Synthesis and Characterization of *C-meso* and *C-racemic* Isomers of a Reinforced Tetraaza Macrocycle and Their Copper(II) Complexes

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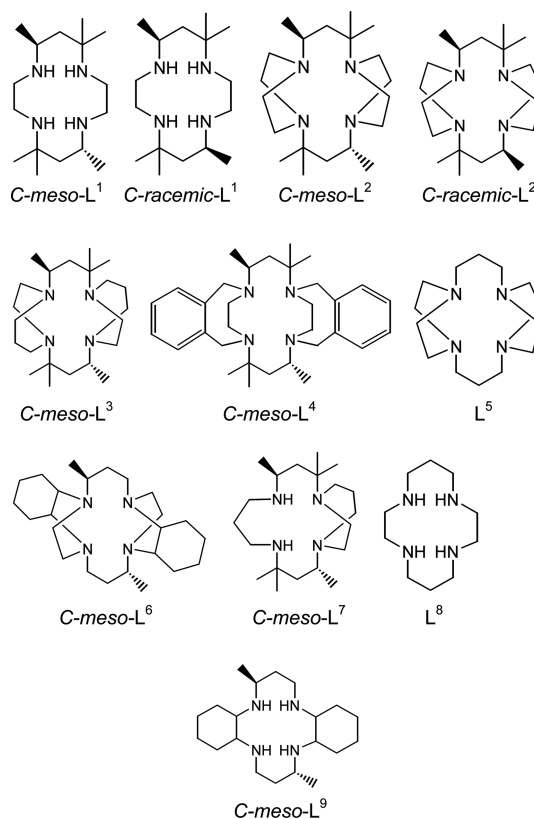
Two isomers of a new tetraaza macrotricycle 2,2,4,9,9,11-hexaazamethyl-1,5,8,12-tetraazatricyclo[10.2.2$^{5.8}$]-octadecane (L^2) containing additional N-CH$_2$CH$_2$-N linkages, *C-meso*-L^2 and *C-racemic*-L^2, have been prepared by the reaction of 1-bromo-2-chloroethane with *C-meso*-L^1 or *C-racemic*-L^1 (L^1 = 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane). Both *C-meso*-L^2 and *C-racemic*-L^2 react with copper(II) ion to form [Cu(*C-meso*-L^2)]$^{2+}$ or [Cu(*C-racemic*-L^2)]$^{2+}$ in dehydrated ethanol, but do not with nickel(II) ion under similar conditions. Crystal structure of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$ shows that the complex has distorted square-pyramidal coordination geometry with an apically coordinated water molecule. Unexpectedly, the Cu-N distances [2.016(3)-2.030(3) Å] of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$ are longer than those [1.992(3)-2.000(3) Å] of [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$. As a result, [Cu(*C-racemic*-L^2)(H$_2$O)]$^{2+}$ exhibits weaker ligand field strength than [Cu(*C-racemic*-L^1)(H$_2$O)]$^{2+}$. The copper(II) complexes readily react with CN$^-$ ion to yield the cyano-bridged dinuclear complex [Cu$_2$(*C-meso*-L^2)$_2$CN]$^{3+}$ or [Cu$_2$(*C-racemic*-L^2)$_2$CN]$^{3+}$. Spectra and chemical properties of [Cu(*C-meso*-L^2)]$^{2+}$ and [Cu$_2$(*C-meso*-L^2)$_2$CN]$^{3+}$ are not quite different from those of [Cu(*C-racemic*-L^2)]$^{2+}$ and [Cu$_2$(*C-racemic*-L^2)$_2$CN]$^{3+}$, respectively.

Key Words : Reinforced macrocycles, Cyano-bridged dinuclear complexes, Crystal structure, Copper(II) complexes

Introduction

Reinforced tetraaza macrocyclic compounds, in which each pair of donor nitrogen atoms is linked together by an additional bridging chain (*e.g.* -(CH$_2$)$_n$-), have received much attention because of their interesting chemical properties.[1-15] Various adjacent-bridged macropolycycles, such as *C-meso*-L^3, *C-meso*-L^4, L^5, and *C-meso*-L^6, have been prepared and investigated.[10-14] It has been revealed that chemical properties of such compounds are quite different from those of *C-meso*-L^1, *C-meso*-L^8, and *C-meso*-L^9 and are affected significantly by their structural characteristics. For instance, *C-meso*-L^3, *C-meso*-L^4, and *C-meso*-L^6 do not react with Ni^{2+} ion in wet or dry methanol,[12-14] though L^5 readily forms the square-planar complex [NiL^5]$^{2+}$ in wet methanol.[11] Although *C-meso*-L^6 forms its copper(II) complex [Cu(*C-meso*-L^6)]$^{2+}$ in dry ethanol,[14] *C-meso*-L^4 does not react with Cu^{2+} ion under similar experimental conditions.[13] Furthermore, the reactivity of *C-meso*-L^3 is quite different from that of *C-meso*-L^4 or *C-meso*-L^6; in the presence of Cu(OAc)·H$_2$O, *C-meso*-L^3 undergoes C-N bond cleavage to form [Cu(*C-meso*-L^7)]$^{2+}$ as the only product.[12] It has also been reported that the ligand field strengths of [NiL^5]$^{2+}$ and [Cu(*C-meso*-L^6)]$^{2+}$ are distinctly stronger than those of [NiL^8]$^{2+}$ and [Cu(*C-meso*-L^9)]$^{2+}$, respectively.[11,14] As far as we know, the preparation of copper(II) complex of L^5 has not been reported. Until now, the effects of the structural characteristics of such macropolycyclic compounds on their chemical properties are not thoroughly investigated. There-fore, we have been interested in the preparation and chemical properties of various types of structurally constrained tetraaza macropolycycles.

