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Note

Synthesis of two configurational isomers of a 14-membered tetraaza macrocycle bearing *N*-$CH_2CH_2CONH_2$ pendent arms and their copper(II) complexes: Crystal structures of the complexes

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Abstract

Two isomers of 1,8-bis(*N*-carbamoylethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^2) bearing two *N*-$CH_2CH_2CONH_2$ groups, *C-meso*-L^2 and *C-racemic*-L^2, have been prepared and characterized. Each isomer reacts with Cu(II) ion to form a five-coordinate complex, [Cu(*C-meso*-L^2)]$(ClO_4)_2$ (**1**) or [Cu(*C-racemic*-L^2)]$(ClO_4)_2$ (**2**), in which only one pendent amide group is coordinated to the metal ion. The crystal structure of **1** · CH_3CN shows that the complex possesses *trans*-III-type *N*-configuration and has a slightly distorted square-pyramidal coordination geometry with a relatively long axial Cu–O (*N*-$CH_2CH_2CONH_2$) bond (2.207(3) Å). On the other hand, **2** exhibits *trans*-V configuration and has a slightly distorted trigonal bipyramidal coordination geometry with a very short equatorial Cu–O (*N*-$CH_2CH_2CONH_2$) bond (2.007(3) Å); the Cu–O distance is distinctly shorter than the Cu–N distances (2.062(4)–2.090(4) Å). The complex **1** exhibits a d–d transition band at approximately 565 nm, whereas the band for **2** is observed at approximately 770 nm.

Keywords: Macrocyclic compounds; Configurational isomer; Copper(II) complexes; Functional pendent arms; Crystal structure; *N*-Carbamoylethyl groups

1. Introduction

There has been considerable interest in the chemical properties and structures of polyaza macrocyclic compounds containing functional pendent arm(s) because they can play an important role in various fields, such as in medicinal chemistry, catalysis, and the chemical industry [1–9]. In general, chemical properties and structures of such compounds are strongly influenced by the nature and number of functional groups. Some polyaza macrocycles bearing pendent amide groups, such as L^3 [3], L^4 [3], and L^5 [4], and their copper(II) and/or nickel(II) complexes have been prepared and investigated [3–9]. However, examples of 14-membered tetraaza macrocyclic compounds bearing pendent *N*-$CH_2CH_2CONH_2$ groups are relatively few, and their coordination behaviors are not thoroughly investigated.

A variety of work has been concerned with the isolation and chemical properties of *C*- and/or *N*-configurational isomers of polyaza macrocyclic compounds in recent years [10–15]. The interest in such compounds mainly depends on the effects of *C*- and/or *N*-configuration on their chemical properties and coordination behaviors. The 14-membered macrocycle L^1 is known to exist as two *C*-configurational isomers, *C-meso*-L^1 and *C-racemic*-L^1 [11]. In this work, we prepared two configurational isomers of 1,8-bis(*N*-carbamoylethyl)-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane (L^2), *C-meso*-L^2 and *C-racemic*-L^2, to see how their coordination behaviors are influenced by the *C*-configuration. Somewhat surprisingly, it was found that the *N*-configuration and the

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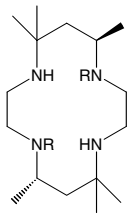
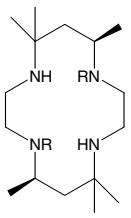
coordination geometry of $[Cu(C\text{-}meso\text{-}L^2)](ClO_4)_2$ (**1**) and $[Cu(C\text{-}racemic\text{-}L^2)](ClO_4)_2$ (**2**) are strongly influenced by the *C*-configuration. Synthesis and characterization of *C-meso*-L^2 and *C-racemic*-L^2 and their copper(II) complexes are reported, along with the crystal structures of **1** · CH_3CN and **2**.



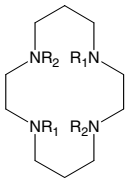
C-meso-L^1: R =H



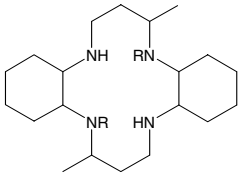
C-racemic-L^1: R = H

C-meso-L^2: R =$CH_2CH_2CONH_2$

C-racemic-L^2: R =$CH_2CH_2CONH_2$



L^3: $R_1 = R_2 = CH_2CH_2CONH_2$



L^5: R = CH_2CONH_2

L^4: R_1 = H; $R_2 = CH_2CH_2CONH_2$

2. Experimental

2.1. Measurements and materials

Electronic absorption spectra were measured with an Analytikjena Specord 200 UV/Vis spectrophotometer, infrared spectra with a Shimadzu IR-440 spectrophotometer, ^{13}C NMR spectra with a Varian Mercury 300 NMR spectrometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses and mass spectral analysis were performed at the Korea Basic Science Institute, Daegu, Korea. The macrocycles *C-meso*-L^1 and *C-racemic*-L^1 were prepared by the reported method [15].

