Nickel(II) Complexes of Saturated and Unsaturated 14-Membered Tetraaza Macrocycles Having Two *cis*-1,2-Diaminocyclohexane Subunits: Crystal Structure and Coordination Behaviors of the Saturated Complex

Shin-Geol Kang* **and Jong Hwa Jeong**[†]

Department of Chemistry, Daegu University, Gyeongsan 712-714, Korea
[†]Department of Chemistry, Kyungpook National University, Daegu 702-701, Korea

Received November 9, 2002

Key Words : Nickel(II) complex, Macrocyclic compounds, Diaminocyclohexane subunit, X-ray structure

There has been considerable interest in the preparation of various types of *C*- and/or *N*-configurational isomers of polyaza macrocyclic complexes.[1-11] In particular, 14-membered macrocyclic complexes having one or two 1,2-diaminocyclohexane subunit(s) theoretically occur as various *C*-configurational isomers because the diaminocyclohexane subunit exists as either *cis*- or *trans*-isomer. Although both [Ni(**3t**)]$(ClO_4)_2$ and [Ni(**3c**)]$(ClO_4)_2$ have a square-planar coordination geometry, reports indicate tat their chemical properties and stereochemistry vary with the isomeric structure of the 1,2-diaminocyclohexane subunit (Chart 1).[8] Furthermore, the chemical properties of [Ni(**4s**)]$^{2+}$ are different from those of [Ni(**4a**)]$^{2+}$, even though both of them contain *cis*-1,2-diaminocyclohexane subunits.[10] *C*-methylated complexes, [Ni(**1t**)]$^{2+}$ and [Ni(**2t**)]$^{2+}$, containing two *trans*-1,2-diaminocyclohexane subunits have been also reported.[11-13] However, relatively few isomers of such compounds have been prepared,[7-13] and discussions of their chemical properties are not sufficient.[8-10]

To gain further insight into the chemistry of such macrocyclic compounds, we prepared the nickel(II) complexes of **1c** and **2c**, having two *cis*-1,2-diaminocyclohexane subunits. It was found that the axial coordination of a solvent molecule, such as MeCN or DMF, is much easier to [Ni(**2c**)]$^{2+}$ than to [Ni(**2t**)]$^{2+}$. The coordination behavior of [Ni(**2c**)]$^{2+}$ is also considerably different from that of [Ni(**3c**)]$^{2+}$. To investigate the differences, the crystal structure of [Ni(**2c**)]$(ClO_4)_2$ was determined. The structure and chemical properties of [Ni(**2c**)]$(ClO_4)_2$ were compared with those of [Ni(**2t**)]$^{2+}$, [Ni(**3c**)]$^{2+}$, and other related nickel(II) complexes.

Experimental Section

Measurements. IR spectra were recorded on a Shimadzu IR-440 spectrophotometer and electronic spectra with an Analytik Jena Specord 200 UV/vis spectrophotometer. Conductance measurements were taken with a Metrohm Herisau Conductometer E518, mass spectra were measured with a Shimadzu GCMSD-QP5050 spectrometer, and NMR spectra were recorded with a Varian Mercury 300 FT NMR spectrometer. Elemental analyzes were performed at the Center for Laboratory Facilities, Daegu University, Kyungsan, Korea.

Synthesis. [$H_2$1c](ClO_4)$_2$. To a cooled (~4 °C) ethanol (30 mL) solution of *cis*-1,2-diaminocyclohexane (7.0 mL, 50 mmol) was added 60% perchloric acid (5.0 mL, 50 mmol) with stirring. After the addition of methyl vinyl ketone (4.5 mL, 50 mmol) over a period of 1 h, the mixture was stirred for 2 h at room temperature and then stored in a refrigerator. The white solid, which had been formed, was filtered, washed with ethanol, and dried in air. Yield: ~20%. Found: C, 44.80; H, 7.17; N, 10.41. Calc. for $C_{20}H_{38}N_4Cl_2O_8$: C,

