

## Synthesis and Characterization of Tetraaza Macrocyclic Nickel(II) and Copper(II) Complexes Bearing Two Tetrazole Pendant Arms

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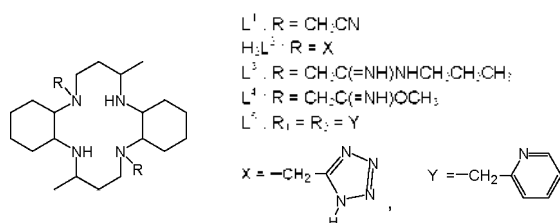
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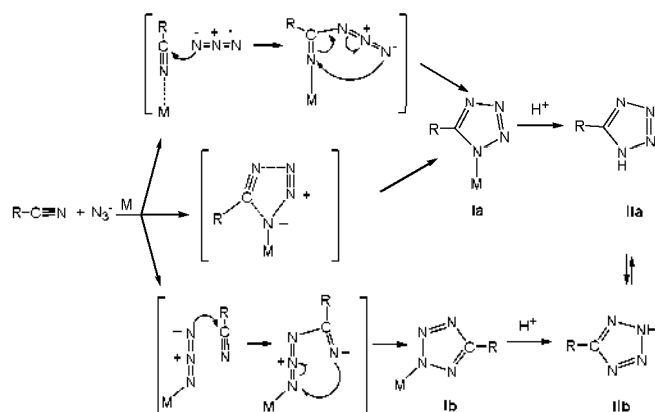
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Organic and inorganic compounds containing tetrazole group(s) have received considerable attention because of their potential applications in various fields, such as medicine, explosive, materials sciences, photography, and sweetener.<sup>1-7</sup> Various types of substituted tetrazoles have been prepared from the reaction of organic nitriles (R-CN) with azide (N<sub>3</sub><sup>-</sup>) ion in the presence of a transition metal ion. It has been suggested that the reaction of coordinated R-CN with free N<sub>3</sub><sup>-</sup> ion would produce the tetrazolato complex **Ia**, while **Ib** as well as **Ia** could be prepared from the reaction of coordinated N<sub>3</sub><sup>-</sup> with free R-CN (Scheme 1).<sup>6,7</sup> It is well known that the cyclization reaction is catalyzed by the metal ion. In the presence of an acid, the tetrazolato complexes **Ia** and **Ib** are readily decomposed to produce the metal-free tetrazoles **IIa** and **IIb**, respectively. Therefore, coordination behaviors of neutral tetrazoles are not thoroughly investigated.



There has been continuing interest in the synthesis of polyaza macrocyclic compounds bearing various types of functional pendant arms, since chemical properties of such compounds



Scheme 1

are influenced by the nature of the functional groups.<sup>8-15</sup> In this work, we examined the reaction of N<sub>3</sub><sup>-</sup> with the N-CH<sub>2</sub>CN pendant arms of [NiL<sup>1</sup>]<sup>2-</sup> and [CuL<sup>1</sup>]<sup>2-</sup> and successfully prepared [Ni(H<sub>2</sub>L<sup>2</sup>)]<sup>2-</sup> and [Cu(H<sub>2</sub>L<sup>2</sup>)]<sup>2-</sup> bearing two coordinated tetrazole pendant arms. The tetrazolato complexes [NiL<sup>2</sup>] and [CuL<sup>2</sup>] were also prepared. Herein, we report the synthesis, characterization, and chemical properties of the new functionalized macrocyclic nickel(II) and copper(II) complexes, along with the crystal structure of [Ni(H<sub>2</sub>L<sup>2</sup>)](ClO<sub>4</sub>)<sub>2</sub>.

### Experimental

**Measurements.** Infrared spectra were recorded using a Shimadzu IR-440 spectrophotometer, electronic absorption spectra with an Analytikjena Specord 200 UV/Vis spectrophotometer, and conductance measurements with a Metrohm Herisau Conductometer E518. Elemental analyses were performed at the Research Center for Instrumental Analysis, Daegu University, Gyeongsan, Korea. FAB mass spectra were performed at the Korea Basic Science Institute, Daegu, Korea. Magnetic moments were calculated from magnetic susceptibility data obtained at 20 °C using a Johnson Matthey MK-1 magnetic susceptibility balance.

