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# 3D Extended Supramolecular Structures via H-Bonded Linkages of 2D Sheetlike or 1D Zigzag Coordination Polymers

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Two 3D supramolecular complexes $[Cu_2(\textit{trans}\text{-oxpn})(phth)]_n\cdot 2nH_2O$, **1**, and $[Cu_2(\textit{trans}\text{-oxpn})(\mu\text{-OH})(\mu\text{-}H_2O)]_n\text{-}Br_n\cdot 2nH_2O$, **2** [$H_2$oxpn = *N,N′*-bis(3-aminopropyl)oxamide, phth = phthalate], were synthesized and characterized by single-crystal X-ray crystallography, thermal analyses, and magnetic measurements. **1** crystallizes in the monoclinic space group $P2_1/c$ with $a = 8.578(2)$ Å, $b = 15.596(2)$ Å, $c = 15.657(2)$ Å, $\beta = 101.29(2)°$, $Z = 4$; **2** crystallizes in the trigonal space group $R\bar{3}c$ with $a = 15.266(2)$ Å, $b = 15.266(2)$ Å, $c = 34.953(5)$ Å, and $Z = 18$. The neutral 2D sheetlike coordination polymer $[Cu_2(\textit{trans}\text{-oxpn})(phth)]_n$ in **1** contains alternate *trans*-oxamidate and phthalate bridges and then is joined together by $H_2O$ molecules via the hydrogen bond linkage Cu(oxpn)···$H_2O$···$H_2O$···(oxpn)Cu to produce a 3D supramolecular structure. The cationic chains $[Cu_2(\textit{trans}\text{-oxpn})(\mu\text{-OH})(\mu\text{-}H_2O)]_n^{n+}$ in **2** contain alternate *trans*-oxamidate, $\mu$-OH, and $\mu$-$H_2O$ bridges and are arranged in three directions, intersecting with one another to yield an extended network via the interchain hydrogen bonds formed by metal-coordinated $OH^-$ with the linkages Cu(oxpn)−OH···OH−Cu(oxpn). Magnetic calculations showed the presence of antiferromagnetic exchange interactions for both complexes. The 2D magnetic coupling system of **1** was simplified into interacting dimers Cu(*trans*-oxpn)Cu, with the coupling via phth as an interdimer interaction and the data were interpreted with a modified Bleaney−Bowers equation leading to $J = -456.7$ cm$^{-1}$ and $\theta = 22.0$ K. **2** was analyzed qualitatively by an alternating chain model taking into account the interchain interaction in a molecular model with $J_1 = -309.6$ cm$^{-1}$, $J_2 = -63.5$ cm$^{-1}$, and $\theta = -12.9$ K, where $J_1$ and $J_2$ denote the coupling constants of the bridges oxamidate and $\mu$-OH, respectively.

## Introduction

The crystal engineering of solid-state metal coordination supramolecules is one of the most active research topics of current chemistry and molecular science due to the theoretical aspects related to the topologies of novel networks with inner cavities and channels,[1] as well as their potential applications in catalysis,[2] host−guest chemistry,[3] and molecular electronics.[4] The strategies used for the architecture of functional systems depend on the nature of the interactions responsible for networking. One of the best strategies to fabricate 3D supramolecular systems is to utilize the hydrogen bonding of the coordinated ligands in addition to their coordination capability to interlink the 1D or 2D coordination molecules via the hydrogen interactions, though networks assembled by this way have not yet attracted enough attention.[5]

N,N′-Disubstituted oxamides are well-known to be versatile ligands which can chelate as well as bridge metal ions to build polynuclear and low-dimensional molecules.[6] One of the most outstanding character of these ligands is the easy transformation of cis−trans conformations, which makes it practical to design tunable molecular materials with extended structures and desired properties. On the one hand, the bidentate character of the mononuclear metal complexes CuL of *cis*-oxamidates makes them useful bidentate paramagnetic ligands toward transition-metal and rare-earth cations, yielding bi-,[7] tri-,[8] tetra-,[9] and even pentanuclear[10] homo- and heterometallic molecular entities. On the other hand, the bis-tridentate character of *trans*-oxamidates favors the formation of *trans*-oxamidato-bridged binuclear units with vacant coordinated sites, which may act as convenient building blocks to be further linked by more bridging groups to construct extended systems as shown in Chart 1.[11,12] When

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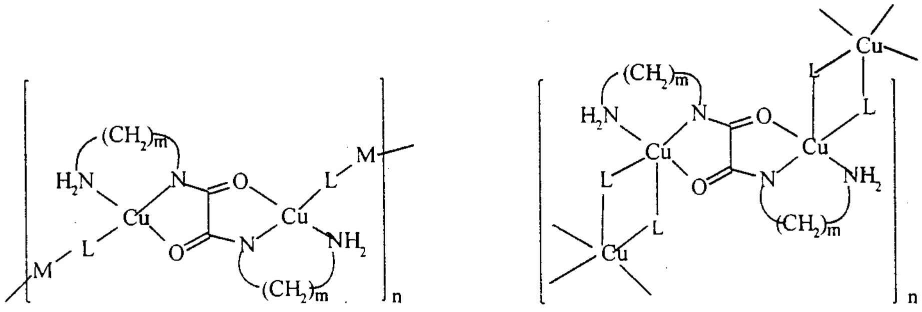
**Chart 1**

