A Novel Hybrid Supramolecular Network Assembled from Perfect π−π Stacking of an Anionic Inorganic Layer and a Cationic Hydronium-Ion-Mediated Organic Layer

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The synthesis and characterization of a three-dimensional inorganic-organic hybrid network $[\{Cu_2(CA)_3\}\{(H_3O)_2(phz)_3\}\cdot G]_n$ (**1**; H_2CA = chloranilic acid, phz = phenazine; G = $2CH_3COCH_3\cdot 2H_2O$) is described. The crystal structure of **1** shows that the 3D network assembly is based on a combination of two types of grid-building sub-units of (6,3) topology: an anionic metal-organic coordination honeycomb grid, and a cationic hydronium-ion-mediated organic honeycomb grid. The inorganic and organic honeycomb nets are perfectly π–π-stacked, creating an infinite number of open-end channels (channel size about 8 Å in diameter). The solid framework of **1** retains its rigidity upon removal of the guest molecules under high vacuum to form compound $[\{Cu_2(CA)_3\}\{(H_3O)_2(phz)_3\}]_n$ (**2**) as revealed by a single-crystal X-ray diffraction analysis. Compounds $[\{M_2(CA)_3\}\{(H_3O)_2(phz)_3\}\cdot G]_n$ (M = Cd, **3**; M = Zn, **4**; M = Co, **5**; G = $2CH_3COCH_3\cdot 2H_2O$) were also prepared and characterized as isostructures of **1** [crystal data for **1**: $Cu_2(CA)_3(H_3O)_2(phz)_3\cdot G$, trigonal, space group $P\bar{3}1m$, formula mass = 1478.86, a = 13.7593(2) Å, c = 9.1869(2) Å, V = 1506.22(5) Å^3, Z = 1; crystal data for **2**: $Cu_2(CA)_3(H_3O)_2(phz)_3$, trigonal, space group $P\bar{3}1m$, formula mass = 1326.62, a = 13.7565(4) Å, c = 9.1544(5) Å, V = 1500.3(1) Å^3, Z = 1]. The magnetic-exchange coupling between the copper centers for compound **1** was analyzed on the basis of the Curie–Weiss expression and a dinuclear magnetic model. The negative values of the Weiss constant and the magnetic-exchange coupling constant indicate an antiferromagnetic interaction between the copper centers.

Introduction

The use of noncovalent interactions, (e.g. metal−ligand coordination, hydrogen bonding, π−π stacking, etc.) to arrange molecular building blocks has evolved into one of the most useful and flexible strategies for the crystal-engineering design of extended networks that have versatile functions.[1−14] Successful examples of this method include highly porous metal-organic frameworks with controllable pore sizes and channel properties,[15−25] porous magnetic networks with guest-tunable magnetism,[26,27] chiral porous networks with enantioselective catalytic properties,[28−32] and guest-responsive dynamic frameworks.[33,34] Inorganic-organic hybrid materials that have potential hybrid properties are of great importance in crystal engineering design due to their possible applications.[35−37] Typically, however, it is difficult to prepare a crystalline material containing more than two components as the entropy effect may induce unpredictable crystal structures.[38] However, it is a route to the generation of materials that have novel properties which are not characteristic of the individual components.

It is known that the chloranilate (CA) ligand and its homologues, which contain two chelating coordination sites, are capable of bridging metal centers to form monomeric molecules, chains, sheets, or 3D structures.[37,39−47] Studies based on CA-containing magneto-networks have also been carried out with respect to the propagation of magnetic superexchange interactions between the paramagnetic metal centers through the CA bridges.[37,39−47] The benefits derived from the phenazine ligand are twofold. First, it contains two pyridine donor sites capable of participation in coordination and hydrogen-bonding interactions, and second, the three fused aromatic rings of the phenazine ligand facilitate π−π stacking interactions. As part of our continuous efforts in the design and synthesis of functional crystalline materials,[13,48−51] we report herein on new supramolecular extended networks, $[\{M_2(CA)_3\}\{(H_3O)_2(phz)_3\}]_n$ (M = Cu, Cd, Zn, and Co), assembled from the

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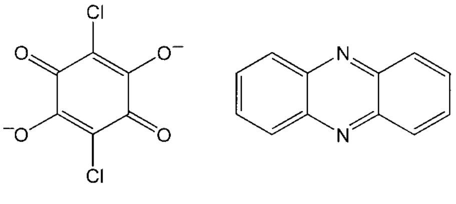
perfect π−π stacking of alternate inorganic and organic 2D hexagonal grid (6,3) nets.[11] The chloranilate and phenazine ligands play key roles in the formation of the inorganic and the organic honeycomb building subunits as well as in the construction of unusually robust ionic 3D networks which contain neutral nanoscale 1D channels.