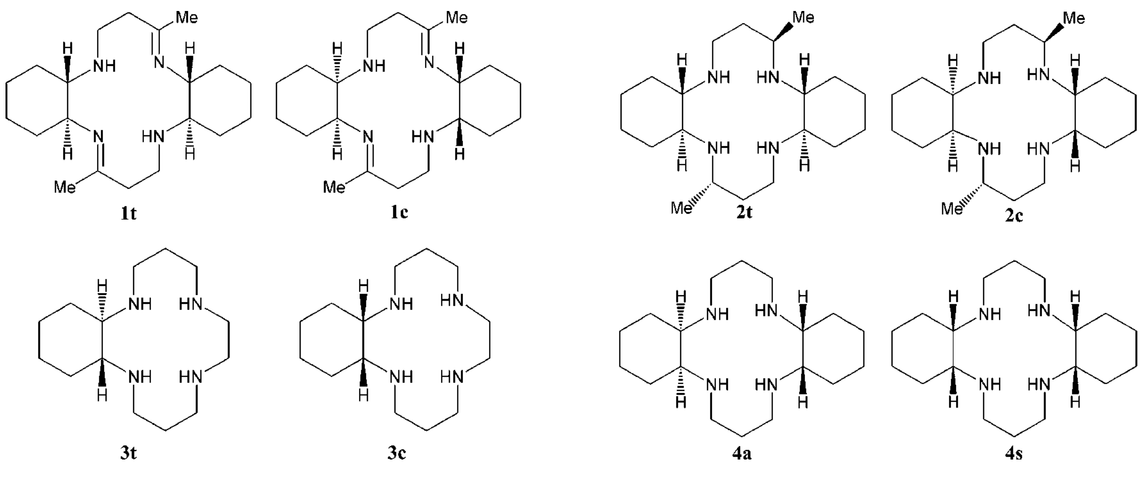

Chart 1

44.99; H, 7.12; N, 10.50%. IR (cm^{-1}): 1660 (ν (C=N)) and 3150 (ν (N-H)).

2c. This compound was prepared by the reaction of [H$_2$**1c**](ClO$_4$)$_2$ with NaBH$_4$ in the presence of NaOH, following the procedure reported for [H$_2$**1t**](ClO$_4$)$_2$.[12] Yield: ~80%. Found: C, 71.40; H, 11.85, N, 16.52. Calc. for $C_{20}H_{40}N_4$: C, 71.37; H, 11.98; N, 16.65%. Mass (*m/z*): 336. IR (cm^{-1}): 3250 (ν (N-H)) and 3290 (ν (N-H)). ^{1}H NMR (CDCl$_3$): δ 0.95 (*d*, Me). ^{13}C NMR (CDCl$_3$): δ 19.7 (Me), 20.2, 24.7 (*d*), 26.3 (*d*), 38.3, 46.9, 54.4, 56.9 ppm.

[Ni(L)](ClO$_4$)$_2$ (L=1c or 2c). After refluxing a methanol suspension (25 mL) of Ni(OAc)$_2$·4H$_2$O (2.0 g) and [H$_2$**1c**](ClO$_4$)$_2$ (1.5 g) or **2c** (1.0 g) for 30 min, an excess of HClO$_4$ or NaClO$_4$ was added to the solution. The yellow solid, which had been formed, was filtered and recrystallized from the hot acetonitrile-water (1 : 3) mixture. Yield: ~80%. **[Ni(1c)](ClO$_4$)$_2$** (Found: C, 40.55; H, 6.17; N, 9.44. Calc. for $C_{20}H_{36}N_4NiCl_2O_8$: C, 40.67; H, 6.10; N, 9.49%. IR (cm^{-1}): 1640 (ν (C=N)) and 3210 (ν (N-H)).) **[Ni(2c)](ClO$_4$)$_2$** (Found: C, 40.38; H, 6.77; N, 9.42 Calc. for $C_{20}H_{40}N_4NiCl_2O_8$: C, 40.39; H, 6.73; N, 9.43%. IR (cm^{-1}): 3160 (ν (N-H)) and 3220 (ν (N-H)).