**Preparation of [Ni(H<sub>2</sub>L<sup>2</sup>)](ClO<sub>4</sub>)<sub>2</sub>·2CH<sub>3</sub>SOCH<sub>3</sub> (**1**).** *Caution!* Perchlorate salts of metal complexes with organic ligands are often explosive and should be handled with great caution! To a warm acetonitrile suspension (20 mL) of [NiL<sup>1</sup>](ClO<sub>4</sub>)<sub>2</sub><sup>13</sup> (1.0 g, 1.5 mmol) was added NaN<sub>3</sub> (1.5 g, 23 mmol). The mixture was stirred in a hot water bath (60 ~ 70 °C) for ca. 10 min. During this time the orange-red solid went to the solution, and then a purple solid was precipitated. After the addition of concentrated HClO<sub>4</sub> (ca. 1.5 mL) dissolved in water (20 mL), the resulting solution was stored in a refrigerator for > 5 h to precipitate a pale purple solid. The solid was filtered, washed with methanol, and dried in air. The crude product was recrystallized from hot DMSO solution containing 3 ~ 5 drops of concentrated HClO<sub>4</sub>. Yield: ~80%. *Anal.* Found: C, 36.79; H, 6.48; N, 18.73. *Calc.* for C<sub>28</sub>H<sub>36</sub>Cl<sub>2</sub>N<sub>12</sub>NiO<sub>10</sub>S<sub>2</sub>: C, 36.77; H, 6.17; N, 18.38%. IR (cm<sup>-1</sup>): 3250 [ν(N-H)], 3117 [ν(N-H)], 1655 (tetrazole), 1570 (tetrazole), and 1100 (*br*, ClO<sub>4</sub><sup>-</sup>). μ<sub>eff</sub> = 2.88 μ<sub>B</sub> at 20 °C.

**Preparation of [NiL<sup>2</sup>] (**2**).** The addition of triethylamine (0.3 mL) or 1.0 M NaOH aqueous solution (20 mL) to a warm DMSO solution (ca. 20 mL) of **1** (0.5 g, 0.7 mmol) produces a pale purple solid. The product was filtered, washed with water, and dried in air. Yield: ~90%. *Anal.* Found: C, 51.32; H, 8.01; N, 30.60.

Calc. for  $C_{23}H_{42}Cl_2N_{12}Ni$ : C, 51.72; H, 7.60; N, 30.16%. IR ( $cm^{-1}$ ): 3261 [v(N-H)], 1655(tetrazole), 1585(tetrazole), and 1100 (*br.*,  $ClO_4^-$ ).  $\mu_{eff} = 2.86 \mu_B$  at 20 °C.

**Preparation of  $[Cu(H_2L^2)](ClO_4)_2 \cdot 2CH_3SOCH_3$  (3).** An acetonitrile suspension (30 mL) of  $[CuL^1](ClO_4)_2^{13}$  (1.0 g, 1.5 mmol) and  $NaN_3$  (1.5 g, 23 mmol) was refluxed for > 28 h and then cooled to room temperature. After the addition of 1.0 M  $HClO_4$  aqueous solution (*ca.* 20 mL), the resulting solution was evaporated at room temperature to precipitate a blue-purple solid. The product was collected by filtration, washed with methanol, and dried in air. It was recrystallized by the addition of 0.1 M  $HClO_4$  aqueous solution to a warm DMSO solution of the crude product. Yield: ~60%. *Anal.* Found: C, 36.31; H, 6.63; N, 18.34. Calc. for  $C_{28}H_{56}Cl_2N_{12}NiO_{10}S_2$ : C, 36.58; H, 6.14; N, 18.28%. FAB mass (*m/z*): 662.2 for  $[Cu(H_2L^2) + ClO_4]^-$ , 562.2 for  $[Cu(H_2L^2) - H]^-$ . IR ( $cm^{-1}$ ): 3229 [v(N-H)], 3151 [v(N-H)], 1640 (tetrazole), and 1575 (tetrazole).

**Preparation of  $[CuL^2]$  (4).** To a DMSO solution (20 mL) of **3** (0.5 g, 0.7 mmol) was added triethylamine (0.1 mL). The pale blue solution was slowly evaporated at room temperature to produce a pale blue solid. The product was collected by filtration, washed with methanol, and dried in air. Yield: ~80%. *Anal.* Found: C, 50.79; H, 7.93; N, 29.43. Calc. for  $C_{24}H_{42}N_{12}Cu$ : C, 51.27; H, 7.53; N, 29.29%. IR ( $cm^{-1}$ ): 3218 [v(N-H)], and 1655 (tetrazole), and 1570 (tetrazole).

