676 *Inorg. Chem.* **1992**, *31*, 676–685

Contribution from the Department of Applied Fine Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan, and Niihama National College of Technology, Yagumo-cho 7-1, Niihama, Ehime 792, Japan

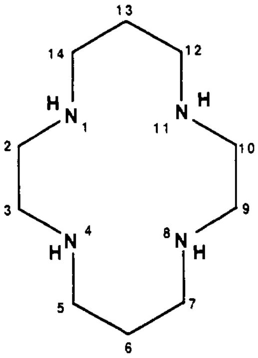
# Synthesis and Molecular Structures of Nickel(II) Alkyl-Substituted Cyclam Complexes

Kazuya Kobiro,*,† Atsuyoshi Nakayama, Toshitaka Hiro, Mitsuhito Suwa, and Yoshito Tobe

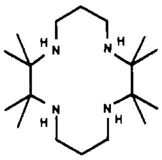
*Received September 13, 1991*

Sterically congested cyclam derivatives **2**, **3s**, **3a**, **4**, **5c**, and **5t** and their Ni(II) complexes have been synthesized. Magnetic susceptibility measurements of the complexes in the solid state and in water solution indicate that the less congested complexes Ni(**1**)$^{2+}$ and Ni(**5t**)$^{2+}$ are high-spin species in the solid state and Ni(**1**)$^{2+}$, Ni(**5c**)$^{2+}$, and Ni(**5t**)$^{2+}$ are mixtures of high-spin species and low-spin species in solution. On the other hand, highly congested complexes Ni(**2**)$^{2+}$, Ni(**3s**)$^{2+}$, and Ni(**4**)$^{2+}$ are shown to be low-spin species in both the solid state and in solution. Ni(**3a**)$^{2+}$ has been shown to be a high-spin species in the solid state, while it is a low-spin species in solution. Electronic spectra of Ni(**1**)$^{2+}$, Ni(**2**)$^{2+}$, Ni(**3s**)$^{2+}$, Ni(**3a**)$^{2+}$, Ni(**4**)$^{2+}$, Ni(**5c**)$^{2+}$, and Ni(**5t**)$^{2+}$ measured in $H_2O$ and in 5 M $NaClO_4$ solution supported the above observations. Half-wave potentials for the $Ni^{II}/Ni^{III}$ redox change ($E_{1/2}(Ni^{II,III})$) were determined for Ni(**1**)$X_2$, Ni(**2**)$X_2$, Ni(**3s**)$X_2$, Ni(**3a**)$X_2$, Ni(**4**)$X_2$, Ni(**5c**)$X_2$, and Ni(**5t**)$X_2$ (X = $NO_3$, $ClO_4$, Cl). It appeared that Ni(II) complexes with sterically congested ligands (Ni(**2**)$^{2+}$, Ni(**3s**)$^{2+}$, Ni(**3a**)$^{2+}$, Ni(**4**)$^{2+}$) show higher half-wave potentials than those of the complexes with less congested ligands (Ni(**1**)$^{2+}$, Ni(**5t**)$^{2+}$, Ni(**5c**)$^{2+}$). Molecular structures of Ni(**2**)$(NO_3)_2$, Ni(**3s**)$(NO_3)_2$, Ni(**3a**)$(NO_3)_2$, Ni(**4**)$(NO_3)_2{\cdot}H_2O$, and Ni(**5t**)$(NO_3)_2$ were determined by X-ray crystal structure analyses, and the steric effects of the peripheral substituents on the coordination are discussed. In Ni(**5t**)$(NO_3)_2$, two axial nitrate anions coordinate to the central Ni atom to give six-coordinate octahedral geometry, while in Ni(**4**)$(NO_3)_2{\cdot}H_2O$ one axial nitrate anion semicoordinates to the central Ni atom to give five-coordinate square pyramidal geometry. Two types of unique structures exist in a unit cell of Ni(**2**)$(NO_3)_2$. One of the structures A has four-coordinate square planar geometry, while in the other structure B one axial nitrate anion semicoordinates to the central Ni atom to give a five-coordinate square pyramidal geometry around the Ni atom. Ni(**3a**)$(NO_3)_2$ possesses six-coordinate octahedral geometry, while Ni(**3s**)$(NO_3)_2$ has four-coordinate square planar geometry with trans-I geometry of the cyclam ring.

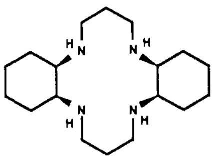
Recently, various tetraaza macrocycles have been prepared, and some very versatile chemistry of their nickel complexes has been described.[1] Among them, the most fascinating is 1,4,8,11-tetraazacyclotetradecane (cyclam) (**1**) because of (i) the beautiful and highly symmetrical structure, (ii) the extremely strong coordinative interactions with 3d metal ions, (iii) the intriguing application for catalytic oxidation,[2] and (iv) the control of the coordination geometry of nickel(II) ion by changing the steric environment of the coordination axis by substituents on the cyclam rings.[3] In connection with the above reasons, a large number of cyclam derivatives with methyl group(s) on the 1, 4, 5, 7, 8, 11, 12, 13, and 14 positions have been synthesized and they have been shown to control the accessibility of the axial ligands to the coordinated nickel(II) ion due to the steric barrier of the methyl group(s).[1]



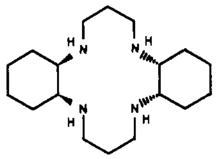
**1**



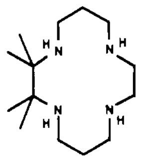
**2**



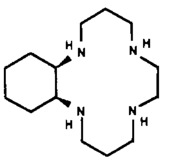
**3s**



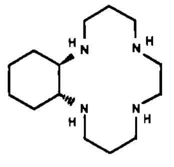
**3a**



**4**



**5c**



**5t**

In this context, we have designed new types of sterically congested cyclams, 2,2,3,3,9,9,10,10-octamethyl-1,4,8,11-tetraazacyclotetradecane (octamethylcyclam) (**2**) and 2,2,3,3-tetramethyl-1,4,8,11-tetraazacyclotetradecane (tetramethylcyclam) (**4**), with eight or four methyl groups on either or both of the ethylene bridges (2/3 and 9/10 positions). HGS and CPK molecular model examinations of the Ni(**2**)$^{2+}$ complex suggest that two pseudo axial methyl groups on the 2 and 3 (or 9 and 10) positions stick up and down the cyclam ring to affect the steric environment of the axial coordination sites. On the other hand, pseudo axial methyl groups on the trimethylene bridge (5 and 7 or 12 and 14 positions) would not have much effect on the steric environment of the axial coordination site, because there is left an open space in the opposite side of the molecule (C12–C14 or C5–C7). Therefore, it is expected that the geminal methyl groups on the ethylene bridge (2, 3, 9, and 10 positions) would prevent axial ligand(s) from contacting the central Ni ion more effectively than the methyl groups on the trimethylene bridge (5, 6, 7, 12, 13, and 14 positions).

As a preliminary report,[4] we previously reported on the synthesis of new types of sterically congested cyclam derivatives, octamethylcyclam (**2**), tetramethylcyclam (**4**), and their related compounds, 2,3:9,10-*cis-syn-cis*-dicyclohexano-1,4,8,11-tetraazacyclotetradecane (*cis-syn-cis*-dicyclohexanocyclam) (**3s**),[5] 2,3:9,10-*cis-anti-cis*-dicyclohexano-1,4,8,11-tetraazacyclotetradecane (*cis-anti-cis*-dicyclohexanocyclam) (**3a**),[5] 2,3-*cis*-cyclohexano-1,4,8,11-tetraazacyclotetradecane (*cis*-cyclohexanocyclam) (**5c**), and 2,3-*trans*-cyclohexano-1,4,8,11-tetraazacyclotetradecane

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† Present address: Niihama National College of Technology.

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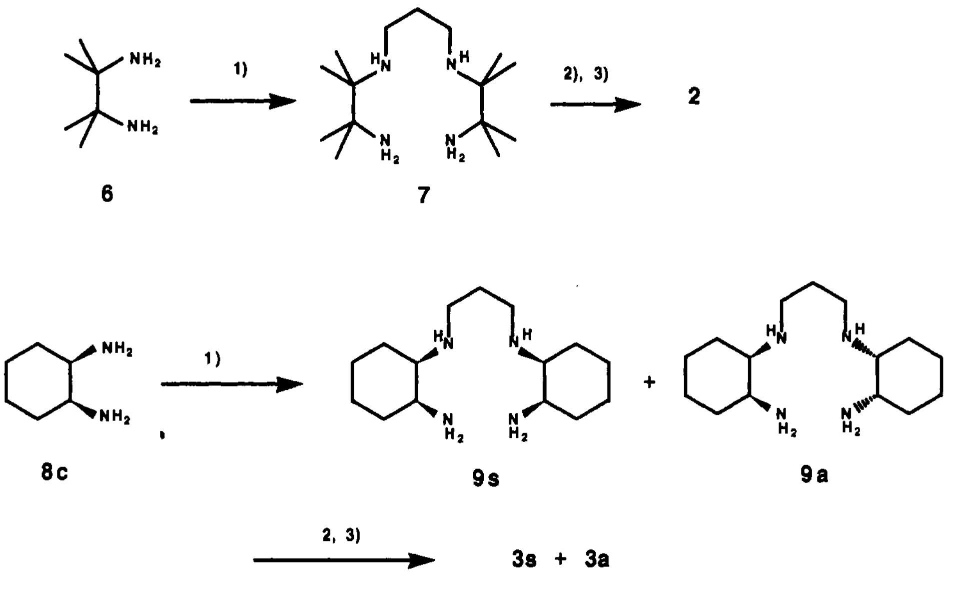
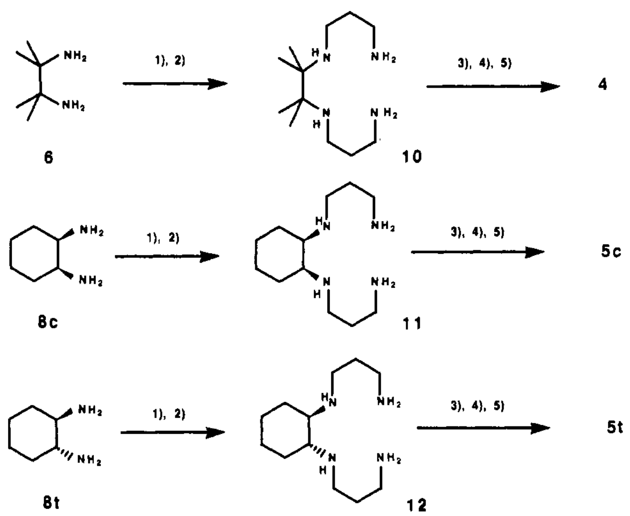
Scheme I



1) $BrCH_2CH_2CH_2Br$, $Na_2CO_3$, 2) $BrCH_2CH_2CH_2Br$, 3) KOH.

Scheme II



1) $CH_2CHCN$, 2) $H_2$, Raney-Ni, 3) OHCCHO, $Ni(ClO_4)_2 \cdot 6H_2O$, 4) $NaBH_4$, 5) NaCN.