C-meso-L^1 *C-racemic*-L^1 *C-meso*-L^2 *C-racemic*-L^2

C-meso-L^3 *C-meso*-L^4 L^5

C-meso-L^6 *C-meso*-L^7 L^8

C-meso-L^9

There has been considerable interest in the isolation of various types of *C*- and/or *N*-conformational isomers of tetraaza macrocyclic compounds.[15-24] The interest mainly depends upon the fact that, in general, *C*- and/or *N*-configuration of such compounds have a strong effect on their chemical properties. The macrocycle L^1 exists as two *C*-conformational isomers, *C-meso*-L^1 and *C-racemic*-L^1, that exhibit different chemical properties.[16,24] In this work, we prepared *C-meso*-L^2 and *C-racemic*-L^2 containing two additional N-CH_2CH_2-N chains to see how their chemical properties are affected by the *C*-configuration and the nature of the chains. Herein synthesis and chemical properties of the two isomers of L^2 and their copper(II) complexes are reported. Chemical properties of *C-meso*-L^2 and *C-racemic*-L^2 are also compared with those of *C-meso*-L^3, *C-meso*-L^4, and *C-meso*-L^6.

Experimental

Measurements. Elemental Analyzes were performed at the Research Center for Instrumental Analysis, Daegu University, Korea. GC-MS spectra were measured with a Shimadzu GCMSD-QP5050 spectrometer. FAB MS spectra were performed at the Korea Basic Science Institute, Daegu, Korea. Infrared spectra were recorded using a Genesis II FT-IR spectrometer, electronic absorption spectra with an Analytic Jena Specord 200 UV/vis spectrophotometer, and NMR spectra with a Varian Mercury 300 FT NMR spectrometer. Conductance measurements were taken with a Z18 Oyster Conductivity/Temperature meter.

Safety Note: Perchlorate salts of transition metal complexes with organic ligands are often explosive and should be handled with caution.

Preparation of *C-meso*-L^2 (L^2 = 2,2,4,9,9,11-hexamethyl-1,5,8,12-tetraazatricyclo[10.2.2$^{5.8}$]octade-cane). To a toluene (30 mL) solution of *C-meso*-L^1 [Ref. 24] (2.0 g, 7.0 mmol) was added 98% 1-bromo-2-chloroethane (3.5 mL, 42 mmol). The solution was refluxed for 48 h. After the addition of KOH (5.6 g, 0.1 mol), the mixture was refluxed for 4 h and then cooled to room temperature. 98% 1-Bromo-2-chloroethane (3.5 mL, 42 mmol) and KOH (5.6 g, 100 mmol) were added to the reaction solution, and the mixture was refluxed for *ca.* 48 h. The resulting slurry was filtered to remove white solid. The filtrate was evaporated on a rotary evaporator, and the residue was dissolved in minimum volume of warm methanol-acetonitrile (1:1). The solution was evaporated in an open beaker at room temperature to precipitate a white solid. It was collected by filtration, washed with acetonitrile, and dried in air. The crude product usually contains a considerable amount of the reactant *C-meso*-L^1. The pure product was isolated by the recrystallization of the crude product from methanol. Yield: 0.45 g, 20%. *Anal.* Calc. for $C_{20}H_{40}N_4$: C, 71.37; H, 11.98; N, 16.65. Found: C, 70.98; H, 11.75; N, 16.82%. GC MS (*m/z*): 336. ^{1}H NMR (CDCl₃) δ 0.82 (*d*, Me), 1.11 (*s*, Me), 1.23 (*s*, Me). ^{13}C NMR (CDCl₃) δ 14.6 (Me), 26.2 (Me), 31.6 (Me), 41.8 (N-CH_2-CH_2-N), 42.7 (N-CH_2-CH_2-N), 43.9 (N-CH_2-CH_2-

N), 45.4 (N-CH_2-CH_2-N), 54.1 (N-CH(Me)-CH_2CH(Me)₂-N), 55.7 (N-CH(Me)-CH_2CH(Me)₂-N), and 58.2 (N-CH(Me)-CH_2CH(Me)₂-N).

