Open and Closed Conformations of Binuclear Cu(II) Complexes with a Bimacrocyclic Ligand Linked by a Tetramethylene Chain

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A binuclear Cu(II) complex with a bimacrocyclic ligand, $[Cu_2(OH_2)_2L](ClO_4)_4 \cdot 4H_2O$ (L: 7,7'-tetramethylene-bis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]) has the open conformation, in which the tetramethylene chain is staircase-like so that two macrocycles are as far apart as possible. $[Cu_2Cl_2L](ClO_4)_2 \cdot H_2O$ adopts the closed conformation, in which the tetramethylene chain is folded so that the two macrocycles face each other.

A number of binuclear metal complexes with bimacrocyclic ligands in which two macrocycles are linked by a polymethylene chain[1-8] are good systems for studies on metal-metal interactions and the effects of the proximate location of two metal ions. Linking two macrocycles often causes interesting problems in the structure of the bridged complex. For these bimacrocyclic complexes, two limiting conformations have been considered because of flexibility of the polymethylene bridges (see below): *i. e.*, (1) the open conformation where the polymethylene bridge elongates like a staircase and the two macrocycles are as far apart as possible, (2) the closed conformation where the bridge is folded and the two macrocycles face each other. Although bimacrocyclic complexes, linked by an *o*-phenylene[9] or *o*-xylene[10] bridge, in the closed conformation have been reported, all the bimacrocyclic complexes with a polymethylene bridge isolated and characterized by X-ray crystallography so far have been limited to the open conformation, to our knowledge.[3-5] In this communication, we report the first example of a bimacrocyclic Cu(II) complex in the closed conformation.

In order to investigate the conformation of polymethylene bridged bimacrocycles, we chose the bicopper(II) complex with the bimacrocyclic ligand linked with a tetramethylene chain,[1,2] because molecular models suggest that the tetramethylene chain is suitable, neither too long nor so short, for the formation of both open and closed conformations, and the closed conformation was necessary for the detail analysis of the seven-line hyperfine splitting of the ESR signal observed for the bicopper(II) complex.[3,7] Recrystallization of the perchlorate[1,2] of the bicopper(II) complex from water gave purple crystals of the complex with the open conformation[11] (Figure 1), which had a very similar structure to that reported for the bimacrocyclic Ni(II) complex[3] with the same ligand L, in spite of the coordination of the water molecules to the axial site. The two macrocycles are as

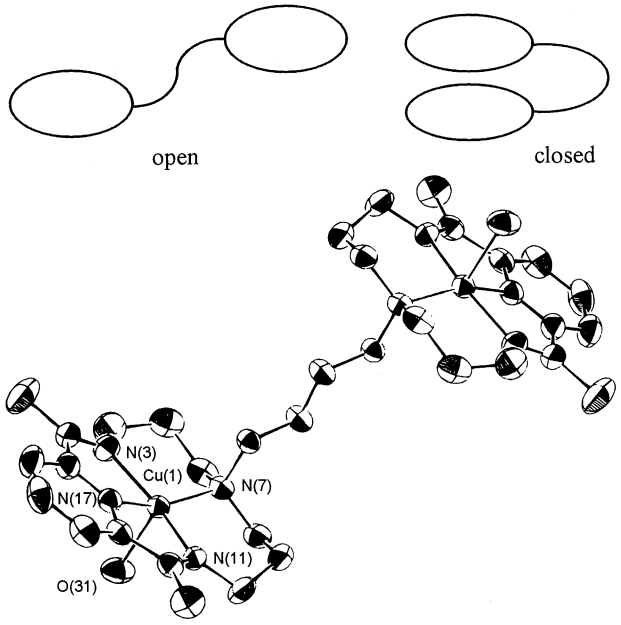

Figure 1. An ORTEP drawing for the complex cation in the open conformation, $[Cu_2L(OH_2)_4]^{4+}$. Selected bond distances (Å) and bond angles (°): Cu(1)-N(17) 1.929(5), Cu(1)-N(11) 2.022(5), Cu(1)-N(7) 1.976(5), Cu(1)-O(31) 2.227(6), Cu(1)-N(3) 2.023(7), N(17)-Cu(1)-N(11) 80.3(3), N(17)-Cu(1)-N(7) 156.4(3), N(17)-Cu(1)-O(31) 102.5(3), N(17)-Cu(1)-N(3) 79.9(3), N(11)-Cu(1)-N(7) 98.7(2), N(11)-Cu(1)-O(31) 95.8(2), N(11)-Cu(1)-N(3) 159.8(3), N(7)-Cu(1)-O(31) 101.0(3), N(7)-Cu(1)-N(3) 98.1(3), O(31)-Cu(1)-N(3) 91.9(3).

