Two-Dimensional Sheets of Rugged Hexagonal Grids of $[Cu_6(\textit{trans}\text{-oxen})_3(\mu_3\text{-OH})_2(H_2O)_2]_n^{4n+}$ with Copper(II) Bridged by *trans*-Oxamidate (oxen) and μ_3-OH^- Groups

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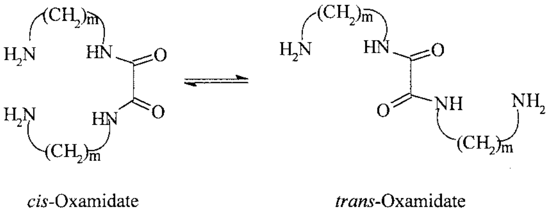
Introduction

The development of synthetic strategies for the architecture of inorganic materials with zeolite-like inner cavities or channels is of immense current interest.[1] The building-block approach has been utilized for the rational assembly of such inorganic and organometallic crystalline solids.[1,2] Construction of the structures with microporous materials based on organic building blocks is attractive, since the shape, size, and function of the cavity become designable. Extended bridging ligands have frequently been used in recent years in order to obtain polymeric frameworks having potential functions such as electrical conductivity,[3] magnetism,[4] clathration ability[5] and catalysis,[6] and ion-exchange properties.[7] On variation of the lengths of these molecular rods and the metal salts employed, a number of polymeric systems have been isolated, displaying various interesting geometries.[8] Among them, *N,N′*-disubstituted oxamidate has proven to be able to give an alternating 1D chain or 2D sheetlike framework.[9,10]

Scheme 1



m = 2; H_2oxen [N,N'-bis(2-aminoethyl)oxamide]
m = 3; H_2oxpn [N,N'-bis(3-aminopropyl)oxamide]

Oxamidate derivatives are known to be versatile organic ligands which can chelate as well as bridge the metal ions to construct discrete and extended structures, depending on the conformation it exhibits[11] (Scheme 1). The *cis*-oxamidates usually give discrete polynuclear species whereas the *trans*-isomers can afford extended structures (Scheme 2). The bis-tridentate character of these ligands in *trans*-conformation allows the formation of *trans*-oxamidato-bridged binuclear copper units which behave as building blocks to be linked together by other bridging groups such as azide,[9a,10b] cyanate,[9b] 4,4′-bipyridine,[10a] pyrimidine,[10a,10d] carboxylate,[10c,10f] cyanide,[10e] and hydroxyl ion,[12] etc., to construct extended 1D or 2D polymers. For example, the 2D sheetlike polymers $[Cu_2(\text{oxen})(4,4'\text{-bipyridine})_2]_{2n}(ClO_4)_{2n}$ and $[Cu_2(\text{oxen})(\text{pyrimidine})_2]_{2n}(ClO_4)_{2n}$ [H_2oxen = *N,N′*-bis(2-aminoethyl)oxamide][10a] were generated by the linkage of the Cu(*trans*-oxen)Cu units with the linear bidentate *N,N′*-donor ligands 4,4′-bipyridine and pyrimidine, respectively. Thus, the size of the cavities becomes controllable by the use of rodlike bridging groups to connect the dimeric units via equatorial−axial linkage.[10a−10e] Herein is described a novel two-dimensional sheetlike polymer $[Cu_6(\textit{trans}\text{-oxen})_3(\mu_3\text{-OH})_2(H_2O)_2]_nBr_{4n}\cdot 3nH_2O$ with rugged hexagonal grids,

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[1] (a) Hoskins, B. F.; Robson, R. *J. Am. Chem. Soc.* **1990**, *112*, 1546. (b) Robson, R.; Abrahams, B. F.; Batten, S. R.; Gable, R. W.; Hoskins, B. F.; Liu, J. *Supramolecular Architecture*; American Chemical Society: Washington, DC, 1992; Chapter 19. (c) Yaghi, O. M.; Li, G. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 207. (d) Black, J. R.; Champness, N. R.; Levason, W.; Reid, G. *Inorg. Chem.* **1996**, *35*, 4432.

[2] Müller, A.; Reuter, H.; Dillinger, S. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2328.

[3] Aumuller, A.; Erk, P.; Klebe, G.; Hunig, S.; von Schutz, J. U.; Werner, H.-P. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 740.

[4] See for examples: (a) Fallah, M. S. E.; Rentschler, E.; Caneschi, A.; Sessoli, R.; Gatteschi, D. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1947. (b) Miyasaka, H.; Matsumoto, N.; Okawa, H.; Re, N.; Gallo, E.; Floriani, C. *J. Am. Chem. Soc.* **1996**, *118*, 981.