Preparation of *C-racemic*-L^2. This compound was prepared by a method similar to that for *C-meso*-L^2, except that *C-racemic*-L^1 [Ref. 24] was reacted instead of *C-meso*-L^1. The crude product often contains the reactant *C-racemic*-L^1. The pure product was isolated by the recrystallization of the crude product from methanol. Yield: 0.68 g, 30%. *Anal.* Calc. for $C_{20}H_{40}N_4$: C, 71.37; H, 11.98; N, 16.65. Found: C, 71.80; H, 11.72; N, 16.35%. GC MS (*m/z*): 336. ^{1}H NMR (CDCl₃) δ 0.83 (*d*, Me), 1.13 (*s*, Me), 1.24 (*s*, Me). ^{13}C NMR (CDCl₃) δ 14.7 (Me), 26.2 (Me), 31.5 (Me), 41.9 (N-CH_2-CH_2-N), 42.7 (N-CH_2-CH_2-N), 43.9 (N-CH_2-CH_2-N), 45.4 (N-CH_2-CH_2-N), 54.1 (N-CH(Me)-CH_2CH(Me)₂-N), 55.7 (N-CH(Me)-CH_2CH(Me)₂-N), and 58.2 (N-CH(Me)-CH_2-CH(Me)₂-N).

Preparation of [Cu(*C-meso*-L^2)(H₂O)](PF₆)₂. An ethanol suspension (20 mL) of Cu(OAc)₂·H₂O (2.4 g, 10.0 mmol) and CH(OEt)₃ (7.5 mL, 40.0 mmol) was refluxed for 2 h. After the addition of *C-meso*-L^2 (1.0 g, 3.0 mmol), the resulting suspension was refluxed for *ca.* 15 h and then cooled to room temperature. The addition of excess NH₄PF₆ dissolved in water (10 mL) to the solution produced a purple solid. The product was filtered, washed with cold water, and recrystallized from hot methanol. Yield based on *C-meso*-L^2: 1.45 g, 70%. *Anal.* Calc for $C_{20}H_{42}N_4CuOP_2F_{12}$: C, 33.93; H, 5.98; N, 7.91. Found: C, 34.21; H, 6.00; N, 8.10%. FAB MS (*m/z*): 544.2 ([CuL³ + PF₆]⁺) and 399.3 ([CuL³ − H]⁺). IR (cm⁻¹): 3530 (v_{O-H}), 1620 {δ(H₂O)}, 850 (v_{P-F}).

Preparation of [Cu(*C-racemic*-L^2)(H₂O)](PF₆)₂. This compound was prepared by a method similar to that for [Cu(*C-meso*-L^2)(H₂O)](PF₆)₂, except that *C-racemic*-L^2 was reacted instead of *C-meso*-L^2. Yield based on *C-racemic*-L^2: 1.04 g, 50%. *Anal.* Calc for $C_{20}H_{42}N_4CuOP_2F_{12}$: C, 33.93; H, 5.98; N, 7.91. Found: C, 33.78; H, 5.73; N, 7.94%. FAB MS (*m/z*): 544.2 ([CuL³ + PF₆]⁺) and 399.2 ([CuL³ − H]⁺). IR (cm⁻¹): 3530 (v_{O-H}), 1650 {δ(H₂O)}, 850 (v_{P-F}).

Preparation of [Cu(*C-meso*-L^2)(H₂O)](ClO₄)₂. To an acetonitrile solution (10 mL) of [Cu(*C-meso*-L^2)(H₂O)]-(PF₆)₂ (0.5 g) was added excess NaClO₄ dissolved in water (10 mL). The mixture was evaporated in an open beaker to precipitate a purple solid. The product was collected by filtration, washed with cold water, and dried in air. Yield: 0.35 g, 80%. *Anal.* Calc for $C_{20}H_{42}N_4CuCl_2O_9$: C, 38.93; H, 6.86; N, 9.08. Found: C, 39.46; H, 6.98; N, 9.46%. IR (cm⁻¹): 3400 (v_{O-H}), 1650 {δ(H₂O)}, 1100 (v_{Cl-O}).

Preparation of [Cu(*C-racemic*-L^2)(H₂O)](ClO₄)₂. To an acetonitrile solution (10 mL) of [Cu(*C-racemic*-L^2)(H₂O)]-(PF₆)₂ (0.5 g) was added excess NaClO₄ dissolved in water (10 mL). The mixture was evaporated in an open beaker to precipitate a purple solid. The product was collected by filtration, washed with cold water, and dried in air. Yield: 0.36 g, 80%. *Anal.* Calc for $C_{20}H_{42}N_4CuCl_2O_9$: C, 38.93; H, 6.86; N, 9.08. Found: C, 39.16; H, 6.94; N, 9.64%. IR (cm⁻¹): 3400 (v_{O-H}), 1650 {δ(H₂O)}, 1100 (v_{Cl-O}).

