DOI: 10.1002/ejic.200701090

Structural and Magnetic Properties of Two Copper(II) Complexes Based on Dinuclear Copper(II) Metallacyclophane

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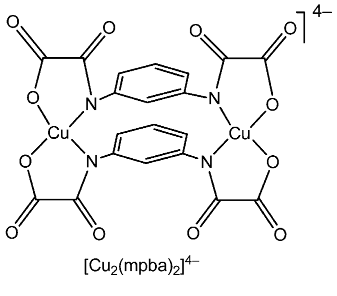
Keywords: Oxamates / Crystal structures / Metallacyclophanes / Azides / Magnetic properties

Two new oxamato-bridged copper(II) complexes of formula $Na_{10}[\{Cu_2(mpba)_2\}_2(\mu_{1,1}\text{-}N_3)_2]\cdot 18H_2O$ (**1**) and $[\{Cu_2(mpba)_2\}\text{-}Cu_2(H_2O)_8]\cdot 6H_2O$ (**2**) [mpba = 1,3-phenylenebis(oxamato-*N*,*N′*)] have been synthesized and characterized. X-ray crystallographic studies of complex **1** reveal a metallamacrocycle structure in which two dinuclear copper(II) metallacyclophane anions are linked by two single symmetric azido ligands in an end-on mode at axial–axial positions. These metallamacrocycle units are self-assembled through sodium cations and water molecules, affording an intricate 3D network. Complex **2** consists of 2D brick-wall-like layers assembled from dinuclear metallacyclophane $[Cu_2(mpba)_2]^{4-}$ anions and copper(II) cations. Magnetic susceptibility measurements of complex **1** in the temperature range 2–300 K show dominating ferromagnetic coupling mediated by the *m*-phenylenediamide bridge and weak antiferromagnetic interaction transmitted by the azido ligand.

Introduction

The design and construction of solid-state architectures of varying dimensionalities from specifically tailored paramagnetic building blocks have proven to be very successful for the preparation of molecular-based magnetic materials.[1] Self-assembly of suitable building blocks with transition-metal ions allows the creation of molecular architectures with defined geometry and new intriguing physical properties.[2–5] In this context, the mononuclear copper(II) complexes with *N*,*N′*-substituted bis(oxamato) ligands, which are versatile bridges to link two or more metal ions and good mediators to transmit magnetic coupling, have evoked considerable interest.[6–8] By employment of this kind of complex as ligand, a number of interesting species such as ordered bimetallic chains,[9] two-dimensional ferrimagnets,[10] 3d–4f compounds,[11] and complexes with interlocked structure[12] have been prepared and characterized in terms of crystal structures and magnetic properties.

Recently, a new (oxamato)copper(II) dinuclear complex built with the dinuclear ligand 1,3-phenylenebis(oxamato-*N*,*N′*) $\{[Cu_2(mpba)_2]^{4-}$, Scheme 1} has been used as a building block for the design and synthesis of polynuclear complexes with a high-spin ground state.[13] This dinuclear copper(II) metallacyclophane anion is potentially a tetrakis-bidentate ligand, which can coordinate up to four metal ions through the free carbonyl oxygen atoms of the oxamate groups. The reaction of this complex as ligand with metal ions can result in an extended network.[14] On the other hand, the copper(II) ions of this dinuclear metallacyclophane anion still have potential coordination sites. When suitable bridging ligands are used, new complexes with unique structures can be obtained. Considering the high affinity of the azido ligand for the copper(II) ion, and the fact that the azido ligand is certainly one of the most interesting magnetic couplers known in molecular chemistry,[15–19] we decided to investigate the new system formed by this dinuclear copper(II) metallacyclophane anion $\{[Cu_2(mpba)_2]^{4-}\}$ in the presence of azide. In this paper, we report the synthe-



Scheme 1.

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ses and crystal structures of two new complexes, $Na_{10}[\{Cu_2(mpba)_2\}_2(\mu_{1,1}-N_3)_2]\cdot 18H_2O$ (**1**) and $[\{Cu_2(mpba)_2\}Cu_2(H_2O)_8]\cdot 6H_2O$ (**2**), which incorporate dinuclear copper(II) metallacyclophane anions. Complex **1** is a 3D network where two dinuclear copper(II) metallacyclophane anions are bridged by two azido ligands in a rare apical–apical end-on coordination fashion to form a metallamacrocycle, and complex **2** is composed of 2D wall-like corrugated layers. The magnetic properties of complex **1** are investigated.