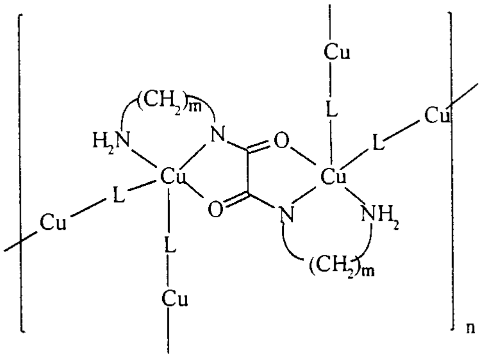


1D Chain Structure

**(A)**

1D Chain Structure

**(B)**



2D Sheet-like Structure

**(C)**

m = 2, $H_2$oxen [N,N'-bis(2-aminoethyl)oxamide]

$H_2$oxap [N,N'-bis(2-aminopropyl)oxamide]

m = 3, $H_2$oxpn [N,N'-bis(3-aminopropyl)oxamide]

these remaining coordinated sites are occupied by terminal ligands, the products isolated are discrete binuclear dimers.[13] It is found that these building blocks can easily be linked together by bridging ligands such as azide,[11a,c,12b] cyanate,[11b] cyanide,[12e] pyrimidine,[12a,d] 4,4′-bipyridine,[12a] and carboxylate[11d,e,12c,f] to construct coordination polymers. Moreover, the strong H-bonding character of these ligands with N and O donors makes the design of 3D supramolecular structures via H bond linkages of the *trans*-oxamidato-bridged 1D chains or 2D sheets possible.[14−16] Herein are reported two 3D supramolecular complexes $[Cu_2(trans\text{-oxpn})(phth)]_n \cdot 2nH_2O$, **1**, and $[Cu_2(trans\text{-oxpn})(\mu\text{-OH})(\mu\text{-}H_2O)]_nBr_n \cdot 2nH_2O$, **2** [$H_2$oxpn = *N,N′*-bis(3-aminopropyl)oxamide, phth = phthalate], the former formed via H bonds joining the 2D coordination sheets whereas the latter via H bonds cross-linking the zigzag coordination chains.

## Experimental Section

The ligand $H_2$oxpn and its mononuclear compound Cu(oxpn) were prepared according to the literature method.[17]

**Synthesis of $[Cu_2(trans\text{-oxpn})(phth)]_n \cdot 2nH_2O$ (1).** To 40 mL of an aqueous solution of Cu(oxpn) (1.0 mmol, 0.264 g) was added 5 mL

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**Table 1.** Crystallogaphic Data for Complexes **1** and **2**

| | **1** | **2** |
|---|---|---|
| empirical formula | $C_{16}H_{24}Cu_2N_4O_8$ | $C_8H_{24}BrCu_2N_4O_6$ |
| fw | 527.47 | 479.30 |
| space group | $P2_1/c$ | $R\bar{3}c$ |
| $a$, Å | 8.578(2) | 15.266(2) |
| $b$, Å | 15.596(2) | 15.266(2) |
| $c$, Å | 15.657(2) | 34.953(5) |
| $\beta$, deg | 101.29(2) | |
| $V$, Å$^3$ | 2054.1(6) | 7054(2) |
| $Z$ | 4 | 18 |
| $T$, °C | 22 | 22 |
| $\lambda$ (Mo K$\alpha$), Å | 0.710 73 | 0.710 73 |
| $\rho_{calcd}$, g cm$^{-3}$ | 1.706 | 2.031 |
| $\mu$, cm$^{-1}$ | 21.22 | 52.92 |
| $R^a$ | 0.0323 | 0.0350 |
| $wR_2{}^b$ | 0.0644 | 0.0741 |

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR_2 = [\sum[w(|F_o|^2 - |F_c|^2)^2]/\sum[wF_o{}^4]]^{1/2}$. $w = [\sigma^2(F_o{}^2) + (0.0333P)^2]^{-1}$ (**1**); $w = [\sigma^2(F_o{}^2) + (0.0415P)^2]^{-1}$ (**2**); $P = [(F_o{}^2)_{max} + 2F_c{}^2]/3$.

of the aqueous solution of $CuBr_2$ (1.0 mmol, 0.224 g) with stirring while the solution changes color from violet-red to blue. Several minutes later, 10 mL of an aqueous solution of phthalic acid (1.0 mmol, 0.166 g) and sodium hydroxide (2.0 mmol, 0.08 g) was added to yield a dark blue solution. After it was stirred for 10 min more, the solution was filtered and the filtrate allowed to stand at room temperature for several days to give blue black crystals. Yield: 38%. IR (KBr, cm$^{-1}$): 491 (s), 575 (s), 617 (s), 653 (s), 702 (s), 772 (s), 835 (s), 864 (s), 927 (s), 988 (m), 1046 (s), 1082 (s), 1145 (s), 1271 (m), 1321 (s), 1356 (s), 1440 (s), 1581 (s), 1616 (s), 2853 (s), 2889 (s), 2931 (s), 3149 (s), 3240 (s), 3296 (m), 3451 (s). Anal. Calcd. for $C_{16}H_{24}N_4O_8$-$Cu_2$: C, 36.40; H, 4.55; N, 10.62. Found: C, 36.12; H, 4.69; N, 10.65%.