[Ni(L)](PF$_6$)$_2$ (L=1c or 2c). An excess of NH$_4$PF$_6$ was added to a warm acetonitrile (10 mL) solution of [Ni(L)](ClO$_4$)$_2$ (0.5 g). After filtering the mixture, water (10 mL) was added to the filtrate. The yellow solid was filtered, washed with water, and dried in air. **[Ni(1c)](PF$_6$)$_2$**. ^{1}H NMR (CD$_3$NO$_3$): δ 2.10 (*s*, Me). ^{13}C NMR (CD$_3$NO$_2$): δ 18.6, 23.4, 23.6, 24.5, 27.2, 39.9, 42.6, 61.3, 66.6, and 186.1 (C=N) ppm. **[Ni(2c)](PF$_6$)$_2$**. ^{1}H NMR (CD$_3$NO$_3$): δ 1.20 (*d*, Me). ^{13}C NMR (CD$_3$NO$_2$): δ 18.7, 20.1, 23.7, 23.9, 24.1, 35.3, 45.7, 51.1, 58.7, and 61.0 ppm.

X-ray crystal structure determination. A yellow crystal suitable for X-ray crystallography was mounted on a CAD4 diffractometer. Intensity data, 4650, were collected and were corrected for Lorentz and polarization effects as well as for absorption corrections with ψ scans. The structure was determined by direct methods and refined by full-matrix least-squares on F^2 with reflections above 2σ level using SHLEXS-97 and SHLEXL-97.[14] All non-hydrogen atoms were refined anisotropically. All hydrogen atoms were calculated using riding models except H(1) and H(2) that were refined isotropically. The crystal and refinement data are listed in Table 1, and the selected bond distances and angles are in Table 3.

Results and Discussion

General characterization. Infrared, mass, and/or NMR spectral data of the compounds prepared in this work are listed in the Experimental Section with the elemental analyses. ^{1}H NMR spectra of [Ni(**1c**)](PF$_6$)$_2$ and [Ni(**2c**)](PF$_6$)$_2$ show only one singlet and doublet, respectively, for the two methyl groups. ^{13}C NMR spectra of the complexes show ten peaks, indicating that each complex prepared in the present work is one of the diastereoisomers with ten pairs of inequivalent carbon atoms. The IR spectrum of [Ni(**1c**)](ClO$_4$)$_2$ shows only one ν (C=N) or ν (N-H), as does that of *N-rac*-[Ni(**1t**)](ClO$_4$)$_2$.[12] In the IR spectrum of [Ni(**2c**)](ClO$_4$)$_2$, however, two bands arising from the secondary amino groups are observed at 3160 and 3220 cm^{-1}. This corresponds to the crystallographic determination that the environment of the amino group involving the N(2) atom is considerably different from that involving the N(1) atom (*see* below). The molar conductance values of the complexes measured in water (180-200 Ω^{-1}mol^{-1}cm^2) and acetonitrile (230-250 Ω^{-1}mol^{-1}cm^2) indicate that the complexes are 1 : 2 electrolytes.

The wavelengths and molar absorption coefficients (Table 2) of the *d-d* transition band for [Ni(**1c**)](ClO$_4$)$_2$ and [Ni(**2c**)](ClO$_4$)$_2$ measured in nitromethane are quite similar to those for the square-planar complexes *N-rac*-[Ni(**1t**)](ClO$_4$)$_2$ and [Ni(**2t**)](ClO$_4$)$_2$,[12] indicating that the ligand-field strengths of the complexes are not affected significantly by the *C*-configuration. The visible spectrum of [Ni(**2c**)](ClO$_4$)$_2$ is also comparable with that of [Ni(**4a**)](ClO$_4$)$_2$.[10] However, the wavelength is distinctly longer than those for [Ni(**3c**)](ClO$_4$)$_2$ and [Ni(**4s**)](ClO$_4$)$_2$.[9,10]

Crystal structure of [Ni(2c)](ClO$_4$)$_2$. The ORTEP view (Figure 1) of [Ni(**2c**)]$^{2+}$ shows that the complex cation has a square-planar coordination geometry with an inversion center at the metal. The macrocyclic ligand contains two *cis*-1,2-diaminocyclohexane subunits. The five-membered chelate rings have a *gauche* conformation, and the six-member chelate rings have a chair one. The two -(CH$_2$)$_4$- parts of the