[5] See for examples: (a) Schwarz P.; Siebel, E.; Fischer, R. D.; Apperley, D. C.; Davies, N. A.; Harris, R. K. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1197. (b) Yuge, H.; Noda, Y.; Iwamoto, T. *Inorg. Chem.* **1996**, *35*, 1842. (c) Soma, T.; Iwamoto, T. *Inorg. Chem.* **1996**, *35*, 1849. (d) Kawata, S.; Kitagawa, S.; Kumagai, H.; Kudo, C.; Kamesaki, H.; Ishiyama, T.; Suzuki, R.; Kondo, M.; Katada, M. *Inorg. Chem.* **1996**, *35*, 4449. (e) Zhang, H.; Wang, X.; Teo, B. K. *J. Am. Chem. Soc.* **1996**, *118*, 11813.

[6] Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151.

[7] Yaghi, O. M.; Davis, C. E.; Li, G.; Li, H. *J. Am. Chem. Soc.* **1997**, *119*, 2868.

[8] Examples: (a) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi A. *J. Chem. Soc., Chem. Commun.* **1994**, 2755. (b) Carlucci, L.; Ciani, G.; Proserpio, D. M.; Sironi, A. *Inorg. Chem.* **1995**, *34*, 5698. (c) Kawata, S.; Kitagawa, S.; kondo, M.; Furuchi, I.; Munakata, M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1759. (d) Keller, S. W. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 247. (e) Hoskins, B. F.; Robson, R.; Slizys, D. A. *J. Am. Chem. Soc.* **1997**, *119*, 2952.

[9] (a) Lloret, F.; Julve, M.; Real, J. A.; Faus, J.; Ruiz, R.; Mollar, M.; Castro, I.; Bois, C. *Inorg. Chem.* **1992**, *31*, 2956. (b) Lloret, F.; Julve, M.; Faus, J.; Ruiz, R.; Castro, I.; Mollar, M.; Philoche-Levisalles, M. *Inorg. Chem.* **1992**, *31*, 784. (c) Real, J. A.; Ruiz, R.; Faus, J.; Lloret, F.; Julve, M.; Journaux, Y.; Philoche-Levisalles, M.; Bois, C. *J. Chem. Soc., Dalton Trans.* **1994**, 3769. (d) Sanz, J. L.; Cervera, B.; Ruiz, R.; Bois, C.; Faus, J.; Lloret, F.; Julve, M. *J. Chem. Soc., Dalton Trans.* **1996**, 1359. (e) Dominguez-Vera, J. M.; Galvez, N.; Colacio, E.; Cuesta, R.; Costes, J.-P.; Laurent, J.-P. *J. Chem. Soc., Dalton Trans.* **1996**, 861. (f) Bencini, A.; Benelli, C.; Fabretti, A. C.; Franchini, G.; Gatteschi, D. *Inorg. Chem.* **1986**, *25*, 1063.

[10] (a) Chen, Z. N.; Fu, D. G.; Yu, K. B.; Tang, W. X. *J. Chem. Soc., Dalton Trans.* **1994**, 1917. (b) Chen, Z. N.; Qiu, J.; Wu, Z. K.; Fu, D. G.; Yu, K. B.; Tang, W. X. *J. Chem. Soc., Dalton Trans.* **1994**, 1923. (c) Chen, Z. N.; Liu, S. X.; Qiu, J.; Wang, Z. M.; Huang, J. L.; Tang, W. X. *J. Chem. Soc., Dalton Trans.* **1994**, 2989. (d) Chen, Z. N.; Qiu, J.; Tang, W. X.; Yu, K. B. *Inorg. Chim. Acta* **1994**, *224*, 171. (e) Chen, Z. N.; Wang, J. L.; Qiu, J.; Miao, F. M.; Tang, W. X. *Inorg. Chem.* **1995**, *34*, 2255. (f) Chen, Z. N.; Tang, W. X.; Miao, F. M.; Wang, J. L. *Polyhedron* **1994**, *13*, 2543.

[11] Ojima, H.; Nonoyama, K. *Coord. Chem. Rev.* **1988**, *92*, 85.

[12] Chen, Z. N.; Zhang, H. X.; Yu, K. B.; Zheng, K. C., Cai, H.; Kang, B. S. *J. Chem. Soc., Dalton Trans.* **1998**, 1133.

