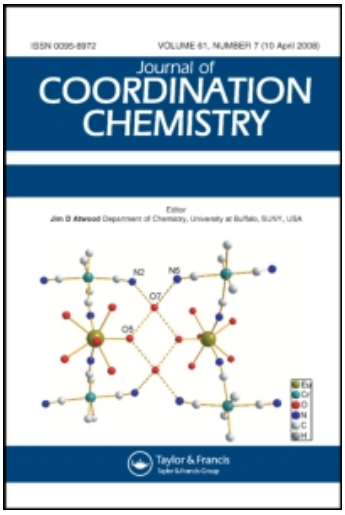


Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

HYDROGENATION OF A DELOCALIZED DIIMINATE SIX-MEMBERED CHELATE RING IN TETRAAZAMACROCYCLIC NICKEL(II) COMPLEXES BY SODIUM BOROHYDRIDE IN WATER—EFFECT OF PROTONATION-DEPROTONATION EQUILIBRIA AND STEREOSELECIVE REDUCTION

Katsura Mochizuki[a]; Takesi Kondo[a]; Shinobu Manaka[a]; Takashi Kajiwara[b]; Tasuku Ito[b]
[a] Department of Chemistry, Yokohama City University, Yokohama, Japan [b] Department of Chemistry, Faculty of Science, Tohoku University, Sendai, Japan

To cite this Article Mochizuki, Katsura , Kondo, Takesi , Manaka, Shinobu , Kajiwara, Takashi and Ito, Tasuku(1996) 'HYDROGENATION OF A DELOCALIZED DIIMINATE SIX-MEMBERED CHELATE RING IN TETRAAZAMACROCYCLIC NICKEL(II) COMPLEXES BY SODIUM BOROHYDRIDE IN WATER—EFFECT OF PROTONATION-DEPROTONATION EQUILIBRIA AND STEREOSELECIVE REDUCTION', Journal of Coordination Chemistry, 37: 1, 205 — 216
To link to this Article: DOI: 10.1080/00958979608023553
URL: http://dx.doi.org/10.1080/00958979608023553

J. Coord. Chem., 1996, Vol 37, pp. 205–216
Reprints available directly from the publisher
Photocopying permitted by license only

HYDROGENATION OF A DELOCALIZED DIIMINATE SIX-MEMBERED CHELATE RING IN TETRAAZAMACROCYCLIC NICKEL(II) COMPLEXES BY SODIUM BOROHYDRIDE IN WATER – EFFECT OF PROTONATION-DEPROTONATION EQUILIBRIA AND STEREOSELECTIVE REDUCTION

KATSURA MOCHIZUKI, TAKESI KONDO, SHINOBU MANAKA,

Department of Chemistry, Yokohama City University, Yokohama 236, Japan

TAKASHI KAJIWARA and TASUKU ITO*

Department of Chemistry, Faculty of Science, Tohoku University, Aramaki, Aoba-ku, Sendai 980-77, Japan

(Received February 23, 1995; in final form July 25, 1995)

Charge delocalized diiminate six-membered chelate rings in the 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane-4,6-dienatonickel(II) ion(**1**) and the α,α'-bis(5,7-dimethyl-1,4,8,11-tetraaza-cyclotetradeca-4,6-dienato-6-yl)-xylenedinicke(II) ion(**2**) were hydrogenated in aqueous media by sodium borohydride. In the reduction reactions, control of the pH of the reaction mixture was essential, and the pH of the solution was kept during the reaction at 3 and at 5–6 for hydrogenations of **1** and **2**, respectively. The delocalized diiminate chelate ring is in protonation-deprotonation equilibrium with the β diimine form and the pK_a of the equilibrium for **2** was determined to be 9.0 for **2a** (*o*-xylylene bridged complex), 9.3 for **2b** (*m*-xylylene bridged complex), and 10.0 for **2c** (*p*-xylylene bridged complex). The appropriate pH values in the hydrogenation reactions were based on the pK_a's. X-ray structure analyses on two reduction products of **1** show that the chirality of the two asymmetric carbons in the cyclam ring is of the meso-form in the major reduction product whereas that in the minor product is of the racemic form. In the major reduction product of **2**, two chiral carbons in each cyclam ring take the meso-form.

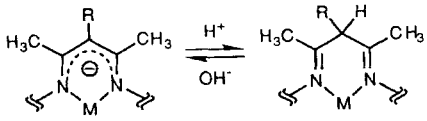
KEYWORDS: chelate complex, tetraaza nickel(II), cyclam, stereoselective

INTRODUCTION

Tetraaza macrocyclic complexes derived by metal-template reactions from acetylacetone and linear tetraamines have the charge delocalized diiminate six-membered chelate ring (**I**).[1,2] Under strongly acidic media, protonation occurs at the central carbon atom to afford the β-diimine chelate ring (**II**). Generally, **II** reverts readily

*Author for correspondence

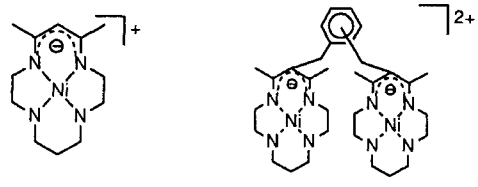
to **I** upon addition of base and the process can be regarded as an acid-base equilibrium (Eq 1). Cummings reported that the acidity of the metal chelate is markedly dependent on the kind of metal ions and that the pK_a of the 14-membered macrocyclic Ni(II) complex, 5,7,-dimethyl-1,4,8,11-tetraazacyclotetradecane-4,6-dienatonickel(II) (complex (**1**)), and its Cu(II) analog are 6.45 and 9.3, respectively.[2] Hydrogenation of chelate ring **I** should afford a fully saturated chelate ring which is less reactive and convenient for certain purposes.