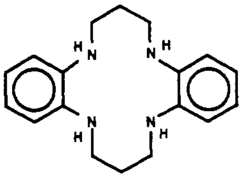
(*trans*-cyclohexanocyclam) (**5t**). In addition, we have measured the electronic spectra, magnetic susceptibilities, and half-wave potentials for the $Ni^{II/III}$ redox change of the nickel complexes. These results suggested that the alkyl groups (methyl or *cis*-cyclohexyl groups) on the 2, 3, 9 and 10 positions of sterically congested cyclamnickel(II) complexes prevent the axial ligands such as anions or water molecules from accessing the coordinated nickel ion to give the low-spin species with four-coordinate square planar or five-coordinate square pyramidal geometry.

In order to establish the effect of the sterically bulky alkyl groups in cyclam ring on the coordination of axial ligands, we selected representative congested complexes $Ni(\mathbf{2})(NO_3)_2$ and $Ni(\mathbf{4})(NO_3)_2$ with bulky tetramethylethane subunits, a different type of congested complex $Ni(\mathbf{3s})(NO_3)_2$ and $Ni(\mathbf{3a})(NO_3)_2$, with two *cis*-cyclohexane subunits, and the probably much less congested complex $Ni(\mathbf{5t})(NO_3)_2$, and the study of their structures was undertaken by the X-ray diffraction method. In this paper we wish to draw possible comparisons of the structural parameters of the congested cyclam complexes with those of known $Ni(\mathbf{1})(NO_3)_2$,[6b] which would reveal the effect of the alkyl groups of the cyclam ring on coordination of the axial ligands.

## Results and Discussion

**Synthesis of Sterically Congested Cyclams.** The results of these synthetic studies show that the sterically congested cyclams can be readily synthesized by simple procedure i, a two-step reaction of 1,2-diamines and 1,3-dibromopropane (Scheme I), or procedure ii, a Ni(II)-template reaction of two-arm amines and glyoxal (Scheme II). Cyclams with bulky substituents on both sides of the cyclam ring were synthesized according to Scheme I. Reaction of an excess of 2,3-dimethylbutane-2,3-diamine (**6**) with 1,3-dibromopropane in the presence of $Na_2CO_3$ as a base gave the hexamethyl tetraamine **7** in 67% yield. Reaction of **7** and 1,3-dibromopropane gave octamethylcyclam (**2**) in 19% yield (mp 131–132 °C). According to a similar procedure, *cis-syn-cis*-dicyclohexanocyclam (**3s**) and *cis-anti-cis*-dicyclohexanocyclam (**3a**) were synthesized from *cis*-cyclohexane-1,2-diamine (**8c**), both in 3% yields.

Stereochemical determination of the syn and anti isomers was done by the X-ray molecular structure analyses of $Ni(\mathbf{3s})Cl_2$,[4] $Ni(\mathbf{3s})(NO_3)_2$, and $Ni(\mathbf{3a})(NO_3)_2$ as discussed in the following section. Sakata and Moriguchi reported the synthesis of two isomers of dicyclohexanocyclam (mp 158.5–161.0 °C and mp 194.5–196.0 °C both recrystallized from petroleum ether) by hydrogenation of dibenzocyclam (**13**).[5] They assigned the structure of the former cis-syn-cis isomer and the latter cis-anti-cis or trans-anti-trans isomer by $^{13}C$ NMR spectroscopic consideration of their complexes with Ni(II) and Co(III) ions. The reported $^{13}C$ NMR spectra of the complexes were in complete agreement with those of the cis-syn-cis and cis-anti-cis isomers (**3s**, **3a**) prepared by us, respectively, thus confirming the above assignment.



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Cyclams with bulky substituents on one side of the cyclam ring, **4**, **5c**, and **5t**, were synthesized according to a method similar to

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**Table I.** Reaction Solvents, Recrystallization Solvents, Melting Points, and Elemental Analyses of Ni(L)$X_2$ (X = $NO_3$, $ClO_4$, Cl)

| L | X | reacn solvent | recryst solvent | mp | anal., %[a] C | H | N | Cl |
|---|---|---|---|---|---|---|---|---|
| **2** | $NO_3$ | DMSO | $H_2O$/EtOH | 270–280 (dec) | 43.64 (43.65) | 8.19 (8.14) | 16.83 (16.97) | |
| **2** | $ClO_4$ | DMSO | $H_2O$ | 286–303 (dec) | 37.94 (37.92) | 7.13 (7.07) | 9.61 (9.83) | 12.46 (12.44) |
| **2** | Cl | DMSO | EtOH | *c* | 43.49 (43.56) | 8.37 (8.36) | 14.50 (14.52) | 17.99 (18.37) |
| **3s** | $NO_3$ | DMSO | $H_2O$/EtOH | 255–265 (dec) | 44.12 (44.01) | 7.47 (7.39) | 16.92 (17.11) | |
| **3s** | $ClO_4$ | DMSO | $H_2O$ | >300 (dec) | 38.44 (38.19) | 6.49 (6.41) | 9.74 (9.90) | 12.28 (12.53) |
| **3s** | Cl | DMSO | $H_2O$/EtOH | >295 (dec) | 48.14 (49.35) | 8.58 (8.28) | 13.44 (12.79) | |
| **3a** | $NO_3$ | DMSO | $H_2O$/EtOH | 295–305 (dec) | 44.23 (44.01) | 7.59 (7.39) | 16.92 (17.11) | |
| **3a** | $ClO_4$ | DMSO | $H_2O$ | >300 (dec) | 38.33 (38.19) | 6.49 (6.41) | 9.74 (9.90) | 12.28 (12.53) |
| **3a** | Cl | DMSO | $H_2O$/EtOH | >300 (dec) | 49.28 (49.35) | 8.29 (8.28) | 12.68 (12.79) | |
| **4**[b] | $NO_3$ | MeOH | $CHCl_3/Et_2O$ | 275–285 (dec) | 37.02 (36.78) | 7.52 (7.50) | 18.41 (18.38) | |
| **4** | Cl | EtOH | EtOH/acetone | *c* | 43.49 (43.56) | 8.73 (8.36) | 14.56 (14.52) | 17.99 (18.37) |
| **5c** | $NO_3$ | MeOH | $CHCl_3$ | 205–210 (dec) | 38.46 (38.47) | 6.88 (6.92) | 19.05 (19.23) | |
| **5c** | Cl | EtOH | MeOH/acetone | *c* | 43.69 (43.79) | 7.87 (7.87) | 14.32 (14.59) | 18.29 (18.46) |
| **5t** | $NO_3$ | MeOH | $CHCl_3/Et_2O$ | 205–210 (dec) | 38.13 (38.47) | 6.87 (6.92) | 18.93 (19.23) | |
| **5t** | Cl | MeOH | MeOH/acetone | *c* | 43.43 (43.79) | 7.75 (7.87) | 14.23 (14.59) | 18.44 (18.46) |

[a] Calculated values were given in parentheses. [b] Monohydrate. [c] Hygroscopic.

that reported by Barefield et al.[7] as shown in Scheme II. Reaction of diamine **6** and acrylonitrile followed by hydrogenation gave two-arm tetramethyl tetraamine **10** in 54% yield. The Ni(II)-templated reaction of tetraamine **10** with glyoxal followed by hydride reduction gave the Ni(**4**)$(ClO_4)_2$ complex in 40% yield (mp >285 °C dec). The template cyclization was achieved at 40–55 °C, while no reaction took place at room temperature. Tetramethylcyclam (**4**) was liberated by treatment of the Ni(**4**)$(ClO_4)_2$ complex with NaCN in 70% yield. According to a similar procedure, except for the temperature of cyclization (reactions took place at room temperature), *cis*-cyclohexanocyclam (**5c**) and *trans*-cyclohexanocyclam (**5t**) were synthesized in 47 and 37% overall yields from *cis*-cyclohexane-1,2-diamine (**8c**) and *trans*-cyclohexane-1,2-diamine (**8t**), respectively.

**Complexation.** Unsubstituted cyclam (**1**) gave the purple nickel(II) nitrate complex easily by reaction with $Ni(NO_3)_2 \cdot 6H_2O$ in methanol at room temperature as reported.[8] Similarly, tetramethylcyclam (**4**), *cis*-cyclohexanocyclam (**5c**), and *trans*-cyclohexanocyclam (**5t**), bearing one bulky group on the cyclam ring, formed the corresponding complexes under similar conditions except for **5c** for which ethanol was used as the solvent. On the other hand, octamethylcyclam (**2**), *cis-syn-cis*-dicyclohexanocyclam (**3s**), and *cis-anti-cis*-dicyclohexanocyclam (**3a**), bearing sterically bulky groups on both sides of the cyclam ring, gave unidentified greenish powdery products under similar conditions. When dimethyl sulfoxide (DMSO) was used instead of methanol, however, crystalline complexes were obtained successfully. According to a similar procedure, complexes with $NiX_2$ (X = $ClO_4$, $Cl_2$) were prepared as listed in Table I.

**Spin State of Complexes in the Solid State and in Solution.** In order to clarify the effect of the substituent(s) on the ethano bridge of the cyclam ring on the spin state of the coordinated Ni(II) ion, magnetic susceptibilities of the complexes were measured in the solid state and in water solution by Gouy's[9] and Evans'[10] methods, respectively. In the solid state, as shown in Table II, in the case of the less congested complexes Ni(**1**)$(NO_3)_2$ and Ni(**5t**)$(NO_3)_2$ with no steric barrier or with *trans*-cyclohexyl group on only one side of the molecules, the values of $\mu_{eff}$ are 3.2 $\mu_B$. On the other hand, in the case of the complexes Ni(**2**)$(NO_3)_2$ and Ni(**3s**)$(NO_3)_2$ bearing bulky alkyl groups on both sides, the values of $\mu_{eff}$ are 0.4 $\mu_B$. $\mu_{eff}$ of Ni(**4**)$\cdot H_2O$ is 0.7 $\mu_B$. These results indicate clearly that the complexes Ni(**1**)$(NO_3)_2$ and Ni(**5t**)$(NO_3)_2$ are high-spin complexes, while the complexes Ni(**2**)$(NO_3)_2$, Ni(**3s**)$(NO_3)_2$, and Ni(**4**)$(NO_3)_2$ are low-spin ones. It should be noted that $\mu_{eff}$ of the anti isomer Ni(**3a**)$(NO_3)_2$ is 3.2 $\mu_B$, indicating it is a high-spin complex in the solid state.

**Table II.** Magnetic Susceptibilities of Ni(L)$(NO_3)_2$ and Visible Absorption Maxima of Ni(L)$(ClO_4)_2$

| L | $\mu_{eff}$, $\mu_B$ solid state | solution | $\lambda_{max}$, nm ($\epsilon$) $H_2O$ | 5 M $NaClO_4$ |
|---|---|---|---|---|
| **1** | 3.2 | 1.65 | 455 (40) | 455 (50) |
| **5c** | *a* | 0.90 | 446 (70) | 446 (70) |
| **5t** | 3.2 | 1.94 | 455 (40) | 455 (70) |
| **4** | 0.7[b] | <0.3 | 452 (80) | 452 (80) |
| **3s** | 0.4 | <0.3 | 440 (80) | 440 (80)[c] |
| **3a** | 3.2 | <0.3 | 455 (60) | *d* |
| **2** | 0.4 | <0.3 | 452 (70) | 452 (70)[c] |

[a] Hygroscopic. [b] Monohydrate. [c] In 1 M solution. Complex was salted-out in 5 M solution. [d] Complex was salted-out in 1 M solution.