**Synthesis of $[Cu_2$(*trans*-oxpn)($\mu$-OH)($\mu$-$H_2O)]_nBr_n\cdot 2nH_2O$ (2).** To 40 mL of an aqueous solution of Cu(oxpn) (1.0 mmol, 0.264 g) was added 5 mL of the aqueous solution of $CuBr_2$ (1.0 mmol, 0.224 g). After it was stirred for several minutes, 10 mL of the aqueous solution of sodium carbonate (1.0 mmol, 0.106 g) was added and the solution was filtered 10 min later. The dark blue filtrate was allowed to stand at room temperature for several days to give blue black crystals. Yield: 30%. IR (KBr, cm$^{-1}$): 414 (m), 463 (s), 505 (s), 646 (s), 723 (s), 793 (s), 835 (s), 885 (s), 927 (s), 1046 (s), 1096 (s), 1152 (s), 1180 (m), 1271 (m), 1314 (s), 1363 (s), 1398 (s), 1454 (s), 1574 (s), 1616 (s), 1735 (m), 1918 (m), 2024 (w), 2868 (m), 2924 (m), 2959 (s), 3156 (m), 3254 (m), 3296 (w), 3409 (w). Anal. Calcd. for $C_8H_{24}N_4O_6$-$BrCu_2$: C, 20.03; H, 5.01; N, 11.68. Found: C, 19.87; H, 4.74; N, 11.55%.

**Crystal Structure Determination.** Single crystals with suitable dimensions were mounted on glass fibers and data collections were performed on a Siemens P4 diffractometer by $\omega$ scan technique using graphite-monochromated Mo K$\alpha$ radiation ($\lambda$ = 0.710 73 Å). Intensity data were collected in $2\theta$ ranges of 4−50°. Of the 3625 and 1385 measured independent reflections for **1** and **2**, 2564 and 945 were considered observed, respectively, with $I \geq 2\sigma(I)$, and used for the structure refinements. The crystallographic data are summarized in Table 1.

**Table 2.** Selected Atomic Distances (Å) and Bond Angles (deg) for Complex **1**[a]

| | | | |
|---|---|---|---|
| Cu(1)−N(1) | 1.957(3) | Cu(1)−O(2) | 1.970(2) |
| Cu(1)−O(1) | 1.979(2) | Cu(1)−N(2) | 1.991(3) |
| Cu(1c)−O(5) | 2.432(2) | Cu(2)−N(3) | 1.953(3) |
| Cu(2)−O(5) | 1.961(2) | Cu(2)−N(4) | 1.968(3) |
| Cu(2)−O(6) | 1.983(2) | Cu(1)···Cu(1b) | 5.257 (2) |
| Cu(1)···Cu(2) | 7.511(3) | Cu(1)···Cu(1c) | 8.303(3) |
| Cu(1c)···Cu(2) | 3.574(2) | O(1)···O(8) | 2.856(2) |
| O(4)···O(8) | 2.755(2) | O(7a)···O(8) | 2.777(3) |
| O(3a)···O(7a) | 2.784(3) | | |
| N(1)−Cu(1)−O(1) | 83.48(10) | O(2)−Cu(1)−O(1) | 93.70(9) |
| N(1)−Cu(1)−N(2) | 94.53(13) | O(2)−Cu(1)−N(2) | 87.72(12) |
| O(1)−Cu(1)−N(2) | 175.4(2) | N(1)−Cu(1)−O(5a) | 109.64(10) |
| O(2)−Cu(1)−O(5a) | 78.10(8) | O(1)−Cu(1)−O(5a) | 93.92(9) |
| N(2)−Cu(1)−O(5a) | 90.62(14) | N(1)−Cu(1)−O(2) | 171.87(10) |
| N(3)−Cu(2)−N(4) | 95.32(12) | N(3)−Cu(2)−O(5) | 166.58(10) |
| N(3)−Cu(2)−O(6) | 83.97(10) | O(5)−Cu(2)−N(4) | 92.97(11) |
| N(4)−Cu(2)−O(6) | 168.57(12) | O(5)−Cu(2)−O(6) | 89.96(9) |

Hydrogen Bond Geometry

| D−H···A | H···A, Å | D−H, Å | D···A, Å | D−H···A, deg |
|---|---|---|---|---|
| O(8)−H(8Ob)···O(1) | 2.072 | 0.788 | 2.856 | 173.8 |
| O(8)−H(8Oa)···O(4) | 1.937 | 0.818 | 2.755 | 173.1 |
| O(7a)−H(7Oc)···O(8) | 1.941 | 0.854 | 2.777 | 165.8 |
| O(7a)−H(7Od)···O(3a) | 1.932 | 0.866 | 2.784 | 167.1 |

[a] Symmetry transformations used to generate equivalent atoms: a = $x$, $-y + 1/2$, $z - 1/2$; b = $-x + 1$, $-y$, $-z$; c = $x$, $-y + 1/2$, $z + 1/2$; d = $-x + 1$, $-y$, $-z + 1$.

