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# Tetraaza Macrocyclic Metal Complexes Containing a Medium-Sized Chelate Ring. 1. Syntheses and Characterization of Nickel(II) Complexes with 1,4,7,10-Tetraazacyclotetradecane, -cyclopentadecane, and -cyclohexadecane

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Three new macrocyclic ligands, 1,4,7,10-tetraazacyclotetradecane, -cyclopentadecane, and -cyclohexadecane, and their nickel(II) complexes have been synthesized and characterized. The complexes, which involve a seven-, eight-, or nine-membered chelate ring, are obtained in two different species, a yellow, diamagnetic four-coordinate complex with perchlorate and a violet to green, paramagnetic six-coordinate complex with halide or pseudohalide ions. All the complex perchlorates in water exist in equilibrium between four-coordinate and diaqua six-coordinate species. Equilibrium constants between the two species for each of the three complex perchlorates have been obtained by analyzing the temperature-dependent electronic spectra. Electronic spectra of a series of the *trans*-dichloro complexes indicate that an average ligand field strength of the macrocyclic ligand decreases with an increase in the ring size.

Extensive work has been done on metal complexes with macrocyclic ligands. However, all of these complexes seem to comprise five- and/or six-membered chelate rings except for those recently reported by Martin et al.,[2] which consist of two six- and two seven-membered chelate rings. The formation of chelate rings will become disadvantageous with the increasing ring members owing to an increase in ring strain and a decrease in the probability of ring closure. In particular, the medium-sized (8-11 members) chelate rings would involve severe ring strain, by analogy with cycloalkanes. Ogino and Fujita[3] investigated the products yielded by reactions between *cis*- or *trans*-$[CoCl_2(en)_2]^+$ (en = ethylenediamine) and a series of diamines, $NH_2(CH_2)_nNH_2$ ($n$ = 2-14), in dimethyl sulfoxide and found that the diamines with $n$ = 5-8 do not form a chelate ring but act as a unidentate or a bridging ligand. A similar result was obtained for Pd(II) and Pt(II) complexes with diphosphines, $(t\text{-}C_4H_9)_2P(CH_2)_nP(t\text{-}C_4H_9)_2$.[4] Thus the medium-sized chelate rings seem to be hardly formed in the metal complexes. However, such chelate rings might be found in metal complexes with appropriate macrocyclic ligands, since macrocyclic complexes are often stabilized to a great extent by the macrocyclic effect "multiple juxtapositional fixedness".[5] With this expectation, three new tetraaza macrocyclic ligands that can form three five-membered chelate rings and one seven-, eight-, or nine-membered ring when coordinated to a metal ion have been synthesized. This paper reports syntheses and properties of the ligands and their four- and six-coordinate Ni(II) complexes.[6]

Throughout this paper, the abbreviations $N_4$7, $N_4$8, and $N_4$9 are used for 1,4,7,10-tetraazacyclotetradecane, 1,4,7,10-tetraazacyclopentadecane, and 1,4,7,10-tetraazacyclohexadecane, respectively. The formation of the medium-sized chelate rings has been confirmed by X-ray crystal structure analyses on *trans*-$[NiCl_2(N_47)]\cdot H_2O$,[7] $[Ni(N_48)](ClO_4)_2$,[7] *trans*-$[NiCl_2(N_49)]$,[7] and *cis*-$[Ni(NCS)_2(N_47)]$.[8]

## Experimental Section

**Preparation of Ligands.** The macrocyclic ligands were prepared according to the synthetic route given in Scheme I.

***N,N′,N″,N‴*-Tetrakis(*p*-tolylsulfonyl)triethylenetetramine (2) and Its Disodium Salt (3).** A solution of *p*-toluenesulfonyl chloride (TsCl) (228.9 g, 1.2 mol) in diethyl ether (600 mL) was added dropwise to a vigorously stirred aqueous solution (250 mL) containing purified triethylenetetramine (**1**) (43.8 g, 0.3 mol) and sodium hydroxide (72 g, 1.8 mol). The mixture was stirred for 1 h. The resulting white precipitate of **2** was filtered and washed with water; yield 85-95%. ($^1$H NMR ($CDCl_3$) $\delta$ 2.13 (s, 12, $CH_3$), 2.8-3.4 (m, 12, $CH_2$), 7.45 (d, 8, phenyl), 7.75 (d, 8, phenyl).) The precipitate (152 g) was mixed with ethanol (500 mL), and the mixture was refluxed for 2 h. To this was added an ethanol solution (320 mL) of 11 g of sodium. The mixture was further refluxed for 2 h and then filtered to remove a small amount of a white solid. The filtrate was rotoevaporated to ca. two-thirds its initial volume. The white crystalline precipitate of **3** produced upon standing overnight was filtered and washed with ethanol; yield 57%.