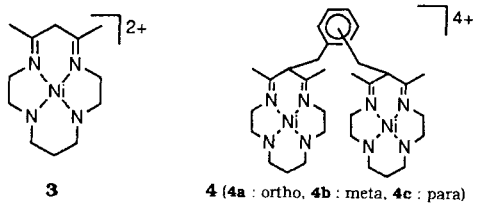
(1)

I **II**

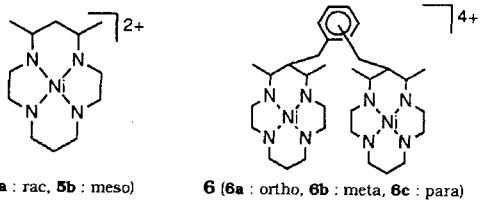
To our knowledge, however, there has been no report on hydrogenation for delocalized chelate ring **I**, although Holtman and Cummings reported catalytic reduction for the protonated diimine form of **1** and its 13-membered analog with use of Raney nickel.[3] This paper reports hydrogenation of 14-membered mononuclear and dinuclear Ni(II) complexes with this type of delocalized chelate ring. **1** and α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato-6-yl)-xylenedinickel(II) (**2**). While Holtman and Cummings described one isomer of **5** which is the only species they isolated,[3] two isomers were isolated in this study. Preliminary results on the structure of **6a** has been published.[4] Detailed chemistry of the reduced



1 **2** (**2a** : ortho, **2b** : meta, **2c** : para)



3 **4** (**4a** : ortho, **4b** : meta, **4c** : para)



5 (**5a** : rac, **5b** : meso) **6** (**6a** : ortho, **6b** : meta, **6c** : para)

complexes **5** including electrocatalytic activity of CO_2 reduction and equilibria between four and six-coordinate species in solution will be reported in a separate paper.[5]

RESULTS AND DISCUSSION

In this study, we used as the hydrogenating reagent, sodium borohydride, which is widely used in organic chemistry and has also been conveniently used in reduction of unsaturated bonds in coordinated organic ligands of metal complexes. For example, the imine bonds in Ni(II) complexes with the Curtis type tetraaza macrocyclic diene ligands can readily be hydrogenated by adding solid $NaBH_4$ portionwise to an aqueous or aqueous methanol solution.[6] We tried to reduce the delocalized chelate rings in **1** and **2** in a similar way, but were totally unsuccessful even though the reactions were carried out at higher temperatures (70–80°C) and a large excess of $NaBH_4$ was used. As mentioned above, the charge delocalized chelate ring (**I**) is in equilibrium with the isolated diimine form (**II**) which may be susceptible to hydrogenation with $NaBH_4$. In actual fact, the charge delocalized chelate rings in **1** and **2** were reduced when acidified solution of **1** or **2** was allowed to react with a large excess of $NaBH_4$. In this hydrogenation reaction, it is necessary to control the pH of the solution within a relatively narrow optimum region. In the hydrogenation by $NaBH_4$, the pH of the solution gradually increases as the reaction proceeds, and hence the equilibrium (1) shifts toward the charge delocalized form. In the actual experimental procedure, the pH of the solution was adjusted with hydrochloric acid to the desired value after every portionwise addition of $NaBH_4$ (see Experimental). The optimal pH for the reaction depends on the pK_a of each system. We found for the first time that the pK_a is strongly dependent on the ligand structure as discussed below. $NaBH_4$ decomposes under acidic conditions, hence portionwise addition of a large excess of $NaBH_4$ is required in the procedure.

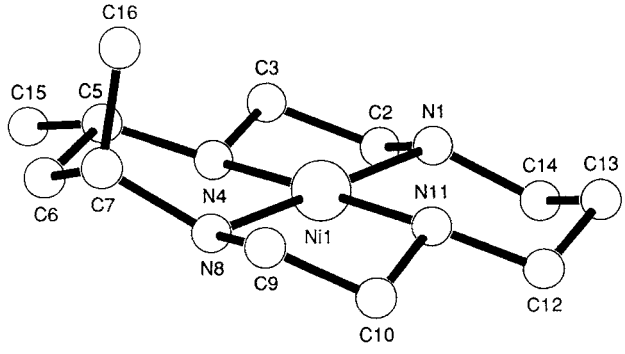


Figure 1 A perspective view of the cation in [**5a**]$(ClO_4)_2$. Selected bond distances (Å) and angles (deg):Ni(1)-N(1), 1.95(1); Ni(1)-N(4), 1.937(10); Ni(1)-N(8), 1.89(1); Ni(1)-N(11), 1.93(1); N(1)-Ni(1)-N(4), 87.3(5); N(1)-Ni(1)-N(8), 178.7(5); N(1)-Ni(1)-N(11), 92.8(5); N(4)-Ni(1)-N(8), 93.7(5); N(4)-Ni(1)-N(11), 178.3(4); N(8)-Ni(1)-N(11), 86.2(5).

*Hydrogenation of the 5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane-4,6-dienatonickel(II) ion (**I**) and the stereochemistry of the reduction product (**5**).*

Holtman and Cummings reported hydrogenation for the protonated diimine form of **1**, that is, hydrogenation of **3**, by Raney nickel but they did not report isomers of the product nor identified its stereochemistry. Hydrogenation of such a chelate ring should give rise to asymmetry at the methylated carbon centers and the combination of chirality of two asymmetric carbons should afford C*-racemic and C*-meso isomers. As described below, the present results were quite different from those by Holtman and Cummings in the presence of isomer **5** and in the stereochemistry of the major reduction product.