**Crystal structure analysis.** Single crystals of **1** suitable for the X-ray crystallography were obtained from warm DMSO solution containing 3 ~ 5 drops of concentrated  $HClO_4$ . Intensity data were collected with CAD4 diffractometer using Mo-K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). Absorption corrections were applied with  $3\psi$  scans. The structures were solved by direct methods and refined by full-matrix least-squares methods based on  $F^2$  using SHELXS-97 and SHELXL-97.<sup>16</sup> Non-hydrogen atoms were refined anisotropically and all hydrogen atoms were included in calculated positions.

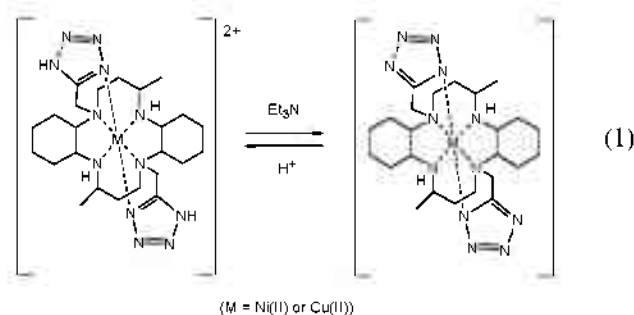
Crystal and refinement data:  $C_{23}H_{56}Cl_2N_{12}NiO_{10}S_2$ ,  $M = 914.55$ , Monoclinic,  $P2_1/c$ ,  $a = 8.3841(3)$ ,  $b = 15.3563(6)$ ,  $c = 15.4446(6) \text{ \AA}$ ,  $\beta = 102.798(1)^\circ$ ,  $V = 1939.1(2) \text{ \AA}^3$ ,  $Z = 4$ ,  $D_{calc} = 1.566 \text{ g cm}^{-3}$ ,  $\mu = 8.16 \text{ cm}^{-1}$ , Theta range =  $1.89 \sim 28.30^\circ$ ,  $-11 \leq h \leq 10$ ,  $-17 \leq k \leq 19$ ,  $-16 \leq l \leq 19$ , GOF on  $F^2 = 1.097$ , Final  $R_1 = 0.0334$ ,  $wR_2 = 0.0822$  ( $I > 2\sigma(I)$ ),  $R_1 = 0.0370$ ,  $wR_2 = 0.0840$  (all data), Largest diff. Peak and hole =  $0.424$  and  $-0.417 \text{ e \AA}^{-3}$ .

## Results and Discussion

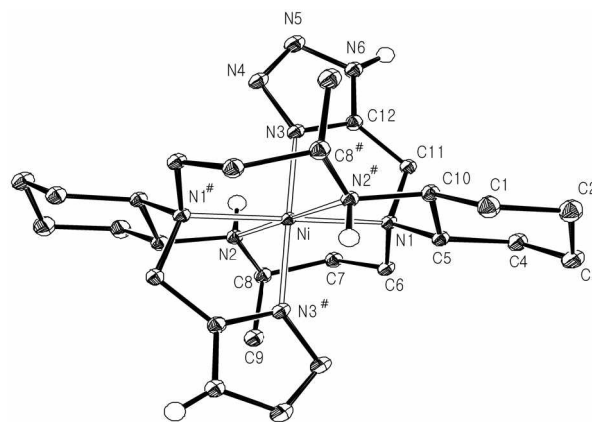
**Synthesis.** As described in the Experimental section, the nickel(II) complex **1** bearing two tetrazole pendant arms was prepared readily by the reaction of  $[NiL^1](ClO_4)_2$  with  $NaN_3$ . The reaction was found to be completed within 10 min at 60 ~ 70 °C. The copper(II) complex **3** bearing two tetrazole pendant arms was also prepared by the reaction of  $[CuL^1](ClO_4)_2$  with  $NaN_3$ . However, the preparation of the copper(II) complex requires much longer reaction time (> 24 h) under similar conditions, indicating that the reaction is strongly influenced by the nature of the central metal ion. This also supports the suggestion that the reaction of  $NaN_3$  with the *N*- $CH_2CN$  groups in  $[NiL^1](ClO_4)_2$  or  $[CuL^1](ClO_4)_2$  may be initiated by the formation of *trans*-octahedral species as an intermediate, in which  $N_3^-$  ions

and/or the pendant nitrile groups are coordinated to the central metal ion. The slower reaction of the copper(II) complex, compared to that of the nickel(II) complex, can be attributed to the relatively weak axial Cu- $N_3$  (or Cu-nitrile group) interaction of the *trans*-octahedral intermediate caused by the Jahn-Teller distortion.

The addition of a base to DMSO solution of **1** or **3** produces **2** or **4** where the pendant five-membered rings are deprotonated (Eq.(1)).