***O,O*-Bis(*p*-tolylsulfonyl)-1,ω-alkanediol (4).** These diol derivatives were prepared by the following general method. *p*-Toluenesulfonyl chloride (120 g, 0.6 mol) was added in small portions to a chilled pyridine solution (200 mL) of a diol (0.3 mol), the solution being kept below 20 °C. The solution was stirred for 3 h at ca. 20 °C and then poured slowly into vigorously stirred cold 2.6 M hydrochloric acid (780 mL). After a while, the white crystals that precipitated were filtered and washed with water; yields 73, 88, and 85% for $n$ = 4, 5, and 6, respectively. $^1$H NMR ($CDCl_3$): for $n$ = 4, $\delta$ 1.6-2.0 (br, 4, $C\text{-}CH_2\text{-}C$), 2.45 (s, 6, $CH_3$), 3.9-4.3 (br, 4, $O\text{-}CH_2$), 7.39 (d, 4, phenyl), 7.81 (d, 4, phenyl); for $n$ = 5, $\delta$ 1.1-1.9 (m, 6, $C\text{-}CH_2\text{-}C$), 2.13 (s, 6, $CH_3$), 4.01 (t, 4, $O\text{-}CH_2$), 7.40 (d, 4, phenyl), 7.84 (d, 4, phenyl); for $n$ = 6, $\delta$ 1.1-2.0 (br, 8, $C\text{-}CH_2\text{-}C$), 2.47 (s, 6, $CH_3$), 4.03 (t, 4, $O\text{-}CH_2$), 7.41 (d, 4, phenyl), 7.85 (d, 4, phenyl).

**1,4,7,10-Tetrakis(*p*-tolylsulfonyl)-1,4,7,10-tetraazacycloalkane (5).** An *N,N*-dimethylformamide (DMF) solution (500 mL) of **4** (0.1 mol) was added dropwise to a stirred DMF solution (1 L) of **3** (80.7 g, 0.1 mol) at 110 °C over a period of 3-5 h. After the addition of **4**, the solution was further stirred for 30 min. The resulting pale yellow solution, which contained a small amount of white solid, was rotoevaporated to ca. 300 mL. On addition of 700 mL of water the concentrate gave a pastelike white or pale yellow precipitate, which solidified when the solution was stirred overnight. The solid thus obtained was filtered and washed with water: yields 75, 93, and 56% for $n$ = 4, 5, and 6, respectively; mp 186, 110, and 94 °C for $n$ = 4, 5, and 6. $^1$H NMR ($CDCl_3$): for $n$ = 4, $\delta$ 1.8 (br, 4, $C\text{-}CH_2\text{-}C$), 2.44 (s, 12, $CH_3$), 2.8-3.8 (m, 16, $N\text{-}CH_2$), 7.55 (d, 8, phenyl), 7.71, 7.77 (dd, 8, phenyl); for $n$ = 5, $\delta$ 1.5 (br, 6, $C\text{-}CH_2\text{-}C$), 2.45 (s, 12,

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**Table I.** Elemental Analyses for the Trihydrobromides of the Ligands and the Ni(II) Complexes and Magnetic Moments for the Ni(II) Complexes

| | % C | | % H | | % N | | |
|---|---|---|---|---|---|---|---|
| compd[a] | calcd | found | calcd | found | calcd | found | $\mu_{eff}$, $\mu_B$ |
| $N_47 \cdot 3HBr$ | 27.11 | 26.96 | 6.14 | 6.25 | 12.64 | 12.38 | |
| $N_48 \cdot 3HBr$ | 28.90 | 28.51 | 6.40 | 6.49 | 12.26 | 12.30 | |
| $N_49 \cdot 3HBr$ | 30.60 | 30.48 | 6.63 | 6.59 | 11.89 | 11.86 | |
| $[Ni(N_47)](ClO_4)_2$ | 26.23 | 26.17 | 5.28 | 5.12 | 12.23 | 12.05 | diamag |
| $[NiCl_2(N_47)] \cdot H_2O$ | 34.52 | 34.70 | 6.95 | 7.22 | 16.10 | 16.02 | 3.26 |
| $[NiBr_2(N_47)]$ | 28.68 | 28.78 | 5.78 | 5.99 | 13.38 | 13.61 | 3.14 |
| $[Ni(NCS)_2(N_47)]$ | 38.42 | 38.34 | 6.45 | 6.43 | 22.40 | 22.31 | 3.10 |
| $[Ni(N_48)](ClO_4)_2$ | 27.99 | 27.61 | 5.55 | 5.40 | 11.87 | 11.94 | diamag |
| $[NiCl_2(N_48)]$ | 38.41 | 38.21 | 7.61 | 7.66 | 16.28 | 16.49 | 3.30 |
| $[Ni(NCS)_2(N_48)]$ | 40.12 | 40.15 | 6.73 | 6.92 | 21.61 | 22.40 | 3.22 |
| $[Ni(N_49)](ClO_4)_2 \cdot H_2O$ | 28.60 | 28.85 | 6.00 | 5.63 | 11.11 | 10.87 | diamag |
| $[NiCl_2(N_49)]$ | 40.26 | 40.22 | 7.88 | 8.02 | 15.65 | 15.83 | 3.22 |
| $[NiBr_2(N_49)]$ | 32.25 | 32.44 | 6.32 | 6.59 | 12.54 | 12.64 | 3.27 |
| $[Ni(NCS)_2(N_49)]$ | 41.70 | 41.45 | 7.00 | 6.85 | 20.84 | 20.46 | 3.25 |

[a] Abbreviations: $N_47 = C_{10}H_{24}N_4$; $N_48 = C_{11}H_{26}N_4$; $N_49 = C_{12}H_{28}N_4$.