**Table 3.** Selected Atomic Distances (Å) and Bond Angles (deg) for Complex **2**[a]

| | | | |
|---|---|---|---|
| Cu−O(2) | 1.933(3) | Cu−N(1) | 1.954(4) |
| Cu−N(2) | 1.999(5) | Cu−O(1) | 2.016(3) |
| Cu−O(4) | 2.675(2) | Cu···Cu(a) | 3.264(3) |
| Cu···Cu(b) | 5.298(5) | O(2)···O(2a) | 2.899(3) |
| O(2)···O(2b) | 2.899(3) | O(3)···O(4) | 2.962(6) |
| O(2)−Cu−N(1) | 174.26(13) | O(2)−Cu−N(2) | 90.0(2) |
| N(1)−Cu−N(2) | 95.0(2) | O(2)−Cu−O(1) | 92.83(9) |
| N(1)−Cu−O(1) | 82.85(14) | N(2)−Cu−O(1) | 168.4(2) |
| Cu−O(2)−Cu(a) | 115.1(2) | Cu−O(4)−Cu(a) | 75.2(3) |

Hydrogen Bond Geometry

| D−H···A | H···A, Å | D−H, Å | D···A, Å | D−H···A, deg |
|---|---|---|---|---|
| O(4)−H(4Oa)···O(3) | 2.177 | 0.848 | 2.962 | 153.7 |
| O(2a)−H(2Oa)···O(2) | 2.132 | 0.850 | 2.899 | 150.1 |
| O(2)−H(2O)···O(2b) | 2.132 | 0.850 | 2.899 | 150.1 |
| O(2b)−H(2Ob)···O(2a) | 2.132 | 0.850 | 2.899 | 150.1 |

[a] Symmetry transformations used to generate equivalent atoms: a = $x - y + {}^1/_3$, $-y + {}^2/_3$, $-z + {}^1/_6$; b = $-x + 2$, $-y + 1$, $-z$.

The coordinates of the metal atoms were determined by direct methods and the remaining non-hydrogen atoms were located from successive difference Fourier syntheses. The structures were refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. For **1**, the hydrogen atoms were located from $\Delta F$ map except those for N(4), C(4), C(14), C(15), C(15′), C(16), and C(16′), which were isotropically added to the structure factor calculations. Atoms C(15), C(15′), C(16) and C(16′) are disordered with the average occupancy of 0.5. For **2**, the space group was determined by systematic absences. The H atoms of O(4), C(2) and N(2) were determined from Fourier-difference map while the others were added theoretically with a common thermal parameter [except that of O(3), which was not determined]. The H atom of O(2) is disordered with the average occupancy of 0.5. Atoms C(3), C(3′), C(4), and C(4′) are disordered, and the occupancy is 0.5. All calculations were performed on an IBM PC computer with the Siemens SHELXL-93 program package.[18] The final $R$ values were $R = 0.0323$ ($R_w = 0.0644$) and $R = 0.0350$ ($R_w = 0.0741$) and the extinction coefficents were 0.0018(2) and 0.00006(3) for **1** and **2**, respectively. The scattering factors were taken from ref 19. The selected atomic distances and bond angles including the hydrogen bond geometries are presented in Tables 2 and 3 for **1** and **2**, respectively. Complete crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles are gathered in the Supporting Information.

**Physical Measurements.** IR spectra were obtained from a Perkin-Elmer 577 spectrophotometer as KBr pellets. Variable-temperature

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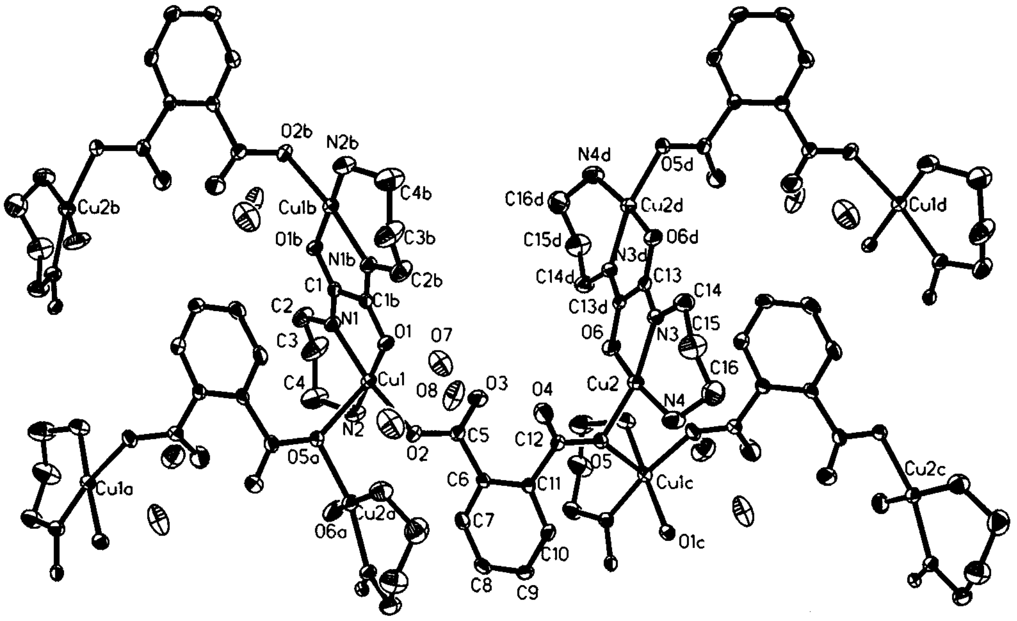

**Figure 1.** View of five units of [$Cu_2$(*trans*-oxpn)(phth)] for **1** with atom-labeling scheme. Thermal ellipsoids are plotted at the 30% probability level.

magnetic susceptibilities in the temperature range 70−300 K were measured on a CAHN-2000 Faraday-type magnetometer at a magnetic field of 5.0 T with the powdered samples kept in capsules for weighing. The magnetic data were corrected for Pascal's constants and the temperature-independent paramagnetism (TIP) per copper(II) ion was assumed to be $60 \times 10^{-6}$ $cm^3$ $mol^{-1}$. Thermal behavior was monitored on a Perkin-Elmer TGS-2 thermogravimetric analyzer.