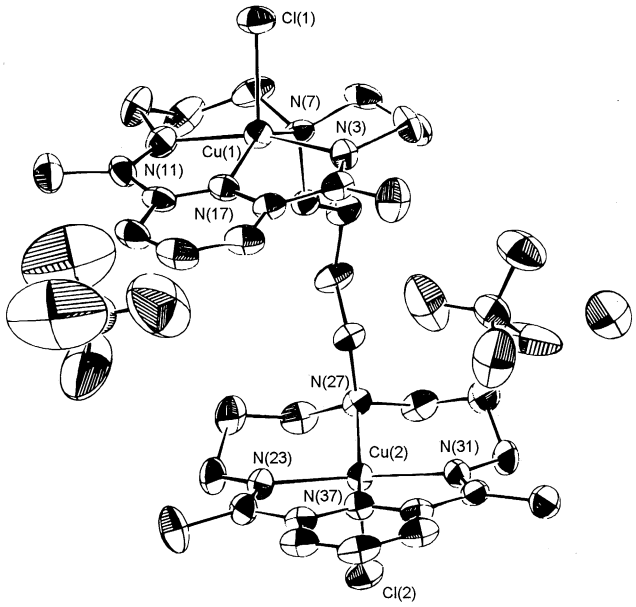

Figure 2. An ORTEP drawing for the complex in the closed conformation, $[Cu_2LCl_2](ClO_4)_2 \cdot H_2O$. Selected bond distances (Å) and bond angles (°): Cu(1)-Cl(1) 2.401(3), Cu(1)-N(7) 2.026(6), Cu(1)-N(17) 1.949(6), Cu(1)-N(11) 2.012(7), Cu(1)-N(3) 2.018(7), Cu(2)-Cl(2) 2.443(3), Cu(2)-N(27) 2.030(6), Cu(2)-N(31) 2.007(7), Cu(2)-N(37) 1.958(6), Cu(2)-N(23) 2.024(7), Cl(1)-Cu(1)-N(7) 103.4(2), Cl(1)-Cu(1)-N(17) 108.6(3), Cl(1)-Cu(1)-N(11) 96.7(2), Cl(1)-Cu(1)-N(3) 94.7(3), N(7)-Cu(1)-N(17) 148.0(3), N(7)-Cu(1)-N(11) 98.8(3), N(7)-Cu(1)-N(3) 96.0(3), N(17)-Cu(1)-N(11) 79.3(4), N(17)-Cu(1)-N(3) 80.1(3), N(11)-Cu(1)-N(3) 158.7(3), Cl(2)-Cu(2)-N(27) 100.4(2), Cl(2)-Cu(2)-N(31) 97.1(2), Cl(2)-Cu(2)-N(37) 109.4(2), Cl(2)-Cu(2)-N(23) 94.5(2), N(27)-Cu(2)-N(31) 98.9(3), N(27)-Cu(2)-N(37) 150.3(3), N(27)-Cu(2)-N(23) 97.7(3), N(31)-Cu(2)-N(37) 78.7(3), N(31)-Cu(2)-N(23) 157.6(3), N(37)-Cu(2)-N(23) 79.5(3).

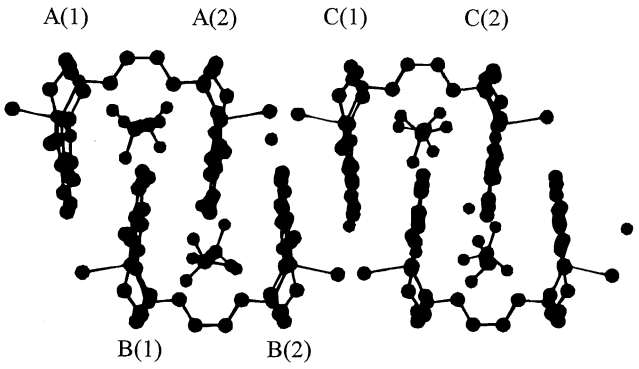

Figure 3. The stacking of the closed complex by partial overlap of pyridine rings: the distance between pyridine rings; 3.653 B(1)-A(2), 3.730 A(2)-B(2), 3.542 Å B(2)-C(1).

