A New Dinuclear Copper(II) Complex of a Bis-macrocyclic Ligand: Synthesis, Characterization, Crystal Structure and Magnetic Properties

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A new dinuclear Cu(II) complex, $[Cu_2L(N_3)_2](ClO_4)_{1.5}\cdot(OH)_{0.5}\cdot2H_2O\cdot0.5C_2H_5OH$ (1), of a bis-macrocyclic ligand, 2,6-bis(1,4,7,10-tetraazacyclododecan-10-ylmethyl)-methoxybenzene (L), has been synthesized, characterized and structurally determined by X-ray diffraction analysis. Complex 1 crystallizes in orthorhombic crystal system, $Pca2(1)$ space group with $a = 1.5371(3)$, $b = 1.6641(3)$, $c = 3.0950(6)$ nm, $V = 7.917(3)$ nm^3, $F_w = 904.62$, $Z = 8$, $D_c = 1.529$ g/cm^3, and final $R = 0.0568$, $wR = 0.1406$ for 10410 observed reflections with $I \geqslant 2\sigma(I)$. Both Cu(II) centers in the structure are coordinated by four nitrogen atoms of 1,4,7,10-tetraazacyclododecane (cyclen) and a nitrogen donor of the axial azide anion. Each Cu(II) center is in a square-pyramidal coordination environment, and the intra- and nearest inter-molecular Cu···Cu nonbonding distances are 0.9855 and 0.7298 nm, respectively. Variable temperature magnetic susceptibility measurements in the range of 4.2—300 K indicate that there exists weak intra- and inter-molecular antiferromagnetic coupling between the Cu(II) centers with $2J = -4.2$ cm^{-1} and $\Theta = -0.47$ K.

Keywords   Binuclear Cu(II) complex, bis-macrocyclic ligand, crystal structure, magnetic properties

Considerable attention and effort have been devoted to the study of transition metal complexes with di-, tri- and tetra-azacyclic polyamines[1-3] and bis-macrocyclic ligands.[4-6] The ligands comprising two macrocycles can form a variety of stable dinuclear complexes with metal ions such as Mn(II/III), Fe(II/III), Co(II/III), Cu(II) and Zn(II).[7] Complexes of these kinds of ligands are interesting not only for the electronic interactions that take place between the metal ions, but also for their reactivity towards small molecules. They may show interesting magnetic behavior,[8] especially for dinuclear Cu(II) complexes, which exemplify the simplest case that two unpaired electrons at two paramagnetic ions are separated by organic spacer ligands, or may serve as models for metalloenzymes.[9]

Although macrocycles linked *via* polymethylene bridges have been well studied,[10] the ligands containing two macrocycles bridged by phenyl groups are relatively rare.[11,12] As a continuation of our work, we report herein the synthesis, characterization, crystal structure, and magnetic properties of a new dinuclear Cu(II) complex of 2,6-bis(1,4,7,10-tetraazacyclododecan-10-ylmethyl) methoxybenzene (L) (Scheme 1).

Experimental
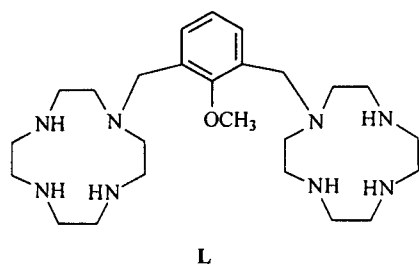
Materials and general methods

The ligand L was synthesized according to the literature method.[11] All other reagents and solvents for syntheses were of analytical grade. FT-IR spectra (KBr pellets) were taken on a FT-IR 170 SX (Nicolet) spectro-

Scheme 1

L

oeter and electronic absorption spectra on a Hitachi UV-3010 spectrophotometer. Carbon, hydrogen, and nitrogen analyses were performed on a Perkin-Elmer 240C analyzer. Conductivity measurement was taken at room temperature using a DDS 11A conductometer. The variable temperature magnetic susceptibilities were measured on a SQUID magnetometer in the 4.2—300 K temperature range. The susceptibilities were corrected for diamagnetism with Pascal's constants for all the constituent atoms, and magnetic moments were calculated by the equation $\mu_{eff} = 2.828(\chi_M T)^{1/2}$.