Results and Discussion

Synthesis

Complex **1** has been prepared by means of a "one-pot" method in which NaOH, $Cu(NO_3)_2\cdot 3H_2O$, and NaN_3 were successively added to the suspension of H_2Et_2mpba in water, and the yield of the obtained complex is high. We also tried to get the dinuclear complex $Na_4[Cu_2(mpba)_2]$ to directly react with (azido)sodium; however, complex **1** could not be obtained. Complex **2** was isolated by the slow diffusion method by using an H-shaped tube in the presence of the azido ligand. Nevertheless, the azido ligand is absent in **2**. We carried out the above reaction with $Cu(NO_3)_2\cdot 3H_2O$ instead of sodium azide, but complex **2** could not be obtained. It seems that the azide group plays an important role in the formation of **2**. On the other hand, although the reaction was repeated at least seventy times, we did not obtain enough complex **2** to perform magnetic measurements. In this reaction, some green powder is obtained, but the infrared spectrum and chemical analysis of this green powder were inconsistent with those of complex **2**.

Structure Description of Complex 1

Complex **1** consists of $[\{Cu_2(mpba)_2\}_2(\mu_{1,1}-N_3)_2]^{10-}$ anions, sodium cations, and water molecules. The $[\{Cu_2(mpba)_2\}_2(\mu_{1,1}-N_3)_2]^{10-}$ anion is a metallamacrocycle in which two dinuclear copper(II) metallacyclophane anions are linked by two single symmetric azido bridging ligands in an end-on mode (Figure 1). Selected bond parameters are listed in Table 1. The coordination environment of each copper(II) ion is a square pyramid with a τ factor value of 0.008 ($\tau = 0$ and 1 for ideal square-pyramidal and trigonal-bipyramidal geometries, respectively).[20] The basal plane of the square pyramid is formed by two amidate nitrogen atoms with Cu–N distances of 1.966–1.986 Å and two carboxylate oxygen atoms with Cu–O distances of 1.956–2.007 Å from the oxamate groups of the $mpba^{4-}$ ligands. The apical positions are occupied by two nitrogen atoms from two azide groups with longer Cu–N bond lengths of 2.464–2.468 Å. Each azide group adopts an end-on fashion to bridge two copper ions in apical–apical positions, thus a metallamacrocycle is formed. The angle Cu(1)–N(5)–Cu(2) is 123.9(3)°, and the Cu···Cu(2) distance is 4.353 Å. Within the dinuclear copper(II) metallacyclophane unit, the dihedral angle and the average separation of two benzene planes are 8.8° and 3.4 Å, respectively. Thus two aromatic rings are in an almost parallel arrangement and perform a perfect face-to-face π–π alignment, which is similar to those reported in related compounds.[13] The copper basal planes are disposed almost perpendicularly to the phenylene planes (dihedral angles of 81.7–89.3°), and the Cu···Cu separation is 6.703 Å.

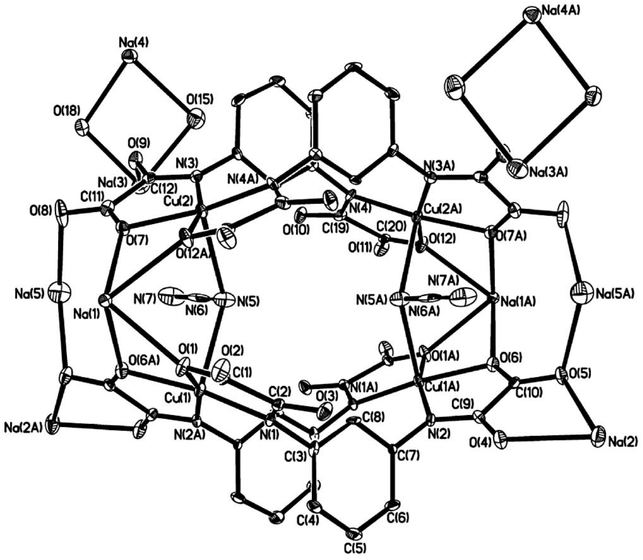

Figure 1. Molecular structure of complex **1** with 30 % thermal ellipsoids and the atom labeling.