On the basis of the reported pK_a value (6.45),[2] $NaBH_4$ hydrogenation for **1** was carried out by controlling pH of the reaction mixture at approximately 3 throughout the reaction. The reduction was successfully accomplished with total isolation yield of *ca.* 45%. When the reduction products were subjected to cation-exchange chromatography (SP Sephadex C-25, eluting agent: a mixed solution containing 0.05 M NaI and 0.05 M NaCl), two components were separated as a first orange trace band and a second brown-orange main band. From each band, square-planar four-coordinate nickel(II) complexes, **5a** and **5b**, were isolated as perchlorate salts, and further free ligands of **5a** and **5b** were also isolated by treating them with CN^-, (see Experimental). It was found, as shown below, that **5a** and **5b** contain C*-racemic and C*-meso ligands, respectively. Both **5a**$(ClO_4)_2$ and **5b**$(ClO_4)_2$ showed FAB-mass peaks at the same positions, m/z = 385 [M-ClO_4]. The free ligands of **5a** and **5b** showed a FAB-mass peak at m/z = 229 [M + H] and both of their ^{13}C NMR spectra consisted of the expected seven signals due to one methyl, five methylene, and one methine carbon, where carbon atoms within each macrocyclic ligand are pairwise equivalent.

Single crystal X-ray analyses were carried out on [**5a**]$(ClO_4)_2$ and [**5b**$(H_2O)_2$]$Cl_2 \cdot 2H_2O$, the latter of which was obtained as described in the Experimental section.[7] Atomic coordinates for both structures are given in Tables 1 and 2. Figures 1 and 2 show X-ray structures of $[\mathbf{5a}]^{2+}$ and $[\mathbf{5b}(H_2O)_2]^{2+}$, respectively.

Complex $[\mathbf{5a}]^{2+}$ is a square planar four-coordinate complex whereas $[\mathbf{5b}(H_2O)_2]^{2+}$ is a *pseudo* octahedral complex with two aquo ligands occupying the axial positions. It should be noted that the counter anions of $[\mathbf{5b}(H_2O)_2]^{2+}$ are chloride which is normally a better ligand than H_2O to this type of Ni(II) complex. To our knowledge, $[\mathbf{5b}(H_2O)_2]^{2+}$ is the first example that has two aquo ligands at axial coordination sites in Ni(II) complexes containing a cyclam ring skeleton. In $[\mathbf{5b}(H_2O)_2]^{2+}$, there exists a *pseudo* mirror plane passing through the metal and the central carbon atoms on two six-membered chelate rings. Coordination bond distances in $[\mathbf{5a}]^{2+}$ and $[\mathbf{5b}(H_2O)_2]^{2+}$ are typical of low-spin and high-spin nickel(II) complexes, respectively (see Figure captions). Both structures revealed the following facts: (1) The cyclam ring skeleton in both compounds takes the most stable "*trans* III" conformation,[8] irrespective of four or six-coordination; (2) Two methyl groups on the chiral carbon atoms, C(5) and C(7), are disposed in $[\mathbf{5a}]^{2+}$ at equatorial and axial positions with respect to the chair form of the six-membered chelate ring, giving the C*-racemic form, whereas those in $[\mathbf{5b}(H_2O)_2]Cl_2 \cdot 2H_2O$ both take the equatorial orientation, affording the C*-meso form.

Table 1 Positional Parameters of [**5a**]$(ClO_4)_2$

atom	*x/a*	*y/b*	*z/c*
Ni(1)	-0.02817(10)	-0.1153(1)	-0.2110(2)
Cl(1)	-0.5550(2)	-0.1324(2)	-0.2143(5)
Cl(2)	-0.4184(2)	-0.1493(2)	-0.7606(4)
O(1)	-0.506(2)	-0.0557(9)	-0.174(2)
O(2)	-0.499(1)	-0.2069(10)	-0.216(2)
O(3)	-0.605(1)	-0.115(1)	-0.343(2)
O(4)	-0.618(1)	-0.157(2)	-0.106(3)
O(5)	-0.337(2)	-0.165(2)	-0.687(4)
O(6)	-0.3939(7)	-0.0681(6)	-0.822(2)
O(7)	-0.410(1)	-0.2254(8)	-0.831(2)
O(8)	-0.490(1)	-0.1452(8)	-0.683(2)
N(1)	0.0387(7)	-0.0776(6)	-0.379(1)
N(4)	-0.1141(7)	-0.1798(6)	-0.333(1)
N(8)	-0.0929(7)	-0.1493(7)	-0.046(1)
N(11)	0.0595(7)	-0.0546(6)	-0.089(1)
C(2)	0.007(1)	-0.1378(10)	-0.495(2)
C(3)	-0.097(1)	-0.151(1)	-0.475(2)
C(5)	-0.2111(8)	-0.1928(9)	-0.302(2)
C(6)	-0.2306(9)	-0.213(1)	-0.143(2)
C(7)	-0.1984(9)	-0.1475(10)	-0.042(2)
C(9)	-0.054(1)	-0.0986(10)	0.078(2)
C(10)	0.047(1)	-0.0915(9)	0.055(2)
C(12)	0.1598(8)	-0.047(1)	-0.123(2)
C(13)	0.1754(8)	-0.009(1)	-0.265(2)
C(14)	0.140(1)	-0.0.71(1)	-0.380(2)
C(15)	-0.260(1)	-0.260(2)	-0.399(3)
C(16)	-0.238(1)	-0.058(1)	-0.071(3)

Stereochemical information for **5a** and **5b** was also obtained from ^{13}C NMR spectra of their perchlorate salts in CF_3COOD. **5a** showed 12 signals indicating that all carbon atoms within the ligand are inequivalent, while **5b** showed 7 pairwise equivalent signals. Assuming that the cyclam ring skeleton in both **5a** and **5b** takes the "*trans*-III" form in solution, the meso form should have a mirror plane, whereas the racemic complex should have no symmetry. Thus **5a** and **5b** are assigned to the C*-rac and C*-meso complex, respectively.