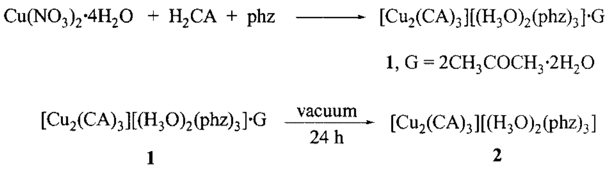


CA phz

Results and Discussion

Synthesis

The ligand CA was chosen as a bridging ligand and phenazine as a π-stacking moiety. Compound **1** was obtained as dark-purple crystals in a mixed-solvent system at room temperature (Scheme 1) and formulated as $[\{Cu_2(CA)_3\}\{(H_3O)_2(phz)_3\}\cdot G]_n$ (**1**; G = $2CH_3COCH_3\cdot 2H_2O$) by elemental and TG analyses. The self-assembly of **1** was achieved by the combination of two types of grid-building sub-units of a (6,3) topology: an anionic metal-organic coordinated honeycomb grid, and a cationic hydronium-ion-mediated organic honeycomb grid. Compound **1** is insoluble in most common solvents such as water, ethanol, acetonitrile, THF, DMF, acetone, etc. $[\{Cu_2(CA)_3\}\{(H_3O)_2(phz)_3\}]_n$ (**2**) was obtained by removing the guest molecules from **1** under vacuum and identified by X-ray single-crystal diffraction techniques and TG analysis. According to a similar synthetic strategy, compounds $[\{M_2(CA)_3\}\{(H_3O)_2(phz)_3\}\cdot G]_n$ (M = Cd, **3**; M = Zn, **4**; M = Co, **5**; G = $2CH_3COCH_3\cdot 2H_2O$) were also synthesized from $Cd(NO_3)_2\cdot 4H_2O$, $Zn(ClO_4)_2\cdot 6H_2O$ and $Co(NO_3)_2\cdot 6H_2O$, respectively.



Scheme 1

Structural Analysis

A single-crystal X-ray analysis reveals that **1** exists in a trigonal crystal lattice (space group $P\bar{3}1m1$) with a formula of $[Cu_2(CA)_3(H_3O)_2(phz)_3]\cdot G$ (G = $2CH_3COCH_3\cdot 2H_2O$). The results of the X-ray analysis of **2** were similar to those for **1** except for the absence of the guests. Crystals of compounds **3**−**5** were also grown and characterized by X-ray diffraction analysis. Selected interatomic bond lengths and angles for **1** and **2** are given in Table 1. An analysis of the local site symmetry reveals that each Cu^{II} center is positioned on a special symmetry site containing a mutually perpendicular threefold rotation axis and a twofold rotation axis. The Cu^{II} center is chelated by three CA ligands that are related by the site symmetry to form a propeller-like arrangement, resulting in an octahedral CuO_6 coordination environment (Figure 1).

Table 1. Selected bond lengths [Å] and angles [°] for **1** and **2**[a]

1		**2**	
Cu(1)−O(1)	2.088(3)	Cu(1)−O(1)	2.088(2)
Cl(1)−C(2)	1.734(4)	Cl(1)−C(2)	1.734(3)
C(1)−O(1)	1.247(4)	C(1)−O(1)	1.251(2)
C(1)−C(2)	1.394(4)	C(1)−C(2)	1.395(2)
C(1)−C(1)#1	1.536(6)	C(1)−C(1)#1	1.531(4)
C(3)−N(1)	1.344(4)	C(3)−N(1)	1.341(2)
O(2)−H(3)	0.92(8)	O(2)−H(3)	1.08(7)
O(1)#1−Cu(1)−O(1)	77.6(1)	O(1)#1−Cu(1)−O(1)	77.76(7)
O(1)−Cu(1)−O(1)#2	175.4(1)	O(1)−Cu(1)−O(1)#2	175.37(8)
O(1)−Cu(1)−O(1)#3	98.90(9)	O(1)−Cu(1)−O(1)#3	98.76(5)
O(1)−Cu(1)−O(1)#5	84.8(1)	O(1)−Cu(1)−O(1)#5	84.87(9)

[a] Symmetry transformations used to generate equivalent atoms: #1: $-x + y + 1, y, -z$; #2: $-y + 1, -x + 1, -z$; #3: $-y + 1, x - y, z$; #4: $-x + y + 1, -x + 1, z$; #5: $x, x - y, -z$; #6: $x - y, -y, z$; #7: y, x, z; #8: $-y + 1, -x + 1, -z - 1$.

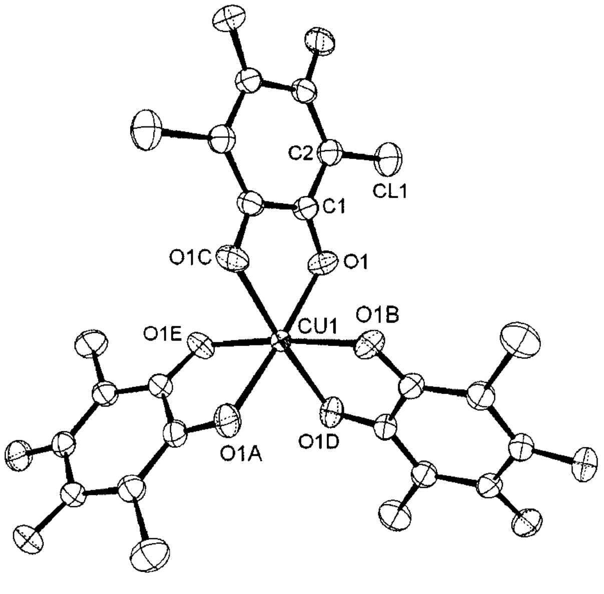


Figure 1. Coordination environment of the Cu^{II} center of compound **1** with atom numbering scheme