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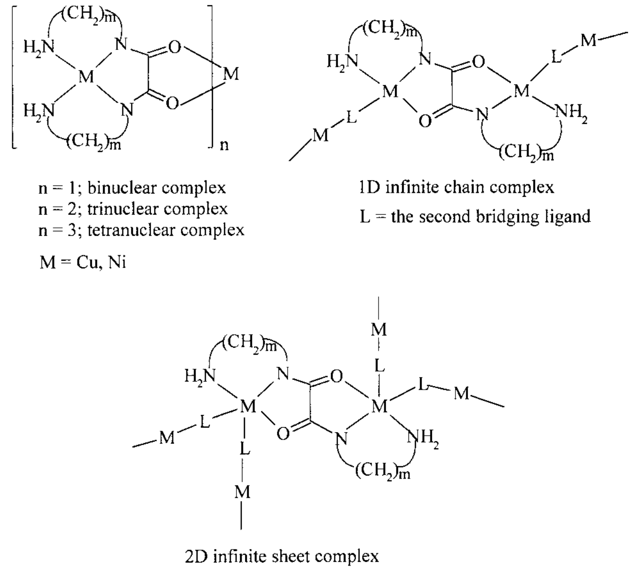
Scheme 2



where the μ_3-OH$^-$ group is equatorially bound to the binuclear unit Cu(*trans*-oxen)Cu in a unique bridging mode.

Experimental Section

The ligand H$_2$oxen and its mononuclear compound Cu(oxen)·2H$_2$O were prepared according to the literature.[13]

Preparation of [Cu$_6$(*trans*-oxen)$_3$(μ_3-OH)$_2$(H$_2$O)$_2$]$_n$Br$_{4n}$·3nH$_2$O. To 40 mL of an aqueous solution of Cu(oxen)·2H$_2$O (1.0 mmol, 0.272 g) was added 5 mL of an 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 pyrazine (2.0 mmol, 0.160 g) was added to give a blue-green solution which was then filtered and the filtrate allowed to stand at room temperature for several days to give dark blue-green crystals. Yield: 65%. Anal. Calcd for $C_{18}H_{48}Br_4Cu_6N_{12}O_{13}$: C, 16.11; H, 3.61; N, 12.53. Found: C, 16.43; H, 3.81; N, 12.87%. IR (KBr, cm^{-1}): 3456 (m), 3318 (m), 3261(m), 3212 (s), 2931 (w), 2882 (w), 2832 (w), 1693 (s), 1651 (s), 1581 (m), 1525 (w), 1447 (m), 1349 (m), 1314 (s), 1117 (m), 1039 (m), 850 (w), 674 (w), 526 (w), 463 (w), 414 (w).

Crystal Structure Determination. A single crystal with dimensions 0.28 × 0.32 × 0.34 mm^3 was mounted on a glass fiber, and data collection was performed on a Siemens P4 diffractometer by the ϖ scan technique using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Intensity data were collected in the 2θ range 2−50°. Of the 3681 measured independent reflections, 2929 were considered observed with $I \geq 2\sigma(I)$ and used for the structure refinement. The crystallographic data are summarized in Table 1.

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 structure was refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms. The positions of the hydrogen atoms were isotropically added to the structure factor calculations but not refined. Br(1), Br(1)′, Br(4), and Br(4)′ are disordered with the occupancy factors 0.9 and 0.1 for Br and Br′, respectively. Atoms O(4W) and O(4W)′ are disordered with the average occupancy of 0.5. All calculations were performed on an IBM PC/486 computer with the Siemens SHELTXL/PC program package.[14] The coordinates for all the non-hydrogen atoms are listed in Table 2, and selected atomic distances and bond angles in Table 3. Complete crystallographic data, atomic coordinates, thermal parameters, and bond distances and angles are gathered in the Supporting Information.

Table 1. Crystallographic Data for the Complex

formula	$C_{18}H_{48}Br_4Cu_6N_{12}O_{13}$
fw	1341.56
space group	*Cc*
a, Å	18.473(3)
b, Å	10.805(4)
c, Å	20.863(3)
β, deg	98.940(6)
V, Å^3	4113.9(18)
Z	4
T, °C	20
λ(Mo Kα), Å	0.710 73
ρ_{calcd}, g·cm^{-3}	2.166
μ, cm^{-1}	69.98
R^a	0.0440
wR^b	0.1079

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum|w(F_o^2)^2|]^{1/2}$; $w = (\sigma^2(F_o^2) + (0.0768P)^2 + 0.0000P)^{-1}$. $P = (F_o^2 + 2F_c^2)/3$.