Meanwhile, in solution, the less congested complexes, Ni(**1**)$(NO_3)_2$, Ni(**5c**)$(NO_3)_2$, and Ni(**5t**)$(NO_3)_2$, showed the $\mu_{eff}$ values of 0.90–1.94 $\mu_B$, which indicate that they are mixtures of low-spin and high-spin species. The more congested cyclam complexes, Ni(**4**)$(NO_3)_2$, Ni(**3s**)$(NO_3)_2$, Ni(**3a**)$(NO_3)_2$, and Ni(**2**)$(NO_3)_2$, exhibited values less than 0.3 $\mu_B$, indicating they are all low-spin complexes. It is noteworthy that the complex Ni(**4**)$(NO_3)_2 \cdot H_2O$ having only one tetramethylethane subunit turned out to be a low-spin complex.

As for the mixture of low-spin and high-spin complexes, Fabbrizzi et al. reported that Ni(**1**)$(ClO_4)_2$ existed in aqueous solution as an equilibrium mixture of high-spin diaquo octahedral species $[Ni(\mathbf{1})(H_2O)_2]^{2+}$ and low-spin diamagnetic square species $[Ni(\mathbf{1})]^{2+}$

$$[Ni(\mathbf{1})(H_2O)_2]^{2+} \rightleftharpoons [Ni(\mathbf{1})]^{2+} + 2H_2O$$

and that the equilibrium was displaced to the right by increasing the ionic strength, since ions of the inert electrolyte were thought to compete for the water molecules coordinated to the Ni(II) ion.[11] In the sterically congested cyclam complexes, it is expected that the steric bulkiness of the alkyl groups on cyclam ring would prevent axial water molecules from interacting with the deeply embedded $Ni^{2+}$ ion. To estimate the facility of coordination of the axial ligand to the $Ni^{2+}$ ion, electronic spectra were measured in water and in 5 M (or 1 M) $NaClO_4$ solutions. As can be seen in Table II, in the case of less congested complexes Ni(**1**)$(ClO_4)_2$ and Ni(**5t**)$(ClO_4)_2$, the values of the molar extinction coefficient ($\epsilon$) at about 450 nm due to low-spin square species increased in $NaClO_4$ solution. On the other hand, more congested complexes Ni(**2**)$(ClO_4)_2$, Ni(**3s**)$(ClO_4)_2$, and Ni(**4**)$(ClO_4)_2$ exhibited similar $\epsilon$ values in both water and $NaClO_4$ solution. In accord with the magnetic susceptibility measurements by Evans' method in water solution, these results indicate that in solution the complexes

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**Table III.** Half-Wave Potentials for the $Ni^{II}/Ni^{III}$ Redox Change of $Ni(L)X_2$ ($X = NO_3$, Cl, $ClO_4$)

| L | $E_{1/2}(Ni^{II,III})$ vs SCE, V | | |
|---|---|---|---|
| | $Ni(NO_3)_2$ | $NiCl_2$ | $Ni(ClO_4)_2$ |
| **1** | $0.79_1$ | $0.41_8$ | $0.98_9$ |
| **5c** | $0.81_8$ | $0.42_9$ | $1.01_9$ |
| **5t** | $0.78_2$ | $0.43_9$ | $0.98_0$ |
| **4** | $0.88_5$[a] | $0.51_0$ | $1.09_6$ |
| **3s** | $1.07_9$ | [b] | $1.07_8$ |
| **3a** | $0.84_5$ | $0.52_0$ | $1.10_6$ |
| **2** | [b] | $0.89_5$ | $1.41_3$ |

[a] Monohydrate. [b] Irreversible.

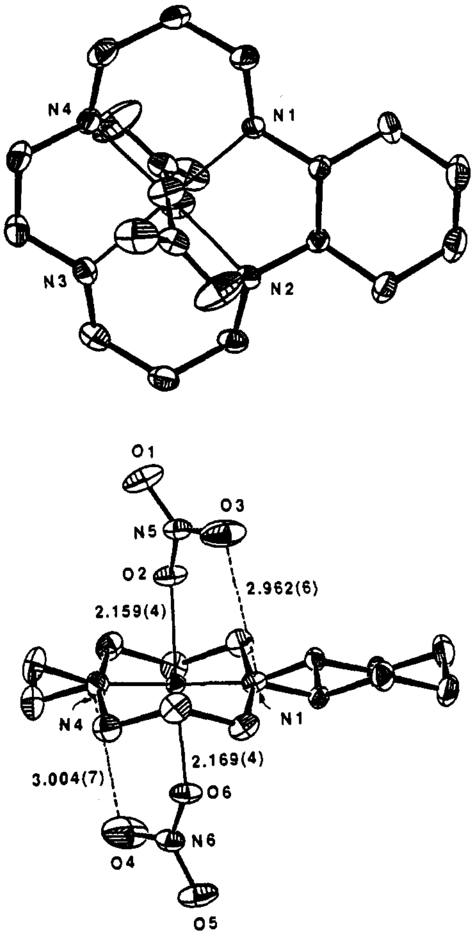

**Figure 1.** Top view and side view of the $Ni(\mathbf{5t})(NO_3)_2$ complex. The ORTEP drawings are shown with 30% probability ellipsoids.

$Ni(\mathbf{1})(ClO_4)_2$ and $Ni(\mathbf{5t})(ClO_4)_2$ are mixtures of low-spin square and high-spin octahedral species, while the complexes $Ni(\mathbf{2})(ClO_4)_2$, $Ni(\mathbf{3s})(ClO_4)_2$, and $Ni(\mathbf{4})(ClO_4)_2$ are all low-spin square species.

**Half-Wave Potentials for the $Ni^{II}/Ni^{III}$ Redox Change.** Busch et al. reported that the positive shifts of half-wave potentials for the $Ni^{II}/Ni^{III}$ redox change ($E_{1/2}(Ni^{II,III})$) of the nickel complexes of methyl-substituted cyclam derivatives were ascribed to the nonbonding interaction between the extraplanar ligands such as solvent which coordinate to the Ni(III) ion and the axially oriented methyl groups on the six-membered chelate ring.[12] In order to estimate the effect of bulky substituents on the ethano bridge of cyclam on the $Ni^{II}/Ni^{III}$ redox behavior, half-wave potentials were measured by cyclic voltammetric method. As shown in Table III, the *trans*-cyclohexanocyclam complexes $Ni(\mathbf{5t})X_2$ ($X = NO_3$, Cl, $ClO_4$) showed half-wave potentials similar to those of the corresponding $Ni(\mathbf{1})X_2$. On the other hand, $Ni(\mathbf{4})X_2$ bearing one tetramethylethane subunit and $Ni(\mathbf{2})X_2$, $Ni(\mathbf{3s})X_2$, and $Ni(\mathbf{3a})X_2$ having two bulky groups on both sides of the cyclam ring showed higher potentials than those of $Ni(\mathbf{1})X_2$ and $Ni(\mathbf{5t})X_2$. *cis*-Cyclohexanocyclam complexes $Ni(\mathbf{5c})X_2$ are intermediate between them. Especially, $Ni(\mathbf{2})Cl_2$ and $Ni(\mathbf{2})(ClO_4)_2$ bearing two tetramethylethane subunits showed very high values, 0.895 and 1.413 V, respectively, indicating that the axial coordination sites of the Ni(III) species were highly hindered by the methyl groups of the cyclam ring.

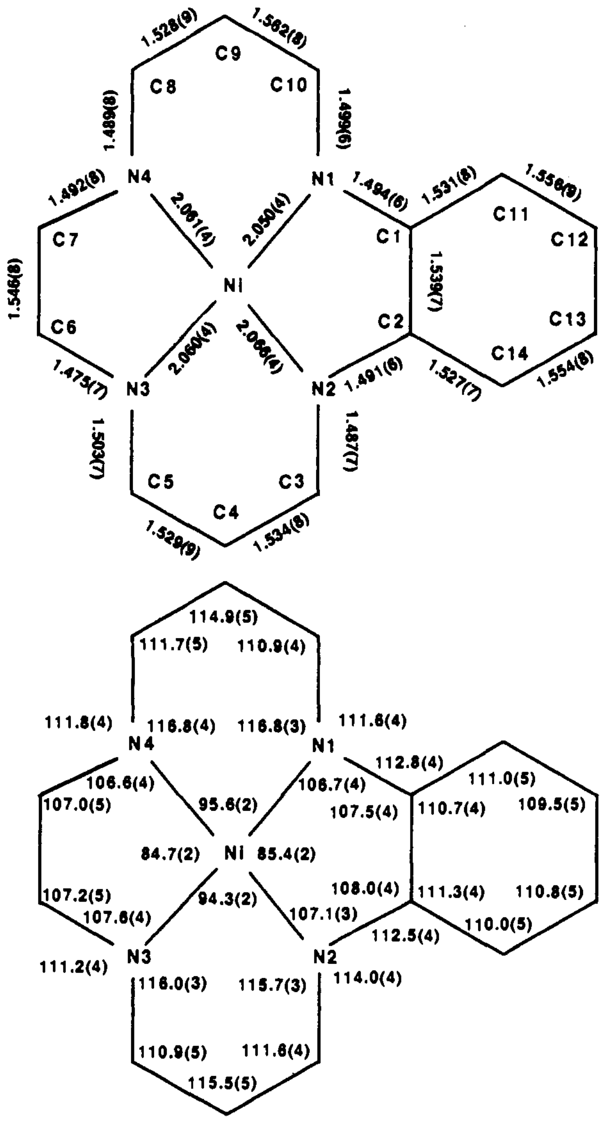

**Figure 2.** Selected bond lengths and angles of the $Ni(\mathbf{5t})(NO_3)_2$ complex.

The above magnetic susceptibility measurements, electronic spectra, and half-wave potentials for the $Ni^{II}/Ni^{III}$ redox change in solution clearly support that, in the sterically congested cyclam complexes $Ni(\mathbf{2})^{2+}$, $Ni(\mathbf{4})^{2+}$, $Ni(\mathbf{3s})^{2+}$, and $Ni(\mathbf{3a})^{2+}$, the axial coordination sites are hindered by steric bulkiness of substituents on the cyclam rings.

**X-ray Structure Analyses.** In order to obtain the structural information of the complexes in the solid state and to clarify the effect of the sterically bulky alkyl groups in the cyclam rings on the axial coordination axis, X-ray structure analyses of $Ni(\mathbf{2})(NO_3)_2$ and $Ni(\mathbf{4})(NO_3)_2 \cdot H_2O$ with tetramethylethane subunit(s), along with related complexes $Ni(\mathbf{3s})(NO_3)_2$ and $Ni(\mathbf{3a})(NO_3)_2$ with two *cis*-cyclohexane subunits and $Ni(\mathbf{5t})(NO_3)_2$ with one *trans*-cyclohexane subunit, were made and the structural parameters were compared.

**Structure of $Ni(\mathbf{5t})(NO_3)_2$.** First of all, the least congested cyclam complex $Ni(\mathbf{5t})(NO_3)_2$ was investigated by the X-ray diffraction method. ORTEP views of the complex are shown in Figure 1. The atomic numbering and selected bond lengths and

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(12) Lovecchio, F. V.; Gore, E. S.; Busch, D. H. *J. Am. Chem. Soc.* **1974**, *96*, 3109.