The oxygen atom of the hydronium ion also positioned at an identical type of symmetry site as the Cu^{II} ion, which is translated 4.593 Å (half the *c* axis) from the copper centers. The three hydrogen atoms of the hydronium ion are related by site symmetry, and form a strong O−H···N hydrogen-bonding interaction with three phz ligands [O···N distance of 2.583(3) Å, O−H distance of 0.921(0) Å and O−H···N angle of 180.0(1)°] (Figure 2). The short O···N distances between the hydronium ion and the phz ligands cause the phz ligands to assume a propeller-like arrangement.

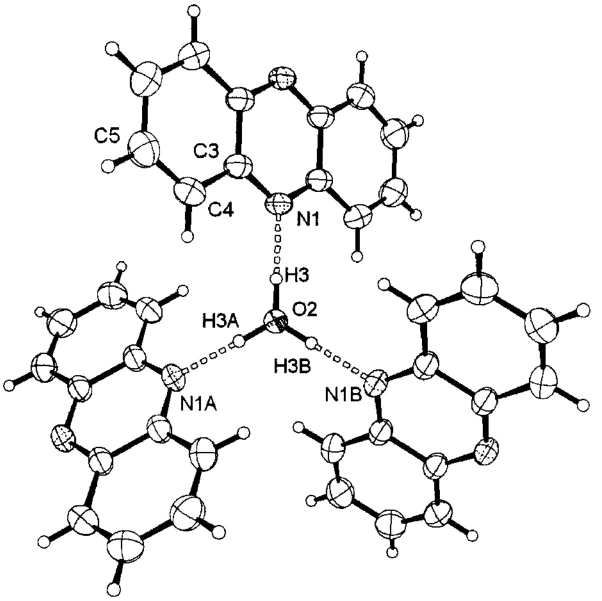


Figure 2. Propeller-like arrangement of hydronium ion and phenazine ligands of compound **1**

Based on the Cu−CA coordination and H_3O−phz hydrogen-bonding interactions, the self-assembly of the two types of two-dimensional grid building subunits with a (6,3) topology occurs. As shown in Figure 3a and 3b, a twelve-membered-ring pore is formed in both the anionic $[Cu_2(CA)_3]^{2-}$ metal-organic coordination layer and the cationic $[(H_3O)_2(phz)_3]^{2+}$ organic hydrogen-bonding layer. Infinite tubular channels with a pore diameter of about 8 Å are observed along the [001] direction (Figure 3c), which can be attributed to the alternate $\pi-\pi$ stacking of the two types of grid-building subunits (Figure 3d) with a very short interplanar distance of 3.29 Å.[47] The propeller-like arrangement around the copper and hydronium ion centers is responsible for this perfect-layer $\pi-\pi$-stacking mechanism. The crystal-packing diagrams are shown in Figure 4. The results of an X-ray diffraction analysis of compounds **3**−**5** reveal that these compounds are isomorphous with **1**. It is noteworthy that a considerable residual density of guest molecules is observed within the channels. However, attempts to resolve these disordered solvent molecules were not successful.

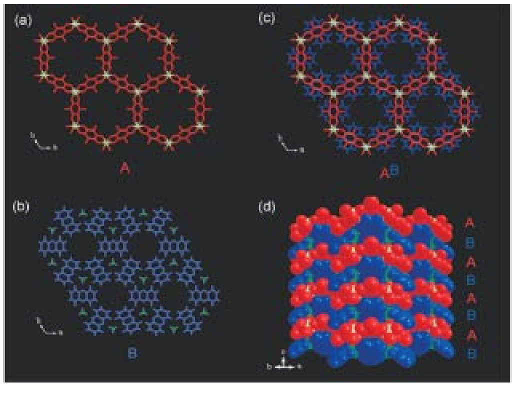


Figure 3. Perspective view of: (a) twelve-membered rings in the $[Cu_2(CA)_3]^{2-}$ metal-organic coordination layers; (b) twelve-membered rings in the $[(H_3O)_2(phz)_3]^{2+}$ organic hydrogen-bonding layers; (c) top-view and (d) side-view of the tubular channel formed by the alternate $\pi-\pi$ stacking of the $[Cu_2(CA)_3]^{2-}$ (red) and $[(H_3O)_2(phz)_3]^{2+}$ (blue) grid-building subunits (channel size about 8 Å in diameter); the Cu^{II} ion is yellow, and the hydronium oxygen atom is green

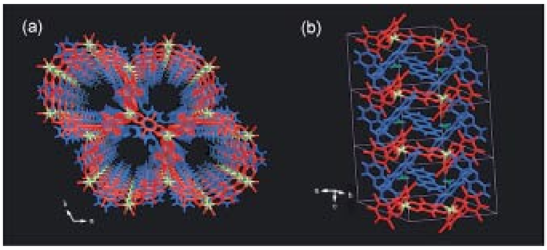


Figure 4. Crystal packing diagrams of **1** showing the perfect $\pi-\pi$ stacking and (a) the honeycomb channels along the [001] direction and (b) the arrangement of Cu^{2+} (pale-yellow) and H_3O^+ (green)