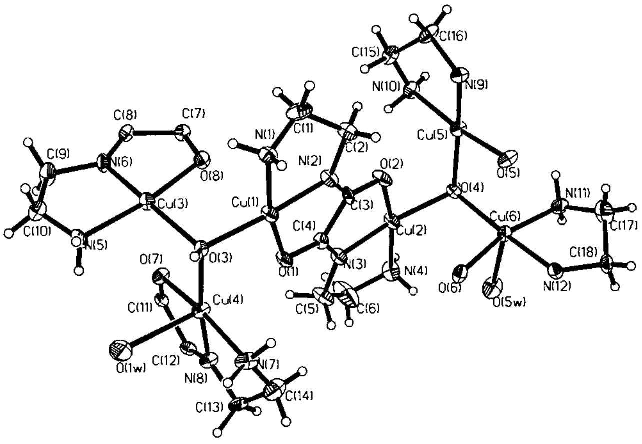


Figure 1. View of one asymmetric unit of the cation [Cu$_6$(*trans*-oxen)$_3$(μ_3-OH)$_2$(H$_2$O)$_2$]$_n^{4n+}$ with the atom-labeling scheme. The ellipsoids represent a 30% probability.

Physical Measurements. The IR spectrum was obtained from a Perkin-Elmer 577 spectrophotometer as a KBr pellet. Variable-temperature magnetic susceptibilities in the temperature range 4−300 K were measured on a model CF-1 superconducting extracting sample magnetometer at a magnetic field of 5.0 T with the powdered sample kept in a capsule for weighing. The temperature was raised gradually from 4.2 to 300 K. Data were recorded at an applied field gradient $H(dH/dX)$ of 1.4 × 10^7 Oe × Oe/cm. An interval of 30 s was kept between data collections, and each measurement took 10 s.

Results and Discussion

The crystal structure of the complex contains cation [Cu$_6$(*trans*-oxen)$_3$(μ_3-OH)$_2$(H$_2$O)$_2$]$_n^{4n+}$, anions Br$^-$, and solvated H$_2$O molecules. The cation [Cu$_6$(*trans*-oxen)$_3$(μ_3-OH)$_2$(H$_2$O)$_2$]$_n^{4n+}$ exhibits a two-dimensional sheetlike structure of copper(II) ions bridged by both *trans*-oxamidate (oxen) and μ_3-OH$^-$ groups. A perspective view of one asymmetric unit with the atom-labeling scheme is depicted in Figure 1.

The asymmetric unit consists of six copper(II) atoms with the formula [Cu$_6$(oxen)$_3$(μ_3-OH)$_2$(H$_2$O)$_2$]$^{4+}$, where four of the copper(II) centers [Cu(1), Cu(2), Cu(3), Cu(5)] are located in square-planar environments of N$_2$O$_2$ while Cu(4) and Cu(6) are in square-based pyramidal geometries with the equatorial plane built by N$_2$O$_2$ donors and the pyramidal apexes occupied by weakly coordinated water molecules. The mean coordination planes of Cu(1) and Cu(3), which have a dihedral angle of 83.4°, form two nearly equal dihedral angles of 96.6° with the least-

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(13) Ojima, H.; Yamada, K. *Nippon Kagaku Zasshi* **1968**, *89*, 490.

(14) Sheldrick, G. M., *SHELXTL-PC*; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990. (b) Sheldrick, G. M. In *Computational Crystallography*; Sayer, D., Ed.; Oxford University Press: New York, 1982.

Table 2. Atomic Coordinates ($\times 10^4$) and Isotropic Thermal Factors ($\mathrm{Å}^2 \times 10^3$) for the Complex