Preparation of [Cu₂(*C-meso*-L^2)₂CN](ClO₄)₃. A water-

acetonitrile (1:1) solution (10 mL) of [Cu(*C-meso*-L^2)(H$_2$O)]-(ClO$_4$)$_2$ (1.0 g) and NaCN (0.3 g, 5.8 mmol) was stirred for *ca.* 10 min at room temperature. The addition of excess NaClO$_4$ to the solution produced a blue solid. The product was collected by filtration, dried in air, and recrystallized from water. Yield: ~80%. *Anal.* Calc for C$_{41}$H$_{80}$N$_9$Cu$_2$Cl$_3$O$_{12}$: C, 43.79; H, 7.17; N, 11.21. Found: C, 43.47; H, 6.89; N, 11.44%. FAB MS (*m/z*): 1023.9 ([Cu$_2$(L^3)(CN) + 2ClO$_4$]$^+$), 925.1 ([Cu$_2$(L^3)(CN) − H + ClO$_4$]$^+$), and 824.2 ([Cu$_2$(L^3)(CN) − 2H]$^+$). IR (cm^{-1}): 2120 (ν_{CN}), 1100 (ν_{Cl-O}).

Preparation of [Cu$_2$(*C-racemic*-L^2)$_2$CN](ClO$_4$)$_3$. This compound was prepared by a method similar to that for [Cu$_2$(*C-meso*-L^2)$_2$CN](ClO$_4$)$_3$, except that [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$ was reacted instead of [Cu(*C-meso*-L^2)-(H$_2$O)](ClO$_4$)$_2$. Yield: ~80%. *Anal.* Calc for C$_{41}$H$_{80}$N$_9$Cu$_2$Cl$_3$O$_{12}$: C, 43.79; H, 7.17; N, 11.21. Found: C, 43.50; H, 6.96; N, 11.38%. FAB MS (*m/z*): 1024.0 ([Cu$_2$(L^3)(CN) + 2ClO$_4$]$^+$), 925.1 ([Cu$_2$(L^3)(CN) − H + ClO$_4$]$^+$), and 824.2 ([Cu$_2$(L^3)(CN) − 2H]$^+$). IR (cm^{-1}): 2123 (ν_{CN}), 1100 (ν_{Cl-O}).

X-ray Crystal Structure Determination of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$. Single crystals of the complex were grown from acetonitrile-water. A single crystal in a thin-walled glass capillary was mounted on an Enraf-Noius CAD-4 diffractometer with Mo *K*α radiation (λ = 0.71073 Å). Unit cell parameters were determined by least-squares analysis of 25 reflections (10° < θ < 13°). Intensity data were collected with θ range of 2.02-25.47° in ω/2θ scan mode and three standard reflections were monitored every 1 h during data collection. Absorption corrections were applied with 3ψ scans. The structure was solved by direct methods and refined by full-matrix least-squares methods based on *F*^{2} using SHELXS-97 and SHELXL-97.[25] Non hydrogen atoms were refined anisotropically except disordered oxygen atoms
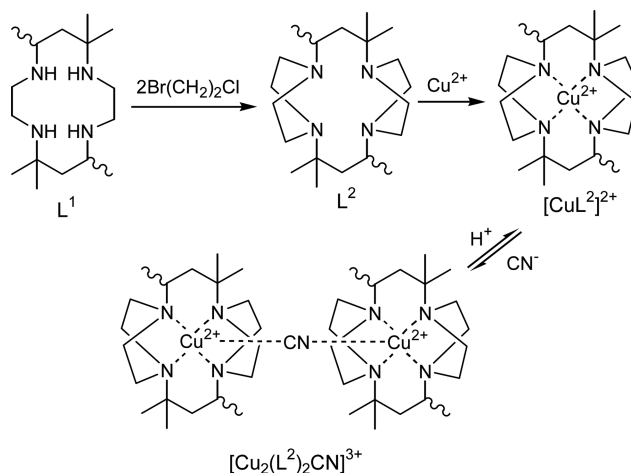
at ClO$_4$ anions which were refined with half occupancies isotropically. All hydrogen atoms were included in calculated positions. Crystallographic data are listed in Table 1.