A weight loss of about 9.5%, corresponding to guest molecules, is observed in the TGA diagram of **1** (Figure 5). The alternating charged layers accommodate neutral guest molecules, which enter the extra-framework area in situ during the self-assembly of the framework. After the removal of the guest molecules from the channels under high vacuum for 24 h, the structural integrity of the guest-free network **2** was maintained (vide infra). We conclude that the size of the channels is sufficiently large to contain some diffused solvents, although the diffused portions of the crystal could not be determined clearly by X-ray diffraction analysis. The elemental analysis and thermogravimetric analysis support the assignment of the guest molecules as $2CH_3COCH_3\cdot 2H_2O$. On the other hand, the acetone, water or THF content of the guests probably varies from crystal to crystal.

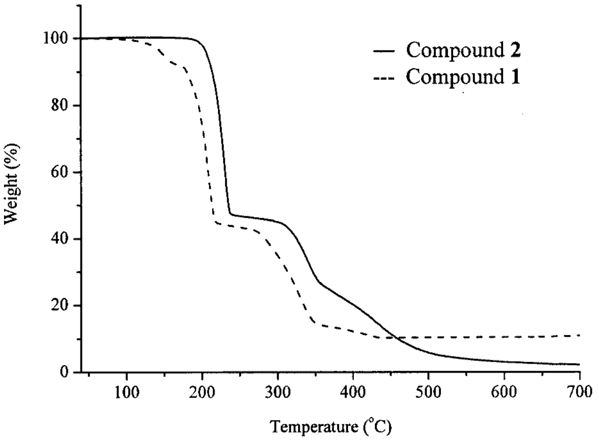


Figure 5. Thermogravimetric-analysis diagrams of **1** and **2**

Removal of Guests

Water, acetone or THF molecules occupy the one-dimensional channels of **1**, which have an estimated diameter of 8 Å (Figures 3 and 4). Attempts were made to remove the guests to form $[\{Cu_2(CA)_3\}\{(H_3O)_2(phz)_3\}]_n$ (**2**) by placing a single crystal of **1** under high vacuum for 24 h. The structure of **2** remained intact, even after the removal of the guest, as evidenced by the single-crystal X-ray analysis

(Table 2). A TGA diagram of the desolvated compound **2** shows no weight loss until 190 °C (Figure 5), indicating that guest molecules can be removed under vacuum. Soaking crystals of **2** in benzene, chlorobenzene, *n*-hexane, or chloroform gave new inclusion compounds, which were characterized by single-crystal X-ray analysis. Surprisingly, the frameworks of these compounds are stable, but the issue of disordered guests remains unresolved.

Magnetic Studies

The magnetic susceptibility (χ_M) and effective moment (μ_B) per mol of copper for complex **1** are given in Figure 6. The effective moment per mol of copper is approximately 1.94 μ_B at 300 K and decreases slowly with decreasing temperature to 30 K. It then decreases sharply at temperatures below 20 K. This behavior indicates a typical weak antiferromagnetically coupled magnetic pair. As a first approximation, we applied the Curie−Weiss law [Equation (1)] to the magnetic-susceptibility data to measure the magnetic coupling interaction; N, g, β, and k_B have their usual meaning and J is the exchange interaction between metal ions.[52]

$$\chi = \frac{Ng^2\beta^2S(S+1)}{3k_BT - 3JS(S+1)} = \frac{C_M}{T-\theta} \qquad (1)$$

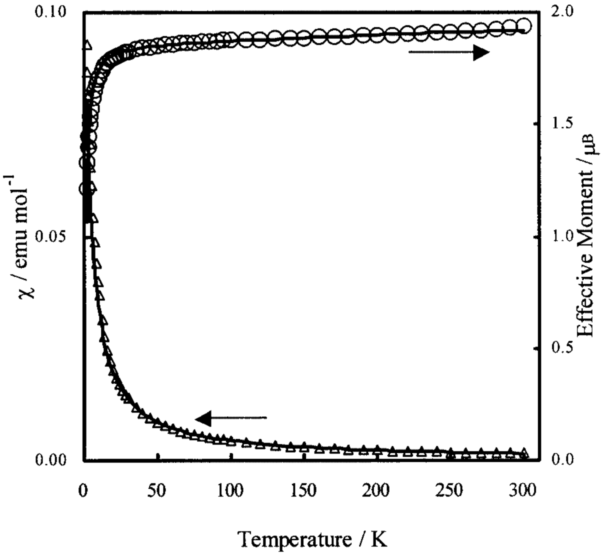


Figure 6. Plots of magnetic susceptibility (χ_M) and the effective magnetic moment (μ_B) per mol of copper versus temperature; the solid line of the magnetic susceptibility is from the fitting results of the Curie−Weiss law and the solid line of the effective magnetic moments is from the fitting results of the dinuclear magnetic equation