atom	x	y	z	U_{eq}[a]
Cu(1)	2900(1)	8047(1)	2164(1)	30(1)
Cu(2)	3820(1)	9631(1)	67(1)	31(1)
Cu(3)	1787(1)	5760(1)	2195(1)	31(1)
Cu(4)	3471(1)	5251(1)	2139(1)	28(1)
Cu(5)	3218(1)	12432(1)	80(1)	29(1)
Cu(6)	4932(1)	11890(1)	127(1)	29(1)
Br(1)	6060(1)	17987(1)	−1774(1)	60(1)
Br(1′)	5592(4)	17616(10)	−1704(4)	82(3)
Br(2)	4139(1)	8696(1)	3189(1)	38(1)
Br(3)	3260(1)	14338(1)	−929(1)	42(1)
Br(4)	2541(1)	8924(1)	−962(1)	62(1)
Br(4')	2105(4)	8462(9)	−1086(4)	71(3)
O(1)	3489(2)	7380(3)	1504(2)	33(1)
O(2)	3248(2)	10279(3)	720(2)	35(1)
O(3)	2800(2)	6375(3)	2519(2)	21(1)
O(4)	3952(2)	11330(3)	−249(2)	22(1)
O(5)	4038(2)	13157(4)	712(2)	32(1)
O(6)	5066(2)	10546(4)	798(2)	36(1)
O(7)	2676(2)	4511(4)	1495(2)	31(1)
O(8)	1645(2)	7130(3)	1540(2)	40(1)
O(1W)	3370(3)	3565(5)	2921(3)	70(2)
O(2W)	4307(3)	1670(6)	2903(5)	133(4)
O(3W)	1946(3)	16218(7)	−662(5)	141(4)
O(4W)	5768(7)	15157(18)	−1398(6)	140(6)
O(4W')	5994(17)	14560(3)	−1565(10)	255(12)
O(5W)	5545(2)	10615(5)	−618(2)	58(2)
N(1)	2291(2)	9048(4)	2674(2)	32(1)
N(2)	2909(2)	9531(2)	1675(1)	28(1)
N(3)	3843(2)	8139(4)	562(2)	31(1)
N(4)	4440(3)	8641(1)	−471(2)	42(2)
N(5)	1763(3)	4202(5)	2733(2)	39(2)
N(6)	897(2)	5117(4)	1705(2)	35(1)
N(7)	4450(1)	5786(5)	2661(1)	40(2)
N(8)	4102(2)	4355(4)	1641(2)	31(1)
N(9)	2614(2)	13329(4)	575(2)	29(1)
N(10)	2273(2)	11891(5)	−420(2)	38(2)
N(11)	5040(3)	13367(5)	−427(3)	43(2)
N(12)	5809(1)	12532(3)	613(2)	31(1)
C(1)	1990(3)	10086(7)	2282(3)	48(2)
C(2)	2536(3)	10615(5)	1872(3)	36(2)
C(3)	3215(3)	9467(5)	1139(3)	30(2)
C(4)	3536(3)	8205(5)	1061(2)	25(2)
C(5)	4209(4)	7079(6)	323(3)	50(2)
C(6)	4360(4)	7322(2)	−325(3)	104(3)
C(7)	1088(3)	6912(5)	1134(3)	29(2)
C(8)	638(3)	5757(5)	1207(3)	27(2)
C(9)	623(2)	3962(5)	1956(1)	52(2)
C(10)	1094(2)	3668(6)	2601(1)	138(3)
C(11)	2930(3)	3896(5)	1079(2)	22(1)
C(12)	3759(3)	3756(5)	1128(3)	27(2)
C(13)	4885(3)	4447(6)	1836(3)	39(2)
C(14)	4994(1)	5656(7)	2221(1)	58(2)
C(15)	1709(3)	12064(6)	−1(3)	35(2)
C(16)	1825(3)	13249(7)	355(3)	41(2)
C(17)	5487(1)	14303(3)	8(2)	56(2)
C(18)	6143(1)	13668(3)	402(2)	38(2)

[a] Equivalent isotropic U_{eq} defined as one-third of the trace of the orthogonalized $\mathbf{U}_{ij}$ tensor.

Table 3. Selected Atomic Distances (Å) and Bond Angles (deg) for the Complex

Cu(1)−N(2)	1.9026(19)	Cu(1)−O(3)	1.971(3)
Cu(1)−N(1)	1.985(5)	Cu(1)−O(1)	2.017(4)
Cu(2)−N(3)	1.911(5)	Cu(2)−O(4)	1.979(4)
Cu(2)−O(2)	1.976(4)	Cu(2)−N(4)	2.030(4)
Cu(3)−N(6)	1.926(4)	Cu(3)−O(3)	2.001(3)
Cu(3)−O(8)	2.004(4)	Cu(3)−N(5)	2.028(5)
Cu(4)−N(8)	1.938(5)	Cu(4)−O(3)	1.987(3)
Cu(4)−O(7)	1.997(4)	Cu(4)−N(7)	2.044(2)
Cu(4)−O(1W)	2.472(4)	Cu(5)−N(9)	1.901(5)
Cu(5)−N(10)	1.978(4)	Cu(5)−O(4)	2.003(4)
Cu(5)−O(5)	2.006(3)	Cu(6)−N(12)	1.903(2)
Cu(6)−O(4)	1.954(3)	Cu(6)−N(11)	1.999(6)
Cu(6)−O(6)	2.005(4)	Cu(6)−O(5W)	2.478(3)
Cu(1)···Br(2)	2.963(2)	Cu(2)···Br(4)	3.033(3)
Cu(3)···Br(1)	3.027(4)	Cu(5)···Br(3)	2.953(3)
O(1w)···O(2w)	2.685(3)	O(3wa)···O(5w)	2.685(2)
O(1w)···N(5)	3.012(3)	O(4w)···N(7)	3.055(3)
O(1w)···Br(3a)	3.330(3)	O(2w)···Br(1a)	3.225(4)
O(3w)···Br(3)	3.278(3)	O(3w)···Br(4b)	3.219(4)
O(4w)···Br(1)	3.224(4)	O(4w)···Br(4a)	3.522(2)
Cu(1)···Cu(2)	5.222(4)	Cu(1)···Cu(3)	3.220(4)
Cu(1)···Cu(4)	3.203(4)	Cu(3)···Cu(4)	3.178(4)
Cu(2)···Cu(5)	3.226(4)	Cu(5)···Cu(6)	3.206(4)
Cu(2)···Cu(6)	3.180(2)		