Preparation of title complex **1**

[$Cu_2L(N_3)_2$](ClO_4)$_{1.5}$ · (OH)$_{0.5}$ · 2H$_2$O · 0.5C$_2$H$_5$OH (**1**), was synthesized by mixing Cu(ClO$_4$)$_2$ · 6H$_2$O (76 mg, 0.2 mmol) and L · 7HBr · 2H$_2$O (104 mg, 0.1 mmol) in water/ethanol (25 mL). The pH value of this solution was adjusted to *ca.* 7—8 with dilute NaOH aqueous solution. The mixture was heated to ~ 80 ℃ with stirring, and then a water solution of excess NaN$_3$ (26 mg, 0.4 mmol) was added. The reaction mixture was filtered and left to stand at room temperature. Blue single crystals suitable for X-ray diffraction analysis were obtained by slow evaporation of the solvent (yield: 50%). FT-IR (KBr pellet) ν: 3442m, 2942w, 2126w, 2037s, 1630m, 1475m, 1459m, 1086vs, 638m, 626m cm^{-1}. Anal. calcd for C$_{26}$H$_{55.5}$Cl$_{1.5}$Cu$_2$N$_{14}$O$_{10}$: C 34.5, H 6.2, N 21.7; found: C 34.4, H 6.3, N 21.6. Λ$_M$(H$_2$O): 256 cm^2 · Ω^{-1} · mol^{-1}.

Crystallographic study

The reflection data were collected on a Bruker Smart 1000 CCD diffractometer equipped with a graphite crystal monochromator situated in the incident beam. The determination of unit cell parameters and data col-

lections were performed with Mo K_α radiation (λ = 0.071073 nm). Reflections in the range 1.22 ≤ θ ≤ 25.05° were collected at room temperature. The structure was solved by direct methods and semi-empirical absorption corrections were applied by SADABS program. Cu(II) atoms in the complex were located from E-maps. All non-hydrogen atoms were determined by successive Fourier syntheses and refined isotropically. The final structure was refined by full matrix least-squares methods with anisotropic thermal parameters for non-hydrogen atoms on F^2. The hydrogen atoms were added theoretically, riding on the concerned atoms and refined with fixed thermal factors. The crystallographic and refinement data for **1** are summarized in Table 1.

Table 1   Crystallographic data and the structure refinement summary for complex **1**

Formula	C$_{26}$H$_{55.5}$Cl$_{1.5}$Cu$_2$N$_{14}$O$_{10}$
F_w	904.62
Crystal system	orthorhombic
Space group	$Pca2(1)$
a (nm)	1.5371(3)
b (nm)	1.6641(3)
c (nm)	3.0950(6)
V (nm^3)	7.917(3)
Z	8
D_c (g/cm^3)	1.529
μ (mm^{-1})	1.243
T (K)	298(2)
No. of unique data	13961
No. of observed data [$I \geq 2\sigma \geq (I)$]	10410
Parameters refined	955
R	0.0568
wR	0.1406
S	1.003
Max residual peak and hole (e/nm^3)	987 and − 510

Results and discussion

Synthesis and general characterization

The synthesis of **1** was achieved by the reaction of the acid-free ligand **L** with Cu(ClO$_4$) · 6H$_2$O. Since the corresponding ligand is of HBr salt, it must be neutralized with NaOH prior to complexation. The electrical conductance value in water solution indicates that **1** behaves as a 2 : 1 electrolyte,[13] which is consistent with the

crystal structure in solid state. The IR spectrum shows absorption bands resulting from the skeletal vibrations of benzene ring in 1400—1600 cm^{-1} region. The absorption bands of ClO_4^- appear at 1086 and 626 cm^{-1} and it exhibits strong absorption bands at 2126, 2037 and 638 cm^{-1} due to the ν_{N-N} stretch of the apical coordination azide anions. The electronic spectrum in aqueous solution shows a *d-d* absorption peak at 605 nm, which is typical for penta-coordinated Cu(II) complex with distorted square-pyramidal geometry.[14] In addition, several strong characteristic absorptions at 200—350 nm can be assigned to the $\pi \rightarrow \pi^*$ transitions of the ligand.