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

Cu(1)–O(1)	1.956(5)	Cu(2)–O(12)	1.961(5)
Cu(1)–N(2A)	1.966(6)	Cu(2)–N(3)	1.967(6)
Cu(1)–N(1)	1.986(6)	Cu(2)–N(4)	1.978(6)
Cu(1)–O(6A)	2.007(5)	Cu(2)–O(7)	1.991(5)
Cu(1)–N(5)	2.468(7)	Cu(2)–N(5)	2.464(8)
O(1)–Cu(1)–N(2A)	164.3(2)	O(12A)–Cu(2)–N(3)	164.3(2)
O(1)–Cu(1)–N(1)	83.3(2)	O(12A)–Cu(2)–N(4A)	82.9(2)
N(2A)–Cu(1)–N(1)	106.0(2)	N(3)–Cu(2)–N(4A)	106.4(2)
O(1)–Cu(1)–O(6A)	85.7(2)	O(12A)–Cu(2)–O(7)	85.0(2)
N(2A)–Cu(1)–O(6A)	82.6(2)	N(3)–Cu(2)–O(7)	83.1(2)
Cu(2)–N(5)–Cu(1)	123.9(3)	N(7)–N(6)–N(5)	176.4(10)

[a] Symmetry transformations used to generate equivalent atoms: A: $-x + 2$, y, $-z + 3/2$.

Each $[\{Cu_2(mpba)_2\}_2(\mu_{1,1}-N_3)_2]^{10-}$ anion is linked by two sodium cations [Na(1), Na(1A)] to form a 1D chain (Figure 2). The Na(1) is six-fold coordinated by four oxygen atoms [O(1), O(7), O(6A), O(12A)] of the oxamato ligands and two oxygen atoms [O(2), O(11)] from another metallamacrocycle. The Na(1)···Na(1A) distance is 3.625 Å. Furthermore, these 1D chains are self-assembled through Na(2), Na(3), Na(4), Na(5), and water molecules to give a three-dimensional network (Figure 3). Interestingly, in this 3D network, there exist linear tetranuclear sodium units in which the adjacent sodium ions are bridged by two water molecules, and this linear tetranuclear sodium unit links two metallamacrocycle entities through two sodium cations [Na(3), Na(3A)] (Figure S1).

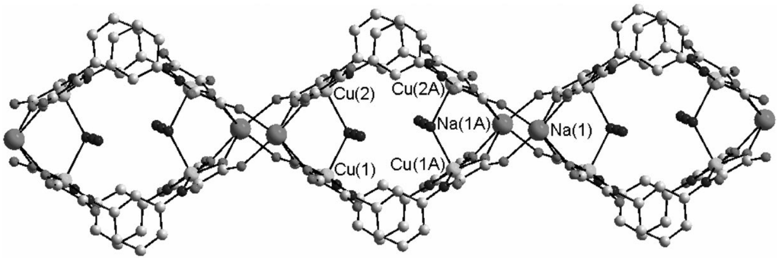

Figure 2. Perspective view of the 1D chain of the $[\{Cu_2(mpba)_2\}_2(\mu_{1,1}\text{-}N_3)_2]^{10-}$ anion linked by Na(1) and Na(1A).

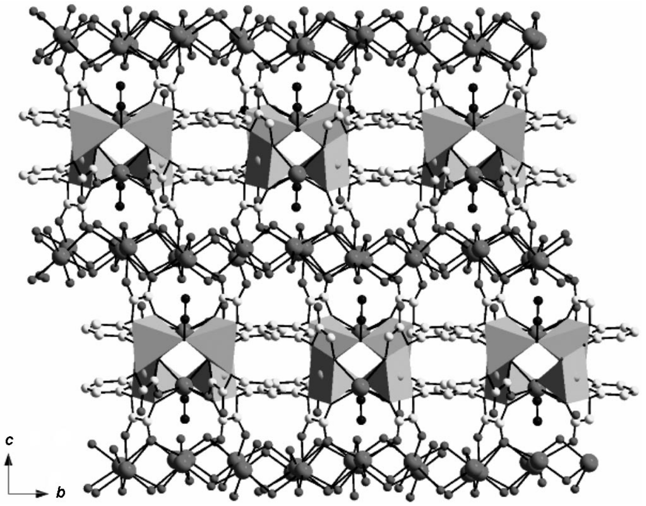

Figure 3. The 3D framework of **1** along the *a* axis.

It should be emphasized that this kind of structure, that is, first, a metallamacrocycle formed by oxamato-bridged dinuclear copper, and second, the supramolecular three-dimensional architecture through hydrated Na^+ cations, is very rare.