Results and Discussion

Synthesis. The macrotricycles *C-meso*-L^2 and *C-racemic*-L^2 were prepared by reacting *C-meso*-L^1 or *C-racemic*-L^1 with excess amount of Cl(CH$_2$)$_2$Br. The synthetic procedure is not quite different from that for *C-meso*-L^6, which has been prepared from the reaction of *C-meso*-L^9 with Cl(CH$_2$)$_2$Br.[14] However, the yield (20-30%) was found to be much lower than that reported for *C-meso*-L^6 (~80%). In the present work, the crude product contains a considerable amount of the reactant *C-meso*-L^1 or *C-racemic*-L^1. The solubility of *C-meso*-L^2 or *C-racemic*-L^2 in methanol is distinctly lower than that of *C-meso*-L^1 or *C-racemic*-L^1. Therefore, the pure product can be isolated by the fractional crystallization of the crude product from methanol. ^{13}C NMR, infrared, and MS spectra of *C-meso*-L^2 and *C-racemic*-L^2 as well as the elemental analyzes are corresponding to their structures. In the infrared spectra of the compounds, no peak corresponding to ν_{N-H} was observed.

The macrotricycles *C-meso*-L^3 and *C-meso*-L^4 have been prepared by reacting *C-meso*-L^1 with 1,3-dibromopropane or 1,2-bis(bromomethyl)benzene.[12,13] In this work, we also attempted the preparation of *C-racemic*-L^3 and *C-racemic*-L^4 from the reaction of *C-meso*-L^1 with 1,3-dibromopropane or 1,2-bis(bromomethyl)benzene under similar conditions, but failed.

Our initial attempts to prepare copper(II) and nickel(II) complexes of *C-meso*-L^2 or *C-racemic*-L^2 from the reaction (reflux > 10 h) of the macrotricycles with Cu(OAc)$_2$·H$_2$O or Ni(OAc)$_2$·4H$_2$O in methanol or ethanol were unsuccessful. The addition of NaClO$_4$ to the reaction solutions produced *C-meso*-L^2·2HClO$_4$ or *C-racemic*-L^2·2HClO$_4$. As described in the Experimental section, the copper(II) complexes of *C-meso*-L^2 and *C-racemic*-L^2 could be prepared by the reaction of dehydrated copper(II) ion in dry ethanol; the reagent HC(OEt)$_3$ reacts with H$_2$O to produce HCO$_2$Et and EtOH.[14]

Table 1. Crystal and structure refinement data for [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)

Formula (*M*)	C$_{20}$H$_{42}$Cl$_2$CuN$_4$O$_9$ (617.02)
Crystal system	orthorhombic, *Pbca* (No 61)
a/*b*/*c* (Å)	16.126(2)/16.999(3)/20.004(3)
α/β/γ (°)	90/90/90
U (Å^3)	5482.8(2)
Z	8
D$_c$ (g cm^{-3})	1.495
μ (cm^{-1})	10.45
F(000)	2600
Θ ranges (°)	2.02-25.47
Index ranges	−19 ≤ *h* ≤ 0, 0 ≤ *k*, ≤ 20, 0 ≤ *l* ≤ 24
Reflections collected	5294
Independent reflections	5094 [R(int) = 0.0098]
Data Completeness	1.000
Data/restraints/parameters	5094 / 0 / 323
Goodness-of-fit on *F*^{2}	1.003
Final R indices [*I* > 2σ(*I*)]	*R$_1$* = 0.0462, *wR$_2$* = 0.1329
R indices (all data)	*R$_1$* = 0.1006, *wR$_2$* = 0.1453
Largest diff. peak and hole (e/Å^3)	0.675 and −0.564

Scheme 1. The route for the synthesis of the copper(II) complexes.

However, we could not prepare any nickel(II) complex of *C-meso*-L^2 or *C-racemic*-L^2 under similar experimental conditions. The reactivity of *C-meso*-L^2 and *C-racemic*-L^2 is similar to that of *C-meso*-L^6, but is quite different from that of *C-meso*-L^3 or *C-meso*-L^4.[12-14] As described in the Introduction section, *C-meso*-L^3 reacts with hydrated copper(II) ion to form [Cu(*C-meso*-L^7)]$^{2+}$, whereas *C-meso*-L^4 does not react with the metal ion even in dehydrated condition.[12,13] One of the reasons for the difference in the reactivity of *C-meso*-L^2, *C-meso*-L^3, and *C-meso*-L^4 may be the steric hindrance of the additional bridging groups. The synthesis and reaction of the copper(II) complexes are shown in Scheme 1.

Crystal Structure of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$. The crystal structure (Fig. 1) of [Cu(*C-racemic*-L^2)(H$_2$O)]-(ClO$_4$)$_2$ shows that the complex has distorted square-pyramidal coordination geometry with a water molecule at the apical position. The Cu atom is displaced by 2.653(3) Å from the mean N$_4$ plane toward the apical water molecule. The apical water molecule and the methyl group attached to C(5) or C(15) atom are *anti* with respect to the N4 plane. The 1,4-diaminocyclohexane subunits have a boat conformation, whereas the six-membered chelate rings adopt a chair form.