Description of crystal structure

The structure of the title complex consists of discrete $[Cu_2L(N_3)_2]^{2+}$ cations, ClO_4^-/OH^- counter anions, and water/ethanol solvate molecules. It is noted that two symmetry-independent units without significant difference are presented in this structure.

An ORTEP plot of $[Cu_2L(N_3)_2]^{2+}$ is presented in Fig. 1, and the selected bond distances and ngles are listed in Table 2. Each Cu(II) center is peñ__-coordinated by four nitrogen donors of cyclen forming the basal plane and a nitrogen atom of the azide anion occupying the axial site. The coordination geometry around each Cu(II) center can be best described as a square pyramid close to C_{4v} symmetry, which can be reflected by τ value defined by Addison *et al*. ($\tau = 0$ for an ideal square-pyramid, and $\tau = 1$ for an ideal trigonal bipyramid).[15]

In this complex, the τ values for Cu(1) and Cu(2) are 0.095 and 0.043, respectively, indicating slight distortion from ideal square-pyramidal coordination geometry for both Cu(II) centers. The Cu(1) and Cu(2) atoms are 0.05356 and 0.05565 nm above the relative least-square planes defined by four N atoms of the cyclen, which are nearly in parallel position with the dihedral angle of 152°. The dihedral angles between the phenyl ring plane and the two N_4 planes are 13.7° and 15.0°, respectively. The methoxy group does not take part in coordination with the Cu(II) centers due to its lower coordination ability and steric hindrance between the two cyclen rings, which is similar as a related complex reported in literature.[11]

In this complex, the Cu—N bond distances are in the range of 0.2008(7)—0.2147(12) nm, which are normal Cu—N coordination bonds. The axial Cu—N_{azide} bond distances are slightly longer than those of the Cu—N_{cyclen} bonds in the basal plane probably due to the Jahn-Teller effect. The two Cu(II) centers are separated at 0.9855 nm, which may offer a good model system for the study of two almost independent metal centers in one complex. The intermolecular Cu···Cu nonbonding distances of two independent $[Cu_2L(N_3)_2]^{2+}$ cations are 0.7298 and 0.9612 nm, respectively, even shorter than the intramolecular Cu···Cu distance. Another notable feature of **1** is that it is in the chiral non-centric space group $Pca2(1)$ with flack parameter of 0.0226 (near zero), indicating the correct absolute configuration.
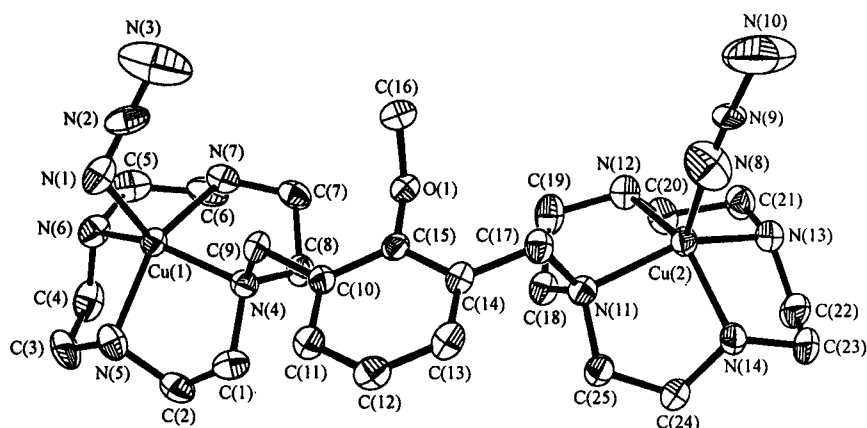

Fig. 1 ORTEP view of $[Cu_2L(N_3)_2]^{2+}$ with 30% probability thermal ellipsoids.