Table 1. Crystal and Refinement Data for [Ni(**2c**)](ClO$_4$)$_2$

Formula	$C_{20}H_{40}Cl_2N_4NiO_8$
M	594.17
Crystal system	Monoclinic
Space group	*C*2*c*
a (Å)	19.806(2)
b (Å)	12.270(2)
c (Å)	12.608(2)
β (°)	112.82(1)
V (Å^3)	2600.1(4)
Z	4
D_c (g cm^{-3})	1.518
μ (cm^{-1})	10.03
F(000)	1256
Crystal size (mm)	0.45 × 0.45 × 0.40
θ range (°)	2.00-25.47
Index ranges	$-23 \le h \le 22$, $-14 \le k \le 0$, $0 \le l \le 14$
Reflections collected	4650
Independent reflections	2408
Reflections observed (>2σ)	1095
Data completeness	1.00
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2408 / 0 / 169
Goodness-of-fit on F^2	0.853
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0511$, $wR_2 = 0.0852$
Largest diff. peak and hole	0.485 and -0.528 eÅ^{-3}

$R_1 = \Sigma || F_o| - | F_c|| / \Sigma | F_o|$.
$wR_2 = [\Sigma w(F_o^2 - F_c^2)^2 / \Sigma[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$; $P = (F_o^2 + 2F_c^2)/3$.

Table 2. Electronic Absorption Spectra and Percentage of Square-Planar Species of the Nickel(II) Complexes in Various Solutions at 20 °C

Complex	Solvent	λ_{max}, nm (ε, M^{-1} cm^{-1})	% Square-planar[a]
[Ni(**1t**)](ClO$_4$)$_2$ [b]	$MeNO_2$	439(77)	
	Me_2SO	436(77)	~100
	H_2O	440(73)	95
	MeCN	442(73)	95
	DMF	443(50)	65
[Ni(**1c**)](ClO$_4$)$_2$	$MeNO_2$	445(75)	
	Me_2SO	445(75)	~100
	H_2O	445(75)	~100
	MeCN	447(65)	87
	DMF	446(48)	64
[Ni(**2t**)](ClO$_4$)$_2$ [c]	$MeNO_2$	463(73)	
	Me_2SO	460(73)	~100
	H_2O	459(70)	96
	MeCN	465(66)	90
	DMF	463(70)	96
[Ni(**2c**)](ClO$_4$)$_2$	$MeNO_2$	465(75)	
	Me_2SO	463(75)	~100
	H_2O	460(60)	80
	MeCN	467(19)	25
	DMF	460(27)	36
[Ni(**3t**)](ClO$_4$)$_2$ [d]	H_2O	455(40)	57
	DMF	676(3.5) 510(8.0) 337(19)	<10
[Ni(**3c**)](ClO$_4$)$_2$ [d]	H_2O	446(70)	~100
	DMF	448(52)	71
[Ni(**4s**)](ClO$_4$)$_2$ [e]	H_2O	440(80)	
[Ni(**4a**)](ClO$_4$)$_2$ [e]	H_2O	455(60)	

[a] Percentage of square-planar species = 100(ε_{obs})/(ε_{sqpl}), where ε_{obs} and ε_{sqpl} are the molar absorption coefficients obtained in coordinating solvents and in nitromethane, respectively. [b] Refs. 7 and 12. [c] Ref. 12. [d] Refs. 9 and 10. [e] Ref. 10.

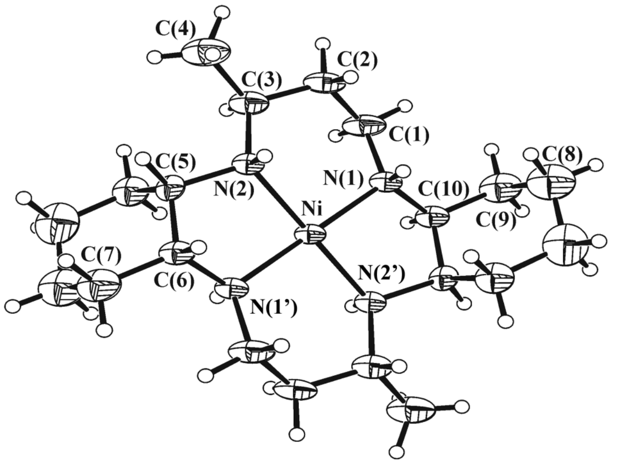

Figure 1. An ORTEP drawing of [Ni(**2c**)]$^{2+}$ in [Ni(**2c**)](ClO$_4$)$_2$ with the atomic labeling scheme.