Selected bond distances and angles of the complex are listed in Table 2. Four Cu-N distances (2.016(3)-2.030(3) Å) of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$ are comparable with those of [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$ and [Cu(*C-meso*-L^6](ClO$_4$)$_2$.[14,26] However, the average Cu-N distance (2.023 Å) is considerably longer than that (1.996 Å) of [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$.[26] This observation is in sharp contrast to the trend that the average Cu-N distance (2.002 Å) of [Cu(*C-meso*-L^6](ClO$_4$)$_2$ containing additional *N*-(CH$_2$)$_2$-*N* bridges is distinctly shorter than that (2.028 Å) of [Cu(*C-meso*-L^9](ClO$_4$)$_2$.[14] The apical Cu-O$_w$ distance (2.281(3) Å)

is considerably longer than the Cu-N distances. The N(1)-Cu-N(3) and N(2)-Cu-N(4) angles (161.3(2) and 156.2(2)°, respectively) are severely deviated from 180°. The angles are comparable with the *trans*-N-Cu-N angles (159.4(1) and 169.2(1)°) of [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$. However, the N(1)-Cu-N(2) and N(3)-Cu-N(4) angles (75.8(2)°) involved in the five-membered chelate rings are distinctly smaller than the N-Cu-N angles (88.5(1)°) involved in the five-membered chelate rings of [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$. On the other hand, the N(2)-Cu-N(3) and N(1)-Cu-N(4) angles (100.1(2) and 100.4(2)°) are larger than the N-Cu-N angles (93.4(1)°) involved in the six-membered chelate rings of [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$. It is obvious that the introduction of -(CH$_2$)$_2$- bridges into [Cu(*C-racemic*-L^1)-(H$_2$O)]$^{2+}$ to give [Cu(*C-racemic*-L^2)(H$_2$O)]$^{2+}$ lengthens the Cu-N distances and causes severe change in the N-Cu-N angles.

Unfortunately, we were unable to grow single crystals of [Cu(*C-meso*-L^2)(H$_2$O)](ClO$_4$)$_2$ suitable for the X-ray crystallography. However, electronic absorption spectra and chemical properties (*see* below) of [Cu(*C-meso*-L^2)(H$_2$O)](ClO$_4$)$_2$ indicate that the coordination geometry and structural features of the complex are similar to those of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$.

Spectra and Properties of [Cu(*C-meso*-L^2)(H$_2$O)]$^{2+}$ and [Cu(*C-racemic*-L^2)(H$_2$O)]$^{2+}$. The infrared and FAB MS spectra of [Cu(*C-meso*-L^2)(H$_2$O)](PF$_6$)$_2$ and [Cu(*C-racemic*-L^2)(H$_2$O)](PF$_6$)$_2$ as well as the elemental analyzes are listed in the Experimental section. The electronic absorption spectra (Table 3) of [Cu(*C-meso*-L^2)(H$_2$O)](ClO$_4$)$_2$ and [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$ measured in water show a *d-d* transition band at *ca.* 540 nm (ε = 420-438 M^{-1}cm^{-1}), indicating that they have square-pyramidal coordination geometry.[20,27,28] Interestingly, the two isomers exhibit similar electronic absorption spectra, indicating that their coordination geometry and the ligand field strength are not affected significantly by the *C*-configuration of L^2. The wavelength of each isomer is longer than that of [Cu(*C-meso*-L^1)(H$_2$O)]-(ClO$_4$)$_2$ (512 nm) or [Cu(*C-racemic*-L^1)(H$_2$O)](ClO$_4$)$_2$ (525 nm). This observation corresponds to the crystallographic result that the average Cu-N distance of [Cu(*C-racemic*-
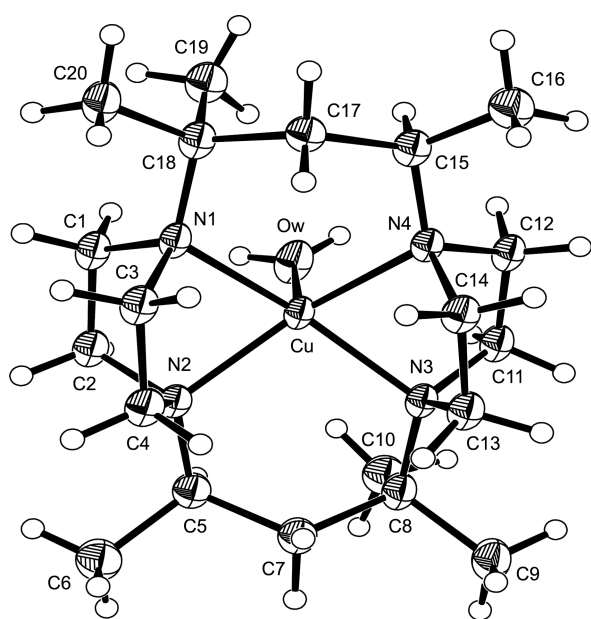

Figure 1. An ORTEP drawing of the cation of [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$ with atomic numbering for the non-hydrogen atoms.