$CH_3$), 3.3 (br, 16, $N-CH_2$), 7.39 (d, 8, phenyl), 7.79 (d, 8, phenyl); for *n* = 6, δ 1.4 (br, 8, $C-CH_2-C$), 2.45 (s, 12, $CH_3$), 3.2 (br, 16, $N-CH_2$), 7.81 (d, 8, phenyl), 7.37 (d, 8, phenyl).

**1,4,7,10-Tetraazacycloalkane Trihydrobromide (6).** A suspension of **5** (0.025 mol) in a mixture of 48% hydrobromic acid (1.2 L) and acetic acid (680 mL) was refluxed until the solid dissolved completely. The time required for the reflux was 24, 65, and 18 h for *n* = 4, 5, and 6, respectively. The resulting pale yellow or red-brown solution was rotoevaporated to ca. 200 mL. On addition of 1 L of an ethanol–diethyl ether mixture (3:1) the crude product **6** was obtained as a pale yellow precipitate, which was filtered. Recrystallization from water–ethanol gave white crystals of **6**, which were filtered, washed with ethanol, and air-dried: yields 68, 57, and 60% for *n* = 4, 5, and 6, respectively; mp 230 °C dec, 225 °C dec, and 215 °C dec for *n* = 4, 5, and 6. $^1H$ NMR ($D_2O$, sodium 4,4-dimethyl-4-silapentanesulfonate (DSS)): for *n* = 4, δ 1.95 (m, 4, $C-CH_2-C$), 3.1–3.8 (m, 16, $N-CH_2$); for *n* = 5, δ 1.72 (m, 6, $C-CH_2-C$), 3.1–3.5 (m, 16, $N-CH_2$). IR (KBr, $cm^{-1}$): *n* = 4, 5, 3250 (NH). $^{13}C$ NMR data are listed in Table II.

**1,4,7,10-Tetraazacycloalkane (7).** Free amine (**7**) was obtained by extracting an aqueous 7–8 M sodium hydroxide solution of **6** with chloroform. The extraction was repeated ten or more times, and the combined extracts were evaporated to give an oily residue. It was dissolved in dichloromethane, and the solution was mixed with anhydrous sodium sulfate, allowed to stand overnight, and filtered. The free amine was obtained as a pale yellow oil by evaporating dichloromethane. The $N_48$ ligand gave white crystals on standing and was recrystallized from dichloromethane (mp 180 °C dec). Other free amines, $N_47$ and $N_49$, were viscous oils even after several trials of purification including recrystallization and GP chromatography. The oily free amines turned yellow-brown gradually, so that the free ligands were stored as trihydrobromides (**6**).

**Preparation of Complexes. (1,4,7,10-Tetraazacyclotetradecane)nickel(II) Perchlorate, $[Ni(N_47)](ClO_4)_2$, and (1,4,7,10-Tetraazacyclopentadecane)nickel(II) Perchlorate, $[Ni(N_48)](ClO_4)_2$.** A methanolic solution of nickel(II) perchlorate hexahydrate was added to a methanolic solution containing an equimolar amount of the ligand with stirring, giving a dark red solution. After 1–2 h, the solution was filtered and concentrated under reduced pressure to yield orange crystals, which were filtered and recrystallized from water; yields 50–60% for $[Ni(N_47)](ClO_4)_2$, 65% for $[Ni(N_48)](ClO_4)_2$. IR (Nujol mull, $cm^{-1}$): $N_47$ complex, 3175 (NH); $N_48$ complex, 3025 (NH), 3200 (sh, NH).

**(1,4,7,10-Tetraazacyclohexadecane)nickel(II) Perchlorate Monohydrate, $[Ni(N_49)](ClO_4)_2 \cdot H_2O$.** A methanolic solution containing equimolar amounts of nickel(II) perchlorate hexahydrate and the $N_49$ ligand was stirred at 50 °C for 1–2 h. The resulting yellow-green solution gave no crystals but an oily product by reduction of its volume under reduced pressure. The product was dissolved in a small amount of water, and the solution was poured onto a column (3-cm i.d. × 30 cm) of SP-Sephadex C-25. The product adsorbed was eluted with an aqueous 0.2 M $NaClO_4$ solution. The yellow-green effluent of the main band was reduced in volume under reduced pressure to yield orange crystals of $[Ni(N_49)](ClO_4)_2 \cdot H_2O$, which were filtered and washed with methanol. The second crop of the complex was obtained from the filtrate by evaporating to dryness, extracting with chloroform, and concentrating the extract; yield 16%. IR (Nujol mull, $cm^{-1}$): 3230 (NH), 3580 (br, OH).

