# Synthesis and Square Planar-Octahedral Equilibrium of Bismacrocyclic Dinickel(II) Complexes with Polymethylene Bridges of Various Lengths

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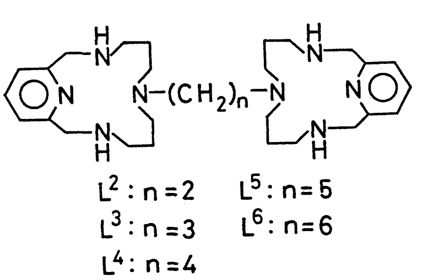
(Received December 6, 1989)

A new series of binuclear nickel(II) complexes with bis(tetraazamacrocycle), 7,7′-polymethylenebis-[3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),13,15-triene]dinickel(II) perchlorates with polymethylene bridges with a length of 2—6-C, was synthesized, as well as the corresponding free ligands. The dinickel(II) complexes were found to be in equilibrium between square planar and octahedral forms in water. The equilibrium shifts toward the octahedral side as the polymethylene bridge becomes short.

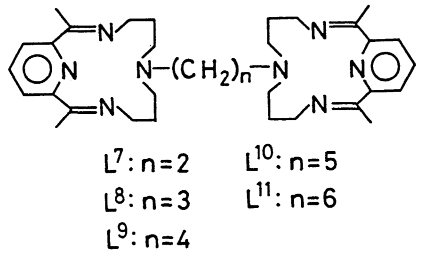
We have recently investigated square planar-octahedral equilibrium, as shown in Equilibrium 1, of binuclear nickel(II) complexes[1] with bismacrocyclic ligands, $L^7$—$L^{11}$, where the same two macrocycles are linked by a methylene chain of various length:[2]

$$[\mathrm{Ni^{II}}_2(L^n)]^{4+} + 2x\mathrm{H_2O} \rightleftarrows [\mathrm{Ni^{II}}_2(L^n)(\mathrm{OH_2})_{2x}]^{4+} \ (x=1,2). \quad (1)$$

Our spectrophotometric study[2] revealed that the equilibrium of the dinickel(II) complexes shifts to the octahedral side as the polymethylene chain becomes short. Furthermore, a quantitative analysis of the equilibrium was achieved by the use of heterometallic Cu(II)Ni(II) complexes.[3] In this analysis, two absorption bands were used: the absorption band (molar absorption coefficient, $\varepsilon$: 100—3500) around 400—500 nm, due to the d-d transition of square planar Ni(II) ions, and that at 700—800 nm due to the octahedral Ni(II) ions. The band at shorter wave length, however, becomes a shoulder of a strong absorption band ($\varepsilon$: ca. 1000—3500 at 395 nm) of charge transfer from C=N bonds to Ni(II) ions. Thus, it is desirable to get rid of the strong band for a direct observation of the d-d band. We tried to reduce the C=N bonds of dinickel(II) complexes, $[\mathrm{Ni^{II}}_2(L^n)]^{4+}$ ($n$=7—11), by the use of sodium borohydride. The reduction proceeded smoothly, but gave a complex mixture due to the generation of two chiral carbon atoms in the ligand.[4]



$L^2$ : n = 2 $L^5$: n = 5
$L^3$ : n = 3 $L^6$: n = 6
$L^4$ : n = 4



$L^7$: n = 2 $L^{10}$: n = 5
$L^8$: n = 3 $L^{11}$: n = 6
$L^9$: n = 4

We successfully prepared a new series of dinickel(II) complexes with $L^2$—$L^6$, formed by the template condensation between 2,6-diformylpyridine and *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,$\omega$-alkanediamine(hereafter, referred to as a branched polyamine). A reduction of C=N bonds in the ligands does not give rise to any chiral carbon atom. By the use of dinickel(II) complexes with the reduced ligands, the d-d bands were observed without interference with other absorption bands.