N(2)−Cu(1)−O(3)	169.42(13)	N(2)−Cu(1)−N(1)	83.21(17)
O(3)−Cu(1)−N(1)	101.75(17)	N(2)−Cu(1)−O(1)	83.30(15)
O(3)−Cu(1)−O(1)	91.24(15)	N(1)−Cu(1)−O(1)	166.37(18)
N(3)−Cu(2)−O(4)	165.77(16)	N(3)−Cu(2)−O(2)	84.09(18)
O(4)−Cu(2)−O(2)	90.42(15)	N(3)−Cu(2)−N(4)	83.51(16)
O(4)−Cu(2)−N(4)	101.24(13)	O(2)−Cu(2)−N(4)	167.48(14)
N(6)−Cu(3)−O(3)	167.27(19)	N(6)−Cu(3)−O(8)	83.93(18)
O(3)−Cu(3)−O(8)	90.10(14)	N(6)−Cu(3)−N(5)	84.5(2)
O(3)−Cu(3)−N(5)	100.84(16)	O(8)−Cu(3)−N(5)	168.22(17)
N(8)−Cu(4)−O(3)	169.89(17)	N(8)−Cu(4)−O(7)	83.10(16)
O(3)−Cu(4)−O(7)	94.31(14)	N(8)−Cu(4)−N(7)	82.56(15)
O(3)−Cu(4)−N(7)	99.73(14)	O(7)−Cu(4)−N(7)	165.64(14)
N(9)−Cu(5)−N(10)	83.78(19)	N(9)−Cu(5)−O(4)	167.16(16)
N(10)−Cu(5)−O(4)	103.45(18)	N(9)−Cu(5)−O(5)	83.72(16)
N(10)−Cu(5)−O(5)	167.44(19)	O(4)−Cu(5)−O(5)	88.63(14)
N(12)−Cu(6)−O(4)	170.20(14)	N(12)−Cu(6)−N(11)	82.17(17)
O(4)−Cu(6)−N(11)	100.65(17)	N(12)−Cu(6)−O(6)	83.64(15)
O(4)−Cu(6)−O(6)	93.59(15)	N(11)−Cu(6)−O(6)	165.74(17)
Cu(1)−O(3)−Cu(4)	108.03(16)	Cu(1)−O(3)−Cu(3)	108.31(15)
Cu(4)−O(3)−Cu(3)	105.65(15)	Cu(6)−O(4)−Cu(2)	107.90(15)
Cu(6)−O(4)−Cu(5)	108.20(16)	Cu(2)−O(4)−Cu(5)	108.23(16)