**Diacido(1,4,7,10-tetraazacyclotetradecane)nickel(II), $[NiX_2(N_47)] \cdot nH_2O$, X = $Cl^-$ (*n* = 1), $Br^-$ (*n* = 0), $NCS^-$ (*n* = 0).** A mixture of $[Ni(N_47)](ClO_4)_2$ (458 mg, 1 mmol) and KX (2 mmol) in methanol (70 mL) was stirred for ca. 30 min at room temperature. The colors of the solutions were yellow-orange, orange-red, and blue for X = $Cl^-$, $Br^-$, and $NCS^-$, respectively. After removal of precipitated $KClO_4$, the solution was evaporated to dryness and the residue was extracted with chloroform. On evaporation the extract gave crystals of the crude complex, which were recrystallized from acetonitrile; yield 40–50%. $[NiCl_2(N_47)] \cdot H_2O$ and $[Ni(NCS)_2(N_47)]$ form blue-violet and violet crystals, respectively. Blue-violet crystals of $[NiBr_2(N_27)]$ are somewhat hygroscopic and change gradually to orange-brown in air. IR (Nujol mull, $cm^{-1}$): X = $Cl^-$, 3500 (OH), 3430 (sh, OH), 3220 (NH), 3240 (NH); X = $Br^-$, 3210 (NH); X = $NCS^-$, 3315 (NH), 3260 (NH), 3210 (s, NH), 2080 (CN).

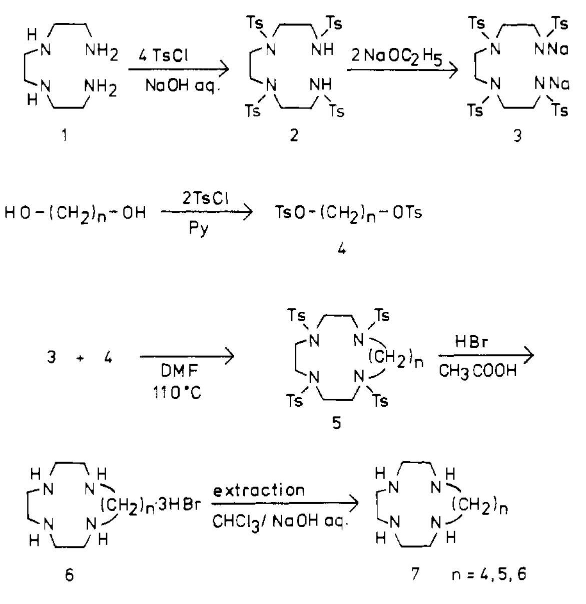
**Diacido(1,4,7,10-tetraazacyclopentadecane)nickel(II), $[NiX_2(N_48)]$, X = $Cl^-$, $Br^-$, $NCS^-$.** These complexes were prepared by a method similar to that for $[NiX_2(N_47)]$. Crystals of pale blue $[NiCl_2(N_48)]$ and blue-violet $[Ni(NCS)_2(N_48)]$ were obtained by recrystallizing the crude products from acetonitrile and a methanol–acetonitrile mixture, respectively. The $[NiBr_2(N_48)]$ complex was obtained only in a chloroform solution. The solution is blue-violet and shows an electronic absorption spectrum characteristic of an octahedral Ni(II) complex. However, the solid obtained by evaporating chloroform was highly hygroscopic and immediately turned into red-brown tarry matter. IR (Nujol mull, $cm^{-1}$): X = $Cl^-$, 3250 (sh, NH), 3210 (NH); X = $NCS^-$, 3310 (NH), 3260 (NH), 3220 (s, NH), 2080 (CN).

**Diacido(1,4,7,10-tetraazacyclohexadecane)nickel(II), $[NiX_2(N_49)]$, X = $Cl^-$, $Br^-$, $NCS^-$.** These complexes were also prepared by a method similar to that for $[NiX_2(N_47)]$. When a methanolic solution (50 mL) of KX (2 mmol) was added to a methanolic solution (30 mL) of $[Ni(N_49)](ClO_4)_2 \cdot H_2O$ (1 mmol), the yellow solution turned immediately pale green (X = $Cl^-$, $Br^-$) or blue (X = $NCS^-$), and gave a pale green (X = $Cl^-$, $Br^-$) or blue (X = $NCS^-$) precipitate along with the precipitation of $KClO_4$. The precipitate was dissolved in chloroform, and undissolved $KClO_4$ was removed by filtration. On evaporation emerald green crystals (X = $Cl^-$, $Br^-$) were obtained and recrystallized from a chloroform–acetonitrile mixture; yields 70 and 90% for X = $Cl^-$ and $Br^-$, respectively. Blue crystals of $[Ni(NCS)_2(N_49)]$ were obtained by recrystallizing from methanol; yield 70%. IR (Nujol mull, $cm^{-1}$): X = $Cl^-$, 3260 (sh, NH), 3250 (NH), 3230 (sh, NH); X = $Br^-$, 3250 (NH), 3230 (sh, NH); X = $NCS^-$, 3210 (NH), 2070 (CN).

Analytical data of the ligands and complexes and magnetic moments for the Ni(II) complexes are given in Table I.

**Measurements.** Infrared spectra were recorded on a Jasco A-3 or a Hitachi 295. $^1H$ NMR spectra were obtained on a JNM-PMX 60 at 60 MHz. $^{13}C$ NMR spectra were obtained at 25 MHz on a JEOL FX-100 spectrometer. Dioxane was used as an internal standard in $D_2O$ solutions. Chemical shift data for $D_2O$ solutions are values

Scheme I



downfield from $Me_4Si$ as $\delta_{dioxane} = 76.4$.

Magnetic moments for the nickel(II) complexes were obtained by using the Evans $^1H$ NMR technique[9] at ambient temperature (33–34 °C), a Varian EM390 being used at 90 MHz. A chloroform solution with an internal reference of 3% (v/v) $Me_4Si$ was used except for the *cis*-$[Ni(NCS)_2(N_47)]$ complex, for which an acetonitrile solution was used because of the solubility. Temperature-dependent volume changes of the solvent were corrected.