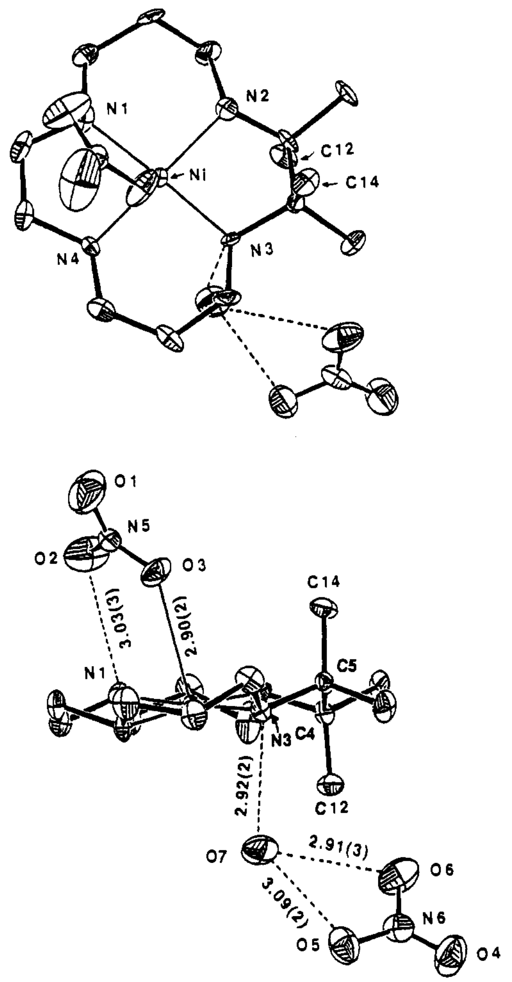


**Figure 3.** Top view and side view of the $Ni(4)(NO_3)_2{\cdot}H_2O$ complex. The ORTEP drawings are shown with 30% probability ellipsoids.

angles are summarized in Figure 2. As expected from the solution data, the Ni atom has six-coordinate octahedral geometry. The Ni atom is situated at the center of the $N_4$ square (N(1), N(2), N(3), N(4)). The cyclam ring has a normal trans-III conformation.[6] The $N_4$ square is planar within 0.02 Å. The Ni–N bond lengths are 2.050 (4), 2.066 (4), 2.060 (4), and 2.061 (4) Å, in accord with the reported high-spin Ni(II) state (2.050 (5) and 2.060 (6) Å for $Ni(\mathbf{1})(NO_3)_2$ complex[6b] and 2.050 and 2.066 Å[13a] or 2.067 (1) and 2.066 (1) Å[13b] for $Ni(\mathbf{1})Cl_2$ complex). The N–Ni–N bond angles are 85.4 (2), 94.3 (2), 84.7 (2), and 95.6 (2)°. Two nitrate anions are located just above and below the Ni atom so that oxygen atoms of nitrate anions coordinate to it. The axial Ni–O bond lengths are 2.159 (4) and 2.169 (4) Å. The distances N(2)–O(3) and N(4)–O(6) are 2.962 (6) and 3.004 (7) Å, respectively, indicating that there exist hydrogen bondings between N–H groups in the cyclam ring (N(2)–H and N(4)–H) and oxygen atoms of the nitrate anions (O(3) and O(6)), respectively. In the case of the $Ni(\mathbf{1})(NO_3)_2$ complex, the corresponding O atoms of nitrate anions made bridged hydrogen bonds with two N–H groups in the cyclam ring.[6b] Thus, although the $Ni(\mathbf{5t})(NO_3)_2$ complex has a *trans*-cyclohexane subunit, it resembles very closely the structure of the prototype complex, $Ni(\mathbf{1})(NO_3)_2$, except for the pattern of the hydrogen bondings between O atoms of nitrate anions and N–H groups of the cyclam ring. From these results, it is deduced that $Ni(\mathbf{5t})(NO_3)_2$ is a low-spin six-coordinate complex with an octahedral geometry around the Ni(II) ion in the solid state and the *trans*-cyclohexane subunit does not interfere with the coordination of nitrate anions of the central Ni atom to give the six-coordinate octahedral complex.

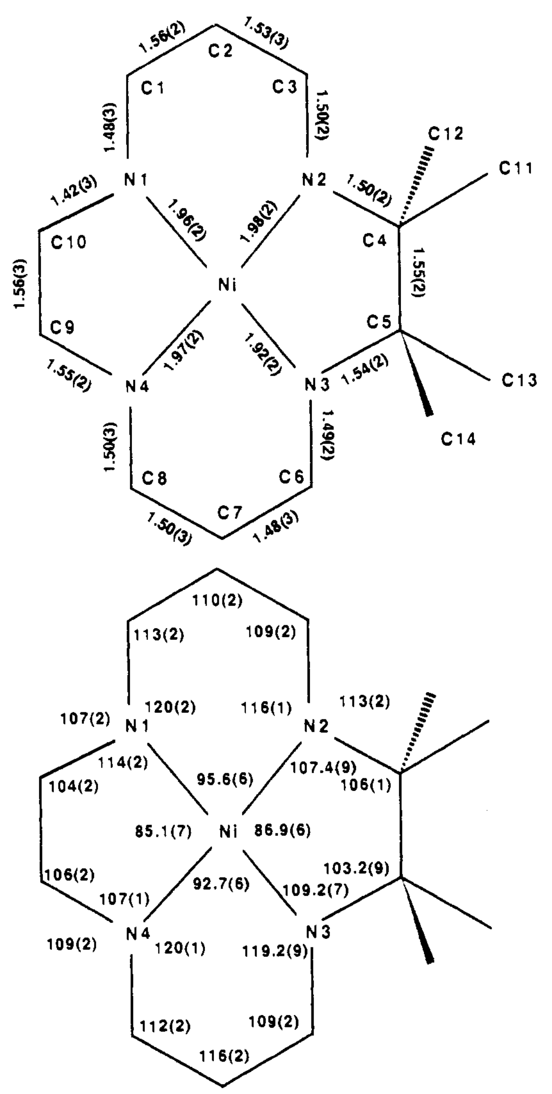
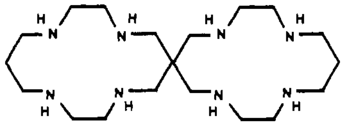


**Figure 4.** Selected bond lengths and angles of the $Ni(4)(NO_3)_2{\cdot}H_2O$ complex.

**Structure of $Ni(4)(NO_3)_2{\cdot}H_2O$.** Next, X-ray analysis of $Ni(4)(NO_3)_2{\cdot}H_2O$ with one tetramethylethane subunit was investigated. The molecular structure of the complex is shown in Figure 3. The atomic numbering and selected bond lengths and angles are summarized in Figure 4. In analogy with $Ni(\mathbf{5t})(NO_3)_2$, the cyclam ring has the trans-III conformation. The $N_4$ plane (N(1), N(2), N(3), N(4)) in the cyclam skeleton is planar within 0.1 Å, and the Ni atom is in the plane. The Ni–N bond lengths are 1.96 (2), 1.98 (2), 1.92 (2), and 1.97 (2) Å, which are shorter than those of $Ni(\mathbf{1})(NO_3)_2$,[6b] $Ni(\mathbf{1})Cl_2$,[13] and $Ni(\mathbf{5t})(NO_3)_2$. These bond lengths are comparable with those of the reported low-spin Ni(II) complex of spirocyclam **14** (1.929–1.960 Å),[14] which are



**14**

in accord with the low-spin Ni(II) state of $Ni(4)(NO_3)_2{\cdot}H_2O$. The N–Ni–N bond angles are 95.6 (6), 86.9 (6), 92.7 (6), and 85.1 (7)°. The Ni(II) ion is five-coordinate with distorted square pyramidal geometry and is weakly coordinated or semicoordi-

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(13) (a) Bosnich, B.; Mason, R.; Pauling, P. J.; Robertson, G. B.; Tobe, M. L. *J. Chem. Soc., Chem. Commun.* **1965**, 97. (b) Ito, T.; Kato, M.; Ito, H. *Bull. Chem. Soc. Jpn.* **1984**, *57*, 2641.

(14) McAuley, A.; Subramanian, S.; Whitcombe, T. W. *J. Chem. Soc., Chem. Commun.* **1987**, 539.

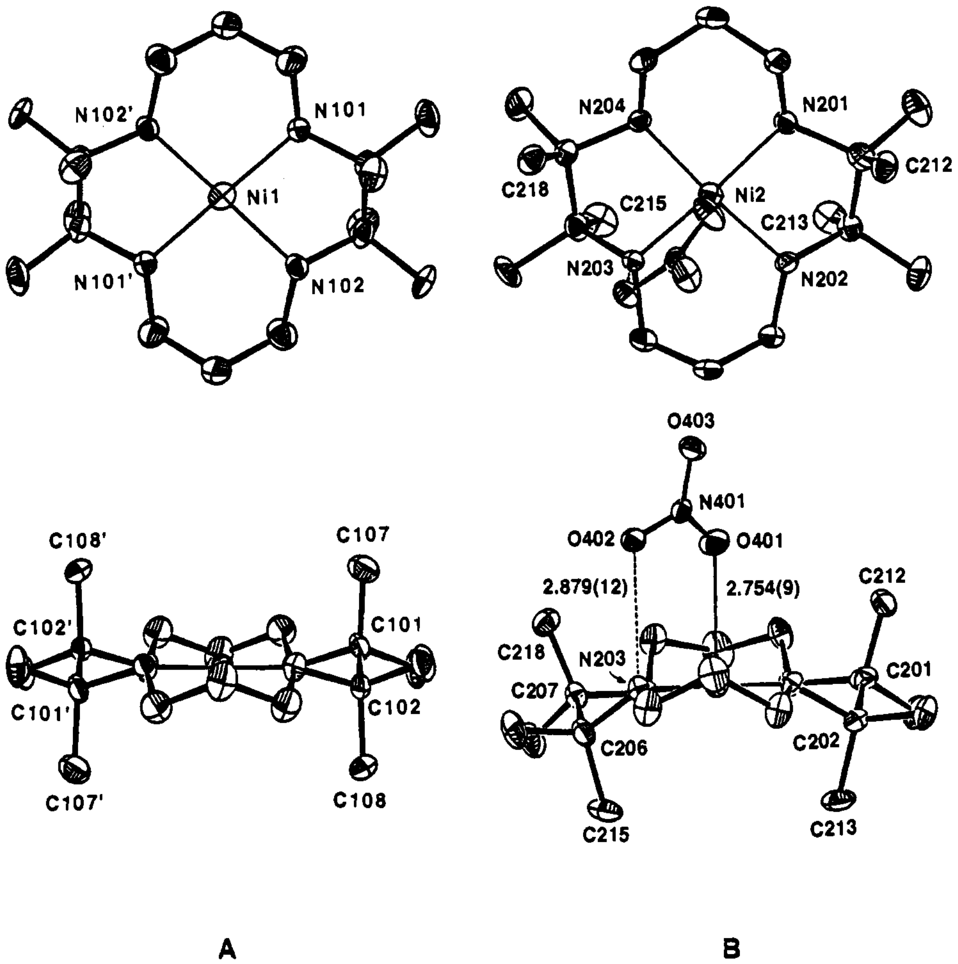

**Figure 5.** Top views and side views of the $Ni(2)(NO_3)_2$ complex: (A) Structure in special positions; (B) structure in general positions. The ORTEP drawings are shown with 30% probability ellipsoids. Uncoordinated nitrate anions are not shown.

nated[15] by one of the O atoms of a nitrate anion (O(3)) from the sterically less encumbered axial direction. The distance between Ni and O(3) is 2.90 (2) Å, and the angle between the Ni···O(3) vector and the $N_4$ plane is 79.3°, which is slightly tilted from the perpendicular axis. Two methyl groups of the tetramethylethane subunit stick out up and below the $N_4$ plane and construct a definite steric barrier against axial coordination, as can be seen in Figure 3. The angles between the vectors C(4)–C(12) and C(5)–C(14) and the $N_4$ plane are 78.2 and 75.5°, respectively. The other nitrate anion, the bottom one in Figure 3, does not coordinate to the Ni atom due to the steric hindrance in this direction. From these results, it is clearly shown that the axial coordination of one of nitrate anions is inhibited due to the axial methyl groups on the cyclam ring and the Ni(II) ion is semicoordinated by one axial ligand to yield a five-coordinate low-spin state with distorted square pyramidal geometry. It has been known that Ni(II) complexes with five-coordinate square pyramidal geometry have both high-spin and low-spin states depending on the nature of the ligands.[16] In the case of Ni(II) complexes with cyclam ligands, however, only the high-spin state has been known.[17] It is, therefore, interesting to note that $Ni(4)(NO_3)_2\cdot H_2O$ represents the first example of a square planar Ni(II) cyclam complex with the low-spin state.