Table 2. Bond distances (Å) and angles (°) for [Cu(*C-racemic*-L^2)(H$_2$O)](ClO$_4$)$_2$

|			
Cu-N(1)	2.030(3)	Cu-N(2)	2.016(3)
Cu-N(3)	2.026(3)	Cu-N(4)	2.021(3)
Cu-OW	2.281(3)	N(1)-C(1)	1.478(5)
N(1)-C(3)	1.498(5)	N(1)-C(18)	1.526(5)
N(2)-C(2)	1.484(5)	N(2)-C(4)	1.489(4)
N(1)-Cu-N(2)	75.8(2)	N(2)-Cu-N(3)	100.1(2)
N(3)-Cu-N(4)	75.8(2)	N(1)-Cu-N(4)	100.4(2)
N(1)-Cu-N(4)	161.3(2)	N(2)-Cu-N(4)	156.2(2)
N(1)-Cu-OW	100.5(2)	N(2)-Cu-OW	100.5(2)
C(1)-N(1)-C(3)	105.4(3)	C(3)-N(1)-C(18)	113.2(3)
N(1)-C(1)-C(2)	108.7(3)	N(2)-C(2)-C(1)	109.1(3)

$L^2)(H_2O)](ClO_4)_2$ is longer than that of [Cu(*C-racemic-*$L^1)(H_2O)](ClO_4)_2$. The present result is quite different from the reported trend that the average Cu-N distance (2.002 Å) and the wavelength (447 nm) of the *d-d* transition band for [Cu(*C-meso-*$L^6)]^{2+}$ containing two N–(CH$_2$)$_2$-N linkages are *ca.* 0.026 Å and 40 nm shorter, respectively, than those of [Cu(*C-meso-*$L^9)]^{2+}$.[14] The molar absorption coefficients for [Cu(*C-meso-*$L^2)(H_2O)](ClO_4)_2$ and [Cu(*C-racemic-*$L^2)(H_2O)]$-$(ClO_4)_2$ measured in water are approximately three times those of [Cu(*C-meso-*$L^1)(H_2O)](ClO_4)_2$ (135 $M^{-1}cm^{-1}$) and [Cu(*C-racemic-*$L^1)(H_2O)](ClO_4)_2$ (174 $M^{-1}cm^{-1}$). This may be related to the severely distorted N-Cu-N angles of the former complexes.

Both [Cu(*C-meso-*$L^2)(H_2O)](ClO_4)_2$ and [Cu(*C-racemic-*$L^2)(H_2O)](ClO_4)_2$ are quite stable even in low pH, like [Cu(*C-meso-*$L^6)]^{2+}$. Visible absorption spectra of each isomer (1.0×10^{-3} M) measured in 0.1 M HClO$_4$ water-acetonitrile (1:1) solution indicated that only less than 1% of the complex was decomposed in 48 h at room temperature. Furthermore, *C-meso-*L^2 and *C-racemic-*L^2 of the copper(II) complexes are not substituted by CN$^-$ ion even in boiling (> 10 h) acetonitrile-water (1:1) solutions containing excess NaCN; this can attributed to the topologically constrained structure of the macrotricycles.[13,14] The only complex obtained from the solution was found to be the cyano-bridged dinuclear complex [Cu$_2$(*C-meso-*$L^2)_2CN]^{3+}$ or [Cu$_2$(*C-racemic-*$L^2)_2CN]^{3+}$. The formation of the five-coordinate mononuclear and dinuclear copper(II) complexes in the present work also shows that *C-meso-*L^2 and *C-racemic-*L^2 containing additional N–(CH$_2$)$_2$-N bridges cannot block the coordination of water molecule or CN$^-$ ion to the axial sites of their copper(II) complexes.

Spectra and Properties of the Dinuclear Copper(II) Complexes. The cyano-bridged dinuclear complexes [Cu$_2$(*C-meso-*$L^2)_2CN](ClO_4)_3$ and [Cu$_2$(*C-racemic-*$L^2)_2CN](ClO_4)_3$ were prepared by the reaction of [Cu(*C-meso-*$L^2)(H_2O)]^{2+}$ or [Cu(*C-racemic-*$L^2)(H_2O)]^{2+}$ with NaCN. Unfortunately, we were unable to grow single crystals of the complexes suitable for X-ray work. However, their formula and coordination geometry can be confirmed by the FAB MS, IR, and electronic absorption spectra of the complexes. The infrared

Table 3. Electronic Absorption Spectral Data of the Complexes[a]

