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$[Cu(L)Mn(N_3)_2]_n$: The First Complex Containing Both Macrocyclic Oxamido and Alternate (μ-1,1 and μ-1,3) Azido Bridges

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A wattle-type heteropolynuclear complex $[(CuL)Mn(N_3)_2]_n$ (**1**) (H_2L = 2,3-dioxo-5,6:15,16-dibenzo-1,4,8,13-tetraazacyclo-pentadeca-7,13-diene), which represents the first system with macrocyclic oxamido and alternate azido bridges, forming a one-dimensional chain structure, has been synthesized and characterized by a low temperature magnetic study. The chains are stacked with interchain hydrogen and lead to the structure of a three-dimensional network.

Over the past two decades, the azido group, N_3, was certainly one of the most interesting magnetic couplers found so far in molecular magnetism. On one hand, the azido ligand has the extreme versatility of its coordination modes,[1] which may coordinate as (i) μ-1,1 (end-on, EO), (ii) μ-1,3 (end-end, EE), (iii) μ-1,1,1 (end-end-end, EEE),[2] and (iv) μ-1,1,3 (end-end-on, EEO).[3] On the other hand, the azido ligand has remarkable ability to transmit a ferro- or antiferro- interaction.[1,4] As a result, the azido ligand has been utilized to assemble a plethora of L−M−azido framework structures. But in these complexes, the L is simply an N-aromatic ligand, such as pyridine, 2,2′-bipyrimidine, 3- and 4-acetylpyridine, or pyrazine, etc.[5,6]

At the same time, it has been found that the oxamido group serves as a pathway through which electron spin interaction takes place. So, polynuclear oxamide bridged complexes have been a focus of magnetic studies. One of the best strategies to design and synthesize polynuclear species is the "complex as a ligand"[7] approach, i.e., using mononuclear complexes that contain potential donor groups for another metal ion. A plethora of oxamido-bridged complexes have been well characterized through this way.[8]

With these facts in mind and in continuation of our interest in polynuclear macrocyclic complexes,[8c−e,9] by using the azido ligand and the prepared macrocyclic oxamide complex ligand, we characterized a one-dimensional complex $[(CuL)Mn(N_3)_2]_n$ (**1**) (H_2L = 2,3-dioxo-5,6:15,16-dibenzo-1,4,8,13-tetraazacyclo-pentadeca-7,13-diene) which includes both alternate azido bridge and oxamido bridge. To our knowledge, this is the first complex including both macrocyclic oxamido and alternated azido bridges.

The complex ligand CuL (H_2L = 2,3-dioxo-5,6:15,16-dibenzo-1,4,8,13-tetraazacyclo-pentadeca-7,13-diene) was prepared as described elsewhere.[10] Single crystals of **1** were grown in a methanol solution by a slow diffusion method

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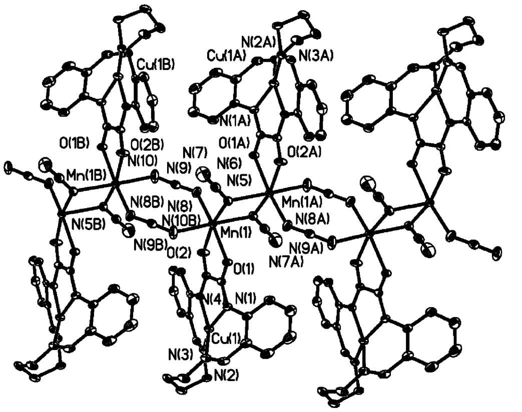

Figure 1. Perspective view of **1**; H atoms are omitted for clarity (thermal ellipsoids are drawn at 30% probability). Selected bond lengths (Å) and angles (deg): Cu1−N1 1.933(2), Cu1−N2 2.000(3), Cu1−N3 1.943(2), Cu1−N4 1.972(2), Mn1−N8 2.202(2), Mn1−N5 2.179(3), Mn1−O1 2.208(2), Mn1−O2 2.224(2), Mn1−N5a 2.223(2), Mn1−N10a 2.218(2), N(1)−Cu(1)−N(3) 158.49(10), N(1)−Cu(1)−N(4) 85.22(9), N(3)−Cu(1)−N(4) 94.87(10), N(1)−Cu(1)−N(2) 90.72(10), N(3)−Cu(1)−N(2) 97.15(10), N(4)−Cu(1)−N(2) 156.72(10), N(8)−Mn(1)−N(5) 99.69(11), N(8)−Mn(1)−O(1) 165.68(9), N(5)−Mn(1)−O(1) 94.35(9).

using an H-shape tube. A mixture of CuL (0.122 g, 0.3 mmol) and NaN$_3$ (0.039 g. 0.6 mmol) which were dissolved in MeOH (3 mL) was added in one arm, and Mn(ClO$_4$)$_2$·6H$_2$O (0.109 g, 0.3 mmol) was added in the other one. Then, MeOH filled in the tube. Deep red crystals, suitable for X-ray determination, were formed after two weeks. IR (KBr) peaks: 2094(vs), 2040(s), 1286(vs), 1610(vs), 1590(s), and 750(s). Anal. Calcd for C$_{20}$H$_{16}$CuMnN$_{10}$O$_2$: C, 43.72; H, 2.91; N, 25.50. Found: C, 43.51; H, 3.03; N, 25.39%.