Structure Description of Complex 2

The molecular structure of complex **2** with the atom labeling is shown in Figure 4. Complex **2** consists of 2D brick-wall-like layers assembled by dinuclear copper(II) metallacyclophane $[Cu_2(mpba)_2]^{4-}$ anions and copper(II) ions. Selected bond lengths and angles are listed in Table 2. There are four crystallographically different copper atoms in **2**: Cu(1), Cu(2), Cu(3), and Cu(4). Cu(3) and Cu(4) have distorted square-pyramidal geometries in which two amidate nitrogen atoms and two carboxylate oxygen atoms from the oxamate groups of two $mpba^{4-}$ ligands are coordinated to the metal atom to form the dinuclear copper metallacyclophane anion. The distortion parameters of the square-pyramidal geometry are τ = 0.11 and 0.13 for Cu(3) and Cu(4), respectively. The average Cu–O and Cu–N distances are 1.983 Å and 1.961 Å, respectively, which are in agreement with those observed in **1**. The apical positions of two square pyramids are occupied by water molecules with Cu–O distances of 2.337(9) Å and 2.370(8) Å, which are significantly longer than the basal ones. The coordination geometry around the Cu(1) atom is a distorted octahedron with additional trigonal distortion with three carboxylate oxygen atoms [O(1), O(10A), O(11A)] from two $mpba^{4-}$ ligands and three water molecules [O(13), O(14), O(15)]. The Cu–O bond lengths span a large range from 2.376(6) Å to 2.434(6) Å. The Cu(2) atom lies in the coordination geometry of a distorted trigonal bipyramid completed by two carboxylate oxygen atoms [O(4), O(7)] from two $mpba^{4-}$ ligands with Cu–O distances of 2.362(6) Å and three water molecules [O(16), O(17), O(18)] with Cu–O distances in the 2.358(8)–2.393(10)-Å range. The τ value is 0.84. Two other oxygen atoms, O(5) and O(8), from the $mpba^{4-}$ ligands are pseudocoordinated to Cu(2) with Cu–O bond lengths of 2.454 and 2.457 Å, respectively.

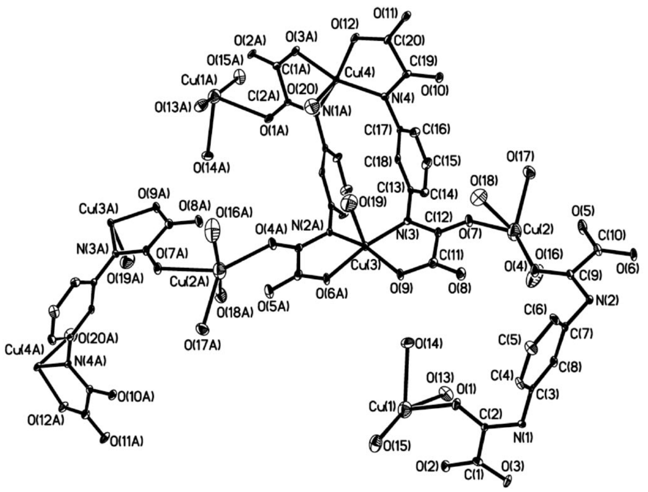

Figure 4. Structure of complex **2** with 30% thermal ellipsoids and the atom labeling. The uncoordinated water molecules are omitted for clarity.

Each brick is formed by slightly distorted Cu_{10} rectangles (Figure 5) in which two dinuclear copper(II) metallacyclophane units act as the two shorter edges (6.568 Å). The length of each longer edge formed by five copper atoms is 21.694 Å, which is equal to the *b* axis of the unit cell. The 2D brick-wall-like sheet shows the corrugated layer, and each layer is packed on top of another, corner to corner, in a perfect stack (Figure S2), similar to that observed in complex $[Co_2Cu_2(mpba)_2(H_2O)_6]\cdot 6H_2O$.[14] The shortest Cu···Cu interlayer distance is 5.655 Å. The uncoordinated water molecules are included between the layers, and hydro-