As shown in Fig. 3, compounds **5a**$(ClO_4)_2$ and **5b**$(ClO_4)_2$ show rather dissimilar electronic absorption spectra in water. Complex **5a** shows a single absorption band at λ_{max} = 453 nm with ε_{max} = 68 $M^{-1}cm^{-1}$, while **5b** shows three bands in the visible region, $\lambda_{max}(\varepsilon_{max})$ = 337 (7.3), 460(22), and 673(2) nm. The major reason for the dissimilarity is a difference in capability for accepting axially-coordinating water molecules between **5a** and **5b**.[5] Holtman and Cummings reported that the reduction product of **1** by their procedure shows an absorption maximum at 452 nm with ε_{max} = 65 $M^{-1}cm^{-1}$ in water.[3] From these absorption spectral data, it is evident that Holtman and Cummings' compound is **5a**, the racemic isomer. Note that **5a** is a trace component of **5** in our case. It should be emphasized that, in the reduction of **1**, catalytic Raney nickel hydrogenation affords the racemic isomer of **5**, whereas $NaBH_4$ hydrogenation in the present procedure gives the meso isomer as a main product.

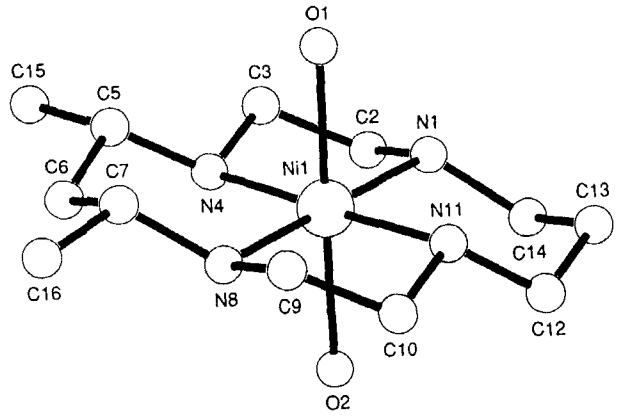


Figure 2 A perspective view of the cation in $[\mathbf{5b}(H_2O)_2]Cl_2 \cdot 2H_2O$. Selected bond distances (Å) and angles (deg): Ni(1)-O(1), 2.181(5); Ni(1)-O(2), 2.196(5); Ni(1)-N(1), 2.055(6); Ni(1)-N(4), 2.071(6); Ni(1)-N(8), 2.066(6); Ni(1)-N(11), 2.073(6); O(1)-Ni(1)-O(2), 178.9(2); O(1)-Ni(1)-N(1), 89.0(2); O(1)-Ni(1)-N(4), 90.5(2); O(1)-Ni(1)-N(8), 90.9(2); O(1)-Ni(1)-N(11), 89.0(2); O(2)-Ni(1)-N(11), 91.1(2); O(2)-Ni(1)-N(4), 89.3(2); N(1)-Ni(1)-N(4), 85.4(3); N(1)-Ni(1)-N(11), 93.4(3); N(8)-Ni(1)-N(1), 178.4(3); N(8)-Ni(1)-N(11), 85.0(3); N(8)-Ni(1)-N(4), 96.1(3); N(11)-Ni(1)-N(4), 178.7(3).

Hydrogenation of α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6-dienato-6-yl)-xylenedinickel(II) ion (2).

The present dinucleating ligand complexes are isolated as the β-diimine form **4** (see Experimental). Figure 4 shows electronic absorption spectra of aqueous solutions of

Table 2 Positional Parameters of $[\mathbf{5b}(H_2O)_2]Cl_2 \cdot H_2O$

atom	*x/a*	*y/b*	*z/c*
Ni(1)	0.98556(9)	0.23800(8)	0.25270(5)
Cl(1)	1.2429(2)	0.2850(2)	−0.0161(1)
Cl(2)	1.0096(3)	0.2940(2)	0.5515(1)
O(1)	1.1155(6)	0.1343(5)	0.1371(3)
O(2)	0.8521(6)	0.3444(6)	0.3674(3)
O(3)	1.1476(9)	−0.1727(7)	0.0636(6)
O(4)	1.3898(8)	0.6524(8)	0.0767(6)
N(1)	0.8370(7)	0.3126(7)	0.1621(3)
N(4)	1.1434(7)	0.4541(6)	0.2812(3)
N(8)	1.1302(7)	0.1572(7)	0.3427(3)
N(11)	0.8253(7)	0.0222(6)	0.2214(4)
C(2)	0.8974(12)	0.4850(9)	0.1856(5)
C(3)	1.0884(11)	0.5196(8)	0.2056(5)
C(5)	1.3259(8)	0.4529(9)	0.2955(5)
C(6)	1.3683(9)	0.3792(12)	0.3714(5)
C(7)	1.3156(8)	0.2012(11)	0.3492(4)
C(9)	1.0687(12)	−0.0155(9)	0.3165(6)
C(12)	0.6447(9)	0.0244(11)	0.2111(6)
C(13)	0.5904(9)	0.0959(12)	0.1366(6)
C(14)	0.6525(9)	0.2721(12)	0.1608(5)
C(15)	1.4333(16)	0.6195(15)	0.3166(9)
C(16)	1.4118(14)	0.1450(19)	0.4222(7)