In addition, there is observed hydrogen bonding for N(1)–H···O(2) (3.03 (3) Å). Interestingly, one hydrate water molecule is situated below the N(3) atom and there exists hydrogen bonding for N(3)–H···O(7) (2.92 (2) Å). Moreover, there are hydrogen bondings between the water molecule and the another nitrate anion (O(7)–H···O(5) = 3.09 (2) and O(7)–H···O(6) = 2.91 (3) Å).

**Structure of $Ni(2)(NO_3)_2$.** The molecular structure of the most congested complex $Ni(2)(NO_3)_2$ is shown in Figure 5. Interestingly, there are two types of unique structures of the complex in a crystal, and Ni atoms were found at both special positions ((0, 0, 0) and $(^1/_2, {}^1/_2, {}^1/_2)$) and general positions.

One of structures is shown in Figure 5A, and its atomic numbering and selected bond lengths and angles are summarized in Figure 6. As shown in Figure 5A, no oxygen atom of the nitrate anion coordinates to the Ni atom, resulting in a four-coordinate square planar geometry for the Ni(II) species. Since the Ni(1) atom is located on a symmetric center, half of the structure is crystallographically independent. The $N_4$ square (N(101), N(102), N(101'), N(102')) is planar, and the Ni(1) atom is in the plane. The cyclam ring has a normal trans-III conformation. The Ni(1)–N bond lengths are 1.994 (8) and 1.965 (8) Å, which are also shorter than those of the $Ni(5t)(NO_3)_2$ complex, indicating the Ni(1) ion is also low-spin species as discussed with $Ni(4)(NO_3)_2\cdot H_2O$. The N–Ni(1)–N bond angles are 84.1 (3) and 95.9 (3)°. It should be pointed out that the four methyl groups of both tetramethylethane subunits stick out up and below the plane of the flattened cyclam ring almost perpendicular to the $N_4$ plane (C(101)–C(107) = 83.6° and C(102)–C(108) = 81.8°), and they construct a strict steric barrier in both faces of axial direction of the cyclam ring. Nonbonded distances between two axial carbon atoms (C(107)···C(108') and C(107')···C(108)) are 5.69 (2) Å.

The other structure is shown in Figure 5B, and its atomic numbering and selected bond lengths and angles are summarized

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(15) (a) Reference 1a, p 604. (b) Procter, I. M.; Hathaway, B. J.; Nicholls, P. *J. Chem. Soc.* **1968**, 1678. (c) Deeth, R. J.; Gerloch, M. *Inorg. Chem.* **1984**, *23*, 3846.

(16) The known low-spin complexes of Ni(II) with five-coordinate square planar geometry have ligands with donor atoms such as P, S, or As: ref 1a, pp 45–68.

(17) For example, see: (a) Iwamoto, E.; Yokoyama, T.; Yamasaki, S.; Yabe, T.; Kumamaru, T.; Yamamoto, Y. *J. Chem. Soc., Dalton Trans.* **1988**, 1935. (b) D'Aniello, M. J., Jr.; Mocella, M. T.; Wanger, F.; Barefield, E. K.; Paul, I. C. *J. Am. Chem. Soc.* **1975**, *97*, 192.

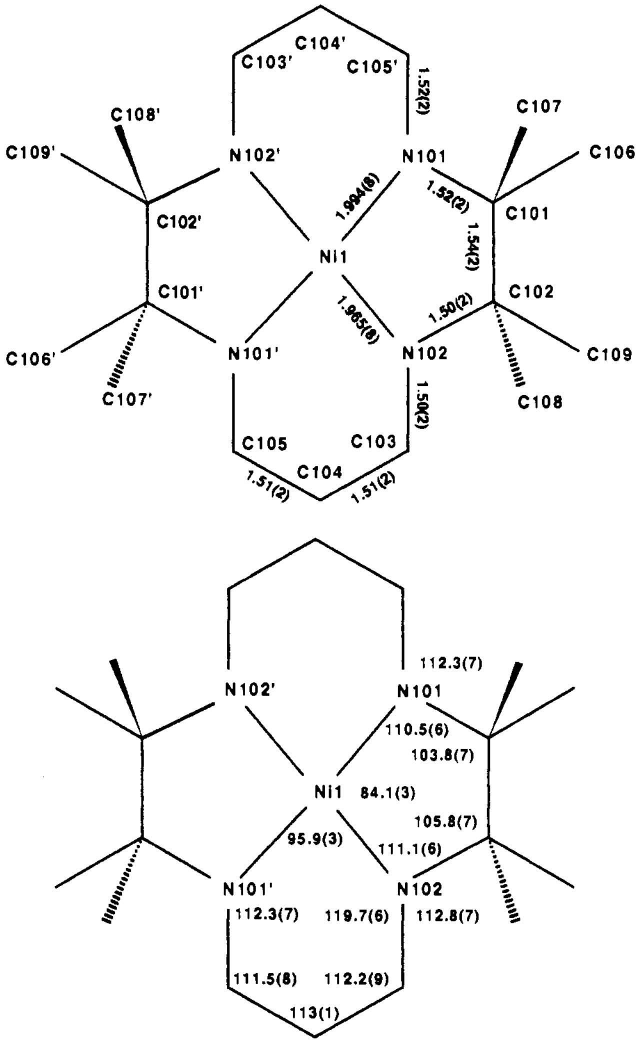

**Figure 6.** Selected bond lengths and angles of the Ni(**2**)$(NO_3)_2$ complex at a special position.

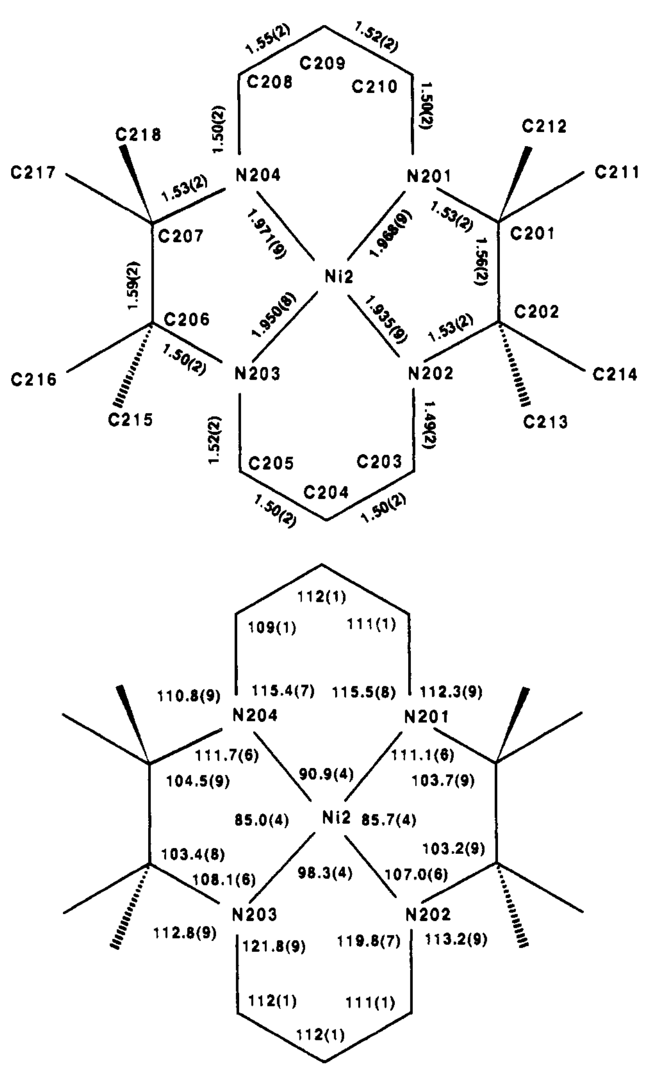

**Figure 7.** Selected bond lengths and angles of the Ni(**2**)$(NO_3)_2$ complex at a general position.

in Figure 7. The $N_4$ square (N(101), N(102), N(103), N(104)) is planar within 0.03 Å, and the Ni(2) atom is located in the plane. The cyclam ring also has the trans-III conformation. The Ni(2)–N bond lengths are 1.968 (9), 1.935 (9), 1.950 (8), and 1.971 (9) Å, which are shorter than those of high-spin complex Ni(**5t**)$(NO_3)_2$. The N–Ni(2)–N bond angles are 85.7 (4), 98.3 (4), 85.0 (4), and 90.9 (4)°. In remarkable contrast with those in structure A, four methyl groups of both tetramethylethane subunits which stick out of the plane of the cyclam ring are inclined relative to the $N_4$ plane, leading to a "V" shape of the barrier (angles between the $N_4$ plane and various vectors are as follows: C(201)–C(212), 71.9°; C(202)–C(213), 73.8°; C(206)–C(215), 74.6°; C(207)–C(218), 68.1°). The nonbonded distance between C(212) and C(218) (6.58 (2) Å) is longer than that between C(213) and C(215) (4.49 (3) Å). The above geometry leaves a space for semicoordination[15] of a nitrate anion in the upper direction of Figure 5B. The distance between Ni(2) and O(401) is 2.754 (9) Å, and the Ni(2)···O(401) vector is slightly tilted from the perpendicular axis to the $N_4$ plane (81.5°). There exists hydrogen bonding for N(203)–H···O(402) (2.879 Å). Despite that there exist two types of structures (A and B) in a crystal, the complex Ni(**2**)$(NO_3)_2$ is on the whole a low-spin complex in the solid state.

From these results, it is clearly demonstrated that the steric bulkiness of four axial methyl groups on two tetramethylethane subunits on the cyclam ring prevents the axial ligands from accessing the central Ni(II) ion, leading to four-coordinate low-spin species with square planar geometry and five-coordinate low-spin species with square pyramidal geometry which is semicoordinated by one axial ligand.