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

Cu(1)–O(1)	2.376(6)	Cu(2)–O(5)	2.454
Cu(1)–O(15)	2.379(8)	Cu(2)–O(8)	2.457
Cu(1)–O(13)	2.383(7)	Cu(3)–N(3)	1.950(7)
Cu(1)–O(10A)	2.398(6)	Cu(3)–N(2B)	1.963(7)
Cu(1)–O(14)	2.407(7)	Cu(3)–O(9)	1.983(6)
Cu(1)–O(11A)	2.434(6)	Cu(3)–O(6B)	1.981(6)
Cu(1)–O(2)	2.452	Cu(3)–O(19)	2.337(9)
Cu(2)–O(18)	2.358(8)	Cu(4)–N(1B)	1.954(7)
Cu(2)–O(7)	2.362(6)	Cu(4)–O(12)	1.976(6)
Cu(2)–O(4)	2.362(6)	Cu(4)–N(4)	1.977(7)
Cu(2)–O(17)	2.383(8)	Cu(4)–O(3B)	1.991(6)
Cu(2)–O(16)	2.393(10)	Cu(4)–O(20)	2.370(8)
O(1)–Cu(1)–O(11A)	141.5(2)	N(3)–Cu(3)–N(2B)	103.6(3)
O(15)–Cu(1)–O(14)	110.2(3)	O(6B)–Cu(3)–O(9)	88.5(2)
O(1)–Cu(1)–O(13)	89.3(3)	O(6B)–Cu(3)–N(3)	170.8(3)
O(15)–Cu(1)–O(10A)	91.6(3)	N(3)–Cu(3)–O(19)	95.3(3)
O(7)–Cu(2)–O(4)	146.6(2)	N(4)–Cu(4)–O(12)	82.2(3)
O(18)–Cu(2)–O(16)	164.5(4)	N(4)–Cu(4)–O(20)	97.3(3)
O(7)–Cu(2)–O(17)	77.0(2)	O(12)–Cu(4)–O(20)	92.4(3)
O(7)–Cu(2)–O(18)	89.2(3)	N(4)–Cu(4)–O(3B)	161.7(3)

[a] Symmetry transformations used to generate equivalent atoms: A: $x + 1, y, z$; B: $-x + 1, y + 1/2, -z + 1/2$.

gen bonding interactions are present in **2** by the coordinated and free water molecules linking the carboxylate oxygen atoms of the oxamate moieties.

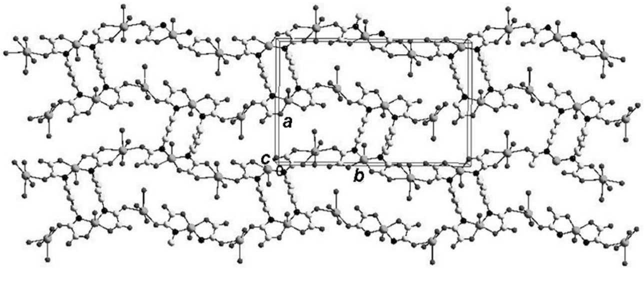

Figure 5. View of the structure of the 2D brick-wall-like layer. The uncoordinated water molecules are omitted for clarity.

Magnetic Properties

The magnetic susceptibilities of complex **1** were measured in the range 2–300 K in an external magnetic field of 1000 Oe, and the magnetic behavior is shown in Figure 6. The value of μ_{eff} at 300 K is 3.77 μ_B; as the temperature decreases, the μ_{eff} values gradually increase and reach a maximum of 3.99 μ_B at 9.0 K, then they decrease quickly to 3.40 μ_B at 2.0 K, suggesting an operative ferromagnetic interaction in **1**. The reciprocal susceptibility varies as the temperature follows the Curie–Weiss law in the whole temperature range, with a positive Weiss constant, $\theta = 0.91$ K, and Curie constant, $C = 1.77\ \text{cm}^3\,\text{K}\,\text{mol}^{-1}$. The positive Weiss constant supports the ferromagnetic interaction.