The temperature dependency of the magnetic susceptibility of complex **1** in the range 2.0−300 K was fit to the Curie−Weiss expression with a C_M value of 0.464 emu K/mol and a θ value of −3.80 K, which were determined by least-squares fitting in order to minimize the R agreement factor, defined as $R = \Sigma[(\chi_M)_i^{obs} - (\chi_M)_i^{calc}]^2/\Sigma[(\chi_M)_i^{obs}]^2$ (1.94×10^{-2}). The negative θ value is indicative of antiferromagnetic coupling between the metal sites. The effective moment $\mu_{eff} = (8 \times C_M)^{1/2}$ and exchange coupling constant $J/k_B = \theta/[S(S+1)]$ were calculated to be 1.93 μ_B and −5.06 K, respectively, for complex **1**. The value of μ_{eff} is larger than the spin-only value of 1.73 μ_B; the corresponding g value of 2.22 commonly observed for Cu^{2+} centers is due to the spin-orbital coupling.[53] The magnetic coupling constant J/k_B is around −5.06 K, indicating a weak antiferromagnetic coupling between the copper centers via the CA ligands.

In order to analyze the magnetic exchange coupling interactions between the copper atoms, the susceptibility data of the complex were analyzed using the Bleaney−Bowers dinuclear magnetic equation [Equation (2)], with $H = -2JS_1{\cdot}S_2$ as the Heisenberg exchange Hamiltonian,[54] where TIP is the temperature-independent paramagnetism of the Cu^{2+} ion.

$$\chi = \frac{2Ng^2\beta^2}{k_BT}\frac{1}{3+\exp(\frac{-2J}{k_BT})} + TIP \qquad (2)$$

A reasonable fitting result for the magnetic susceptibility data with $TIP = 200 \times 10^{-6}$ emu/mol was found to be $g = 2.14$, $J = -2.22$ K (-1.58 cm^{-1}) for complex **1**, with an agreement factor R of 1.05×10^{-2}. The absolute value of J is much smaller than the value for $[Cu(CA)]_n$ ($J = -12.3$ cm^{-1}), and is similar to the value for $[\{Cu(CA)(H_2O)\}(L)]_n$ (L = H_2O, dmpyz, phz).[41] Since this antiferromagnetic interaction is very weak, the maximum peak (T_N) of the magnetic susceptibility data would not be observed above 2.0 K. This very weak antiferromagnetic exchange interaction can be attributed to intrinsic structural aspects: because of the site symmetry (D_3) around the copper atom, the magnetic orbital is no longer pure $d_{x^2-y^2}$ and is mixed with the d_{z^2} orbital. This induces a reversal of 90° around the O−Cu−O axis of the magnetic orbital, and, consequently, reduces the extent of the antiferromagnetic interactions. Because of the weak antiferrromagnetic interactions within complex **1**, the Curie−Weiss law and the Bleaney−Bowers expression for the dimer both give reasonable fitting results. However, the values of the exchange coupling parameter J obtained from the two approximations are slightly different, which is due to the fact that both are not complete expressions of the honeycomb structure.

Conclusion

A novel robust supramolecular network $[\{Cu_2(CA)_3\}\{(H_3O)_2(phz)_3\}]_n$ has been synthesized and analyzed. The perfect π−π stacking of an alternating anionic inorganic layer and a cationic organic layer leads to an infinite number of one-dimensional, open-ended channels. The alternating charged layers are able to contain guests within the channels; these guests can be removed under high vacuum. This type of compound may have potential for use in vivo as guest adsorption/desorption and micro-reaction vessels for catalysts. The results of the magnetic study indicate the presence of an antiferromagnetic network.

Experimental Section

General Remarks: Chloranilic acid, phenazine and metal nitrate salts were purchased commercially and used as received without further purification. Thermogravimetric analyses were performed under nitrogen with a Perkin−Elmer TGA-7 analyzer. Powder-diffraction measurements were recorded with a Siemens D-5000 diffractometer at 40 kV (30 mA) with Cu-K_α radiation (λ = 1.5406 Å), with a step size of 0.02° in θ and a scan speed of 1 s per step size. Variable-temperature dc magnetic susceptibility data were collected for a polycrystalline sample of complex **1** in an applied field of 1.0 kG in the temperature range 2.0−300.0 K with a SQUID magnetometer (Quantum Design, MPMS-7). The sample was embedded in eicosane wax to prevent any torquing of the polycrystalline material in the magnetic field. Pascal's constants were used to estimate the diamagnetic corrections.[55]