Electronic absorption spectra in solution were obtained on a Hitachi 340 spectrophotometer equipped with a data printer. In equilibrium studies, the temperature of a sample solution was thermostated within ±0.1 °C by use of a temperature-controlled circulating bath, Neslab RTE-8, and measured immediately before and after each spectral measurement with a copper–constantan thermocouple and a digitial thermometer, Takeda TR-2121. Electronic absorption spectra in the solid state were recorded on a Hitachi 323 spectrophotometer using Nujol mulls mounted between polyethylene films.

## Results and Discussion

**Syntheses of Ligands and Nickel(II) Complexes.** Three new tetraaza macrocyclic ligands, $N_47$, $N_48$, and $N_49$, were prepared by a method similar to that for other analogous tetraazacycloalkanes.[10,11] The synthetic route is given in Scheme I. The cyclization of **3** with **4** proceeds in fairly good yield (60–90%), giving tetrakis(*p*-tolylsulfonyl) derivatives of the 14-, 15-, and 16-membered cyclic amine ligands. The free $N_48$ amine is obtained as a white crystalline solid, while $N_47$ and $N_49$ are highly viscous oily substances.

The ligands form orange Ni(II) complex perchlorates by mixing with $Ni(ClO_4)_2 \cdot 6H_2O$ in methanol. All the perchlorates show a fairly strong single d–d band around 22 000 cm$^{-1}$, which is characteristic of a four-coordinate, square-planar $[Ni^{II}N_4]$ chromophore.[12]

Table II. $^{13}C$ NMR Spectral Data

| compd | assignt | chem shift (rel intens)[a] |
|---|---|---|
| $N_47 \cdot 3HBr$ | C-*C*-C | 21.1 (1) |
| | N-*C*-C | 42.3 (1), 43.8 (2), 45.5 (1) |
| $N_48 \cdot 3HBr$ | C-*C*-C | 22.5 (1), 23.6 (2) |
| | N-*C*-C | 43.9 (2), 44.3 (2), 45.8 (2), 46.8 (2) |
| $N_49 \cdot 3HBr$ | C-*C*-C | 23.4 (1), 23.7 (1) |
| | N-*C*-C | 43.2 (1), 44.3 (1), 45.9 (1), 46.3 (1) |
| $[Ni(N_47)](ClO_4)_2$ | C-*C*-C | 29.9 (1) |
| | N-*C*-C | 49.2 (1), 52.3 (1), 55.8 (1), 57.3 (1) |
| $[Ni(N_48)](ClO_4)_2$ | C-*C*-C | 23.5 (1), 24.8 (2) |
| | N-*C*-C | 49.7 (2), 50.7 (2), 52.1 (2), 53.8 (2) |
| $[Ni(N_49)](ClO_4)_2$ | C-*C*-C | 26.9 (1), 27.8 (1) |
| | N-*C*-C | 48.8 (1), 51.8 (2), 53.3 (1) |

[a] Chemical shifts in ppm from $Me_4Si$. The data for trihydrobromides of the ligands were obtained in $D_2O$ with dioxane (67.4 ppm from $Me_4Si$) as an internal standard and those for the Ni(II) complexes in $CD_3NO_2$ with an internal $Me_4Si$ standard.

Table II lists $^{13}C$ NMR data for trihydrobromides of the free ligands in $D_2O$ and the four-coordinate Ni(II) complexes in $CD_3NO_2$. The number of observed signals suggests that all the compounds are cyclic in structure and have either a twofold axis or a symmetry plane. The assignment for each carbon cannot be made, but that for the carbon atoms bonded and not bonded to the nitrogen atoms can be done from the relative intensity as shown in Table II. Both free ligands and Ni(II) complexes show signals due to the methylene groups bonded to the nitrogen atoms at a lower field than those not bonded to the nitrogen atoms. The signals of the free ligand appear at a higher field than the corresponding signals of its Ni(II) complex.

The four-coordinate complexes, $[NiL](ClO_4)_2$, afford six-coordinate complexes, $[NiX_2L]$, by treatment with appropriate potassium salts such as KCl, KBr, or KSCN. The $[NiX_2L]$ complexes are violet to green, depending on the kinds of $X^-$ and the macrocyclic ligand, and show three to four d–d absorption bands in the near-infrared to visible region. Such a spectral pattern is characteristic of a six-coordinate, octahedral Ni(II) complex.[11,12] Magnetic moments of the $[NiX_2L]$ complexes are normal for high-spin Ni(II) (Table I). A solid-state spectrum of $[NiX_2L]$ is almost the same as that in a chloroform solution, $[NiX_2L]$ retaining the composition in this solvent. However, the spectra of $[NiX_2L]$ in water, alcohols, acetonitrile, and dimethyl sulfoxide solutions exhibit in general absorption bands corresponding to both square-planar and octahedral Ni(II) complexes.[13] Thus $[NiX_2L]$ gives an equilibrium mixutre of four- and six-coordinate species in these solvents, although the composition and structure of the latter species depend on the kinds of complexes and solvents.