**Crystal Structure of **1**.** A perspective view of the cation of **1** is given in Fig. 1. Two tetrazole pendant arms are coordinated to the metal ion through the nitrogen atoms ( $N(3)$  and  $N(3^{\#})$ ), and the complex has distorted *trans*-octahedral coordination geometry with an inversion center. The cyclohexane rings and



**Figure 1.** A view of  $[Ni(H_2L^2)]^{2+}$  in **1**. H atoms attached to the carbon atoms are omitted for clarity.

**Table 1.** Selected Bond Distances [ $\text{\AA}$ ] and Angles [ $^\circ$ ] for **1**

Ni(1)-N(1)	2.136(2)	Ni(1)-N(2)	2.100(2)
Ni(1)-N(3)	2.122(2)	C(6)-N(1)	1.497(2)
C(11)-N(1)	1.496(2)	C(12)-N(3)	1.313(2)
C(12)-N(6)	1.324(2)	N(3)-N(4)	1.366(3)
N(4)-N(5)	1.292(2)	N(5)-N(6)	1.350(2)
N(1)-Ni-N(1 <sup>#</sup> )	180.0(1)	N(1)-Ni-N(2)	96.3(1)
N(1)-Ni-N(3)	80.0(1)	N(2)-Ni-N(3)	85.3(1)
Ni-N(3)-N(4)	140.1(2)	Ni-N(3)-C(12)	113.3(2)
N(4)-N(5)-N(6)	107.3(2)	N(2 <sup>#</sup> )-Ni-N(3)	94.7(2)
C(12)-N(3)-N(4)	106.6(2)	C(12)-N(6)-N(5)	108.2(2)
N(3)-N(4)-N(5)	109.3(3)	N(3)-C(12)-N(6)	108.7(3)
N(3)-C(12)-C(11)	123.4(2)		

**Table 2.** Electronic Absorption Spectral Data for the Complexes

Complex	$\lambda_{\text{max}}$ , nm ( $\epsilon$ , $\text{M}^{-1}\text{cm}^{-1}$ ) <sup>a</sup>
<b>1</b>	520 (4.7) 790 (4.1)
<b>2</b>	520 <sup>b</sup>
$[\text{NiL}^3](\text{ClO}_4)_2^c$	510 (8) <sup>d</sup> 800 (7.5) <sup>d</sup>
$[\text{NiL}^4](\text{ClO}_4)_2^e$	513 (12) 800 (5.5)
$[\text{NiL}^5](\text{ClO}_4)_2^f$	530 (6.0)
<b>3</b>	570 (105) 580 <sup>b</sup>
<b>4</b>	584 <sup>b</sup>
$[\text{CuL}^4](\text{ClO}_4)_2^g$	587 (65) <sup>g</sup>

<sup>a</sup>Measured in DMSO at room temperature unless otherwise specified. <sup>b</sup>Measured in Nujol mull. <sup>c</sup>Ref. 14. <sup>d</sup>Measured in water. <sup>e</sup>Ref. 13. <sup>f</sup>Ref. 15. <sup>g</sup>Measured in nitromethane.

the six-membered chelate rings adopt chair conformations. The tetrazole and methyl groups in each six-membered chelate ring are *anti* with respect to the  $\text{NiN}_4$  plane.

Selected bond distances and angles of **1** are listed in Table 1. The C(12)-N(3) bond distance [1.313(2) Å] is shorter than the C(12)-N(6) distance [1.324(2) Å] and is corresponding to the C=N double bond. The N(4)-N(5) double bond distance [1.292(2) Å] is distinctly shorter than the N(3)-N(4) and N(5)-N(6) distances [1.366(3) or 1.350(2) Å]. The N(3) atom is located at the trigonal plane of the Ni, C(12), and N(3) atoms. The axial Ni-N(3) bond is not perpendicular to the in-plane Ni-N bonds. The Ni-N distances [2.100(2) ~ 2.136(2) Å] are typical for high-spin *trans*-octahedral nickel(II) complexes with 14-membered tetraaza macrocyclic ligands.<sup>13-15</sup> Although the axial Ni-N(3) (pendant arm) distance [2.122(2) Å] is longer than the in-plane Ni-N(2) (secondary) distance [2.100(2) Å], it is *ca.* 0.01 Å shorter than the in-plane Ni-N(1) (tertiary) distance [2.136(2) Å]. It is also seen that the Ni-N(3) distance is *ca.* 0.13 Å shorter than the axial Ni-N (pyridine) distance (2.255(4) Å) of  $[\text{NiL}^5]\text{Cl}_2$ .<sup>15</sup> This clearly shows that the five-membered tetrazole pendant arms in **1** bind the metal ion more strongly than the pyridine groups in  $[\text{NiL}^5]\text{Cl}_2$ . However, the coordination ability of the tetrazole group is weaker than that of the imidate ester or amidine pendent arm in  $[\text{NiL}^3](\text{ClO}_4)_2$  or  $[\text{NiL}^4](\text{ClO}_4)_2$ : the Ni-N(3) distance is considerably longer than the axial Ni-N distance of  $[\text{NiL}^3](\text{ClO}_4)_2$  [2.088(3) Å] or  $[\text{NiL}^4](\text{ClO}_4)_2$  [2.100(3) Å].<sup>13,14</sup>