**Structure of Ni(3a)$(NO_3)_2$.** A different type of sterically congested cyclam complex Ni(**3a**)$(NO_3)_2$ was investigated. The structure of the complex is shown in Figure 8, and the atomic numbering and selected bond lengths and angles are summarized in Figure 9. Since the Ni atom is located on a symmetric center, half of the structure is crystallographically independent. In accord with the magnetic susceptibility determined in the solid state, the Ni atom has six-coordinate octahedral geometry. The Ni atom is situated at the center of the $N_4$ plane (N(1), N(2), N(1′), N(2′)), and the $N_4$ plane is planar. The cyclam ring has the normal trans-III conformation. The Ni–N bond lengths are 2.074 (3) and 2.058 (3) Å, and they are comparable with those of Ni(**5t**)$(NO_3)_2$, supporting the high-spin Ni(II) state. The N–Ni–N bond angles are 95.8 (1) and 84.2 (1)°. Two nitrate anions are located above and below the Ni atom so that oxygen atoms of nitrate anions coordinate to it from the sterically less encumbered direction. The axial Ni–O(1) and Ni–O(1′) bond lengths are 2.186 (3) Å, and the angles between the $N_4$ plane and the Ni···O(1) and Ni···O(1′) vectors are 84.9°, which are only slightly tilted from the perpendicular axis. Two cyclohexane subunits stick out up and below the cyclam ring. The angles between the $N_4$ plane and the C(2)–C(9) and C(2′)–C(9′) bonds are 76.5°, indicating that two cyclohexane subunits do not construct effective steric barriers toward the axial coordination sites. From these results, it became apparent that, although the cyclam ligand **3a** has two steric barriers on opposite sides on each face of the cyclam ring (upper left and lower right of the cyclam ring in Figure 8) due to the *cis*-cyclohexane subunits, two anti-fused *cis*-cyclohexane subunits in Ni(**3a**)$(NO_3)_2$ do not interfere with the coordination of axial ligands to give the six-coordinate octahedral geometry around the Ni(II) ion. As a result, the structure of Ni(**3a**)$(NO_3)_2$

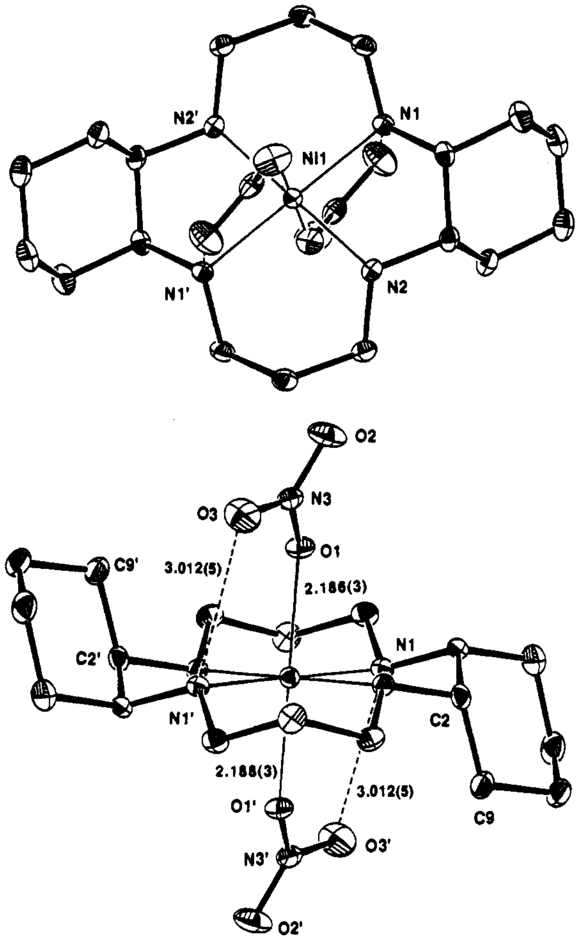

**Figure 8.** Top view and side view of the Ni(**3a**)$(NO_3)_2$ complex. The ORTEP drawings are shown with 30% probability ellipsoids.

resembles very closely that of the less congested cyclam complex Ni(**5t**)$(NO_3)_2$.

**Structure of Ni(3s)(NO$_3$)$_2$.** Finally, another type of sterically congested cyclam complex Ni(**3s**)$(NO_3)_2$ was investigated. The structure of the complex is shown in Figure 10, and the atomic numbering and selected bond lengths and angles are summarized in Figure 11. Apparently, Ni(**3s**)$(NO_3)_2$ has square planar geometry without axial ligand coordination. The Ni–N bond lengths are 1.941 (7), 1.913 (7), 1.931 (7), and 1.914 (7) Å, and they are shorter than those of Ni(**5t**)$(NO_3)_2$, supporting the low-spin Ni(II) state.[6,13,14] The N–Ni–N bond angles are 88.2 (3), 87.9 (3), 88.2 (3), and 95.8 (3)°. Two cyclohexane subunits on cyclam ring which stick out up almost perpendicular to the $N_4$ plane (the angle between the $N_4$ plane and the C(2)–C(14) bond is 83.9°, and that between the $N_4$ plane and the C(6)–C(15) bond, 85.9°) construct an apparent steric barrier against axial coordination. One of the most remarkable structural features of Ni(**3s**)$(NO_3)_2$ is that the cyclam ring has the trans-I conformation[6] in contrast with the conformation of the other complexes (Ni(**5t**)$(NO_3)_2$, Ni(**2**)$(NO_3)_2$, Ni(**4**)$(NO_3)_2 \cdot H_2O$). Because of steric hindrance due to this particular conformation of the cyclam ring, coordination of nitrate anion from the lower direction of the $N_4$ plane would be suppressed, as can be seen in Figure 10.[18] Thus, it should be pointed out that, despite that cyclam ligand **3s** has a steric barrier in only one direction (upper direction in Figure 10) due to the cyclohexane rings, both faces of the coordination sites are hindered due to the additional steric barrier produced by the trans-I conformation of the cyclam ring.

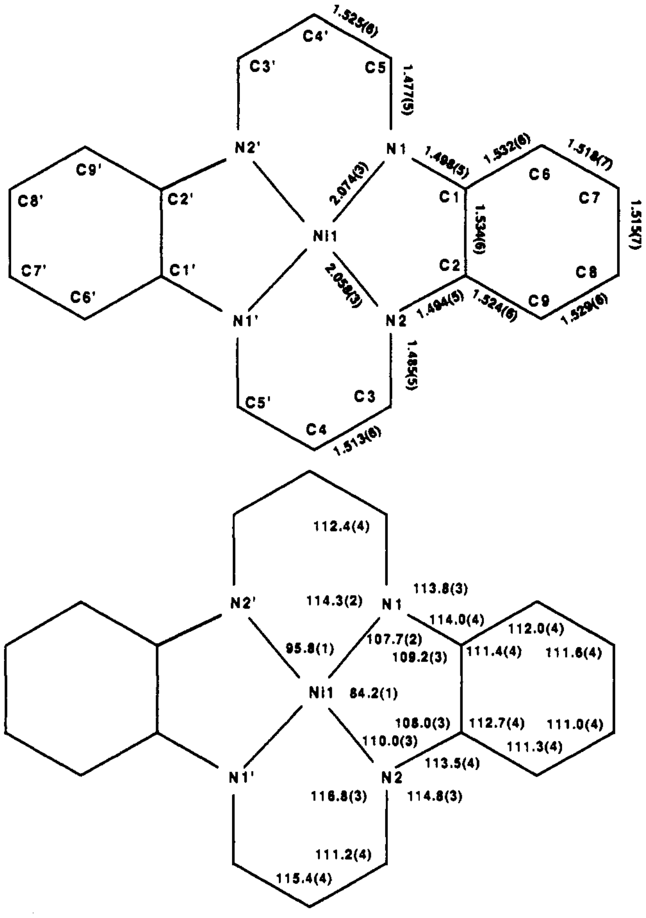

**Figure 9.** Selected bond lengths and angles of the Ni(**3a**)$(NO_3)_2$ complex.

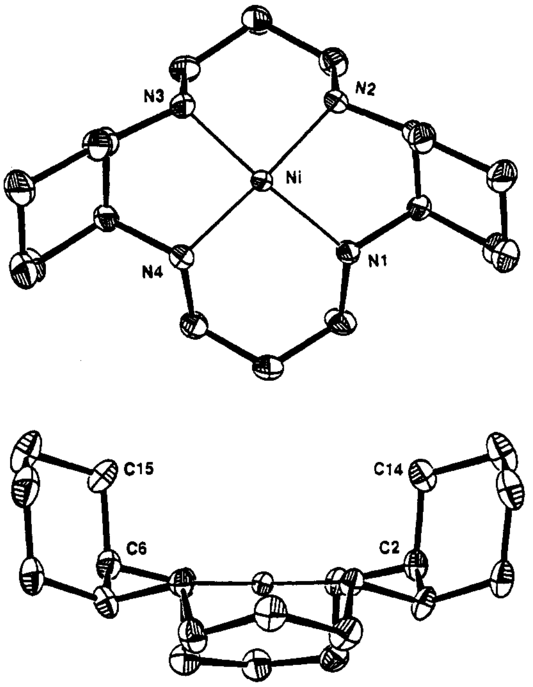

**Figure 10.** Top view and side view of the Ni(**3s**)$(NO_3)_2$ complex. The ORTEP drawings are shown with 30% probability ellipsoids. Uncoordinated nitrate anions are omitted.

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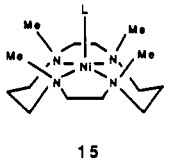
[18] The trans-I conformation was also found in the Ni(II) complex **15**. In this case, the coordination of axial ligand from the lower direction was suppressed to give five-coordinate square pyramidal geometry.[17]



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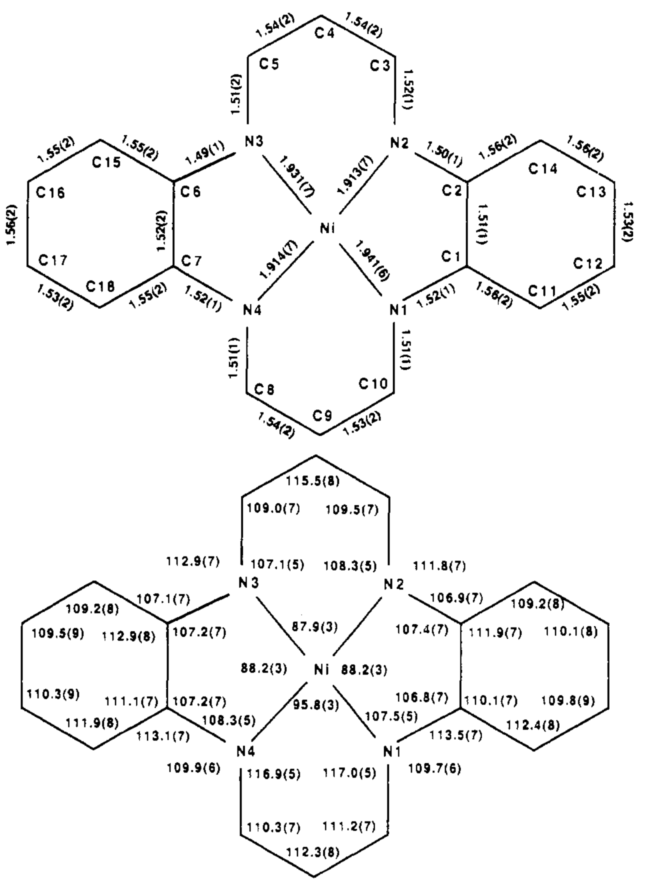

**Figure 11.** Selected bond lengths and angles of the Ni(**3s**)$(NO_3)_2$ complex.

**Conclusion.** It has been proved that the tetramethylethane subunits in cyclam complexes Ni(**2**)$(NO_3)_2$ and Ni(**4**)$(NO_3)_2$ result in a significant change of the accessibility of the axial ligand toward coordinated nickel(II) ion leading to four-coordinate square planar and five-coordinate square pyramidal geometries. It is of worth noting that only one tetramethylethane subunit is enough to effectively prevent axial ligands such as nitrate anions or water molecules from accessing the central nickel(II) ion. Moreover, in *syn*-dicyclohexanocyclam complex Ni(**3s**)$(NO_3)_2$, both faces of the coordination sites are sterically hindered due to both two cyclohexane subunits and the trans-I conformation of the cyclam ring itself to yield four-coordinate square planar geometry.