**Equilibrium between $[NiL]^{2+}$ and $[NiL(H_2O)_2]^{2+}$ in Water ($L = N_47, N_48, N_49$).** It is known that some square-planar tetraaza macrocyclic Ni(II) complexes in water give an equilibrium mixture of yellow, diamagnetic square-planar $[NiL]^{2+}$ and violet (or blue), paramagnetic octahedral $[NiL(H_2O)_2]^{2+}$.[14-21] This is the case for all the present complex perchlorates. The equilibrium in (1) is dependent upon temperature and ionic strength; an increase in either variable makes the equilibrium shift to the left side to increase the

$$[NiL]^{2+} + 2H_2O \underset{}{\overset{K}{\rightleftharpoons}} [NiL(H_2O)_2]^{2+} \qquad (1)$$

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Table III. Thermodynamic Parameters, Equilibrium Constants, and Relative Amounts of Four- and Six-Coordinate Species at 25 °C for the $[NiL]^{2+} + 2H_2O \rightleftharpoons [NiL(H_2O)_2]^{2+}$ System[a]

| L | $-\Delta H$, kJ mol$^{-1}$ | $-\Delta S$, J K$^{-1}$ mol$^{-1}$ | $K_{25\,°C}$[b] | % 4-coord | % 6-coord |
|---|---|---|---|---|---|
| $N_46$[c] | 31 | 126 | 0.15 | 87 | 13 |
| $N_47$ | 20 | 71 | 0.64 | 61 | 39 |
| $N_48$ | 23 | 88 | 0.33 | 75 | 25 |
| $N_49$ | 26 | 84 | 1.26 | 44 | 56 |

[a] $I = 0.1$ ($NaClO_4$). [b] $K = [NiL(H_2O)_2{}^{2+}]/[NiL^{2+}]$. [c] $N_46$ = [13]ane$N_4$.[17]

amount of $[NiL]^{2+}$. The equilibrium is also affected by the kind of salts used for the adjustment of ionic strength.[20]

For the present complex perchlorates, the equilibrium constants ($K = [NiL(H_2O)_2{}^{2+}]/[NiL^{2+}]$) and thermodynamic parameters were determined at an ionic strength of 0.1 ($NaClO_4$) from the temperature dependence of the electronic absorption spectra. Figure 1 shows temperature-dependent electronic spectra of $[Ni(N_49)](ClO_4)_2$ in an aqueous solution. The spectral change is reversible with isosbestic points at 374 and 564 nm. With a rise in temperature, the intensity of the band at 452 nm associated with the four-coordinate species increases and those of other bands associated with the six-coordinate species decrease. Similar temperature-dependent spectra with distinct isosbestic points were also obtained for the $N_47$ and $N_48$ complex perchlorates. The equilibrium constants and $\Delta H$ and $\Delta S$ values for eq 1 were calculated as described previously[20] and are listed in Table III along with values for the $[Ni(N_46)]^{2+}$ complex ($N_46$ = 1,4,7,10-tetraazacyclotridecane).[17]

It has been reported that a 13-membered tetraaza macrocyclic ligand such as $N_46$ provides the best fit cavity size for a square-planar Ni(II) complex.[17] The cavity size will become large with an increase in ring members of the macrocyclic ligand. Since Ni–N bond distances in a paramagnetic macrocyclic Ni(II) complex should be longer than those in the corresponding diamagnetic complex, a larger macrocyclic ligand would facilitate the formation of a paramagnetic, six-coordinate Ni(II) complex. Table III shows that the relative amounts of four-coordinate species are the largest in the $N_46$ complex and decrease with an increase in the ring size except for the $N_48$ complex, for which the four-coordinate species are exceptionally favored. The stability of the four-coordinate $[Ni(N_48)]^{2+}$ complex seems to be attributable to stereochemical features resulting from the eight-membered chelate ring. Although geometrical structures of the $[NiL(H_2O)_2]^{2+}$ complexes are unknown, molecular models indicate that the $[Ni(N_48)(H_2O)_2]^{2+}$ complex involves severe steric hindrance or strain in both cis and trans structures. When the complex has a trans configuration and the eight-membered chelate ring is assumed to adopt the most stable crown-type conformation, the methylene protons adjacent to the nitrogen atoms of the eight-membered chelate ring are disposed in close proximity to the apical coordination site of the Ni(II) ion to hinder the coordination of a water molecule. The cis configuration also involves severe steric hindrance among the amino and methylene protons or strain in the chelate skeleton in any conformer of the $N_48$ ligand. Thus $[Ni(N_48)(H_2O)_2]^{2+}$ would be unstable as compared with $[Ni(N_48)]^{2+}$. In fact, the six-coordinate complex with large bromide ions, $[NiBr_2(N_48)]$, is highly hygroscopic and immediately turns red-brown to form the four-coordinate $[Ni(N_48)]^{2+}$ (Experimental Section).