## Results and Discussion

**Description of the Structure of [$Cu_2$(*trans*-oxpn)(phth)]$_n$·2$n$$H_2O$ (1).** The crystal structure of **1** contains the neutral coordination polymer [$Cu_2$(*trans*-oxpn)(phth)]$_n$ and solvated water molecules. [$Cu_2$(*trans*-oxpn)(phth)]$_n$ exhibits a two-dimensional sheetlike structure of copper(II) ions bridged by both *trans*-oxpn and phth groups. A perspective view of five of the symmetry-related units with the atom-labeling scheme is depicted in Figure 1.

The asymmetric unit consists of binuclear copper(II) with the formula [$Cu_2$(*trans*-oxpn)(phth)], where one copper(II) center [Cu(1)] is located in a square-based pyramid of $N_2O_3$ with the equatorial plane built by $N_2O_2$ and the apex occupied by an oxygen atom from the carboxylate of phth, while the other Cu center [Cu(2)] is located in a square-planar environment. The mean coordination planes of Cu(1) and Cu(2), which have a dihedral angle of 35.5°, form two nearly equal dihedral angles of 147.0° with the least-squares plane of the ligand phth. The *trans*-oxamidate group behaves as a bis-tridentate ligand chelating as well as bridging copper ions to form dimeric Cu(*trans*-oxpn)Cu unit with one five- and one six-membered chelating rings for each copper atom. The deprotonated N [N(1) and N(3)] and their symmetry-related N atoms are $sp^2$ hybridized with the bonds Cu−$N_{amide}$ (average 1.955 Å) shorter than Cu−$N_{amine}$ (average 1.980 Å). The ligand phth affords a unique coordination mode[20] with one of the carboxylate groups ligating in a unidentate equatorial coordination fashion, whereas the other acts as a $\mu_2$-O bridge with one of its oxo atoms with both equatorial and axial bondings to Cu(2) and Cu(1c), respectively. The bridging angle Cu(2)−O(5)−Cu(1c) is 108.37(9)°. The equatorial bond Cu(2)−O(5) [1.961(2) Å] is much shorter than the axial Cu(1c)−O(5) [2.432(2) Å] one but is close to the length of the other equatorial bond Cu(1)−O(2) [1.970(2) Å]. Thus, each phth ligand bridges three copper centers and links the dimeric copper units Cu(*trans*-oxpn)Cu to form the 2D sheets along the *bc* plane. The dihedral angles formed between the carboxylate planes and the phenyl ring in a phth group are 53.0° for C(5)−O(2)−O(3) and 56.0° for C(12)−O(4)−O(5), quite different from those found in the literature.[20] The dihedral angle between the two carboxylate groups is 53.8°. The copper⋯copper separation through the *trans*-oxamidate is 5.257 Å. The Cu⋯Cu distances through the ligand phth are 7.511, 8.303, and 3.574 Å for Cu(1)⋯Cu(2), Cu(1)⋯Cu(1c), and Cu(2)⋯Cu(1c), respectively.

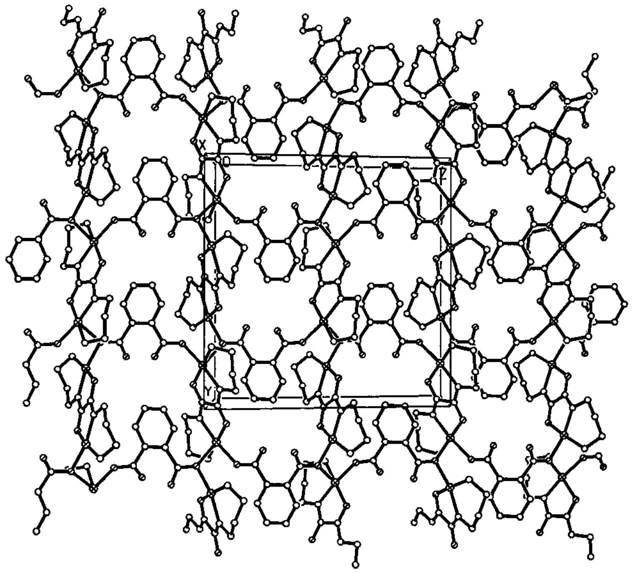

**Figure 2.** Schematic view of the 2D sheet extended along the *bc* plane for **1**.

An extended sheet along the *bc* plane is shown in Figure 2. The inner cavity consists of the linkage of two *trans*-oxamidato-