As described above, the coordination geometry around each copper(II) ion is square-pyramidal. Thus, the magnetic orbitals at copper(II) ions are defined by short equatorial bonds, and they are of $d_{x^2-y^2}$ type, possibly with some d_{z^2} character. Since the azide group links two copper atoms at axial–axial positions and the out-of-plane exchange pathway is involved, the magnetic coupling mediated by the azido ligand should be weak. Therefore, the present tetranuclear magnetic system can be simplified as a dinuclear copper(II) interaction though the cyclophane moiety. The magnetic data are analyzed by the Bleaney–Bowers equation[21] with the Hamiltonian in the form $\hat{H} = -J\hat{S}_1\hat{S}_2$ Considering weak magnetic coupling transmitted by azido ligands, the mean field approximation, zJ', was introduced.[22] The magnetic exchange pathways are presented in Figure 7. The best fitting of the experimental data leads to $g = 2.14$, $J = 15.10\ \text{cm}^{-1}$, $zJ' = -1.12\ \text{cm}^{-1}$and $R = 2.96 \times 10^{-4}$ (R is defined as $\sum[(\chi_M)_{\text{obs}} - (\chi_M)_{\text{calc.}}]^2/\sum[(\chi_M)_{\text{obs}}]^2$. The J value is consistent both in sign and magnitude with those previously reported.[13] The ferromagnetic coupling observed in **1** results from the spin polarization effects, which lead to the alternation of spin density at the double *m*-phenylenediamide bridging framework.[13a,23] The weak antiferromagnetic coupling transmitted by the azido bridging ligands can be ascribed to the larger angle of Cu–N–Cu [123.9(3)°]. As known, the interaction through an end-on azido bridge is ferromagnetic for lower Cu–N–Cu angles and antiferromagnetic for higher angles. The critical angle is 108° according to empirical analyses[24] and 104° accord-

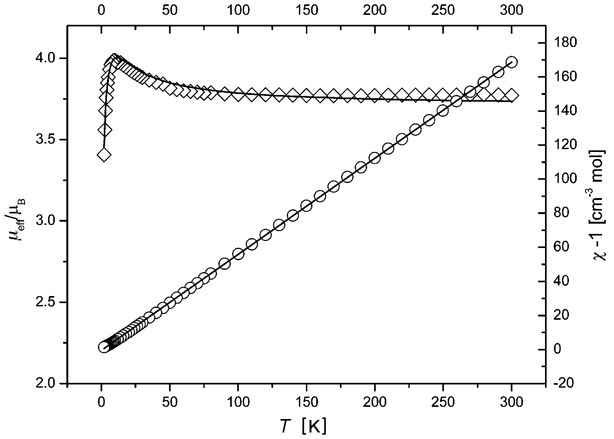

Figure 6. Plots of the μ_{eff} and χ^{-1} vs. T for complex **1**. The solid line represents the curve obtained with the best-fitted parameters.

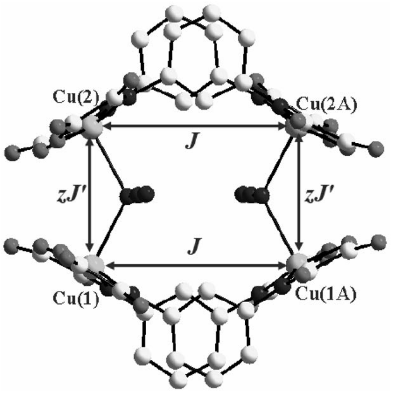

Figure 7. The magnetic exchange pathways between the local spins in complex **1**.

ing to a density functional study.[25] The antiferromagnetic coupling in **1** is in agreement with the above trends. However, it should be noted that the trends are based on the symmetric basal–basal end-on azido bridges, while, in complex **1**, the azide groups are disposed in a symmetric apical–apical end-on fashion. No other magnetic and structural data are available to investigate the magnetostructural correlations for this type of bridge.

Conclusions

Working with the versatile azido ligand, we synthesized two new (oxamato)copper(II) complexes from the dinuclear copper(II) complex of the *meta*-phenylenebis(oxamato) ligand. Complex **1** shows an interesting metallamacrocycle structure bridged by azido ligands. This is the first metallamacrocycle obtained by using dinuclear copper(II) metallacyclophane. In **1**, the azide group adopts an end-on mode to bridge two copper(II) ions in apical–apical positions; to the best of our knowledge, this is first example with this kind of bridging in (azido)copper(II) complexes. Complex **1** exhibits strong ferromagnetic coupling through the *m*-phenylenediamide bridge, owing to spin polarization. Complex **2** is the second example of a brick-wall sheet structure to be found in oxamato-bridged complexes. This contribution exemplifies a strategy to obtain oxamate-based materials with unique interesting structural and magnetic properties.

Experimental Section

Materials: All the starting chemicals were of AR grade and used as received. The ligand 1,3-phenylenebis(ethyl oxamate-*N*,*N′*) (H_2Et_2mpba) and the precursor $Na_4[Cu_2(mpba)_2]\cdot 10H_2O$ were prepared according to literature methods.[13a]

Physical Measurements: Elemental analyses for C, H, and N were carried out with a Perkin–Elmer 240 elemental analyzer. The infrared spectra were recorded from KBr pellets in the range 4000–400 cm^{-1} with a Bruker Tensor 27 IR spectrometer. Variable-temperature magnetic susceptibilities were measured with an MPMS XL-7 SQUID magnetometer. Diamagnetic corrections were made with Pascal's constants for all the constituent atoms.