cyclohexane subunits are *anti* with respect to the macrocyclic plane. The stereochemistry of the four nitrogen atoms in the complex is a *trans*-III form, which is quite similar to that in [Ni(**2t**)](ClO$_4$)$_2$.[11]

As expected from the electronic spectra, the average Ni-N distance (1.944(7) Å) of [Ni(**2c**)](ClO$_4$)$_2$ is similar to that of [Ni(**2t**)](ClO$_4$)$_2$ (1.951 Å).[11] The Ni-N(2) distance (1.959(4) Å) is *ca.* 0.03 Å longer than the Ni-N(1) distance. The N(2)-C(5) (1.513(4) Å) distance involved in the five-member chelate ring is also distinctly longer than the N(1)-C(10) (1.471(5) Å) distance, indicating the severer steric repulsion around the N(2) and C(5) atoms. This may be correlated with the fact that the two hydrogen atoms attached to N(2) and C(5) atoms are *syn* with respect to the five-member chelate ring, whereas those attached to N(1) and C(10) atoms are *anti*. It is interesting to find that such structural features are quite different from those reported for [Ni(**2t**)](ClO$_4$)$_2$, in which the two hydrogen atoms attached to each N-C bond of the five-member chelate ring are *anti*;[11] in the case of [Ni(**2t**)](ClO$_4$)$_2$, the Ni-N (next to the methylated carbon) distance (1.946(3) Å) is slightly shorter than the other Ni-N distance (1.957(3) Å) and, furthermore, the two N-C bond distances [1.500(4) Å and 1.503(4) Å] involved in the five-member chelate ring are nearly the same.[11] The Ni-N(2)-C(3) (124.4(3)°) and Ni-N(1)-C(1) (117.3(3)°) angles are distinctly larger and smaller, respectively, than 120°. This trend is also somewhat different from that reported for [Ni(**2t**)](ClO$_4$)$_2$, in which the two Ni-C-N angles involved in a six-membered chelate ring are 119.4(2)° and 120.9(2)°.[11] The geometry around the nickel ion deviates from the ideal square-planar; the N(1)-Ni-N(2) angle is expended to 93.9(3)°, whereas the N(2)-Ni-N(2A) angle is reduced to 86.1(2)°. The crystallographic results clearly show that, although [Ni(**2c**)](ClO$_4$)$_2$ and [Ni(**2t**)](ClO$_4$)$_2$ have a similar *N*-configuration (*trans*-III), their structural features are significantly affected by the isomeric structure of the 1,2-diaminohexane subunit. This result also contrast with the reported trend that the stereochemistry of the *cis*-isomer [Ni(**3c**)](ClO$_4$)$_2$ is a *trans*-I form and is different from that of [Ni(**3t**)](ClO$_4$)$_2$ (*trans*-III).[8] The conformational difference between [Ni(**2c**)]$^{2+}$ and [Ni(**3c**)]$^{2+}$ is somewhat interesting because the conditions for the preparation of the two complexes are nearly the same.

Coordination of solvent molecule. The absorption spectra (Figure 2) of [Ni(**2c**)](ClO$_4$)$_2$ show that the molar absorption coefficient (at *ca.* 460 nm) measured in coordinating solvents, such as DMF, MeCN, and H_2O, is much smaller than that in $MeNO_2$, a non-coordinating solvent, and is strongly influenced by the nature of the solvent. This can be attributed to the equilibrium of the square-planar [Ni(**2c**)]$^{2+}$ and octahedral [Ni(**2c**)(S)$_2$]$^{2+}$ species in coordinating solvent (S).[7,15-19] The percentages of the square-planar species, which were calculated by reported methods,[15-17] are listed in Table 2, along with those of [Ni(**1c**)]$^{2+}$ and other related complexes. The percentage for the unsaturated complex [Ni(**1c**)]$^{2+}$ in DMF, MeCN, or H_2O is higher than that for the saturated complex [Ni(**2c**)]$^{2+}$, as usual. In each solvent, the percentage of [Ni(**1c**)]$^{2+}$ is not very different from that of [Ni(**1t**)]$^{2+}$. On the other hand, most interestingly, the value for [Ni(**2c**)]$^{2+}$ in