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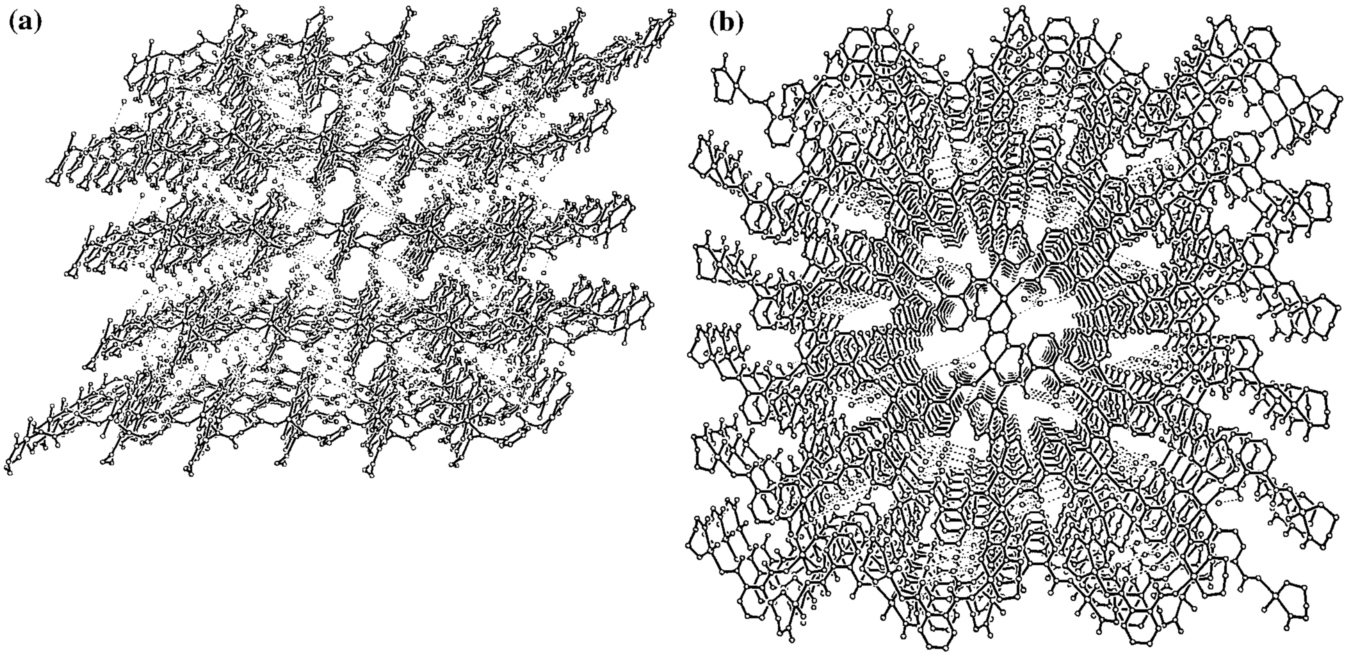

**Figure 3.** View of the packing of the 2D sheets joined together via H-bonded linkages along the (a) *b* axis and (b) *a* axis for **1**.

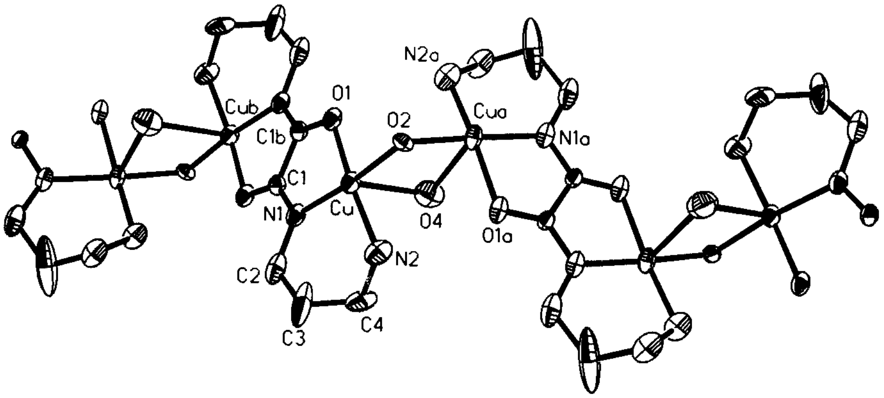

**Figure 4.** View of three symmetry-related units [$Cu_2$(*trans*-oxpn)($\mu$-OH)($\mu$-$OH_2$)]$^-$ showing the zigzag chain structure for **2**. Thermal ellipsoids are plotted at the 50% probability level.

bridged dimeric copper units Cu(*trans*-oxpn)Cu and two phth groups. The solvated $H_2O$ [O(7) and O(8)] molecules intercalate between the layers and pull the sheets together via two H-bonding pathways: O(1)···O(8)···O(7a)···O(3a) and O(4)···O(8)···O(7a)···O(3a) with the distances O(1)···O(8), O(4)···O(8), O(8)···O(7a), and O(7a)···O(3a) of 2.856, 2.755, 2.777, and 2.784 Å, respectively, as illustrated in Figure 3. Hence, a 3D supramolecular structure is constructed with the sheets linked together via a series of interlayer H bonds formed by the solvated water molecules and the oxygen atoms from the oxamidate as well as phth ligands.

**Description of the Structure of [$Cu_2$(*trans*-oxpn)($\mu$-OH)($\mu$-$H_2O$)]$_n$$Br_n$·2$n$$H_2O$ (2).** The structure of **2** contains cation [$Cu_2$(*trans*-oxpn)($\mu$-OH)($\mu$-$H_2O$)]$_n^{n+}$, anions $Br^-$, and solvated water molecules. The cation exhibits a zigzag chain structure with bridging ligands $oxpn^{2-}$, $HO^-$, and $H_2O$, in which the binuclear copper units Cu(*trans*-oxpn)Cu of *trans*-oxamidate are linked by $\mu$-$OH^-$ and $\mu$-$OH_2$ bridges which are symmetrically located in the equatorial and axial sites, respectively, of the copper coordination centers as shown in Figure 4. The bond Cu−O(2) [1.933(3) Å] is much shorter than Cu−O(4) [2.675(2) Å], and the bridging angle Cu−O(2)−Cu(a) [115.1(2)°] is much more obtuse than Cu−O(4)−Cu(a) [75.2(3)°]. An inversion center is located at the middle of bond C(1)−C(1b), and a $C_2$ axis passes through atoms O(2) and O(4). The oxamidate in *trans*-conformation behaves as a bis-tridentate bridge, and the deprotonated amide nitrogen [N(1)] atom is $sp^2$ hybridized. The fact that the bond C(1)−N(1) [1.305(6) Å] is much shorter than N(1)−C(2) [1.448(6) Å] reveals that the former has a certain extent of double-bond character.