squares plane of Cu(4). The *trans*-oxamidate behaves as a bis-tridentate ligand chelating as well as bridging copper ions to form a dimeric Cu(*trans*-oxen)Cu unit with two five-membered chelating rings for each copper atom. The deprotonated N atoms [N(2), N(3), N(6), N(8), N(9), and N(12)] are sp^2-hybridized with the bonds Cu−N$_{\mathrm{amide}}$ (average 1.914 Å) much shorter than Cu−N$_{\mathrm{amine}}$ (average 2.011 Å). The π-electrons of C═O in *trans*-oxamidate are delocalized within the whole amide skeleton forming a conjugated system. The hydroxyl groups O(3)H and O(4)H cap the Cu$_3$ triangles and act as μ_3-bridges to link equatorially the dimeric copper units Cu(*trans*-oxen)Cu along the *ab* plane to extend the 2D sheets. This is different from other low-dimensional complexes of *trans*-oxamidate, such as $[\mathrm{Cu_2(oxen)(L)_2}]_{2n}(\mathrm{ClO_4})_{2n}$[10a] (L = pyrimidine or 4,4′-bipyridine), $[\mathrm{Cu_2(oxen)(pic)(H_2O)}]_n(\mathrm{ClO_4})_n\cdot 2n\mathrm{H_2O}$[10c] (pic = pyridine-4-carboxylate ion), and $[\mathrm{Cu_2(oxpn)Fe(CN)_5(NO)}]_n$[10d] [H$_2$oxpn = *N,N*′-bis(3-aminopropyl)oxamide], where the *trans*-oxamidato-bridged copper dimers are joined together by a second bridging group via equatorial−axial linkages. The average bridging angles Cu−(μ_3-OH)-Cu for HO(3)$^-$ and HO(4)$^-$ are 107.3 and 108.1°, respectively. Accordingly, HO(3)$^-$ and HO(4)$^-$ are located respectively in the apexes of the two reversely oriented trigonal pyramids Cu(1)Cu(3)Cu(4)O(3) and Cu(2)Cu(5)-Cu(6)O(4), with distances 0.711 and 0.691 Å to the pyramidal bases, respectively. The Cu−O(3)H$^-$ and Cu−O(4)H$^-$ distances (in the range of 1.954(3)−2.003(4) Å) are much shorter than Cu(4)−O(1w) (2.472(4) Å) and Cu(6)−O(5w) (2.478(3) Å) and easily distinguished. The average copper···copper separations through the *trans*-oxamidate and the μ_3-OH$^-$ bridges are 5.222 and 3.202 Å, respectively.

An extended sheet along the *ab* plane with rugged hexagonal grids is shown in Figure 2. The inner cavity, derived from the linkage of six *trans*-oxamidato-bridged dimeric copper units as the edges of the hexagon and six μ_3-OH$^-$ groups as the corners,

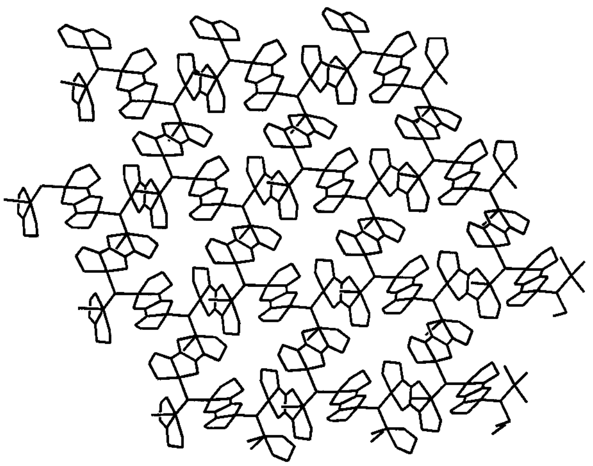

Figure 2. Schematic view of the 2D sheet extended along the *ab* plane, showing the rugged hexagonal grids.

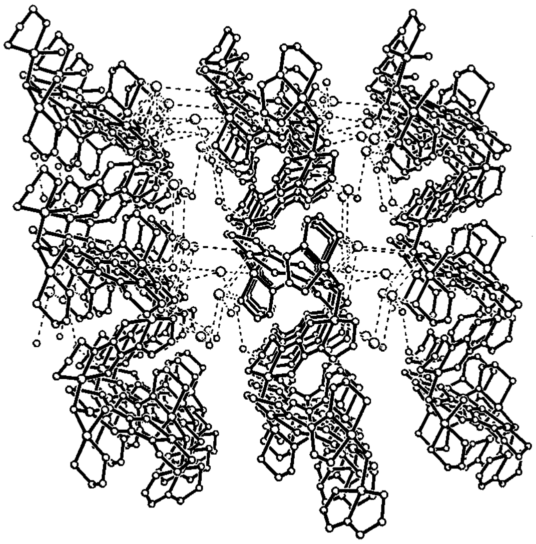

Figure 3. View of the packing of the 2D sheets joined together via H-bonded linkages down the *c*-axis. Large circles indicate the bromide ions, and small ones, the oxygen atoms from H_2O.