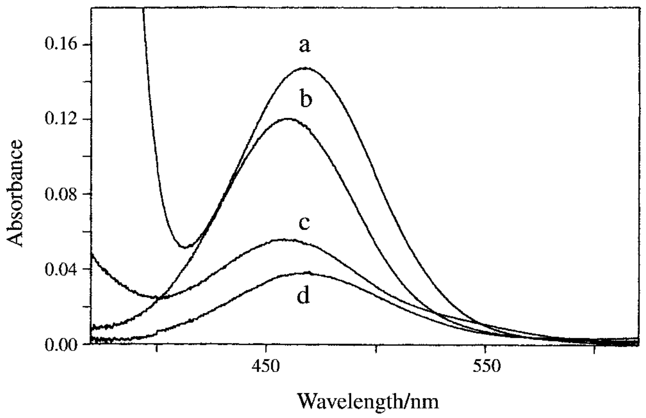

Figure 2. Electronic absorption spectra of [Ni(**2c**)](ClO_4)$_2$ (2.0 × 10^{-3} M) in $MeNO_2$ (a), H_2O (b), DMF (c), and MeCN (d).

Table 3. Bond Distances (Å) and Angles (°) for [Ni(**2c**)](ClO_4)$_2$

Ni-N(1)	1.928(3)	Ni-N(2)	1.959(4)
N(1)-C(1)	1.491(5)	N(1)-C(10)	1.471(5)
N(2)-C(3)	1.497(5)	N(2)-C(5)	1.513(4)
N(1)-Ni-N(1)	180.0(2)	N(2)-Ni-N(2)	180.0(2)
N(1)-Ni-N(2)	93.9(3)	N(1)-Ni-N(2)	86.1(2)
Ni-N(1)-C(1)	117.3(3)	Ni-N(1)-C(10)	110.0(3)
Ni-N(2)-C(3)	124.4(3)	Ni-N(2)-C(5)	108.8(2)
N(1)-C(1)-C(2)	111.7(4)	N(1)-C(10)-C(9)	115.6(4)
N(2)-C(3)-C(2)	110.2(3)	N(2)-C(5)-C(6)	112.2(4)

MeCN (25%) or DMF (36%) is much lower than that for [Ni(**2t**)]$^{2+}$ (≥ 90%). This indicates that the *cis*-isomer binds the solvent molecule much more easily than does the *trans*-isomer. Such a coordination behavior of [Ni(**2c**)]$^{2+}$ may be closely related to the longer Ni-N(2) (next to the methylated carbon atom) distance and/or the more distorted structure, which make the attack of the solvent molecule easier. The present result contrasts with the reported trend that the proportion of the square-planar species in DMF is much higher for the *cis*-isomer [Ni(**3c**)]$^{2+}$ (71%) than for the *trans*-isomer [Ni(**3t**)]$^{2+}$ (<10%).[9]

Table 2 also shows that the relative coordinating ability of the solvent molecules to [Ni(**2c**)](ClO_4)$_2$ ($Me_2SO < H_2O \ll$ DMF < MeCN) differs from that to [Ni(**1c**)](ClO_4)$_2$ (Me_2SO <H_2O < MeCN < DMF). In any case, the coordinating ability of the solvent molecules is not parallel with their inherent basicity (Gutmann's donor number of the solvent decreases in the order of Me_2SO > DMF > H_2O > MeCN). The relatively weak coordinating ability of Me_2SO is the result of the strong self-association and/or the severe steric hindrance of the methyl groups.[7,18] The stronger coordinating ability of MeCN to [Ni(**2c**)]$^{2+}$, compared with that of DMF or H_2O, can be attributed to its rod like geometry and weak basicity toward interactions with the protons of the coordinated secondary amino groups.[17,18] In the case of the unsaturated complex [Ni(**1c**)]$^{2+}$, however, both the solvent-amino group interaction and the steric hindrance caused by the macrocyclic ligand are less significant. Therefore, the inherent basicity (DMF > MeCN) of the solvent molecule may play an important role in the axial coordination of [Ni(**1c**)]$^{2+}$.