**Table 2**   Selected bond distances (10^{-1} nm) and angles (°) of complex **1**

Bond distance			
Cu(1)—N(1)	2.122(8)	Cu(1)—N(4)	2.055(6)
Cu(1)—N(5)	2.017(7)	Cu(1)—N(6)	2.023(7)
Cu(1)—N(7)	2.017(7)	Cu(2)—N(8)	2.141(12)
Cu(2)—N(11)	2.057(7)	Cu(2)—N(12)	2.056(7)
Cu(2)—N(13)	2.012(7)	Cu(2)—N(14)	2.008(7)
Bond angles			
N(5)-Cu(1)-N(7)	146.5(3)	N(5)-Cu(1)-N(6)	85.6(3)
N(7)-Cu(1)-N(6)	86.1(3)	N(5)-Cu(1)-N(4)	85.9(3)
N(7)-Cu(1)-N(4)	86.5(3)	N(6)-Cu(1)-N(4)	152.2(3)
N(14)-Cu(2)-N(13)	84.9(3)	N(14)-Cu(2)-N(12)	146.9(3)
N(13)-Cu(2)-N(12)	87.0(3)	N(14)-Cu(2)-N(11)	85.5(3)
N(13)-Cu(2)-N(11)	149.5(3)	N(12)-Cu(2)-N(11)	85.3(3)

Magnetic properties

The magnetic behavior of complex **1** is illustrated in Fig. 2 by means of $\chi_M(\mu_{eff})$ *vs*. T in the 300—4.2 K temperature range. The room temperature magnetic mo-

ment μ_{eff} is 2.58 μ_B and it decreases slowly upon cooling. The single-triplet energy gap ($2J$) was deduced from the least-squares fit of the experimental data to the temperature for isotropic exchange by using a Bleaney-Bowers equation[16] for coupling Cu(II) dimer:

$$\chi_M = 2Ng^2\beta^2/K(T - \Theta)[3 + \exp(-2J/KT)]^{-1}(1 - \rho) + Ng^2\beta^2\rho/2KT + N_\alpha \qquad (1)$$
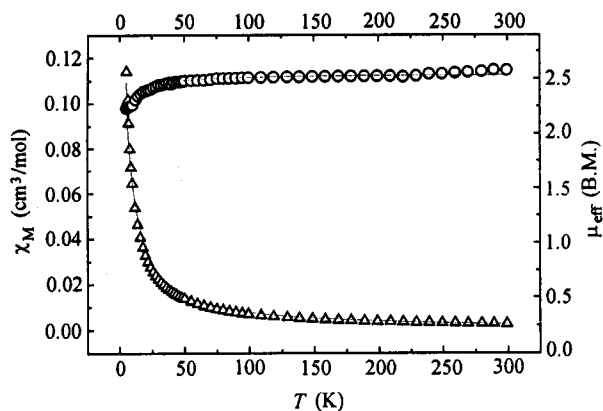
Fig. 2   Magnetic coupling diagram of complex **1**.

Eq. (1) results from a consideration of the eigen-values of $H = -2JS_1S_2$, of the Heisenberg exchange Hamilton for the two interacting $S = 1/2$ centers. N_α is the temperature independent paramagnetism (120×10^{-6} cm^{-1}), ρ represents the fraction of a possible magnetically dilute impurity, Θ is Weiss-type correction of the intermolecular interaction, and other symbols have their usual meanings. The results of the best fit for **1** were using a nonlinear analysis with g, J, ρ, Θ as variables

obtained as $g = 2.08$, $J = -2.1$ cm^{-1}, $\rho = 0.006$ and $\Theta = -0.47$ K. The agreement factor F is defined as $\Sigma[(\chi_M)_{obs} - (\chi_M)_{calc}]^2/\Sigma(\chi_M)_{obs}^2 = 8.4 \times 10^{-5}$. These values imply that there exists a weak intramolecular anti-ferromagnetic interaction within each bimeric cation, which may be due to the fact that the intramolecular Cu···Cu nonbonding distance is rather large and no direct bridges link the two Cu(II) centers. Furthermore, weak antiferromagnetic interaction is also found in inter-molecular Cu···Cu centers, which may be caused by the shorter distances between the Cu(II) centers.[17]

References

1   (a) Grapperhaus, C. A.; Darensbourg, M. Y. *Acc. Chem. Res.* **1998**, *31*, 451.

(b) Bu, X. H.; Du, M.; Shang, Z. L.; Zhang, R. H.; Liao, D. Z.; Shionoya, M.; Clifford, T. *Inorg. Chem.* **2000**, *39*, 4190.

(c) Bu, X. H.; Du, M.; Zhang, L.; Liao, D. Z.; Tang, J. K.; Zhang, R. H.; Shionoya, M. *J. Chem. Soc.*, *Dalton Trans.* **2001**, 593.