The copper atom is located in a distorted square-based pyramidal surrounding with the equatorial plane consisting of amide O(1) and N(1) and amine N(2) from *trans*-oxamidate, and O(2) of the $\mu$-$OH^-$ bridge, and the apical site occupied by O(4) of $\mu$-$OH_2$. The mean coordination planes of Cu and Cu(a) with a dihedral angle of 62.1° form a dihedral angle of 90.0° with the least squares plane defined by the bridging pathway Cu−O(2)−Cu(a)−O(4). The intrachain copper···copper separations through *trans*-oxpn and oxo bridges are 5.298 and 3.264 Å, respectively. The shortest interchain copper···copper distance is 4.704 Å. The coordinated water $H_2O$(4) associates with the lattice water $H_2O$(3) via hydrogen bond with the distance O(4)···O(3) of 2.962 Å. The zigzag chains extending in three different directions which are symmetry-related

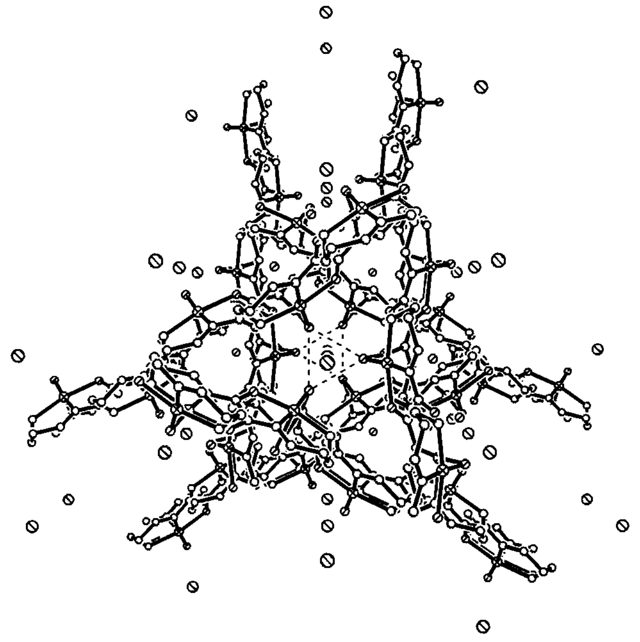

**Figure 5.** View of the arrangement of the zigzag chains extending in three directions with 60° orientation for **2**, showing (i) the reversibly oriented equilateral triangles formed by the intersecting chains, (ii) hexagonal cavity with the $Br^-$ anions located, (iii) the formation of the interchain hydrogen bonds via $\mu$-OH groups.

to one another via an $C_3$ axis intersect one another, affording an interwoven network with a reversibly oriented equilateral triangular arrangement, thus forming hexagonal cavities in which the $Br^-$ ions are located as shown in Figure 5. The $\mu$-OH groups in the three chains form interchain H bonds to one another with O···O distance of 2.899 Å. Thus, the chains packing in three different directions interpenetrate one another to form an extended network via the interchain H bond linkages.

**Thermal Analysis.** The TG curve for **1** shows that the solvate water molecules are lost first in the temperature range 95−115 °C with a weight loss of 7.0%, corresponding to the calculated value (6.8%) of losing two solvated water molecules. It is followed then by the degradation in range 280−285 °C with the weight loss (31.5%) close to the theoretical value (31.1%) for release of the ligand phth. Above 300 °C, the ligand oxpn is degraded and burned. The final pyrolysis product is CuO with the remaining percentage of 30.1%. For **2**, the thermal behavior is quite complicate and the possible degradation process is only predicted tentatively. The dehydration occurring in the temperature range 90−270 °C, following the order: the solvated water first (15.2%) in the range 90−140 °C, then the coordinated water molecule (7.5%) in the range 210−270 °C. The hydroxyl and bromide ions might be lost in the range 310−550 °C with the weight loss of 24.2%, corresponding to the calculated value (23.8%). The sample is then decomposed completely and burned above 550 °C, and the product of the pyrolysis is CuO.

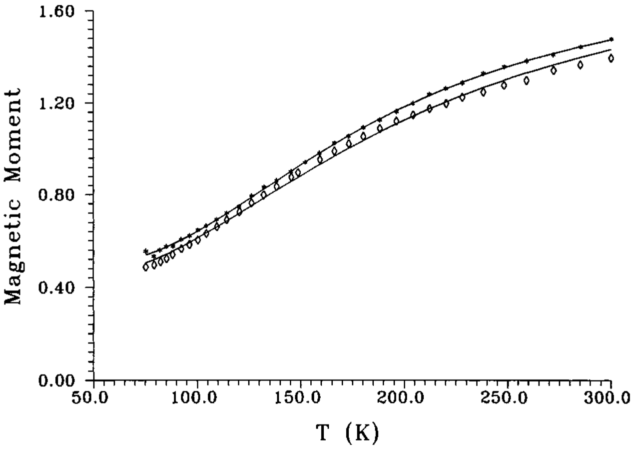

**Figure 6.** Plot of the temperature dependence of the effective magnetic moments $\mu_{\text{eff}}$ for **1** (*) and **2** (◊). The solid lines correspond to the best fit.