CAUTION! Perchlorate salts of metal complexes are potentially explosive and therefore should be prepared in small quantities.

The structure determination reveals that **1** is a one-dimensional chain (Figure 1). The structure consists of neutral, well-isolated chains of manganese atoms bridged by alternate two EO (end-on) parts and two EE (end-end) parts. The shape of one chain of **1** is a wattle, and the alternate azido chain consists of the stem while the oxamido ligands decorate both the sides like the leaves. Each manganese(II) ion has a distorted octahedral coordination, completed by the two oxygen atoms of the complex ligand (CuL). The basal plane comprises the N8 and N10B from the EE azido bridge, N5 from EO azido bridge, and O1 from the complex ligand, whereas apical positions are occupied by O2 of CuL and N5 of EO bridge.[11]

The EO and EE bridges are arranged *cis*. The acute dihedral angle between planes formed by the two neighboring Mn−N units is 80.5°. The Mn−Mn intrachain distances are 5.344(2) Å (EE bridges) and 3.388(2) Å (EO bridges). The Mn1−N5−Mn1A bond angle in the EO mode is 99.91(10)° slightly smaller than the results (100−106.5°)[6,12] usually obtained for this kind of bridging. The four atoms Mn1, N5, N5A, and Mn1A lay strictly on the same plane, but the other nitrogen atoms do not reside within this plane and form 83.5° angles. The Mn−N bond distance is 2.223(3) Å. The N−N distance of the azido ligand ranges from 1.183(3) to 1.152(4) Å (averaging 1.167 Å) and reflects typical double bond character.

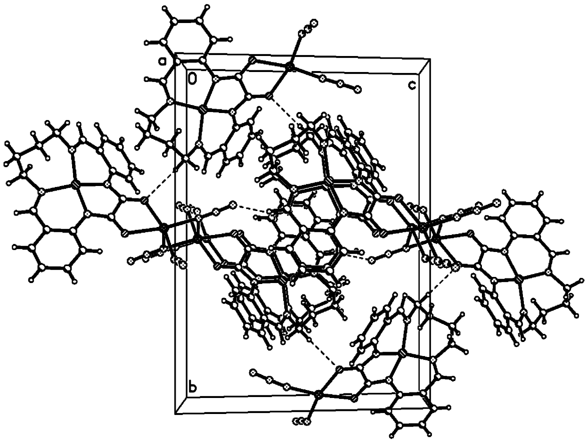

Figure 2. Packing diagram of **1**. There are two kinds of H-bonding. The dashed lines indicate them.

For the EE bridges, the two azido bridges are practically coplanar, and the azido anion is practically linear, N8−N9−N10 = 176.7(3)°, whereas the Mn1−N8−N9, Mn1B−N10−N9 linkages are bent with angles of 130.8(2)° and 132.5(2)°, respectively. The manganese atoms are out of the azido plane (2.1°), giving a chair distortion.

The copper atom is connected to the manganese atom via the oxygen atoms of the oxamido macrocyclic ligands with the Cu−Mn separation of 5.498(2) Å. The Mn−O bond distance is 2.208(2) Å.

The copper(II) atom of the complex ligand is the center of the tetrahedron environment. Four nitrogen atoms deviate from the plane 0.3939(1) Å (N1), −0.3466(1) Å (N2), 0.3329(1) Å (N3), and −0.3803(1) Å (N4). The average distance is 1.962 Å between the copper(II) and nitrogen atom. All copper ions in the macrocyclic oxamido ligands at the same side of the chain are on a line (Figure 1); the minimum Cu−Cu distance is 7.912(2) Å.

There is an intermolecular C−H···O (2.489 Å) and an intermolecular C−H···N (2.607 Å) interaction in the crystal structure, so the molecule forms a 3D framework (Figure 2).

Variable-temperature magnetic susceptibility measurements were performed on a powdered sample with Quantum Design MPMS-7 SQUID magnetometer in an applied field of 5 KOe. The thermal variation of $\chi_M T$ is shown in Figure 3. The observed $\chi_M T$ value is 9.3 cm^3 mol^{-1} K at 300 K, which is lower than the spin-only value 9.50 cm^3 mol^{-1} K for the uncoupled Cu$_2$Mn$_2$ unit. A gradual decrease in $\chi_M T$

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[11] Crystal data for the C20H16CuMnN10O2: $M = 548.92$, monoclinic, space group $P2_1/c$, $a = 7.912(3)$ Å, $b = 19.622(7)$ Å, $c = 14.308(5)$ Å, $\beta = 100.360(6)°$, $V = 2185.2(12)$ Å^3, $Z = 4$, $T = 293(2)$ K, μ(Mo Kα) = 1.593 mm^{-1}, $D_c = 1.669$ Mg·m^{-3}. The data were collected on a Bruker Smart 1000 diffractometer. The structure was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program. Total numbers of measured and observed independent reflections are 12298, 4462 ($R_{int} = 0.0446$). Final R indices [$I > 2\sigma_1$], R1= 0.0389, wR2 = 0.0706.