## Experimental Section

**General Methods.** IR spectra were recorded on a Hitachi 260-10 spectrometer. $^1H$ NMR spectra were measured on JEOL JNM PS-100 and JEOL GSX400 spectrometers, and $^{13}C$ NMR spectra were recorded on a JEOL JNM FX90Q spectrometer in $CDCl_3$ solution. Mass spectra were measured on a Hitachi RMU-6E spectrometer. Electronic spectra were recorded on a Hitachi 356 double-beam spectrophotometer. Magnetic measurements in water solution were performed by Evans' method[10] on a JEOL JNM PS-100 NMR spectrometer.

**Materials.** 2,3-Dimethylbutane-2,3-diamine (**6**) was prepared by the methods described by Sayre.[19] *cis*-Cyclohexane-1,2-diamine (**8c**) and *trans*-cyclohexane-1,2-diamine (**8t**) were separated from a mixture (purchased from Nakarai Tesque) according to the procedure reported by Saito and Kidani.[20] 1,3-Dibromopropane was purchased from Wako Pure Chemical Industries.

**Safety Note.** *Since perchlorate salts are potentially explosive, these should be handled with great caution!*[21]

**Syntheses. 2,3,3,9,9,10-Hexamethyl-4,8-diazaundecane-2,10-diamine (7).** To a stirred mixture of 21.3 g (201 mmol) of $Na_2CO_3$ and 50.0 g (430 mmol) of diamine **6** in 68 mL of ethanol at 0 °C was added a solution of 8.47 g (42 mmol) of 1,3-dibromopropane in 4.3 mL of ethanol during 1 h. The mixture was refluxed for 24 h and then cooled to room temperature. The reaction mixture was diluted with $CH_2Cl_2$ and filtered. The solvent and the unreacted diamine **6** were removed by distillation. The residue was distilled under vacuum to give 7.6 g (67%) of tetraamine **7** as an oil: bp 124 °C (1 mmHg); IR (neat) 3280, 1630 $cm^{-1}$; MS $m/z$ 272 ($M^+$); $^1H$ NMR $\delta$ 0.99 (s, 12 H), 1.04 (s, 12 H), 1.36 (br s, 6 H), 1.54 (quintet, $J$ = 7 Hz, 2 H), 2.59 (t, $J$ = 7 Hz, 4 H). **7**·4HCl salt: mp 273 °C dec (recrystallized from ethanol). Anal. Calcd for $C_{15}H_{40}Cl_4N_4$: C, 43.07; H, 9.64; N, 13.39. Found: C, 42.98; H, 9.51; N, 13.23.

**2,2,3,3,9,9,10,10-Octamethyl-1,4,8,11-tetraazacyclotetradecane (Octamethylcyclam) (2).** A mixture of 1.00 g (3.68 mmol) of tetraamine **7** and 0.74 g (3.70 mmol) of 1,3-dibromopropane in 70 mL of ethanol was heated at reflux for 7 d. Most of the solvent was distilled off, and 900 mg of KOH and 50 mL of ethanol were added. The mixture was refluxed for another 1 h, cooled, diluted with $CH_2Cl_2$, and filtered. The filtrate was condensed in vacuo, and the residue was chromatographed on alumina with $CH_2Cl_2$ as eluent to give 217 mg (19%) of octamethylcyclam (**2**): mp 131–132 °C (recrystallized from $CH_3CN$); IR (KBr) 3260 $cm^{-1}$; MS $m/z$ 312 ($M^+$); $^1H$ NMR $\delta$ 1.05 (s, 24 H), 1.7 (m, 4 H), 2.66 (t, $J$ = 5 Hz, 8 H); $^{13}C$ NMR $\delta$ 20.4 (q, 8 C), 30.6 (t, 2 C), 44.1 (t, 4 C), 58.3 (s, 4 C). Anal. Calcd for $C_{18}H_{40}N_4$: C, 69.13; H, 12.89; N, 17.18. Found: C, 69.28; H, 12.97; N, 17.95.

**1,2:8,9-*cis*-Dicyclohexano-3,7-diazanonane-1,9-diamine (9s, 9a).** Tetraamines **9s** and **9a** were synthesized from *cis*-cyclohexane-1,2-diamine (**8c**) by the method similar to that described for **7** as a mixture in 35% yield: IR (neat) 3260 $cm^{-1}$; MS $m/z$ 269 ($M^+$ + 1); $^1H$ NMR $\delta$ 1.0–1.9 (m, 18 H), 1.96 (br s, 4 H), 2.4–2.9 (m, 4 H), 3.04 (br s, 6 H).

**2,3:9,10-*cis*-*syn*-*cis*-Dicyclohexano-1,4,8,11-tetraazacyclotetradecane (*cis*-*syn*-*cis*-Dicyclohexanocyclam) (3s) and 2,3:9,10-*cis*-*anti*-*cis*-Dicyclohexano-1,4,8,11-tetraazacyclotetradecane (*cis*-*anti*-*cis*-Dicyclohexanocyclam) (3a).** Dicyclohexanocyclams **3s** and **3a** were synthesized both in 3% yields from a mixture of tetraamines **6s** and **6a** by the method similar to that described for **2**. They were separated by chromatography on alumina. Anti isomer **3a** was eluted first, and then syn isomer **3s**, with $CH_2Cl_2$. **3s**: mp 156–157 °C (recrystallized from $CH_3CN$); IR (KBr) 3260 $cm^{-1}$; MS $m/z$ 308 ($M^+$); $^1H$ NMR $\delta$ 1.0–1.8 (m, 20 H), 1.8–2.2 (br s, 4 H), 2.2–3.0 (m, 12 H); $^{13}C$ NMR $\delta$ 22.5 (t, 4 C), 28.0 (t, 4 C), 30.2 (t, 2 C), 49.8 (t, 4 C), 57.6 (t, 4 C). Anal. Calcd for $C_{18}H_{36}N_4$: C, 70.08; H, 11.76; N, 18.16. Found: C, 70.18; H, 11.71; N, 18.07. **3a**: mp 189–190 °C (recrystallized from $CH_2Cl_2$); IR (KBr) 3280 $cm^{-1}$; MS $m/z$ 308 ($M^+$); $^1H$ NMR $\delta$ 1.0–1.9 (m, 24 H), 2.4–3.0 (m, 12 H); $^{13}C$ NMR $\delta$ 22.5 (t, 4 C), 28.3 (t, 4 C), 30.2 (t, 2 C), 43.2 (t, 4 C), 56.9 (t, 4 C). Anal. Calcd for $C_{18}H_{36}N_4$: C, 70.08; H, 11.76; N, 18.16 Found: C, 70.10; H, 11.65; N, 18.10.

**5,5,6,6-Tetramethyl-4,7-diazadecane-1,10-diamine (10).** Tetraamine **10** was synthesized according to the method similar to that described by Barefield et al.[7] To 5.15 g (44.4 mmol) of diamine **6** was added dropwise at 0 °C 6.4 mL (120 mmol) of freshly distilled acrylonitrile over 20 min. The reaction mixture was stirred for 1 h at 0 °C, brought slowly to 100 °C, and maintained at this temperature for 75 h. After being cooled, the excess acrylonitrile was evaporated in vacuo. The crude product was dissolved in 70 mL of absolute ethanol and placed in an autoclave. The solution was saturated with dry ammonia, and 2.5 g of freshly prepared Raney-nickel catalyst (W-4) was added. The suspension was stirred under a pressure of hydrogen (10 atm) for 18 h and filtered. The filtrate was evaporated in vacuo, and the residue was distilled under vacuum to give 5.15 g (54%) of tetraamine **10**: bp 145 °C (3 mmHg); IR (neat) 3250 $cm^{-1}$; $^1H$ NMR $\delta$ 1.00 (s, 12 H), 1.56 (quintet, $J$ = 7 Hz, 4 H), 1.62 (s, 6 H), 2.58 (t, $J$ = 7 Hz, 4 H), 2.76 (t, $J$ = 7 Hz, 4 H).

**(2,2,3,3-Tetramethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Perchlorate Complex (Ni(tetramethylcyclam)$(ClO_4)_2$ Complex) (Ni(4)$(ClO_4)_2$).** Ni(**4**)$(ClO_4)_2$ was synthesized by the procedure similar to that described by Barefield et al.[7] To a stirred mixture of 3.20 g (8.8 mmol) of $Ni(ClO_4)_2{\cdot}6H_2O$ in 48 mL of water was added at 5 °C 2.00 g (8.70 mmol) of tetraamine **10** over 10 min, and the mixture was stirred for 30 min at 5 °C. To this mixture was added 1.36 mL (12.1 mmol) of 40% glyoxal during 5 min, and then the mixture was heated at 40–55 °C for 5 h. The resulting slurry was again cooled to 5 °C and treated with 657 mg (17.4 mmol) of $NaBH_4$, which was added in small portions over 1 h. The mixture was then heated at 90 °C for 20 min, the hot solution was filtered rapidly through a glass filter. The filtrate was acidified with 60% $HClO_4$, and the solvent was evaporated in vacuo. The resulting orange solid was washed with ethanol and ether to give 1.75 g (40%) of Ni(**4**)$(ClO_4)_2$: mp >285 °C dec (recrystallized from water); IR (KBr) 3200, 1100 $cm^{-1}$. Anal. Calcd for $C_{14}H_{32}C_{12}N_4NiO_8$: C, 32.71; H, 6.27; Cl, 13.79; N, 10.90. Found: C, 32.33; H, 6.16; Cl, 13.91; N, 10.52.