[{$Cu_2(CA)_3$}{$(H_3O)_2(phz)_3$}·G]$_n$ (1; G = $2CH_3COCH_3·2H_2O$): The synthesis of **1** was carried out at ambient temperature by carefully layering a solution of H_2CA (0.6 mmol) in acetone (6 mL) on top of a solution of phenazine (0.6 mmol) in THF (2 mL, middle), and a solution of $Cu(NO_3)_2·4H_2O$ (0.4 mmol) in H_2O (2.5 mL, bottom). After the solutions had been allowed to stand for about one week, dark-purple, hexagonal-shaped crystals were formed in 65% yield based on H_2CA, along with a black amorphous powder of unknown composition. The bulk product was washed with deionized water and ethanol, and separated by suction filtration. Hexagonal-shaped crystals, suitable for crystallographic analysis, were separated mechanically from the dark powder and dried in a desiccator at ambient temperature. A powder X-ray diffraction pattern of the isolated crystals was in good agreement with the pattern simulated from single-crystal data (vide infra). [{$Cu_2(CA)_3$}{$(H_3O)_2(phz)_3$}·$2CH_3COCH_3·2H_2O$]$_n$ = $C_{60}H_{46}Cl_6Cu_2N_6O_{18}$ (1478.81): calcd. C 48.73, H 3.14, N 5.68; found C 49.24, H 2.94, N 5.55.

[{$Cu_2(CA)_3$}{$(H_3O)_2(phz)_3$}]$_n$ (2): A single crystal of **2** was obtained by mounting a single crystal of **1** on a glass fiber and keeping it sealed in a Schlenk tube under vacuum (10^{-3} Torr) for 24 h. The resulting crystal was sealed to prevent contact with moisture from the air during the single-crystal X-ray diffraction analysis.

[{$M_2(CA)_3$}{$(H_3O)_2(phz)_3$}·G]$_n$ (M = Cd, 3; M = Zn, 4; M = Co, 5; G = $2CH_3COCH_3·2H_2O$): Cd, Zn, and Co analogs of **1** were synthesized under similar reaction conditions using $Cd(NO_3)_2·4H_2O$, $Zn(ClO_4)_2·6H_2O$, and $Co(NO_3)_2·6H_2O$, respectively, as starting materials. These hexagonal-shaped crystals of the products were small and formed in low yield, along with a black amorphous powder of unknown composition. Crystals with good quality could be selected easily for single-crystal X-ray diffraction analysis. Nevertheless, we were not able to obtain sufficient amounts of pure products for other analyses.

X-ray Crystallographic Study: A hexagonal single crystal of **1** with dimensions of 0.38 × 0.38 × 0.18 mm was mounted on the tip of a glass fiber and placed onto the goniometer head for indexing and intensity data collection using a Bruker Smart CCD diffractometer (Mo-K_α = 0.71073 Å). The raw frame data for **1** were integrated into SHELX format reflection files and corrected for Lorentz and polarization effects with the Denzo program.[56] Corrections for incident- and diffracted-beam absorption effects were applied with the Multiscan method.[57] The structure of **1** was solved by direct methods and refined against F^2 by the full-matrix least-squares technique, using the WINGX,[58] PLATON,[59] and SHELX[60] software packages. The hydrogen atoms of the hydronium ion were located from the difference map and refined isotropically. The remaining hydrogen atoms were calculated and refined as riding atoms; all non-hydrogen atoms were refined with anisotropic displacement parameters. The minimum and maximum residual density of −0.45 and 1.25 e/Å^3 indicated that some guest molecules could be assigned from the difference maps. Nevertheless, attempts to resolve these disordered solvent molecules failed. No further attempts to resolve these diffusion regions were made. To analyze compound **2**, a newly selected crystal of good quality of **1** with dimensions of 0.28 × 0.28 × 0.18 mm was first held under a vacuum and then sealed. A crystallographic determination procedure similar to that described above was then performed. Crystallographic details for compounds **1** and **2** are given in Table 2 and selected bond lengths and angles are shown in Table 1. Compounds **3**, **4** and **5** were also characterized by single-crystal X-ray diffraction analysis and their crystallographic details are also given in Table 2. CCDC-235466 (**1**), -235467 (**2**), -235468 (**3**), -235469 (**4**) and -235470 (**5**) contain the supplementary crystallographic data

Table 2. Crystal data collection and structure refinement

	1	2	3	4	5
Empirical formula	$C_{60}H_{46}Cl_6Cu_2N_6O_{18}$	$C_{54}H_{30}Cl_6Cu_2N_6O_{14}$	$C_{60}H_{46}Cd_2Cl_6N_6O_{18}$	$C_{60}H_{46}Cl_6N_6O_{18}Zn_2$	$C_{60}H_{46}Cl_6Co_2N_6O_{18}$
Formula mass	1478.81	1326.62	1576.58	1482.53	1469.92
Crystal system	trigonal	trigonal	trigonal	trigonal	trigonal
Space group	$P\bar{3}1m$	$P\bar{3}1m$	$P\bar{3}1m$	$P\bar{3}1m$	$P\bar{3}1m$
a [Å]	13.7593(2)	13.7565(4)	14.359(2)	13.7520(6)	13.7930(8)
c [Å]	9.1869(2)	9.1544(5)	8.651(2)	9.1950 (5)	9.1310(7)
V [Å^3]	1506.22(5)	1500.3(1)	1544.7(4)	1506.0(1)	1504.4(2)
Z	1	1	1	1	1
T [°C]	24(2)	24(2)	24(2)	24(2)	24(2)
λ [Å]	0.71073	0.71073	0.71073	0.71073	0.71073
$\rho_{calcd.}$ [g cm^{-3}]	1.630	1.468	1.695	1.635	1.723
μ [mm^{-1}]	1.052	1.042	1.013	1.129	0.884
R_1 [a] [$I > 2\sigma(I)$]	0.0522	0.0472	0.0477	0.0598	0.0669
wR_2 [b] [$I > 2\sigma(I)$]	0.1973	0.1502	0.1512	0.1862	0.1635
R_1 [a] (all data)	0.0585	0.0570	0.0582	0.0731	0.1158
wR_2 [b] (all data)	0.2017	0.1580	0.1602	0.1973	0.1907
GOF	1.290	1.127	1.137	1.195	1.021

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

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].