CAUTION! Although not encountered in our experiments, azido complexes of metal ions are potentially explosive and should be handled with care.

$Na_{10}[\{Cu_2(mpba)_2\}_2(\mu_{1,1}\text{-}N_3)_2]\cdot 18H_2O$ (1): H_2Et_2mpba(0.1 g, 0.26 mmol) was suspended in water (15 mL) in a flask. NaOH (0.05 g, 1.25 mmol) dissolved in water (10 mL) was added. After stirring for 15 min at room temperature until complete dissolution, $Cu(NO_3)_2\cdot 3H_2O$ (0.062 g, 0.26 mmol) in water (5 mL) was added dropwise whilst stirring. After stirring for 10 min, solid NaN_3 (0.032 g, 0.5 mmol) was added. After stirring for 2 h, the resulting deep green solution was filtered, and the filtrate was kept at room temperature so that the solvent could evaporate slowly. Deep green crystals were collected after three weeks. Yield: 76%. $C_{40}H_{52}Cu_4N_{14}Na_{10}O_{42}$ (1885.00): calcd. C 25.48, H 2.78, N 10.40; found C 25.37, H 2.87, N 9.37. IR spectra: ṽ = 2030 (vs), 1687 (vs), 1638 (vs), 1569 (vs), 1480 (m), 1336 (vs), 986 (w), 865 (s), 830 (m) cm^{-1}.

$[\{Cu_2(mpba)_2\}Cu_2(H_2O)_8]\cdot 6H_2O$ (2): Bright green single crystals of **2** were grown in water solution by a slow diffusion method using an H-shaped tube. The starting solution was $Na_4[Cu_2(mpba)_2]\cdot 10H_2O$ in one arm and NaN_3 in the other arm. After one month, a few bright green crystals were separated. IR spectra: ṽ = 1660 (vs), 1481 (m), 1421 (m), 1326 (vs), 996 (w), 866 (s), 757 (m) cm^{-1}.

X-ray Crystallography: Diffraction intensity data for single crystals of **1** and **2** were collected at room temperature with a Bruker SMART 1000 CCD diffractometer employing graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å). The structures were solved by direct methods and refined by full-matrix least-squares on F^2 with the SHELXS 97[26] and SHELXL 97[27] programs, respectively. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were placed in calculated positions and refined isotropically by using riding model. Pertinent crystallographic data and structure refinement parameters are summarized in Table 3.

Table 3. Crystal data and structure refinement for **1** and **2**.

	1	**2**
Empirical formula	$C_{20}H_{26}N_7Na_5O_{21}Cu_2$	$C_{20}H_{36}N_4O_{26}Cu_4$
M_r	942.51	1002.69
T [K]	294(2)	294(2)
λ(Mo-K_α) [Å]	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$C2/c$	$P2_1/c$
a [Å]	13.259(3)	13.9838(18)
b [Å]	20.591(4)	21.694(3)
c [Å]	24.931(5)	11.6684(15)
β [°]	96.201(3)	93.150(2)
V [Å^3]	6767(2)	3534.4(8)
Z	8	4
D_c [g cm^{-3}]	1.850	1.884
μ [mm^{-1}]	1.419	2.478
θ range [°]	1.64–25.02	1.46–25.01
unique reflns./R_{int}	5993/0.0817	6105/0.0417
GOF	1.022	1.052
$R1$[a] [$I > 2\sigma(I)$]	0.0682	0.0873
$wR2$[b] (all data)	0.2106	0.2654

[a] $R1 = \Sigma(||F_0| - |F_c||)/\Sigma|F_0|$. [b] $wR2 = [w(|F_0|^2 - |F_c|^2)^2/(w|F_0|^2)^2]^{1/2}$.

CCDC-649641 and -649642 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supporting Information (see footnote on the first page of this article): View of the linear tetranuclear sodium unit in complex **1** and the stacking of 2D brick-wall-like sheets in complex **2**.

Acknowledgments

This work was supported by the National Science Foundation of China (Nos. 20471032, 50672037).

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Received: October 10, 2007