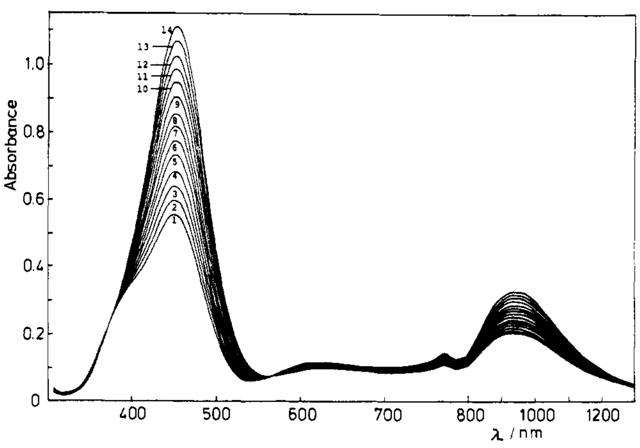

Figure 1. Absorption spectra of $[Ni(N_49)](ClO_4)_2$ in aqueous 0.1 M $NaClO_4$ solution at various temperatures (K): (1) 277.9; (2) 280.7; (3) 283.2; (4) 285.9; (5) 289.0; (6) 291.6; (7) 294.2; (8) 296.2; (9) 299.2; (10) 302.0; (11) 304.5; (12) 307.0; (13) 309.9; (14) 312.6. The concentration of the complex is $1.704 \times 10^{-2}$ M.

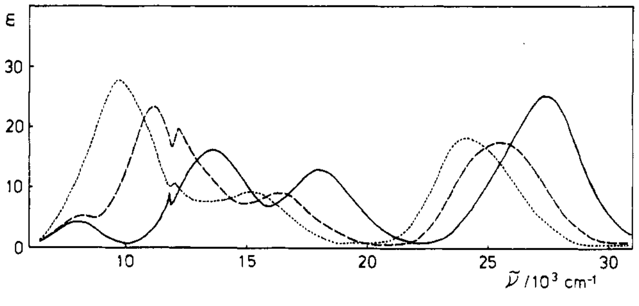

Figure 2. Electronic spectra of $[NiCl_2(N_47)]\cdot H_2O$ (—), $[NiCl_2(N_48)]$ (---), and $[NiCl_2(N_49)]$ (···) in $CHCl_3$.

**Electronic Absorption Spectra of $[NiX_2L]$ ($X = Cl^-, Br^-, NCS^-$; $L = N_47, N_48, N_49$).** Figure 2 shows electronic absorption spectra of a series of the dichloro complexes in chloroform. Table IV lists the spectral data. The dichloro complexes show a similar spectral pattern, and the pattern resembles that of *trans*-diacido Ni(II) complexes formed with a similar tetraaza macrocyclic ligand reported by Martin et

Table IV. Electronic Spectral Data

| complexes | $10^3\tilde{\nu}$, cm$^{-1}$ ($\epsilon$) | | | | | |
|---|---|---|---|---|---|---|
| $[Ni(N_47)](ClO_4)_2$[a] | | | | 21.6 (175.7) | | |
| $[Ni(N_48)](ClO_4)_2$[a] | | | | 21.9 (138.6) | | |
| $[Ni(N_49)](ClO_4)_2\cdot H_2O$[a] | | | | 21.8 (147.2) | | |
| $[NiCl_2(N_47)]\cdot H_2O$[b] | 7.9 (4.4) | | 13.6 (16.4) | | 18.0 (13.0) | 27.4 (25.5) |
| $[NiBr_2(N_47)]$[b] | 7.2 (4.7) | | 13.8 (17.6) | | 17.9 (17.0) | 27.1 (36.9) |
| $[Ni(NCS)_2(N_47)]$[c] | | 10.0 | | | 18.0 | 28.1 |
| $[NiCl_2(N_48)]$[b] | 8.3 (5.3) | | 11.2 (23.5) | | 16.4 (9.1) | 25.6 (17.6) |
| $[NiBr_2(N_48)]$[b] | 7.2 (4.8) | | 13.8 (17.1) | | 17.9 (17.3) | 27.1 (36.7) |
| $[Ni(NCS)_2(N_48)]$[c] | | 11.0 | | | 17.8 | 27.5 |
| $[NiCl_2(N_49)]$[b] | | 9.7 (27.8) | | | 15.2 (9.2) | 24.2 (18.3) |
| $[NiBr_2(N_49)]$[c] | | 10.2 | | | 15.6 | 24.7 |
| $[Ni(NCS)_2(N_49)]$[b] | | 9.8 (42.9) | | | 16.7 (15.5) | 26.2 (25.9) |

[a] In nitromethane. [b] In chloroform. [c] Solid-state spectra.