Acknowledgments

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[1] J.-M. Lehn, J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, *Comprehensive Supramolecular Chemistry*, Pergamon, Oxford, **1996**.
[2] M. J. Zaworotko, *Nature* **1999**, *402*, 242−243.
[3] G. R. Desiraju, *Crystal Engineering. The Design of Organic Solids*, Elsevier, Amsterdam, **1989**.
[4] S. Kitagawa, M. Kondo, *Bull. Chem. Soc. Jpn.* **1998**, *71*, 1739−1753.
[5] M. Eddaoudi, J. Kim, N. Rosi, D. Vodak, J. Wachter, M. O'Keeffe, O. M. Yaghi, *Science* **2002**, *295*, 469−472.
[6] B. J. Holliday, C. A. Mirkin, *Angew. Chem. Int. Ed.* **2001**, *40*, 2022−2043.
[7] G. F. Swiegers, T. J. Malefetse, *Chem. Rev.* **2000**, *100*, 3483−3537.
[8] F. A. Cotton, C. Lin, C. A. Murillo, *Acc. Chem. Res.* **2001**, *34*, 759−771.
[9] S. R. Batten, R. Robson, *Angew. Chem. Int. Ed.* **1998**, *37*, 1460−1494.
[10] B. Moulton, M. J. Zaworotko, *Chem. Rev.* **2001**, *101*, 1629−1658.
[11] R. Robson, *J. Chem. Soc., Dalton Trans.* **2000**, 3735−3744.
[12] G. Ferey, *Chem. Mater.* **2001**, *13*, 3084−3098.
[13] Y.-H. Liu, H.-C. Wu, H.-M. Lin, W.-H. Hou, K.-L. Lu, *Chem. Commun.* **2003**, 60−61.
[14] S. Ferlay, S. Koenig, M. W. Hosseini, J. Pansanel, A. De Cian, N. Kyritsakas, *Chem. Commun.* **2002**, 218−219.
[15] S. Noro, R. Kitaura, M. Kondo, S. Kitagawa, T. Ishii, H. Matsuzaka, M. Yamashita, *J. Am. Chem. Soc.* **2002**, *124*, 2568−2583.
[16] T. J. Prior, D. Bradshaw, S. J. Teat, M. J. Rosseinsky, *Chem. Commun.* **2003**, 500−501.
[17] M. Eddaoudi, D. B. Moler, H. Li, B. Chen, T. M. Reineke, M. O'Keeffe, O. M. Yaghi, *Acc. Chem. Res.* **2001**, *34*, 319−330.
[18] J. Kim, B. Chen, T. M. Reineke, H. Li, M. Eddaoudi, D. B. Moler, M. O'keeffe, O. M. Yaghi, *J. Am. Chem. Soc.* **2001**, *123*, 8239−8247.
[19] W. Mori, S. Takamizawa, *J. Solid State Chem.* **2000**, *152*, 120−129.
[20] S. S.-Y. Chui, S. M.-F. Lo, J. P. H. Charmant, A. G. Orpen, I. D. Williams, *Science* **1999**, *283*, 1148−1150.
[21] Y.-B. Dong, M. D. Smith, H.-C. zur Loye, *Angew. Chem. Int. Ed.* **2000**, *39*, 4271−4273.
[22] H. Li, M. Eddaoudi, M. O'Keeffe, O. M. Yaghi, *Nature* **1999**, *402*, 276−279.
[23] O. R. Evans, W. Lin, *Inorg. Chem.* **2000**, *39*, 2189−2198.
[24] K. Seki, *Chem. Commun.* **2001**, 1496−1497.
[25] M. Eddaoudi, H. Li, O. M. Yaghi, *J. Am. Chem. Soc.* **2000**, *122*, 1391−1397.
[26] M. Kurmoo, H. Kumagai, S. M. Hughes, C. J. Kepert, *Inorg. Chem.* **2003**, *42*, 6709−6722.
[27] G. J. Halder, C. J. Kepert, B. Moubaraki, K. S. Murray, J. D. Cashion, *Science* **2002**, *298*, 1762−1765.
[28] T. J. Prior, M. J. Rosseinsky, *Inorg. Chem.* **2003**, *42*, 1564−1575.
[29] Y. Cui, H. L. Ngo, P. S. White, W. Lin, *Chem. Commun.* **2003**, 994−995.
[30] U. Siemeling, I. Scheppelmann, B. Neumann, A. Stammler, H.-G. Stammler, J. Frelek, *Chem. Commun.* **2003**, 2236−2237.
[31] H. L. Ngo, W. Lin, *J. Am. Chem. Soc.* **2002**, *124*, 14298−14299.
[32] J. S. Seo, D. Whang, H. Lee, S. I. Jun, J. Oh, Y. J. Jeon, K. Kim, *Nature* **2000**, *404*, 982−986.
