Extended Network *via* Axial Cu-Br Linkages of Zig-zag Coordination Chains of Copper(II) Ions Bridged Alternately by *trans*-Oxamidate and End-on Azide Groups

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The zig-zag coordination chains $[Cu_2(trans\text{-oxen})(N_3)(Br)]_n$ [H_2oxen = N,N'-bis(2-aminoethyl)oxamide] with alternating bridges of *trans*-oxamidate and azide in bis-terdentate and end-on mode, respectively, are held together via axial Cu-Br linkage in a unique fashion to form an extended structure.

Crystal engineering and the design of solid-state architectures has become topic of increasing interest over recent years.[1] It offers hope of rationally designing extended solids by linking together molecular building blocks having specific functionality and geometry. A successful strategy leading to the extended supramolecular architectures is the use of metal-containing cations to link relatively stable coordination compounds containing potential bridging units. Following this rational synthetic approach, various homo- and heterometallic systems, ranging from discrete entities to 3D extended structures, can be obtained.

N,N'-disubstituted oxamide derivatives are efficient bridging ligands for the stepwise synthesis of homo- and heteropolynuclear complexes.[2] One of the most outstanding character of these ligands is the transformation of *cis-trans* conformation, which makes it practical to design tunable molecular materials with extended structures and desired properties. The bis-terdentate character of *trans*-oxamidates favors the formation of *trans*-oxamidato-bridged cationic binuclear units which behave as the building blocks to be joined together by a second bridging group to generate an extended system.[3,4] Here is reported a new *trans*-oxamidato-bridged polymeric complex $[Cu_2(trans\text{-oxen})(N_3)(Br)]_n$ [H_2oxen = N,N'-bis(2-aminoethyl)oxamide] with two other bridging groups azide and Br^-.

The complex was prepared by the addition of an aqueous solution of $CuBr_2$ (1 mmol, 10 cm^3) into an aqueous solution of Cu(oxen)·$2H_2O$ [5](1 mmol, 40 cm^3) with stirring, followed then by the addition of an aqueous solution of NaN_3 (1 mmol, 5 cm^3). The deep green-blue solution was filtered after stirring for a while, and kept at room temperature for several days to give well-shaped dark blue crystals. The complex was characterized by elemental analysis,[6] IR spectrum[7] and magnetic measurement and its structure was determined by single crystal X-ray diffraction method.[8]

A view of four symmetry-related asymmetric units of the complex with atom-labeling scheme is depicted in Figure 1. The coordination polymer exhibits an extended structure with the copper(II) ions bridged by three different groups, i.e. *trans*-oxen, N_3^- and Br^-. The zig-zag chains derived from the *trans*-oxamidato-bridged binuclear copper(II) units Cu(*trans*-oxen)Cu linked singly further by azide groups *via* equatorial coordinations, are joined together *via* the axial Cu-Br linkages to produce a 3D extended structure with the inner cavity of dimension 8.8 × 7.0 Å as illustrated in Figure 2.

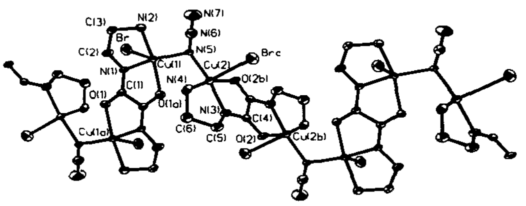

Figure 1. A view of four symmetry-related units of the complex.

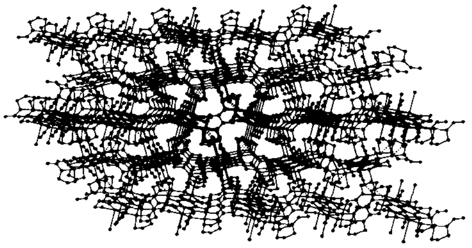

Figure 2. A view of the extended 3D structure down the c axis.

The asymmetric unit contains two different copper atoms, both of which are in elongated square-based pyramidal environments and surrounded by N_3OBr donors. The equatorial planes of Cu(1) [N(2)N(1)O(1a)N(5)] and Cu(2) [N(4)N(3)O(2b)N(5)] with a dihedral angle of 79.9° are built by N_3O donors from two different oriented *trans*-oxen groups and the same azide group, respectively. The axial sites of Cu(1) and Cu(2) are occupied by Br and Br(c) with the bonds Cu(1)-Br and Cu(2)-Br(c) of 2.8252(9) and 2.922(1) Å, respectively.

The deprotonated oxamidato group exhibits a *trans*-conformation, behaving as a bis-terdentate bridging ligand to form a binuclear unit Cu(*trans*-oxen)Cu with two five-membered chelating rings for each copper center. The amide N atoms [N(1) and N(3)] are sp^2 hybridized with the bond Cu-N_{amide} (average 1.915 Å) much shorter than Cu-N_{amine} (average 2.021 Å). The azido group exhibits a *quasi*-symmetric end-on mode bridging equatorially two copper centers with the bonds Cu(1)-N(5) and Cu(2)-N(5) of 1.954(3) and 1.977(3) Å, respectively, and the bridging angle of 112.5(2)°. This is different from the asymmetric end-on mode of double azide groups found in $[Cu_2(mapox)(N_3)_2]_n$ [H_2mapox = N,N'-bis(3-methyl-aminoproyl)oxamide][3a] and $[Cu_2(dmaeoxd)(N_3)_2]_n$ [H_2dmaeoxd = N,N'-bis[2-dimethyl-aminoethyl)oxamide],[3c] but similar to the symmetric end-on fashion found in complex $[Cu_4(oxen)_2(N_3)_3]_n(ClO_4)_n$·$2nH_2O$.[4b] The bromide anion bridges axially the copper centers in a *quasi*-symmetric way with the bonds Cu(1)-Br and Cu(2d)-Br of 2.8252(9) and 2.922(1) Å, respectively, and the bridging angle Cu(1)-Br-Cu(2d) of 123.9(2)°. The average copper···copper distance through *trans*-oxamidate bridges is 5.256 Å, whereas those through azide and Br^- groups are 3.268 and 5.073 Å, respectively.