al.[11] Thus the present dichloro complexes are assumed to have a *trans*-$[NiCl_2N_4]$ structure. This structure has been confirmed by X-ray analyses on $[NiCl_2(N_47)]$ and $[NiCl_2(N_49)]$.[7] Martin et al.[11] studied the electronic absorption spectra of *trans*-diacido tetraaza macrocyclic Ni(II) complexes and assigned the bands on the basis of the tetragonal ligand field model with $D_{4h}$ symmetry. Although the present dichloro complexes have lower symmetry than $D_{4h}$, the observed spectra can be explained according to their model. The bands in the 7000–14 000-cm$^{-1}$ region can be assigned to the electronic transition to the $^3T_{2g}$ state in $O_h$ symmetry, which splits into the lower $^3E_g$ and higher $^3B_{2g}$ states in the tetragonal field. The tetragonal splitting is observed for $[NiCl_2(N_47)]$ and $[NiCl_2(N_48)]$ with magnitudes of 5700 and 2900 cm$^{-1}$, respectively. The magnitude of splitting decreases with an increase in the ring size. In $[NiCl_2(N_49)]$ the splitting is so small that the two bands overlap, giving apparently a single band. According to the tetragonal ligand field model, the transition energy of the second lowest band ($^3B_{2g} \leftarrow {}^3B_{1g}$) corresponds in a first approximation to the in-plane ligand field strength ($Dq^{xy}$).[11] This band is observed at 13 600, 11 200, and 10 200 cm$^{-1}$ for $[NiCl_2(N_47)]$, $[NiCl_2(N_48)]$, and $[NiCl_2(N_49)]$, respectively. The results suggest that the in-plane ligand field strength due to the macrocyclic ligand decreases with an increase in the ring size. The average Ni–N distances of $[NiCl_2(N_47)]$ and $[NiCl_2(N_49)]$ found by X-ray analyses are 2.07 and 2.16 Å, respectively.[7] On the contrary, the lowest energy band ($^3E_g \leftarrow {}^3B_{1g}$) of the $N_47$ complex is observed at lower energy than that of the larger macrocyclic $N_48$ complex, although the energy difference between these bands is very small, and the band of the $N_49$ complex is not observed by overlapping of the strong $^3B_{2g} \leftarrow {}^3B_{1g}$ band. Since the tetragonal ligand field model indicates that the transition energy of the lowest band is proportional to the sum of $Dq^{xy}$ and $Dq^z$ (axial ligand field strength), the $Dq^z$ value of $[NiCl_2(N_47)]$ should be much smaller than that of $[NiCl_2(N_48)]$. Martin et al. observed the same shift in the $^3E_g \leftarrow {}^3B_{1g}$ bands of analogous macrocyclic complexes and concluded that the $Dq^z$ value is not constant but decreases as the $Dq^{xy}$ value increases. They termed it an electronically controlled cis effect.[11] The same cis effect may operate on the present dichloro complexes. The average Ni–Cl and Ni–N distances of 2.55 and 2.07 Å for the $N_47$ complex and 2.43 and 2.16 Å for the $N_49$ complex respectively support the occurrence of the cis effect.[7]

The dibromo complexes show electronic absorption spectra very similar to those of the corresponding dichloro complexes and can be assigned to the same *trans*-dibromo configuration. The spectra of the bis(isothiocyanato) complexes are somewhat different from those of the halogen complexes. The complexes show a single band at nearly the center of the first and second low-energy bands of the halogen complexes. Since the ligand field strength of the isothiocyanate ligand is stronger than that of a halide ligand, the tetragonal splitting would be small even in the trans configuration. The geometrical structures of the bis(isothiocyanato) complexes cannot be assigned unequivocally from the electronic spectra. However, the $[Ni(NCS)_2(N_47)]$ complex has been found to have a cis configuration by X-ray analysis.[8] It is interesting to note that the solubility of $[Ni(NCS)_2(N_47)]$ in a nonpolar solvent such as chloroform is extremely low, while $[Ni(NCS)_2(N_48)]$ and $[Ni(NCS)_2(N_49)]$ are as highly soluble as other *trans*-$[NiX_2L]$ type complexes. These facts may suggest the structural difference among these three NCS complexes. The polarity of the cis complex should be larger than that of the trans complex. Thus coordination geometries of the $N_48$ and $N_49$ complexes would be of the trans type.

In the higher energy region all the complexes show two absorption bands. These bands are shifted to the lower energy side as the ring size increases.

**Registry No.** **1**, 112-24-3; **2**, 55442-07-4; **3**, 56187-06-5; **4** (*n* = 4), 4724-56-5; **4** (*n* = 5), 24293-28-5; **4** (*n* = 6), 4672-50-8; **5** (*n* = 4), 81582-18-5; **5** (*n* = 5), 84194-07-0; **5** (*n* = 6), 84194-08-1; **6** (*n* = 4), 84215-03-2; **6** (*n* = 5), 84194-05-8; **6** (*n* = 6), 84194-06-9; $[Ni(N_47)](ClO_4)_2$, 81599-72-6; $[NiCl_2(N_47)]\cdot H_2O$, 84194-09-2; $[NiBr_2(N_47)]$, 84194-10-5; $[Ni(NCS)_2(N_47)]$, 84180-77-8; $[Ni(N_48)](ClO_4)_2$, 84194-12-7; $[NiCl_2(N_48)]$, 84194-13-8; $[Ni(NCS)_2(N_48)]$, 84194-14-9; $[Ni(N_49)](ClO_4)_2\cdot H_2O$, 84194-17-2; $[NiCl_2(N_49)]$, 84194-18-3; $[NiBr_2(N_49)]$, 84194-19-4; $[Ni(NCS)_2(N_49)]$, 84194-20-7; $HO(CH_2)_4OH$, 110-63-4; $HO(CH_2)_5OH$, 111-29-5; $HO(CH_2)_6OH$, 629-11-8; $[Ni(N_47)(H_2O)_2]^{2+}$, 84194-21-8; $[Ni(N_48)(H_2O)_2]^{2+}$, 84194-22-9; $[Ni(N_49)(H_2O)_2]^{2+}$, 84194-23-0; $[NiBr_2(N_48)]$, 84194-24-1.