**Spectra and Properties.** Both **1** and **3** dissolve in DMSO, but are nearly insoluble in acetonitrile, nitromethane, or water. The tetrazole groups of complexes are not protonated even in 3.0 M  $\text{HClO}_4$  solutions. As described above, however, they readily undergo deprotonation in basic solutions to give the neutral complex **2** or **4**.

The value of magnetic moment of **1** (2.88  $\mu_{\text{B}}$ ) or **2** (2.86  $\mu_{\text{B}}$ ) is consistent with a  $d^8$  electronic configuration in octahedral coordination geometry. The infrared spectrum of **1** shows  $\nu$  (N-H) of the secondary amino groups at 3250 and 3117  $\text{cm}^{-1}$ . Peaks corresponding to the tetrazole groups are also observed at 1655 and 1570  $\text{cm}^{-1}$ . A broad band arising from the presence of perchlorate anions is observed at 1100  $\text{cm}^{-1}$ . The spectrum of **3** is quite similar to that of the corresponding the nickel(II) complex. The electronic absorption spectrum (Table 2) of **1** is not quite different from those of the nickel(II) complexes with

$\text{L}^3$ ,  $\text{L}^4$ , and  $\text{L}^5$ .<sup>13-15</sup> However, the wavelength (520 nm) for **1** is *ca.* 10 nm longer and shorter than those for  $[\text{NiL}^3](\text{ClO}_4)_2$  and  $[\text{NiL}^4](\text{ClO}_4)_2$ , respectively. This trend may be related to the axial Ni-N bond distances of the complexes ( $[\text{NiL}^3](\text{ClO}_4)_2 < \mathbf{1} < [\text{NiL}^4](\text{ClO}_4)_2$ ). The spectrum of **3** measured in DMSO shows a d-d transition band at 570 nm ( $\epsilon = 105 \text{ M}^{-1}\text{cm}^{-1}$ ), which is also comparable with those of  $[\text{CuL}^4](\text{ClO}_4)_2$  and other related *trans*-octahedral copper(II) complexes.<sup>12-15</sup> The value of the molar conductance for **1** ( $58 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) or **3** ( $59 \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) in DMSO indicates that each complex is a 1:2 electrolyte.<sup>17</sup>

The neutral complexes **2** and **4** are nearly insoluble even in DMSO, unlike **1** or **3**. The infrared spectra of **2** and **4** show  $\nu$  (N-H) of the secondary amino groups at 3261 and 3218  $\text{cm}^{-1}$ , respectively; no peak assignable to perchlorate anion is observed. The electronic absorption spectra of **2** (*ca.* 520 nm) and **4** (*ca.* 580 nm) measured in Nujol mull are similar to those of **1** and **3**, respectively, indicating that the pendant tetrazolato groups are also involved in coordination.

## Summary

This work has shown that **1** and **3** bearing two coordinated tetrazole pendant arms can be prepared by the reaction of  $\text{N}_3^-$  ion with  $[\text{NiL}^1](\text{ClO}_4)_2$  or  $[\text{CuL}^1](\text{ClO}_4)_2$ . In the presence of a base, **1** and **3** are readily deprotonated to **2** or **4**. This work also shows that the coordination ability of the tetrazole group in **1** is stronger than the pendant pyridine group in  $[\text{NiL}^5]\text{Cl}_2$ . To the best of our knowledge, **1** and **3** are the first examples of 14-membered tetraaza macrocyclic complexes bearing two coordinated tetrazole pendant arms.

**Supplementary Material.** Crystallographic data of **1** are available from the Cambridge Structural Database (CCDC 748100). Copies of the data can be obtained free of charge, on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (<http://www.ccdc.cam.ac.uk>, fax: +44-1223-336-033, or e-mail: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk)).

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