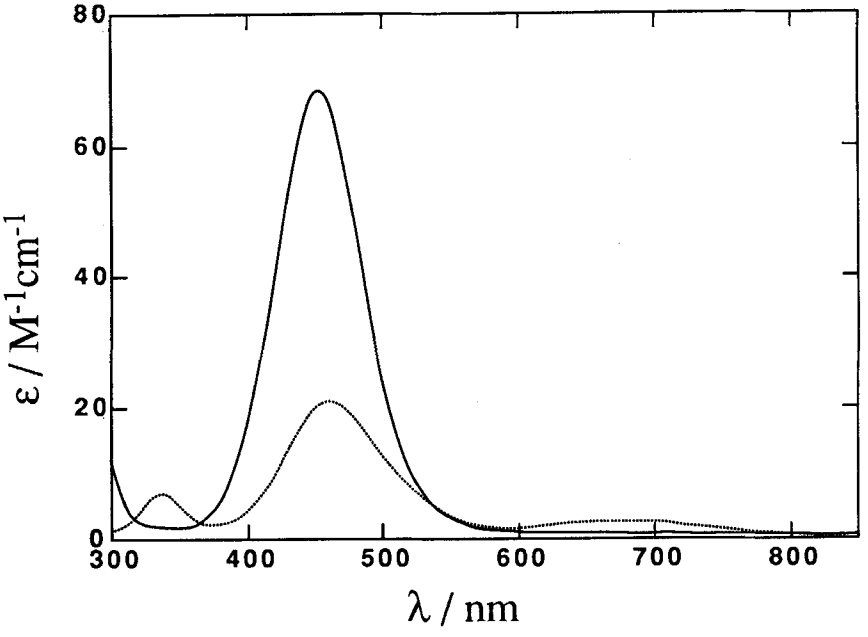


Figure 3 Electronic absorption spectra of **[5a]**$(ClO_4)_2$(solid line) and **[5b]**$(ClO_4)_2 \cdot 2H_2O$ (dashed line) in H_2O.

4b$(ClO_4)_4$ at pH 2.4 and 11.4. The spectrum is strongly pH dependent and the color of the solution was pale yellow at pH 2.4 and violet at pH 11.4. The pH dependency of the spectrum is due to the acid-base equilibrium of Eq (1). From the absorbance *vs.* pH plot at 368 nm, the pK_a for **4b**$(ClO_4)_4$ was determined to be 9.3 (see inset of Fig. 4). At pH 12, the delocalized form (**2b**) decomposed gradually as shown by the spectral decrease.

Very similar pH dependencies of the spectra were observed for aqueous solutions of **4a**$(ClO_4)_4$ and **4c**$(ClO_4)_4$ and their pK_a values were determined in a similar way to be 9.0 and 10.0, respectively. The pK_a values for **4a, 4b**, and **4c** are not much different; however, it should be noted that acid dissociation constants for **4** are smaller by approximately three orders of magnitude than that for **3**. The acidity of the metal chelate as shown in Eq 1 depends strongly, not only on the kind of metal ion,[2] but also on the ligand structure. On the basis of the pK_a values, hydrogenations for **4a, 4b**, and **4c** were carried out by adjusting the pH of the reaction mixture to *ca.* 5-6 with HCl after every portionwise addition of $NaBH_4$. Hydrogenated products (**6**) were isolated as $[Ni_2Cl_2(o\text{-L})](ClO_4)_2 \cdot 1.5H_2O$,[4b] $[Ni_2Cl_4(m\text{-L})] \cdot 3H_2O$,[9] and $[Ni_2Cl_4(p\text{-L})] \cdot 3H_2O$,[10] (L = α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradecane-6-yl)-xylene), respectively, upon addition of a large excess of NaCl to the reaction mixtures. All the data on the products including elemental analyses, IR and UV-vis spectroscopy indicated that hydrogenations for all the *ortho-*, *meta-*, and

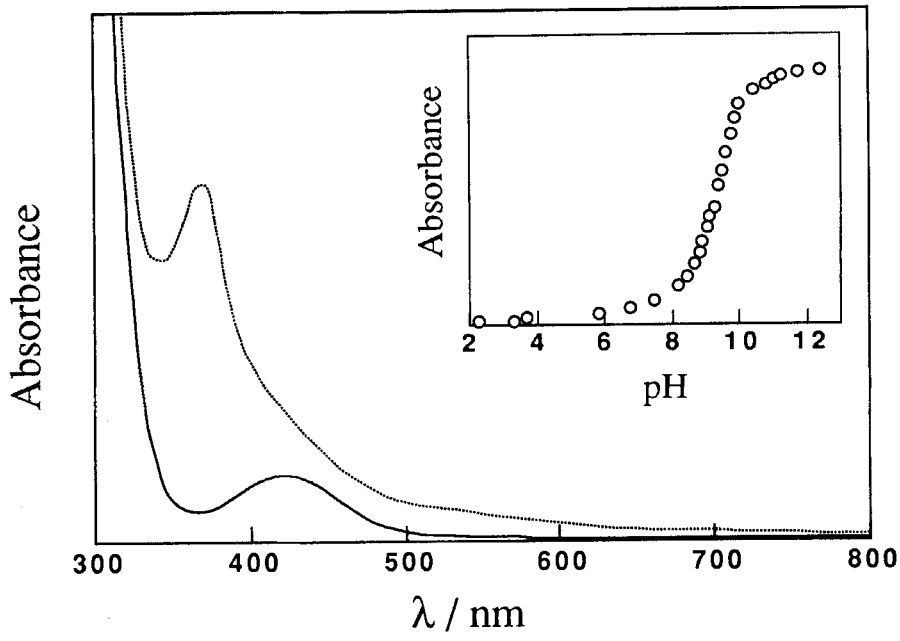


Figure 4 Electronic absorption spectra of [**4b**]$(ClO_4)_4$ at pH 2.42 (solid line) and 11.40 (dashed line) in H_2O. The inset shows the pH dependency of the absorbance at 368 nm.