Concluding remarks. The properties of the unsaturated complex [Ni(**1c**)](ClO_4)$_2$ are similar to those of [Ni(**1t**)](ClO_4)$_2$. However, the conversion of [Ni(**2t**)](ClO_4)$_2$ to its *cis*-isomer [Ni(**2c**)](ClO_4)$_2$ changes the structural characteristics and makes the axial coordination of solvent molecules such as MeCN, DMF, and H_2O much easier. The stereochemistry and the coordination behavior of [Ni(**2c**)](ClO_4)$_2$ is also different from that of [Ni(**3c**)](ClO_4)$_2$, indicating that chemical properties of the saturated 14-membered tetraaza macrocyclic complexes also can be affected significantly by the number of the 1,2-diaminocyclohexane subunits.

Acknowledgments. This work was supported by the Research Grant of Daegu University (2002).

References

1. Maimon, E.; Zilbermann, I.; Golub, G.; Ellern, A.; Shames, A. I.; Cohen, H.; Meyerstein, D. *Inorg. Chim. Acta* **2001**, *324*, 65, and references cited therein.
2. Zimmer, M. *Coord. Chem. Rev.* **2001**, *212*, 133.
3. Curtis, N. F. *Inorg. Chim. Acta* **2001**, *317*, 27.
4. (a) Chen, J.-W.; Chungm, C.-S. *Inorg. Chem*. **1986**, *25*, 2841. (b) Moore, P.; Sachinidis, J.; Willey, G. R. *J. Chem. Soc., Chem. Commun*. **1983**, 522. (c) Szalda, D. J.; Schwarz, C. L.; Creutz, C. *Inorg. Chem*. **1991**, *30*, 586.
5. Misra, T. K.; Chung, C.-S.; Cheng, J.; Lu, T.-H. *Polyhedron* **2001**, *20*, 3249.
6. Edwards, R.; Newman, P. D.; Stephens, F. S.; Vagg, R. S.; Williams, P. A. *Inorg. Chim. Acta* **1993**, *204*, 125.
7. Kang, S.-G.; Kim, M.-S.; Kim, S.-G.; Jeong, J. H. *Inorg. Chim. Acta* **1997**, *254*, 391.
8. Hashimoto, M.; Sakata, K.; Tanoue, Y. *Polyhedron* **2001**, *20*, 409.
9. Sakata, K.; Odamura, T.; Kanbara, Y.; Nibu, T.; Hashimoto, M.; Tsuge, A.; Moriguchi, Y. *Polyhedron* **1998**, *17*, 1463.
10. Kobiro, K.; Nakayama, A.; Hiro, T.; Suwa, M.; Tobe, Y. *Inorg. Chem*. **1992**, *31*, 676.
11. Kang, S.-G.; Kim, M.-S.; Whang, D.; Kim, K. *Inorg. Chim. Acta* **1998**, *279*, 238.
12. Kang, S.-G.; Kweon, J. K.; Jung, S.-K. *Bull. Korean Chem. Soc.* **1991**, *12*, 483.
13. Kang, S.-G.; Kim, M.-S.; Whang, D.; Kim, K. *J. Chem. Soc., Dalton Trans.* **1994**, 853.
14. Sheldrick, G. M. *SHELXS-97, Program for the Solution of Crystal Structure*; University of Göttingen: Göttingen, Germany, 1990; Sheldrick, G. M. *SHELXL-97*, Program for crystal structure refinement; University of Göttingen: Göttingen, Germany, 1997.
15. Suh, M. P.; Kang, S.-G.; Goedken, V. L.; Park, S.-H. *Inorg. Chem*. **1991**, *30*, 365.
16. Suh, M. P.; Kang, S.-G. *Inorg. Chem*. **1988**, *27*, 2544.
17. Iwamoto, E.; Yokoyama, T.; Yamasaka, S.; Kumamaru, T.; Yamamoto, Y. *J. Chem. Soc., Dalton Trans.* **1988**, 1935, and references cited therein.
18. Yokoyama, T.; Iwamoto, E.; Kumamaru, T. *Bull. Chem. Soc. Jpn.* **1991**, *64*, 464.
19. Moore, P.; Sachinidis, J.; Wieley, G. R. *J. Chem. Soc., Dalton Trans*. **1984**, 1323.