(d) Bu, X. H.; Du, M.; Zhang, L.; Shang, Z. L.; Zhang, R. H.; Shionoya, M. *J. Chem. Soc.*, *Dalton*

Trans. **2001**, 729.

(e) Bu, X. H.; Du, M.; Shang, Z. L.; Zhang, L.; Zhao, Q. H.; Zhang, R. H.; Shionoya, M. *Eur. J. Inorg. Chem.* **2001**, 1551.

2 (a) Halcrow, M. A.; Christou, G. *Chem. Rev.* **1994**, *94*, 2421.

(b) Wainwright, K. P. *Chem. Rev.* **1997**, *166*, 35.

3 (a) Kimura, E.; Bu, X. H.; Shionoya, M.; Wada, S.; Maruyama, S. *Inorg. Chem.* **1992**, *31*, 4542.

(b) Bu, X. H.; An, D. L.; Chen, Y. T.; Shionoya, M.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1995**, 2289.

(c) Bu, X. H.; An, D. L.; Cao, X. C.; Zhang, R. H.; Clifford, T.; Kimura, *E. J. Chem. Soc., Dalton Trans.* **1998**, 2247.

(d) Bu, X. H.; Cao, X. C.; An, D. L.; Zhang, R. H.; Clifford, T.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1998**, 431.

4 (a) Bossek, U.; Hummel, H.; Weyermuller, T.; Wieghardt, K.; Russell, S.; van der Wolf, L.; Kolb, U. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1552.

(b) Fallon, G. D.; McLachlan, G. A.; Moubaraki, B.; Murray, K. S.; O'Brien, L.; Spiccia, L. *J. Chem. Soc., Dalton Trans.* **1997**, 2765.

(c) Brudenell, S. J.; Spiccia, L.; Bond, A. M.; Fallon, G. D.; Hockless, D. C. R.; Lazarev, G.; Mahon, P. J.; Tiekink, E. R. T. *Inorg. Chem.* **2000**, *39*, 881.

5 Bu, X. H.; Lu, S. L.; Zhang, R. H.; Liao, D. Z.; Aoki, S.; Clifford, T.; Kimura, E. *Inorg. Chim. Acta* **2000**, *298*, 50.

6 (a) Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem.* **1996**, *29*, 4143.

(b) Haider, R.; Ipek, M.; DasGupta, B.; Yousaf, M.; Zompa, L. J. *Inorg. Chem.* **1997**, *36*, 3125.

7 Zhang, X.; Hsieh, W.; Margulis, T. N.; Zompa, L. J. *Inorg. Chem.* **1995**, *34*, 2883.

8 Kahn, O. *Molecular magnetism*, VCH publishers, New York, **1993**.

9 Sessler, J. L.; Sibert, J. W.; Lynch, V. *Inorg. Chem*, **1990**, *29*, 4143 and references therein.

10 Brudenell, S. J.; Spiccia, L.; Tielink, E. R. K. *Inorg. Chem.* **1996**, *35*, **1974** and references therein.

11 Xu, Q.; Du, M.; Zhang, R. H.; Shen, H. Y.; Bu, X. H.; Bu, W. M. *Chin. J. Chem.* **2000**, *18*, 358.

12 Kimura, E.; Aoki, S.; Koike, T.; Shiro, M. *J. Am. Chem. Soc.* **1997**, *119*, 3068 and references therein.

13 Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

14 McLachlan, G. A.; Fallon, G. D.; Martin, R. L.; Spiccia, L. *Inorg. Chem.* **1995**, *34*, 254.

15 (a) Addison, A. W.; Rao, T. N.; Reedijk, J.; Rijn, J. V.; Verschoor, G. C. *J. Chem. Soc., Dalton Trans.* **1984**, 1349.

(b) O'sullivan, C.; Murphy, G.; Murphy, B.; Hathaway, B. *J. Chem. Soc., Dalton Trans.* **1999**, 1835.

16 Tandon, S. S.; Thompson, L. K.; Manuel, M. E.; Bridson, J. N. *Inorg. Chem.* **1994**, *33*, 5555.

17 Chen, J. T.; Liao, D. Z.; Zhang, R. H.; Zhan, Y. L.; Lu, J. Y. *Chem. J. Chin. Univ.* **1993**, *12*, 1638 (in Chinese).