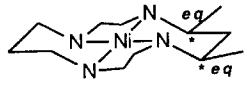
para-isomers of **2** (or **4**) were smoothly accomplished with such experimental procedures.

Hydrogenation for **2** also gives rise to C*-racemic and C*-meso isomers within each cyclam ring in **6**. When the reduction product of **2a**, $[Ni_2Cl_2(o\text{-}L)](ClO_4)_2$ = [**6a**Cl_2]$(ClO_4)_2$, was chromatographed over CM Sephadex C-25 (eluting agent: 0.3 M NaBr), a very weak orange band was separated from the main red-orange second band. The species from the main band was revealed to be the C*-meso form by X-ray analyses of its derivatives.[4] The amount of the isolated minor component was so small that structural characterization was not carried out. It was found that hyrogenation products **6b** and **6c** are also mostly of the C*-meso type. The hydrogenations for **2** are thus stereoselective.

Stereoselectivity of the Hydrogenation Reaction

Hydrogenations for **1** and **2** by the present method afforded reduced compounds of the meso type as a major product in both cases. It has been shown in the X-ray analyses of the main product [**5b**$(H_2O)_2$]$Cl_2 \cdot H_2O$ and dinuclear metal complexes containing the ligand *o*-L, $[Ni_2(\mu\text{-}Br)Br_2(o\text{-}L)]Br$,[4a] $[Zn_2(\mu\text{-}CO_3)(o\text{-}L)](ClO_4)_2$,[4a] and $[Ni_2Cl_2(o\text{-}L)](ClO_4)_2$,[4b] that the hydrogenated tetraaza macrocyclic ring in these compounds have the structure shown in III: (i) The cyclam ring skeleton is of the "*trans*-III" type,[6,8] where the six-membered chelate rings adopt the chair form; (ii) Two methyl

substituents are equatorial with respect to the chair-form chelate rings; (iii) The chirality due to the two asymmetric carbons is of the meso-form.



III

In view of these structural features, it appears that the stereoselective hydrogenations in this study come from the high conformational stability of the "*trans*-III" type in the cyclam ring and the preferential equatorial orientation of the methyl groups in the resulting chair-form six-membered chelate ring.

EXPERIMENTAL

Measurements

Visible absorption spectra and ^{13}C NMR spectra were recorded on a Hitachi-340 spectrophotometer and JEOL JNM-FX90 and JEOL GSX-270 spectrometer, respectively.

*Hydrogenation of 5,7-dimethyl-1,4,8-11-tetraazacyclotetradecane-4,6-dienatonickel(II)(complex (**1**)) and isolation of the isomers (**5a** and **5b**) of the reduction product*

The starting compound **1**(ClO_4) was prepared according to the reported method.[1] Sodium borohydride (Wako Pure Chemical Industries, Ltd.) was used as received. To an aqueous solution (100 mL) containing 2 g of **1**(ClO_4) was added HCl until the solution became pH 3. To the heated solution (60°C) 16 g of solid $NaBH_4$ was added portionwise with stirring over 1.5 h. Immediately after every portionwise addition of $NaBH_4$, the pH of the reaction mixture was adjusted to 3 with HCl. As the reduction proceeded, black precipitates were formed. The solution was stirred at 60 °C for an additional 30 min and the pH was adjusted to 1 with HCl to dissolve the black precipitates. The resulting clear orange solution was adjusted to pH 6 with NaOH, further stirred for 30 min, and evaporated to 20 mL. Ethanol was added to the solution to precipitate white solids comprized mainly of NaCl, which were removed by filtration. The procedure for removal of the white solids (reduction of the solution volume, addition of ethanol, and filtration) was repeated three times. Then, the solution was evaporated to dryness to yield a violet residue, which was dissolved in a minimum of water and was put on top of a SP-Sephadex C-25 column (70 cm, 3 cmϕ). The adsorbed species were eluted with a mixed solution containing 0.05 M NaI and 0.05 M NaCl to give two well separated bands, a first minor orange band and a second main brown orange band, which were identified as the racemic isomer **5a** and the meso isomer **5b**, respectively (see text). They were collected separately and isolated as perchlorate salts after removal of I^- and Cl^-. Yields, 3% for **5a**(ClO_4)$_2$ and 41 % for **5b**(ClO_4)$_2 \cdot 2H_2O$. For **5a**(ClO_4)$_2$. *Anal.* Calcd. for $NiC_{12}H_{28}O_8N_4Cl_2$ (%): C, 29.7; H, 5.8; N, 11.5; Found: C, 29.5; H, 5.8; N, 11.3. ^{13}C NMR (CF_3COOD) δ = 17.7 (CH_3), 19.9 (CH_3), 27.9 (CH_2),

43.4 (CH_2), 49.5 (CH_2), 51.0 ($2CH_2$), 51.3 ($CHCH_3$, CH_2), 52.4 ($CHCH_3$), 53.2 (CH_2), 53.6 (CH_2). For **5b**$(ClO_4)_2 \cdot 2H_2O$. *Anal.* Calcd. $NiC_{12}H_{32}O_{10}N_4Cl_2$ (%): C, 27.6; H, 6.2; N, 10.7; Found: C, 28.0; H, 5.5; N, 10.9. ^{13}C NMR (CF_3COOD) $\delta = 20.4$ (CH_3), 27.9 (CH_2), 45.5 (CH_2), 50.2 (CH_2), 51.0 (CH_2), 53.5 (CH_2), 57.0 ($CHCH_3$).