**2,2,3,3-Tetramethyl-1,4,8,11-tetraazacyclotetradecane (Tetramethylcyclam) (4).** To a stirred mixture of 505 mg (0.98 mmol) of Ni(**4**)$(ClO_4)_2$ in 10 mL of water was added at room temperature 192 mg (3.92

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**Table IV.** Crystallographic Data for Ni(**2**)($NO_3$)$_2$, Ni(**3s**)($NO_3$)$_2$, Ni(**3a**)($NO_3$)$_2$, Ni(**4**)($NO_3$)$_2$·$H_2O$, and Ni(**5t**)($NO_3$)$_2$

| | Ni(**2**)($NO_3$)$_2$ | Ni(**3s**)($NO_3$)$_2$ | Ni(**3a**)($NO_3$)$_2$ | Ni(**4**)($NO_3$)$_2$·$H_2O$ | Ni(**5t**)($NO_3$)$_2$ |
|---|---|---|---|---|---|
| formula | $C_{18}H_{40}N_6NiO_6$ | $C_{18}H_{36}N_6NiO_6$ | $C_{18}H_{36}N_6NiO_6$ | $C_{14}H_{34}N_6NiO_7$ | $C_{14}H_{30}N_6NiO_6$ |
| fw | 495.25 | 491.22 | 491.22 | 457.16 | 437.13 |
| space group | $P2_1/n$ | $P\bar{1}$ | *Pbca* | $Pca2_1$ | $P2_1/n$ |
| *a*, Å | 13.997 (4) | 12.135 (4) | 17.765 (4) | 17.795 (5) | 10.970 (2) |
| *b*, Å | 25.306 (9) | 12.157 (3) | 15.136 (2) | 7.410 (2) | 22.840 (4) |
| *c*, Å | 9.947 (3) | 7.553 (2) | 8.013 (1) | 15.358 (4) | 7.878 (2) |
| $\alpha$, deg | | 91.53 (2) | | | |
| $\beta$, deg | 101.67 (3) | 92.17 (2) | | | 96.55 (2) |
| $\gamma$, deg | | 93.05 (2) | | | |
| *V*, Å$^3$ | 3446 (2) | 1111.4 (5) | 2155 (1) | 2025.1 (8) | 1961.1 (6) |
| *Z* | 6 | 2 | 4 | 4 | 4 |
| $d_{calcd}$, g cm$^{-3}$ | 1.43 | 1.47 | 1.42 | 1.50 | 1.48 |
| $\mu$(Mo K$\alpha$), cm$^{-1}$ | 10.33 | 9.20 | 9.49 | 10.07 | 10.33 |
| *R*, % | 10.7 | 9.4 | 4.2 | 6.7 | 6.4 |
| $R_w$, % | 14.6$^a$ | 11.3$^a$ | 4.2$^b$ | 16.1$^a$ | 9.1$^a$ |

$^a w = [\sigma^2(F_o) + 0.003(F_o)^2]^{-1}$. $^b w = 4F_o^2/\sigma^2(F_o^2)$.

mmol) of NaCN over 5 min. The resulting mixture was refluxed for 3 h with stirring. After the mixture was cooled, 100 mg (2.5 mmol) of NaOH was added, and the mixture was extracted by $CHCl_3$. The organic phase was separated, washed with water, and dried ($Na_2SO_4$). The solvent was evaporated in vacuo. The crude product was recrystallized from $CH_3CN$ to give 175 mg (70%) of **4**: mp 109–110 °C; IR (KBr) 3270, 3220 cm$^{-1}$; MS *m/z* 256 (M$^+$); $^1$H NMR $\delta$ 1.02 (s, 12 H), 1.68 (quintet, *J* = 5 Hz, 4 H), 2.08 (br s, 4 H), 2.6–2.9 (m, 12 H). Anal. Calcd for $C_{14}H_{32}N_4$: C, 65.57; H, 12.85; N, 21.85. Found: C, 65.47; H, 12.47; N, 21.67.

**5,6-*cis*-Cyclohexano-4,7-diazadecane-1,10-diamine (11).** Tetraamine **11** was prepared from **8c** according to the method similar to that described for **10** in 58% yield as an oil. **11**: bp 152 °C (1 mmHg); IR (neat) 3250 cm$^{-1}$; MS *m/z* 228 (M$^+$); $^1$H NMR $\delta$ 1.0–2.0 (m, 18 H), 2.4–2.9 (m, 10 H).

**(2,3-*cis*-Cyclohexano-1,4,8,11-tetraazacyclotetradecane)nickel(II) Perchlorate Complex (Ni(*cis*-cyclohexanocyclam)($ClO_4$)$_2$ Complex) (Ni(5c)($ClO_4$)$_2$).** This complex was synthesized from **11** by the procedure similar to that described for Ni(**4**)($ClO_4$)$_2$ in 67% yield. Ni(**5c**)($ClO_4$)$_2$: mp >270 °C dec (recrystallized from water); IR (KBr) 3100, 1100 cm$^{-1}$. Anal. Calcd for $C_{14}H_{30}C_{12}N_4NiO_8$: C, 32.84; H, 5.91; Cl, 13.85; N, 10.94. Found: C, 33.07; H, 5.91; Cl, 13.70; N, 10.83.

**2,3-*cis*-Cyclohexano-1,4,8,11-tetraazacyclotetradecane (*cis*-Cyclohexanocyclam) (5c).** This compound was synthesized from Ni(**5c**)($ClO_4$)$_2$ by the method similar to that described for **4** in 70% yield. **5c**: mp 137.5–138 °C (recrystallized from $CH_3CN$); IR (KBr) 3250 cm$^{-1}$; MS *m/z* 254 (M$^+$); $^1$H NMR $\delta$ 1.0–2.0 (m, 16 H), 2.4–3.0 (m, 14 H). Anal. Calcd for $C_{14}H_{30}N_4$: C, 66.09; H, 11.89; N, 22.02. Found: C, 66.19; H, 11.89; N, 21.70.

**5,6-*trans*-Cyclohexano-4,7-diazadecane-1,10-diamine (12).** Tetraamine **12** was prepared from *trans*-cyclohexane-1,2-diamine (**8t**) according to the method similar to that described for **10** in 63% yield as an oil. **12**: bp 159 °C (2 mmHg); IR (neat) 3380, 3350 cm$^{-1}$; MS *m/z* 228 (M$^+$); $^1$H HNR $\delta$ 1.12 (quintet, *J* = 9 Hz, 4 H), 1.4–1.8 (m, 12 H), 2.09 (br s, 4 H), 2.3–3.0 (m, 8 H).

**(2,3-*trans*-Cyclohexano-1,4,8,11-tetraazacyclotetradecane)nickel(II) Perchlorate Complex (Ni(*trans*-cyclohexanocyclam)($ClO_4$)$_2$ Complex) (Ni(5t)($ClO_4$)$_2$).** This complex was synthesized by the procedure similar to that described for Ni(**4**)($ClO_4$)$_2$ in 59% yield. Ni(**5t**)($ClO_4$)$_2$: mp >275 °C dec; IR (KBr) 3300, 3180, 1100 cm$^{-1}$. Anal. Calcd for $C_{14}H_{30}C_{12}N_4NiN_8$: C, 32.84; H, 5.91; Cl, 13.85; N, 10.94. Found: C, 32.82; H, 5.95; Cl, 13.90; N, 10.70.

**2,3-*trans*-Cyclohexano-1,4,8,11-tetraazacyclotetradecane (*trans*-Cyclohexanocyclam) (5t).** This compound was synthesized from Ni(**5t**)($ClO_4$)$_2$ by the method similar to that described for **4** in 70% yield. **5t**: mp 218–219 °C (recrystallized from a mixture of $CHCl_3$ and ether); IR (KBr) 3250, 3150 cm$^{-1}$; MS *m/z* 254 (M$^+$); $^1$H NMR $\delta$ 0.6–3.2 (m). Anal. Calcd for $C_{14}H_{30}N_4$: C, 66.09; H, 11.89; N, 22.02. Found: C, 66.12; H, 11.83; N, 21.91.

**Complexation of Cyclam Derivatives with $NiX_2$ (X = $NO_3$, Cl, $ClO_4$). Method A.** Equimolar amounts of cyclam derivative and $NiX_2 \cdot nH_2O$ in methanol were refluxed. Crystals formed on cooling were collected, washed with methanol, dried, and recrystallized from appropriate solvent.

**Method B.** Equimolar amounts of cyclam derivative and $NiX_2 \cdot nH_2O$ in DMSO were heated at 75 °C for 1 or 2 d. The solvent was evaporated in vacuo, and the obtained solids were recrystallized from the appropriate solvent. Reaction solvents, recrystallization solvents, melting points, and elemental analyses are listed in Table I.

**Measurements of Half-Wave Potentials for the Ni$^{II}$/Ni$^{III}$ Redox Change.** Cyclic voltammetric measurements were made with a potentiostat (Hokutodenko HA-301), a function generator (Hokutodenko HB-104), and a standard three-electrode cell. A working electrode (platinum), counter electrode (glassy carbon), and reference electrode (standard calomel electrode) were used. All measurements were made for acetonitrile solutions that were 0.1 M in tetrabutylammonium perchlorate.

**X-ray Crystallographic Studies. Ni(2)($NO_3$)$_2$.** Orange crystals were formed by recrystallization from water/ethanol. Integrated intensities were measured on the Rigaku automated four-circle diffractometer using graphite-monochromatized Mo K$\alpha$ radiation. Unit cell parameters were determined by least-squares refinement of 25 automatically centered reflections. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table IV. Calculations were performed with the XRAY system program.[22] The structure was solved by Patterson techniques. The space group was determined to be $P2_1/n$ (No. 14) from the observed conditions. Two nickel atoms were situated on special positions, (0, 0, 0) and ($^1/_2$, $^1/_2$, $^1/_2$), and four nickel atoms were situated on general positions in the unit cell. No absorption correction was applied. Final refinement was carried out with anisotropic thermal parameters. One nitrate anion was disordered and was refined as two different molecules whose populations were equal to 0.5 and as two rigid groups (N(301), O(301), O(302), and O(303) and N(302), O(304), O(305), and O(306)), while two other anions were unconstrained. Selected bond lengths and angles are given in Figures 6 and 7.

**Ni(3s)($NO_3$)$_2$, Ni(3a)($NO_3$)$_2$, Ni(4)($NO_3$)$_2$·$H_2O$, and Ni(5t)($NO_3$)$_2$.** Orange crystals (Ni(**3s**)($NO_3$)$_2$ from water and Ni(**4**)($NO_3$)$_2$·$H_2O$ from water/ethanol) and violet crystals (Ni(**5t**)($NO_3$)$_2$ from methanol/acetone and Ni(**3a**)($NO_3$)$_2$ from water/ethanol) were obtained by recrystallization. Unit cell parameters were determined by least-squares refinement of 25 automatically centered reflections. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table IV. Calculations were performed with the XRAY system program[22] for Ni(**3s**)($NO_3$)$_2$, Ni(**4**)($NO_3$)$_2$·$H_2O$, and Ni(**5t**)($NO_3$)$_2$ and the TEXSAN crystallographic software package[23] for Ni(**3a**)($NO_3$)$_2$. The nickel atom was determined via Patterson methods. All non-hydrogen atoms were refined anisotropically. In the case of Ni(**3a**)($NO_3$)$_2$, hydrogen atoms were refined isotropically. Selected bond lengths and angles are summarized by Figures 2, 4, 9, and 11.

**Acknowledgment.** We are grateful to the Crystallographic Research Center, Osaka University, for all the crystallographic computations and the Ministry of Education, Science and Culture for the support of the NMR spectral facilities of the Instrumental Analysis Center, Faculty of Engineering, Osaka University.

**Supplementary Material Available:** Figure S1, illustrating crystal packing in a unit cell of Ni(**2**)($NO_3$)$_2$, and Tables S1–S3, S5, S6, S8–S11, S13, S14, S16, and S17, listing crystallographic data and refinement parameters, fractional atomic coordinates and thermal parameters, and bond lengths and bond angles for Ni(**2**)($NO_3$)$_2$, Ni(**3s**)($NO_3$)$_2$, Ni(**3a**)($NO_3$)$_2$, Ni(**4**)($NO_3$)$_2$·$H_2O$, and Ni(**5t**)($NO_3$)$_2$ (45 pages); Tables S4, S7, S12, S15, and S18, listing observed and calculated structure factors (166 pages). Ordering information is given on any current masthead page.

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