has dimension 13.5 Å × 10.7 Å, in which no solvent molecule is clathrated. The solvate H_2O molecules and the Br^- ions are inserted between the sheets via a series of hydrogen bonds of the linkages $Br^- \cdots H_2N$ (amine), $Br^- \cdots H_2O$, and μ_3-$OH^- \cdots Br^-$ with distances in the ranges from 3.1 to 3.6 Å as illustrated in Figure 3, a schematic view with the arrays of the 2D sheets down the *c* axis. Moreover, atoms Br(1), Br(2), Br(3), and Br(4) can be regarded as weakly binding to Cu(3), Cu(1), Cu(5), and Cu(2) via axial coordinations with the Cu−Br distances of 3.027, 2.963, 2.953, and 3.033 Å, respectively. The solvent water molecules also join with the coordinated H_2O and the amine N atoms via intermolecular H-bonds O(1w)$\cdots$O(2w) (2.685 Å), O(3wa)$\cdots$O(5w) (2.685 Å), O(1W)$\cdots$N(5) (3.012 Å) and O(4w)$\cdots$N(7) (3.055 Å). Hence, the sheets are linked together via the interlayer H-bonds formed by the weakly coordinated Br^- and solvated and coordinated H_2O molecules as well as the amine N atoms of oxamidates.

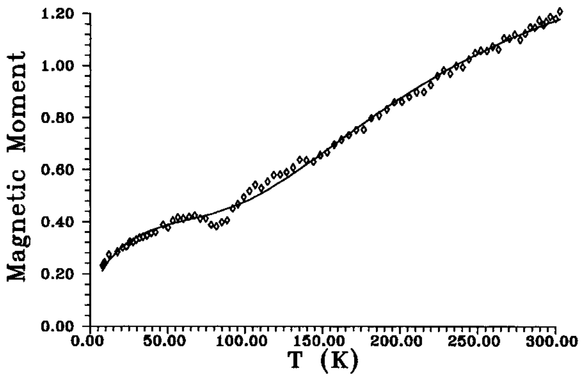

Figure 4. Temperature dependence of the effective magnetic moments μ_{eff} (μ_B) per copper(II) ion. The solid line corresponds to the best fit.

The variable-temperature magnetic behavior with the effective magnetic moments (μ_{eff}) per copper(II) ion vs *T* is plotted in Figure 4. The μ_{eff} is 1.21 μ_B for each copper at 300 K, much smaller than the spin-only value (1.73 μ_B) without exchange interaction. This fact together with the decrease of μ_{eff} with the lowering of temperature reveals a behavior characteristic for strong antiferromagnetic coupling. Many investigations have demonstrated the remarkable ability of the *trans*-oxamidato bridge to transmit exchange interactions between copper(II) ions when the magnetic orbitals are in the plane of the oxamidate ligand.[9,10] The fact that the average bridging angles Cu−(μ_3-OH)−Cu for $HO(3)^-$ (107.3°) and $HO(4)^-$ (108.1°) are more obtuse than the critical angle (97.5°)[15,16] of a bridging OH^- with antiferromagnetic or ferromagnetic exchange shows that the μ_3-OH^- groups in the title complex should also transmit antiferromagnetic exchange interactions. To carry out the quantitative calculation of the 2D coupling system with alternating bridges, the magnetic system was simplified as sheets of interacting dimers Cu(*trans*-oxen)Cu, with the exchange through the μ_3-OH^- bridge creating an interdimeric molecular field. Thus, it should be possible to interpret the data by means of a modified Bleaney−Bowers equation[10b,d] with an intermolecular interaction. Least-squares fitting of the experimental data led to $J = -387.2\ \text{cm}^{-1}$, $g = 2.07$, $\theta = -39.1$ K, $\rho = 0.083$, and $R = 6.6 \times 10^{-4}$ with *R* defined as $\sum(\mu_{\text{obsd}} - \mu_{\text{calcd}})^2/\sum(\mu_{\text{obsd}})^2$, where ρ denotes the percentage of paramagnetic impurities. The curve calculated with these parameters gives a satisfactory fit to the experimental data as shown in Figure 4. The negative value of θ reveals that the μ_3-OH^- bridge exerts an antiferromagnetic contribution, which is in accord with the result estimated from the bridging angle. The bump at −80 K comes from a little oxygen and/or other impurities such as monomeric complex.

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Supporting Information Available: Tables listing detailed crystallographic data, complete bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters (8 pages). Ordering information is given on any current masthead page.

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(15) Mathews, I. I.; Manohar, H. *J. Chem. Soc., Dalton Trans.* **1991**, 2139.

(16) Charlot, M. F.; Jeannin, S.; Jeannin, Y.; Kahn, O.; Lucrece-Aabaul, J.; Frere, L. *Inorg. Chem.* **1979**, *18*, 1675.