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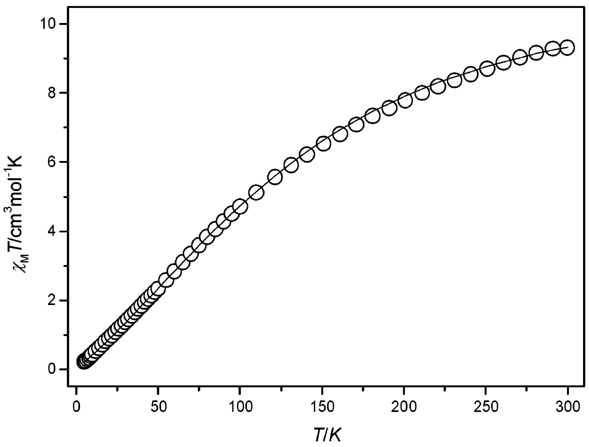
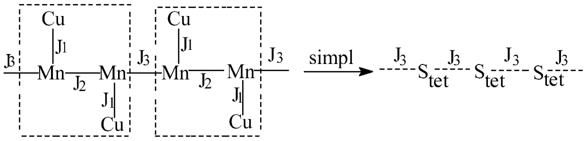


Figure 3. Plot of $\chi_M T$ vs T for **1**. Solid lines correspond to calculated curve.

Scheme 1



is observed as the temperature is decreased, indicating there is a dominant antiferromagnetic interaction in complex **1**.

To the best of our knowledge, no formula to reproduce the magnetic susceptibility of such a complex system is available in the literature, so we used an approximate way[13] to interpret the magnetic behavior. Complex **1** can be regarded as a uniform chain formed by Cu_2Mn_2 tetranuclear units which are indicated in Scheme 1.

In Scheme 1, J_1 is the exchange integral between Cu(II) and Mn(II) through the oximado bridge, J_2 stands for the exchange integral between Mn(II) ions through EO azido bridge, and J_3 stands for that for the EE azido bridge. On the assumption of purely isotropic interactions, the susceptibility of tetranuclear unit (Cu_2Mn_2), χ_{tet} is calculated from eq 1.

$$\chi_{tet} = f(J_1, J_2, g, T) \qquad (1)$$

$f(J_1, J_2, g, T)$ is derived using a method previously reported[14] and is shown in the Supporting Information section. Assuming that S_{tet} is treated as a classical spin, S_{tet} can be calculated from eqs 1 and 2, and the magnetic susceptibility of the chain eq 3 can be described by the classical spin model derived by Fisher.[15]

$$\chi_{tet} = \frac{Ng^2\beta^2}{3KT} S_{tet}(S_{tet} + 1) \qquad (2)$$

$$\chi_M = \frac{Ng^2\beta^2}{3KT} S_{tet}(S_{tet} + 1)\left(\frac{1 + \mu}{1 - \mu}\right) \qquad (3)$$

$$\mu = \coth\left[\frac{J_3 S_{tet}(S_{tet} + 1)}{KT}\right] - \left[\frac{KT}{J_3 S_{tet}(S_{tet} + 1)}\right]$$

The least-squares fit from eq 3 to the data was found with $J_1 = -25.64(1)$ cm^{-1}, $J_2 = 19.80(1)$ cm^{-1}, $J_3 = -4.84(1)$ cm^{-1}, $g = 2.1$. R defined as $\sum[(\chi_M)^{obs} - (\chi_M)^{calc}]^2/\sum[(\chi_M)^{obs}]^2$ is 1.81×10^{-4}. These results call for the EO azido-bridge promoting a ferromagnetic interaction, while the EE bridge gives rise to an antiferromagnetic interaction. From Figure 3, the model provides a very good fit of $\chi_M T$ variation over the temperature range 5−300 K with a discrepancy that does not exceed experimental uncertainty. The ferromagnetic interaction ($J = 19.80$ cm^{-1}) between Mn(II) ions via EO may be explained on the basis of the spin-polarization mechanism which implies that the electron of the bridging nitrogen atom (α spin) is partially delocalized to two Mn(II) orbits. As a result, each unpaired electron of the two Mn(II) ions is likely to have a β spin, favoring ferromagnetic interactions.[16] The exchange integrals through EE azido bridge and oxamido bridge obtained by this model lie in the same range as those previously reported for EE azido bridge[1] and oxamido complexes,[8e] respectively.

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Supporting Information Available: Magnetic susceptibility formula of the tetranuclear unit. Crystallographic file in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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