An aqueous solution of **5b**$(ClO_4)_2$ was passed through a Cl^--form anion-exchange resin and slowly evaporated to afford violet crystals of [**5b**$(H_2O)_2]Cl_2 \cdot 2H_2O$, which were used in X-ray crystallographic work.

*Isolation of free ligands of **5a** and **5b***

Free ligands were obtained by $CHCl_3$ extraction from an aqueous solution in which Ni(II) ions were removed beforehand from each complex with the CN^- treatment. For free ligand of **5a**. ^{13}C NMR ($CDCl_3$) $\delta = 20.1$(CH_3), 29.1 (CH_2), 45.0 (CH_2), 45.8 (CH_2), 49.1 ($CHCH_3$), 49.3 (CH_2), 50.0 (CH_2). For free ligand of **5b**. ^{13}C NMR ($CDCl_3$) $\delta = 21.7$ (CH_3), 29.5 (CH_2), 46.6 (CH_2), 47.2 (CH_2), 50.3 (CH_2), 51.6 (CH_2), 55.6 ($CHCH_3$).

*X-ray Data Collection and Structure Refinement of [**5a**]$(ClO_4)_2$*

Diffraction data were collected at room temperature on a Rigaku AFC5R diffractometer by using graphite monochromated Cu Kα ($\lambda = 1.54178$ Å) radiation. Crystal data for [**5a**]$(ClO_4)_2$: $C_{12}H_{28}N_4NiCl_2O_8$, *fw* = 485.98, orthorhombic, space group $P2_12_12_1$(#19), $a = 14.27(3)$, $b = 14.62(2)$, $c = 9.54(2)$ Å, $U = 1989(5)$ Å^3, $Z = 4$, $D_c = 1.62$ g cm^{-3}, $F(000) = 1016$, μ(Cu-Kα) = 43.16 cm^{-1}. A total of 1726 reflections were collected ($2\theta \leq 120.1°$), of which 1282 independent significant reflections ($I \geq 3\sigma(I)$) were assumed to be observed. The structure was solved by the Patterson method (DIRDIF92 PATTY) and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined anisotropically. The final cycle of refinement including 244 variable parameters was converged at $R = 0.063$ and $R_w = 0.078$ ($w = 1/\sigma^2(F_o)$).

*X-ray Data Collection and Structure Refinement of [**5b**$(H_2O)_2]Cl_2 \cdot 2H_2O$*

Diffraction data were collected at room temperature on a MAC Science MXC-3k diffractometer by using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation. Because the crystal rapidly decomposes in air losing water of crystallization, the specimen ($0.50 \times 0.35 \times 0.25$ mm) was covered with epoxide resin. Crystal data for [**5b**$(H_2O)_2]Cl_2 \cdot 2H_2O$: $C_{12}H_{36}N_4NiCl_2O_4$, fw = 430.04, triclinic, space group $P\bar{1}$(#2), $a = 8.155(2)$, $b = 9.042(5)$, $c = 15.050(6)$ Å, $\alpha = 107.10(3)$, $\beta = 96.03(2)$, $\gamma = 98.69(3)°$, $U = 1035.3(7)$ Å^3, $Z = 2$, $D_c = 1.38$ g cm^{-3}, $F(000) = 460$, μ(Mo-Kα) = 12.210 cm^{-1}. The intensity data were collected by the ω-2θ scan technique in the region $3 < 2\theta < 55°$ and an absorption correction was not applied. A total of 5222 reflections were collected, of which 4089 independent significant reflections ($I \geq 3\sigma(I)$) were assumed to be observed. The structure was solved by direct methods and refined by the full-matrix least-squares method. All the non-hydrogen atoms were refined with anisotropic thermal parameters. The final cycle of refinement including 304 variable parameters was converged at $R = 0.0530$ and $R_w = 0.0797$

($w = \exp(10\sin^2\theta/\lambda^2)/\sigma^2(F_o)$). All the calculations were carried out with use of CRYSTAN, the program package supplied by MAC Science.

Preparation of α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,7-diene-6-yl)-xylenedinickel(II) (4)

Complex **4a** was prepared as follows. To an aqueous solution (150 mL) containing 5.4 g (15.8 mmol) of **1**(NO_3)[1] was added 1.86 g (7.1 mmol) of α,α'-dibromo-*ortho*-xylene, and stirred at 80°C for several hours. As the reaction proceeded, α,α'-dibromoxylene was gradually dissolved to give a clear brown solution. The reaction mixture was cooled to room temperature and a concentrated aqueous solution of $NaClO_4$ (12 g) was added. The resulting brownish yellow precipitates were filtered off, and recrystallized from hot aqueous ethanol (1:1) to give yellow plates of **4a**$(ClO_4)_4$. Yield 4.7 g (ca. 55%). ^{13}C NMR (CD_3NO_2) for **4a**$(ClO_4)_4$ δ = 23.0 (CH_3), 27.3 (CH_2), 34.8 (CH_2), 50.5 (CH_2), 53.7 (CH_2), 55.6 (CH_2), 63.4 (*C*H), 131.1 (phenyl), 135.3 (phenyl), 136.2 (phenyl), 180.9 (CCH_3).

