1; N, 19.1; Cu, 20.0. UV−vis (cm^{-1}): 19150. EPR: $g_\perp = 2.05$, $g_\| = 2.1$. **1·NH_4BF_4**: Yield 15%. Anal. Calcd for $CuB_{0.333}F_{1.333}C_8H_{10}N_{4.333}O_{3.333}$: C, 30.73; H, 3.22; N, 19.41. Found: C, 30.1; H, 3.3; N, 19.4. UV−vis (cm^{-1}): 18900. EPR: $g_{iso} = 2.08$. **1·NH_4PF_6**: Yield 27%. Anal. Calcd for $CuP_{0.333}F_2C_8H_{10}N_{4.333}O_{3.333}$: C, 29.28; H, 3.03; N, 18.56; Cu, 19.14. Found: C, 29.3; H, 3.0; N, 18.3; Cu, 20.1. UV−vis (cm^{-1}): 19300. EPR: $g_{iso} = 2.05$. **1·$CH_3NH_3ClO_4$**: Yield 56%. Anal. Calcd for $CuCl_{0.333}C_{8.333}H_{9.667}N_{4.333}O_{4.167}$: C, 32.02; H, 3.12; N, 19.41. Found: C, 32.1; H, 3.3; N, 19.3.

Preparation of 1·$MClO_4$. Following the same procedure used for the synthesis of **1** but with additional presence of $MClO_4$ (M = Li, K, Rb) salts (1 mmol), dark purple crystals of **1·$MClO_4$** are obtained within 1 day. With M = K, Rb compounds contaminated with ammonium salts where always obtained. **1·$LiClO_4$**: Yield 85%. Anal. Calcd for $CuLi_{0.333}Cl_{0.333}C_8H_{7.333}N_4O_{4.667}$: C, 30.68; H, 2.79; N, 17.89. Found: C, 30.4; H, 2.8; N, 17.9. **1·$KClO_4$**: Yield 74%. Anal. Calcd for $CuK_{0.1667}Cl_{0.333}C_8H_{8.667}N_{4.1667}O_{4.333}$: C, 30.49; H, 2.72; N, 18.37. Found: C, 30.1; H, 2.7; N, 18.3. **1·$RbClO_4$**: Yield 69%. Anal. Calcd for $CuRb_{0.1667}Cl_{0.333}C_8H_{9.333}N_{4.1667}O_{4.667}$: C, 29.28; H, 2.87; N, 17.79. Found: C, 29.2; H, 2.8; N, 18.0.

Instruments. Thermogravimetric analyses were performed on Schimadzu-TGA-50H equipment in the presence of a reactive atmosphere of air. Magnetic susceptibility measurements were performed on polycrystalline samples with a quantum design MPMS-2SQUID magnetometer operating in the range 2.0−300 K at 10000 G. X-band EPR spectra on polycrystalline samples were measured at room temperature on a Brucker 300E instrument operating at a frequency of 9.79 GHz. Electronic spectra on crystalline samples were carried out on a Varian Cary UV−vis−NIR spectrophotometer. Powder X-ray diffractograms were performed on a Philips PW1000 diffractometer using Cu Kα radiation ($\lambda = 1.54018$ Å).

Gas and Salt Sorption. A N_2 sorption isotherm for anhydrous **1** (0.115 g) was performed on automatic Quantachrom Quantasorb Jr. equipment at 77 K, using three different N_2:He mixtures (1:9, 2:8, 3:7). The sample was previously dried by heating it at 373 K on a N_2 stream. Water sorption by anhydrous **1** was studied by means of a Schimadzu-TGA-50H thermobalance employing an isothermal program. Salt sorption isotherms were studied at 25 °C in water solution (50 mg of **1** in 50 mL of solution) with the equilibrium being reached at 48 h of exposure to metal salt solutions. The group 1 metal concentration on the **1** framework was determined by means of atomic emission on an acetylene flame and using the Cu concentration on the samples as the internal standard on Perkin-Elmer Aanalyst 100 equipment.

X-ray Analysis. Crystal data for $\{(Cu(pymo)_2)_3\cdot NH_4ClO_4\cdot 4H_2O\}_\infty$ (**1·NH_4ClO_4**) at 295(2) K: $Cu_3ClC_{84}H_{30}N_{13}O_{14}$, $M = 950.66$, purple cubes, 0.15 × 0.15 × 0.15 mm^3, cubic, space group $Pn\bar{3}m$, $a = 15.7600(3)$ Å, $V = 3914.4(1)$ Å^3, $Z = 4$, $\rho_{calcd} = 1.613$ g cm^{-3}, Mo Kα radiation ($\lambda = 0.71069$ Å), $\mu = 1.76$ mm^{-1}, minimum (maximum) transmission 0.44 (0.77), absorption corrected, Stoe STADI4 system (293 K), 5557 reflections measured, 879 unique, 514 with $F_o^2 > 4\sigma(F_o^2)$ were used to refine 60 parameters to $R1$ ($wR2$) = 0.065 (0.191), GOF = 1.083, and highest peak in difference map = 1.10 eÅ^{-3}. Structure solution was by direct methods and was refined on F^2 in SHELX-97.[24] All non-hydrogen atoms were refined anisotropically with the exception of perchlorate oxygens, water molecules, and ammonium ions. The perchlorate anion was disordered in two positions with half occupancy each. As a result of the high symmetry, ammonium ions and water molecules were found to be distributed respectively in 6 and 12 equivalent positions. Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre supplementary publication no. CCDC-142804. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (Fax: (+44)1223-336-033; E-mail: deposit@ccdc.cam.ac.uk).

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Supporting Information Available: Figures showing the magnetic behavior of **1** and **1·NH_4ClO_4** versus the temperature, XRPD diagrams of intermediate species in the salt sorption processes, and N_2 sorption at 77 K of anhydrous **1**; tables listing atomic coordinates, temperature factors, bond lengths and angles, and details of refinement of the X-ray crystallographic data for compound **1·NH_4ClO_4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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[24] Sheldrick, G. M. *SHELXL97, Program for the Refinement of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.