far apart as possible to minimize the electrostatic repulsion between the Cu(II) ions; the inversion center exists at the center of the tetramethylene bridge. This result led us to expect that the reduction of the electrostatic repulsion should enable the complex to adopt the closed conformation. Therefore, a chloride anion was used as a first trial for the reduction of the formal charge on the Cu(II) ions by the substitution of the coordinated water molecules; *i.e.*, the recrystallization of the perchlorate from water was performed in the presence of various amounts of NaCl. According to our expectations, the recrystallization in the presence of a 100-fold molar excess of NaCl yielded blue crystals of the chloride anion-coordinated square-pyramidal $[Cu_2Cl_2L](ClO_4)_2 \cdot H_2O$ in the closed conformation[11] (Figure 2).

In the closed conformation, the chloride anions actually coordinate to the Cu(II) ions so as to reduce the electrostatic repulsion between the Cu(II) ions. Additionally, the two perchlorates are located between the macrocycles, which can be assumed to attract the two Cu(II)-macrocyclic rings. In contrast to the case of the open conformation, the tetramethylene bridge is folded in the closed conformation so that the two macrocycles, having essentially the same structure, face each other; they are not completely face-to-face but are spread at an angle of ca. 23 degrees away from each other around the tetramethylene bridge. The distance between the Cu(II) ions accordingly becomes considerably shorter in the closed conformation (7.669(2)) than in the open conformation (9.366(1)).

As mentioned above, the reduction of the positive charge of the Cu(II) ions and the location of the perchlorates between the Cu(II) ions should be important for the formation of the closed conformation. One additional motive force toward the closed conformation was observed in the packing view of the crystal.[12] The stacking of pyridine rings is present in the closed conformation. As shown in Figure 3, two complexes overlie each other, and the pyridine rings of one complex partially overlap the pyridine rings of the other. The distance between the pyridine rings are 3.653, 3.730, and 3.542 for B(1)-A(2), A(2)-B(2),and B(2)-C(1), respectively, suggesting the presence of weak interactions between the pyridine rings.

Thus, the closed conformation was first characterized in the present study, and studies on effects of the length of the polymethylene bridge and of other counter anions are now in progress.

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11 Crystal data for $[Cu_2L(OH_2)_2](ClO_4)_4 \cdot 4H_2O$: $C_{34}H_{62}N_8O_{22}Cl_4Cu_2$, FW 1203.81, monoclinic, $P2_1/n$ (No. 14), a=18.35(1), b=10.68(1), c=12.798(8) Å, β=99.51(5) °, V=2473(3) Å^3, Z=2, Dcalcd=1.62 g cm^{-3}, μ=11.62 cm^{-1} for Mo $K\alpha$ radiation (λ=0.71073 Å), 5697 unique reflections measured by 2θ-ω scan, 3247 ($I \geq 3\sigma(I)$) used for LS calculations, R=0.069 and R_w=0.057. Crystal data for $[Cu_2LCl_2](ClO_4)_2 \cdot H_2O$: $C_{34}H_{52}N_8O_9Cl_4Cu_2$, FW 985.74, monoclinic, $P2_1/n$ (No. 14), a=14.404(3), b=26.402(5), c=11.733(3) Å, β=110.99(2) °, V=4166(1) Å^3, Z=4, Dcalcd=1.57 g cm^{-3}, μ=13.41 cm^{-1} for Mo $K\alpha$ radiation (λ=0.71073 Å), 9573 unique reflections measured by 2θ-ω scan, 4575 ($I \geq 3\sigma(I)$) used for LS calculations, R=0.060 and R_w=0.053. The intensity data were collected using a MAC Science MXC3k four-circle diffractometer. The structures were solved by the direct method (SIR92) and refined by the full-matrix least-square method. All the non-hydrogen atoms were refined using anisotropic thermal parameters. Hydrogen atoms were placed in the calculated position with isotropic thermal parameters fixed at 1.1 times those of the carbon and the nitrogen atoms to which they are covalently bonded (weighting scheme, $\omega = \exp(10\sin^2\theta/\lambda^2)/\sigma^2(F_o)$).

12 A hydrogen bond between Cl(2) and the water molecule (Cl---O: 3.236 Å) may also stabilize the closed conformation.