[33] Z. Wang, B. Zhang, H. Fujiwara, H. Kobayashi, M. Kurmoo, *Chem. Commun.* **2004**, 416−417.
[34] J. Y. Lu, A. M. Babb, *Chem. Commun.* **2002**, 1340−1341.
[35] J. W. Ko, K. S. Min, M. P. Suh, *Inorg. Chem.* **2002**, *41*, 2151−2157.
[36] M. P. Suh, K. S. Min, J. W. Ko, H. J. Choi, *Eur. J. Inorg. Chem.* **2003**, 1373−1379.
[37] K. Nagayoshi, M. K. Kabir, H. Tobita, K. Honda, M. Kawahara, M. Katada, K. Adachi, H. Nishikawa, I. Ikemoto, H. Kumagai, Y. Hosokoshi, K. Inoue, S. Kitagawa, S. Kawata, *J. Am. Chem. Soc.* **2003**, *125*, 221−232.
[38] J. D. Dunitz, *Chem. Commun.* **2003**, 545−548.
[39] S. Kitagawa, S. Kawata, *Coord. Chem. Rev.* **2002**, *224*, 11−34.
[40] M. Kawahara, M. K. Kabir, K. Yamada, K. Adachi, H. Kumagai, Y. Narumi, K. Kindo, S. Kitagawa, S. Kawata, *Inorg. Chem.* **2004**, *43*, 92−100.
[41] S. Kawata, S. Kitagawa, H. Kumagai, C. Kudo, H. Kamesaki, T. Ishiyama, R. Suzuki, M. Kondo, M. Katada, *Inorg. Chem.* **1996**, *35*, 4449−4461.
[42] M. K. Kabir, M. Kawahara, H. Kumagai, K. Adachi, S. Kawata, T. Ishii, S. Kitagawa, *Polyhedron* **2001**, *20*, 1417−1422.
[43] S. Kawata, S. Kitagawa, H. Kumagai, T. Ishiyama, K. Honda, H. Tobita, K. Adachi, M. Katada, *Chem. Mater.* **1998**, *10*, 3902−3912.
[44] Y.-T. Li, C.-W. Yan, Y.-J. Zheng, D.-Z. Liao, *Polyhedron* **1998**, *17*, 1423−1427.
[45] H. Kumagai, S. Kawata, S. Kitagawa, *Inorg. Chim. Acta* **2002**, *337*, 387−392.
[46] B. F. Abrahams, J. Coleiro, K. Ha, B. F. Hoskins, S. D. Orchard, R. Robson, *J. Chem. Soc., Dalton Trans.* **2002**, 1586−1594.
[47] A. Yoshino, H. Matsudaira, E. Asato, M. Koikawa, T. Shiga, M. Ohba, H. Okawa, *Chem. Commun.* **2002**, 1258−1259.
[48] Y.-H. Liu, Y.-L. Lu, H.-C. Wu, J.-C. Wang, K.-L. Lu, *Inorg. Chem.* **2002**, *41*, 2592−2597.
[49] Y.-H. Liu, H.-L. Tsai, Y.-L. Lu, Y.-S. Wen, J.-C. Wang, K.-L. Lu, *Inorg. Chem.* **2001**, *40*, 6426−6431.
[50] Y.-H. Liu, Y.-L. Lu, H.-L. Tsai, J.-C. Wang, K.-L. Lu, *J. Solid State Chem.* **2001**, *158*, 315−319.
[51] Y.-H. Liu, C.-S. Lin, S.-Y. Chen, H.-L. Tsai, C. -H Ueng, K.-L. Lu, *J. Solid State Chem.* **2001**, *157*, 166−172.
[52] O. Kahn, *Molecular Magnetism*, VCH, New York, **1993**.
[53] R. L. Carlin, *Magnetochemistry*, Springer-Verlag, New York, **1986**.
[54] S. Ferlay, G. Francese, H. W. Schmalle, S. Decurtins, *Inorg. Chim. Acta* **1999**, *286*, 108−113.
[55] E. A. Boudreaux, L. N. Mulay, *Theory and Application of Molecular Paramagnetism*, John Wiley & Sons, New York, **1976**.
[56] Z. Otwinowsky, W. Minor, "Processing of X-ray Diffraction Data Collected in Oscillation Mode", in *Methods in Enzymology* (Eds.: C. W. Carter, Jr., R. M. Sweet), Academic Press, New York, **1996**, vol. 276, p. 307.
[57] R. H. Blessing, *Acta Crystallogr., Sect. A* **1995**, *51*, 33−38.
[58] L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837−838.
[59] A. L. Spek, *PLATON*, Utrecht University, Utrecht, The Netherlands, **2000**.
[60] G. M. Sheldrick, *SHELX-97* (including SHELXS and SHELXL), University of Göttingen, Germany, **1997**.

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