**Magnetic Properties.** The temperature dependences of the effective magnetic moments $\mu_{\text{eff}}$ per copper(II) atom of complexes **1** and **2** are shown in Figure 6. The fact that $\mu_{\text{eff}}$ reduces gradually with the decrease of the temperature reveals an antiferromagnetic interaction for both the complexes. Obviously, the presence of different bridging paths may induce different magnetic exchange interactions. Oxamidate is known to afford an effective exchange pathway to mediate a strong antiferromagnetic coupling interaction.[11−13] It has been reported that the bridging group phth usually transmit a ferromagnetic exchange interaction between copper(II) ions.[20] As for the asymmatric carboxylate bridging pathway Cu(1c)−O(5)−Cu(2) in **1** with both equatorial (to square planar Cu(2)) and axial (to square-pyramidal Cu(1c)) Cu−O bonds, the exchange interaction is negligible,[11f,12c,21] since the relative orientations of the two magnetic orbitals are particularly unfavorable for trasmitting electronic effects between the copper(II) ions. Thus, it is possible to depict the 2D magnetic coupling system by means of an alternating chain (bridged by *trans*-oxpn and phth transmitting strong antiferromagnetic and ferromagnetic interactions, respectively) model using the empirical expression proposed by Hatfield[22] for alternating chains with

$$H = -J\sum_{i=1}^{n/2}(S_{2i}S_{2i-1} + \alpha S_{2i}S_{2i+1})$$

Unfortunately, no ideal result can be obtained due to the fact that this model is more suitable for expressing alternating chain with both bridges transmitting antiferromagnetic interactions. In fact, there is no ideal model to deal with such system with one bridge transmitting antiferromagnetic whereas the other ferromagnetic exchange. However, in view of the fact that the exchange interaction transmitted by *trans*-oxpn should be much larger than that by phth, and also that in order to interpret reasonably the magnetic behavior, the 2D magnetic system can be simplified as sheets of interacting dimers Cu(*trans*-oxpn)-Cu, with the exchange through phth bridge creating an inter-dimeric molecular field. On this basis, it should be possible to interpret the data by means of a modified Bleaney−Bowers equation[12a,e,23] with an intermolecular interaction. Least-squares fitting of the experimental data led to $J = -456.7\ \text{cm}^{-1}$, $g = 2.18$, $\theta = 22.0$ K, $\rho = 0.011$, and $R = 1.0 \times 10^{-4}$ with $R$ defined as $\Sigma(\mu_{\text{obsd}} - \mu_{\text{calcd}})^2/\Sigma(\mu_{\text{obsd}})^2$. The curve calculated with these parameters gives a satisfactory fit to the experimental data as shown in Figure 6. The positive value of $\theta$ (22.0 K) reveals that the phth bridge exerts a ferromagnetic contribution which is much smaller than that (80 ± 10 $\text{cm}^{-1}$) found in other phth-bridged copper(II) complex.[20] It has been found[20] that the

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dihedral angle $\omega$ between the two carboxylato groups of the phth bridge plays a key role in determining the strength of the exchange interaction, and an $\omega$ value of about 80° should minimize the antiferromagnetic contribution and lead to the largest ferromagnetic exchange. Obviously, the different ferromagetic exchange interactions through phth bridge for **1** and for the reported complex[20] can easily be explained by the fact that the $\omega$ value in the former (53.8°) deviates much greater than that (78.7°) for the complex $[(dien)(ClO_4)Cu(1)(\mu\text{-phth})Cu(2)(dien)](ClO_4)$ reported in the literature.[20] For **2**, the exchange transmitted via $\mu$-OH bridge is antiferromagnetic due to the fact that the bridging angle Cu−($\mu$-OH)−Cu (115.1°) is much larger than 97°—the critical angle for the exchange interaction of a $\mu$-OH bridge to occur.[24] As for the bridging pathway Cu−($\mu$-$OH_2$)−Cu, the magnetic interaction is negligible because of the unfavorable axial coordination. On this basis, the magnetic system of this complex can be described as alternating chains with antiferromagetic coupling for both oxamidate and $\mu$-OH bridges, which can be interpreted by using the empirical expression proposed by Hatfield,[22] taking into account the interchain interaction in a molecular model. This model resulted in an excellent fit to the magnetic data and the best fitting parameters are $J_1 = -309.6$ cm$^{-1}$, $J_2 = -63.5$ cm$^{-1}$, $\theta = -12.9$ K, $g = 2.24$, and $R = 5.6 \times 10^{-4}$ for **2**, where $J_1$ and $J_2$ denote the coupling constants of the bridges oxamidate and $\mu$-OH, respectively, and $\theta$ is the coupling interaction between chains via H bonds.

## Conclusions

The hydrogen bonding interaction involved here is important in construction of higher dimensional metal coordination polymers. Although it is difficult to control the crystal engineering involving hydrogen bonding linkages, the supramolecular pathway is still a good strategy to realize the self-assembly of inorganic materials with zeolite-like cavities or channels. N,N′-Disubstituted oxamidate seems to be a good organic ligand which can afford bridging and chelating coordination as well as hydrogen bonding capability to build three-dimensional supramolecular architectures.

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**Supporting Information Available:** Listings of data collection and refinement details, atomic coordinates including those for hyhrogen atoms, all anisotropic thermal parameters, all bond lengths and angles (8 pages). Ordering information is given on any current masthead page.

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