2.2. Preparation of C-meso-L^2

A methanol solution (ca. 20 ml) of *C-meso*-L^1 (2.0 g, 7.0 mmol) and acrylamide (3.0 g, 42 mmol) was stirred for 48 h at room temperature. During which time, a white solid was produced. The product was collected by filtration and dissolved in a minimum volume of chloroform at room temperature. After the addition of methanol (20 ml), the resulting solution was evaporated at room temperature to produce a white solid. The product was filtered, washed with cold methanol, and dried in air. Yield: ~80%. *Anal.* Calc. for $C_{22}H_{46}N_6O_2$: C, 61.93; H, 10.87; N, 19.70. Found: C, 62.01; H, 10.53; N, 19.56%. Mass (*m*/*z*): 427 (M^+). ^1H NMR ($CDCl_3$): 0.82 (d, Me), 1.02 (s, Me), 1.13 (s, Me). ^{13}C NMR (CD_3CN): δ 11.8, 23.7, 27.8, 33.1, 38.2, 42.3, 44.3, 46.5, 49.8, 53.2, 175.3 (C=O) ppm. IR (cm^{-1}): 3100–3400 (νN–H, broad), 1620–1700 (νC=O, broad), and 1580–1610 (δN–H, broad).

2.3. Preparation of C-racemic-L^2

A methanol solution (ca. 20 ml) of *C-racemic*-L^1 (2.0 g, 7.0 mmol) and acrylamide (3.0 g, 42 mmol) was stirred for 48 h at room temperature and then evaporated at room temperature to dryness. After the addition of acetonitrile (20 ml) to the residue, the white solid was collected by filtration. The product was dissolved in a minimum volume of methanol at room temperature. After the addition of acetonitrile (20 ml), the resulting solution was evaporated at room temperature to produce a white solid. The product was filtered, washed with acetonitrile, and dried in air. Yield: ~80%. *Anal.* Calc. for $C_{22}H_{46}N_6O_2$: C, 61.93; H, 10.87; N, 19.70. Found: C, 61.98; H, 10.59; N, 19.62%. Mass (*m*/*z*): 427 (M^+). ^1H NMR ($CDCl_3$): 0.83 (d, Me), 0.87 (d, Me), 1.02 (s, Me), 1.04 (s, Me), 1.14 (s, Me), 1.15 (s, Me). ^{13}C NMR (CD_3CN): δ 11.8, 13.5, 23.7, 24.3, 27.8, 28.8, 33.1, 34.8, 38.1, 38.4, 42.4, 44.3, 46.5, 46.7, 49.9, 53.0, 53.1, 53.2, 175.3 (C=O), 175.5 (C=O) ppm. IR (cm^{-1}): 3100–3400 (νN–H, broad), 1640–1700 (νC=O, broad), and 1580–1610 (δN–H, broad).

2.4. Preparation of $[Cu(C\text{-}meso\text{-}L^2)](ClO_4)_2$ (**1**)

A methanol suspension (20 ml) of $Cu(OAc)_2 \cdot H_2O$ (2.0 g) and *C-meso*-L^2 (1.0 g) was refluxed for 20 min and then cooled to room temperature. An excess amount of $HClO_4$ was added to the solution to produce a purple solid. The product was filtered, washed with methanol, and dried in air. The crude product was recrystallized by addition of $HClO_4$ to its acteonitrile-water solution. Yield: ~90% based on *C-meso*-L^2. *Anal.* Calc. for $C_{22}H_{46}N_6CuCl_2O_{10}$: C, 38.35; H, 6.73; N, 12.20. Found: C, 38.07; H, 6.67; N, 12.05%. FAB mass (*m*/*z*): 489.2 ($[Cu(C\text{-}meso\text{-}L^2)\text{–}H]^+$) and 588.2 ($[Cu(C\text{-}meso\text{-}L^2)+ClO_4]^+$). IR ($cm^{-1}$): 3355 ($\nu$N–H), 3304 ($\nu$N–H), 3224 ($\nu$N–H), 3210 ($\nu$N–H), 1640–1700 ($\nu$C=O, broad), 1600 ($\delta$N–H), and 1100 ($\nu ClO_4$).

2.5. Preparation of $[Cu(C\text{-}racemic\text{-}L^2)](ClO_4)_2$ (**2**)

A methanol suspension (20 ml) of $Cu(OAc)_2 \cdot H_2O$ (2.0 g) and *C-racemic*-L^2 (1.0 g) was refluxed for 20 min and then cooled to room temperature. An excess amount of $HClO_4$ was added to the solution to produce a light blue-green solid. The product was filtered, washed with methanol, and dried in air. The crude product was recrystallized by addition of $HClO_4$ to its acteonitrile-water solution. Yield: ~90% based on *C-racemic*-L^2. *Anal.* Calc. for $C_{22}H_{46}N_6CuCl_2O_{10}$: C, 38.35; H, 6.73; N, 12.20. Found: C, 38.25; H, 6.51; N, 12.09%. FAB mass (*m*/*z*): 489.2 ($[Cu(C\text{-}racemic\text{-}L^2)\text{-}H]^+$) and 588.2 ($[Cu(C\text{-}racemic\text{-}L^2)+ClO_4]^+$). IR ($cm^{-1}$): 3404 ($\nu$N–H), 3348 ($\nu$N–H),