Compound	λ_{max}, nm (ε, $M^{-1}cm^{-1}$)[a]	
[Cu(*C-meso-*$L^1)](ClO_4)_2$[b]	512(135)	
[Cu(*C-racemic-*$L^1)(H_2O)](ClO_4)_2$[b]	525(174)	
[Cu(*C-meso-*$L^2)(H_2O)](ClO_4)_2$	538(420)	
[Cu(*C-racemic-*$L^2)(H_2O)](ClO_4)_2$	540(438)	
[Cu$_2$(*C-meso-*$L^2)_2CN](ClO_4)_3$	605(990) 605[d]	603(1185)[c]
[Cu$_2$(*C-racemic-*$L^2)_2CN](ClO_4)_3$	600(995) 605[d]	602(1180)[c]
[Cu(*C-meso-*$L^6)](ClO_4)_2$[e]	447(427)[c]	
[Cu(*C-meso-*$L^9)](ClO_4)_2$[f]	487(113)[c]	

[a]Measured in water at 20 °C unless otherwise specified. [b]Ref. 29. [c]In nitromethane. [d]In Nujol mull. [e]Ref. 14. [f]Ref. 30.

spectra of the complexes show ν_{CN} of the bridging ligand at *ca.* 2120 cm^{-1}. The FAB MS spectrum of [Cu$_2$(*C-meso-*$L^2)_2CN](ClO_4)_3$ shows three groups of peaks corresponding to the fragments [Cu$_2$($L^2)_2(CN) + 2ClO_4]^+$, [Cu$_2$($L^2)_2(CN) -$ H + ClO$_4]^+$, and [Cu$_2$($L^2)_2(CN) - 2H]^+$ at *m/z* 1023.9, 925.1, and 824.2, respectively. A similar spectrum was also obtained for [Cu$_2$(*C-racemic-*$L^2)_2CN](ClO_4)_3$. The electronic absorption spectra of the two isomers measured in Nujol mull and various solvents show the *d-d* transition band at 600-610 nm, indicating that they have square-pyramidal coordination geometry in the solid state and in the solvents.[20,28] The wavelengths are *ca.* 100 nm longer than those of [Cu(*C-meso-*$L^2)(H_2O)]^{2+}$ and [Cu(*C-racemic-*$L^2)(H_2O)]^{2+}$. The molar absorption coefficients of the dinuclear complexes measured in water, nitromethane, and acetonitrile are approximately double those of the monomer complexes. The molar conductance values of the dinuclear complexes measured in water (280 and 290, respectively) indicate that they are 1:3 electrolytes.

The dinuclear complexes are extremely stable in the solid states and in various solvents, such as water, methanol, and acetonitrile. In acidic aqueous solutions, however, each dinuclear complex is rapidly decomposed to give the monomer [Cu(*C-meso-*$L^2)(H_2O)]^{2+}$ or [Cu(*C-racemic-*$L^2)(H_2O)]^{2+}$ (Eq. (1)); the only complex obtained after the addition of NaClO$_4$ or HClO$_4$ to the solution was found to be [Cu(*C-meso-*$L^2)(H_2O)](ClO_4)_2$ or [Cu(*C-racemic-*$L^2)(H_2O)](ClO_4)_2$.

$$[(L^2)Cu-CN-Cu(L^2)]^{3+} + H^+ \rightarrow 2[CuL^2(H_2O)]^{2+} + HCN \quad (1)$$
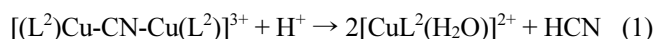
Conclusion

Two isomers of a reinforced macrocycle, *C-meso-*L^2 and *C-racemic-*L^2, and their copper(II) complexes have been prepared and characterized. Unexpectedly, the introduction of two -(CH$_2$)$_2$- groups into [Cu(*C-racemic-*$L^1)(H_2O)]^{2+}$ to give [Cu(*C-racemic-*$L^2)(H_2O)]^{2+}$ lengthens the Cu-N bond distances and weakens the ligand field strength. Both [Cu(*C-meso-*$L^2)(H_2O)]^{2+}$ and [Cu(*C-racemic-*$L^2)(H_2O)]^{2+}$ are quite inert against ligand substitution even in solutions containing excess amount of the anion CN$^-$ ion, but readily form the cyano-bridged dinuclear complexes [Cu$_2$(*C-meso-*$L^2)_2CN]^{3+}$ and [Cu$_2$(*C-racemic-*$L^2)_2CN]^{3+}$, respectively. In contrast to the cases of *C-meso-*L^1 and *C-racemic-*L^1, chemical properties and spectra of the complexes of *C-meso-*L^2 and *C-racemic-*L^2 are not affected significantly by their *C*-configuration. This work clearly supports the conclusion that chemical properties of *C-meso-*L^2, *C-meso-*L^3, *C-meso-*L^4, and *C-meso-*L^6 are strongly influenced by their structural characteristics, such as the *C*-substituents and the length of the additional bridging groups.

Supplementary Materials. Crystallographic data for [Cu(*C-racemic-*$L^2)(H_2O)](ClO_4)_2$ have been deposited with

CCDC (Deposition No. CCDC 980903). These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from CCDC, 12 Union Road, Cambridge CB2 1EZ, UK, E-mail: deposit@ccdc.cam.ac.uk.

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