The temperature dependence of the effective magnetic moment (μ_{eff}) of the complex in the temperature range 300 - 70 K is shown in Figure 3. At 300 K, the μ_{eff} of each copper(II) atom is only 1.40 μ_B, lower than the spin-only value (1.73 μ_B). This fact together with the decrease of μ_{eff} with the lowering of the temperature indicates the complex is characteristic of the antiferromagnetic exchange interaction. The 3D magnetic system could be simplified into alternating chains since the exchange transmitted *via* the Br^- bridge with axial coordination is negligible.[4a] Hence, attempts have been made to fit the magnetic data by the empirical relation proposed by Hatfield,[9] taking into account the interchain interaction in a molecular model.[10] The best fitting parameters from the least-squares calculation led to $g = 2.25$, $J_1 = -366.3$ cm^{-1}, $J_2 = -85.7$ cm^{-1}, and $\theta = -7.2$ K, where J_1 and J_2 are the coupling constants of the bridges oxamidate and azide, respectively, and θ denotes the coupling interactions between chains *via* bridging Br^-.

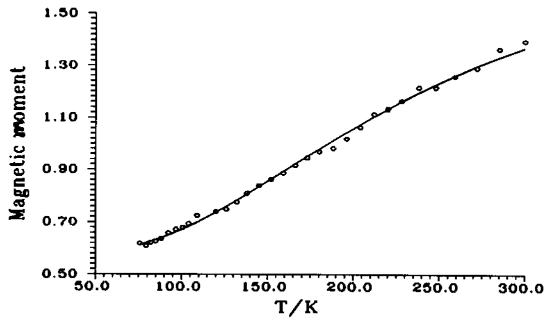

Figure 3. Plot of the temperature dependence of the effective magnetic moments μ_{eff} for the complex. The solid line represents the best fit.

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References and Notes

1 a) R. Robson, B. F. Abrahams, S. R. Batten, R. W. Gable, B. F. Hoskins, and J. Liu, "Supramolecular Achitecture, ACS", Washington DC (1992), Chap 19. b) B. F. Hoskins and R. Robson, *J. Am. Chem. Soc.*, **112**, 1546 (1990).

2 H. Ojima and K. Nonogama, *Coord. Chem. Rev.*, **92**, 85 (1988).

3 a) F. Lloret, M. Julve, J. A. Real, J. Faus, R. Ruiz, M. Mollar, I. Castro, and C. Bois, *Inorg. Chem.*, **31**, 2956 (1992). b) F. Lloret, M. Julve, J. Faus, R. Ruiz, I. Castro, M. Mollar, and M. Philoche-Levisalles, *Inorg. Chem.*, **31**, 784 (1992). c) J. A. Real, R. Ruiz, J. Faus, F. Lloret, M. Julve, Y. Journaux, M. Philoche-Levisalles, and C. Bois, *J. Chem. Soc., Dalton Trans.*, **1994**, 3769. d) J. L. Sanz, B. Cervera, R. Ruiz, C. Bois, J. Faus, F. Lloret, and M. Julve, *J. Chem. Soc., Dalton Trans.*, **1996**, 1359. e) A. Bencini, C. Benelli, A. C. Fabretti, G. Franchini, and D. Gatteschi, *Inorg. Chem.*, **25**, 1063 (1986).

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

5 H. Ojima and K. Yamada, *Nippon Kagaku Zasshi*, **89**, 490 (1968).

6 Anal. Found: C, 16.96; H, 2.99; N, 23.19%. Calcd for $C_6H_{12}BrCu_2N_7O_2$: C, 17.09; H, 2.87; N, 23.27%.

7 IR (KBr, cm^{-1}): 3310(m), 3233(m), 3135(w), 2945(w), 2853(w), 2101(s), 1658(s), 1574(s), 1342(m), 1314(m), 1278(m),1032(m), 660(w), 572(w), 449(w).

8 Crystal data: $C_6H_{12}BrCu_2N_7O_2$, M = 421.22, monoclinic, $P2_1/n$, a = 10.3220(10), b = 12.250(2), c = 10.4360(10) Å, β = 111.040(10)°, V = 1231.6(3) Å^3, Z = 4, D_c = 2.272 g cm^{-3}, R = 0.0365, wR = 0.0882 and S = 0.995 for 180 parameters using 1939 [$F_o > 4\sigma(F_o)$] reflections. The crystal structure was solved by direct method and refined by full-matrix least-squares techniques with anisotropic thermal parameters for all the non-hydrogen atoms using the Siemens SHELXTL/PC program package.[11]

9 W. E. Hatfield, *J. Appl. Phys.*, **52**, 1985 (1981). The equation:
$\chi_M = (Ng^2\mu_B^2)/k(T - \theta) \bullet (A + Bx + Cx^2)/(1 + Dx + Ex^2 + Fx^3)$.

10 T. Watanabe, *J. Phys. Soc. Japan*, **17**, 1856 (1962).

11 G. M. Sheldrick, SHELXTL/PC, Siemens Analytical X-ray Instruments, Inc.; Madison, WI, 1990.