Tetraperchlorate salts of **4b** and **4c** were synthesized in a similar way by use of *meta*- and *para*-derivatives in place of α,α'-dibromo-*ortho*-xylene. ^{13}C NMR (CD_3NO_2) for **4b**$(ClO_4)_4$ δ = 22.6(CH_3), 27.3(CH_2), 37.0(CH_2), 50.6(CH_2), 53.9(CH_2), 55.5(CH_2), 63.6 (*C*H), 131.3 (phenyl), 133.5 (phenyl), 135.0 (phenyl), 137.4 (phenyl), 180.7 (CCH_3). ^{13}C NMR (CD_3NO_2) for **4c**$(ClO_4)_4$ δ = 22.4 (CH_3), 27.2 (CH_2), 36.4 (CH_2), 50.8 (CH_2), 53.6 (CH_2), 55.5 (CH_2), 63.3 (*C*H), 133.9 (phenyl), 136.5 (phenyl), 180.4 (CCH_3).

*Hydrogenation of α,α'-bis(5,7-dimethyl-1,4,8,11-tetraazacyclotradeca-4,6-dienato-6-yl)-ortho-xylenedinickel(II) ion (**2a**) and isolation of the main reduction product (**6a**) and its free ligand*

Complex **4a** is easily transformed to violet **2a** by addition of base, which can be isolated as the perchlorate salt. Hydrogenation was carried out as follows. To an aqueous solution (200 mL) of **4a**$(ClO_4)_4$ (3g) was added 100 mL of saturated NaCl aqueous solution, and the solution was acidified to pH 5–6 with HCl. The solution was heated to boiling and an excess of solid $NaBH_4$ (1.0–1.2 g) was added portionwise slowly. After every portionwise addition of $NaBH_4$, the pH of the reaction mixture was adjusted to pH 5–6 with HCl. As the reaction proceeded, pale violet solids precipitated out. The solution was cooled down to room temperature. Resulting solids were removed by filtration and were recrystallized from water. Yield, 1.5 g. The products consist mostly of $[Ni_2Cl_2(o\text{-L})](ClO_4)_2$. The crude products were purified by cation-exchange chromatography (CM Sephadex C-25, eluting agent 0.3 M NaBr). From the main band, a good quality red orange crystalline compound $[Ni_2(\mu\text{-Br})Br_2(o\text{-L})]Br\cdot H_2O$[4a] was obtained upon reducing the volume of the eluted solution. $[Ni_2(o\text{-L})](ClO_4)_4\cdot 4H_2O$ was obtained as yellow microcrystals by adding concentrated aqueous $NaClO_4$ to an aqueous solution of $[Ni_2(\mu\text{-Br})Br_2(o\text{-L})]Br\cdot H_2O$. *Anal.* for $[Ni_2(o\text{-L})](ClO_4)_4\cdot 4H_2O$. Found: C, 33.4; H, 6.5; N, 9.7%. Calcd for $Ni_2C_{32}H_{70}O_{20}N_8Cl_4$: C, 33.5; H, 6.2; N, 9.8%. The free ligand of **6a** was obtained in a similar manner to the procedure for isolation of free ligands of **5a** and **5b**.[4a] For free ligand of **6a**. ^{13}C NMR ($CDCl_3$) δ = 19.6(CH_3), 26.5 (CH_2), 29.3 (CH_2), 47.2 (CH_2), 50.1 (CH_2), 50.8 (*C*H), 51.1 (CH_2), 61.1 (CCH_3), 125.1 (phenyl), 129.7 (phenyl), 140.9 (phenyl).

Hydrogenations for **2b** and **2c** were carried out in a similar way. ^{13}C NMR data (in $CDCl_3$) for free ligand of **6b** $\delta = 19.2$ (CH_3), 28.4 ($2CH_2$), 46.3 (CH_2), 48.9 (CH_2), 50.1 (CH_2), 51.1 (CH), 59.9 (CCH_3), 124.9 (phenyl), 127.0 (phenyl), 128.8 (phenyl), 142.5 (phenyl). ^{13}C NMR data (in $CDCl_3$) for free ligand of **6c** $\delta = 20.1$ (CH_3), 29.0 (CH_2), 29.5 (CH_2), 47.4 (CH_2), 50.1 (CH_2), 51.1 (CH_2), 52.3 (CH), 61.0 (CCH_3), 128.8 (phenyl), 140.8 (phenyl).

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research No. 04453041 from the Ministry of Education, Science and Culture, Japan.

References

1. J.G. Martin, R.M.C. Wei, and S.C. Cummings, *Inorg. Chem.*, **11**, 475 (1972).
2. J.G. Martin, and S.C. Cummings, *Inorg. Chem.*, **12**, 1477 (1973).
3. M.S. Holtman, and S.C. Cummings, *Inorg. Chem.*, **15**, 660 (1976).
4. Preliminary results on **6a** have been published: (a) T. Kajiwara, T. Yamaguchi, H. Kido, S. Kawabata, R. Kuroda, and T. Ito, *Inorg. Chem.*, **32**, 4990 (1993); (b) T. Kajiwara, T. Yamaguchi, H. Oshio, and T. Ito, *Bull. Chem. Soc. Jpn.*, **67**, 2130 (1994).
5. K. Mochizuki, and T. Kondo, Unpublished.
6. For example, T. Ito, and D.H. Busch, *J. Am. Chem. Soc.*, **95**, 7528 (1973).
7. For **5b**$(ClO_4)_2$, single crystals suitable for X-ray works were not obtained.
8. B. Bosnich, C.K. Poon, and M.L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965).
9. Anal. Found: C, 44.08 H, 7.64; N, 12.78 %. Calcd for $Ni_2C_{32}H_{68}O_3N_8Cl_4$: C, 44.07; H, 7.87; N, 12.85%.
10. Anal. Found: C, 44.07; H, 7.50; N, 12.84 %. Calcd for $Ni_2C_{32}H_{68}O_3N_8Cl_4$: C, 44.07; H, 7.87; N, 12.85%.