## Experimental

**Materials.** A typical procedure for the preparation of the binuclear complexes is as follows.

2,6-diformylpyridine (5.40 g, 0.04 mol) and nickel(II) acetate tetrahydrate (9.95 g, 0.04 mol) were dissolved in 300 cm³ of ethanol-water (1 : 1, v/v). To this solution we then added 100 cm³ of ethanol-water (1 : 1, v/v) containing *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,3-propanediamine (6.05 g, 0.02 mol) which had been neutralized with acetic acid just before the addition. The mixture was stirred for ca. 16 h at 60 °C, left standing at room temperature for 1 h, evaporated to ca. 100 cm³, and then filtered. The filterate was chromatographed with the cation-exchange column (SP-Sephadex C-25, $\phi$=30 mm, 1=1000 mm) with 0.5 mol dm⁻³ sodium chloride solution as an eluant, to give a red band. The red eluate was concentrated to ca. 20 cm³. The sodium chloride, precipitated by the addition of ethanol to the solution, was filtered off. The same procedure was repeated five times. The thus-obtained residue was dissolved in 1000 cm³ of cold methanol-water (2 : 3, v/v), to which was portionwise added sodium borohydride (11.35 g, 0.30 mol). The methanolic solution was heated to 60 °C and sodium borohydride (22.70 g, 0.60 mol) was potionwise added. After the mixture had been stirred for ca. 2 h at 60 °C, 60% perchloric acid was added until the solution became pH 1; the stirred mixture was kept for 2 h at 60 °C. The solution was adjusted to pH 5 by the addition of conc. NaOH, stirred for ca. 1 h at 70 °C, and left standing for 1 h at room temperature. After evaporation, the residue was thoroughly washed with ethanol and suspended in a small amount of water, which was passed through the column of a Cl-form anion-exchange resin (Amberlite IRA410, $\phi$=30 mm, l=300 mm) for the exchange of counter ions. The resulting clear solution was chromatographed with a cation-exchange column (SP-Sephadex C-25, $\phi$=30 mm, l=400 mm) and eluted with a 0.5 mol dm$^{-3}$ sodium chloride solution, to give a reddish orange band. The reddish orange eluate was concentrated to ca. 20 cm$^3$. The sodium chloride precipitated by the addition of ethanol to the solution was filtered off. After repeating the same procedure for five times, the residue was dissolved in a minimum amount of water, to which was added a saturated aqueous sodium perchlorate solution to yield precipitates. The twice recrystallization of the precipitates from a small amount of hot water gave crystals, which were washed well with water and dried over $P_2O_5$ in vacuum. The absence of chloride ions in the complex was confirmed by use of $AgNO_3$.

Hexamethylene, pentamethylene, tetramethylene and ethylene derivatives were prepared by the same procedure described above except for using *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,6-hexanediamine, *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,5-pentanediamine, *N,N,N′,N′*-tetrakis(3-aminopropyl)-1,4-butanediamine, and *N,N,N′,N′*-tetrakis-(3-aminopropyl)-1,2-ethanediamine, respectively.

Free ligands, $L^n$ were obtained by treating dinickel(II) complexes with NaCN in a strong alkaline solution, and subsequent extraction with $CH_2Cl_2$.

The data of elemental analyses and overall isolated yields, after recrystallization, of the new series of dinickel(II) complexes are given below, besides $^{13}$C NMR spectra of the free ligands.

$[Ni^{II}_2(L^3)](ClO_4)_4\cdot H_2O$: Yield: 15.1%. Found: C, 33.21; H,4.69; N, 10.61%. Calcd for $C_{29}H_{48}N_8Ni_2Cl_4O_{16}\cdot H_2O$: C, 33.42; H, 4.84; N, 10.75%. $^{13}$C NMR ($CF_3COOD$, TMS) $\delta$=10.8 (t), 24.6 (t), 50.7 (t), 52.1 (t), 56.3 (t), 62.9 (t), 121.2 (d), 143.9 (d), 160.9 (s).

$L^3$: $^{13}$C NMR ($CDCl_3$, TMS) $\delta$=21.8 (t), 27.3 (t), 46.3 (t), 51.0 (t), 52.1 (t), 54.1 (t), 120.3 (d), 136.2 (d), 159.1 (s).

The dinickel(II) complex with a trimethylene bridge, a template product before the reduction, was also isolated as a perchlorate: Found: C, 33.68; H, 3.93; N, 10.83%. Calcd for $C_{29}H_{40}N_8Ni_2Cl_4O_{16}\cdot H_2O$: C, 33.69; H, 4.10; N, 10.84%. IR (KBr): 1640 (C=N) cm$^{-1}$. $^{13}$C NMR ($CF_3COOD$, TMS) $\delta$= 12.2 (t), 25.2 (t), 45.2 (t), 53.5 (t), 56.9 (t), 131.1 (d), 147.0 (d), 153.9 (s), 169.9 (s).

$[Ni^{II}_2(L^6)](ClO_4)_4$: Yield: 11.7%. Found: C, 36.08; H, 5.05; N, 10.46%. Calcd for $C_{32}H_{54}N_8Ni_2Cl_4O_{16}$: C, 36.05; H, 5.11; N, 10.51%. $^{13}$C NMR ($CF_3COOD$, TMS) $\delta$=19.2 (t), 24.3 (t), 27.1 (t), 51.8 (t), 52.6 (t), 56.0 (t), 62.8 (t), 121.0 (d), 143.5 (d), 160.4 (s).

$L^6$: $^{13}$C NMR ($CDCl_3$, TMS) $\delta$=25.0 (t), 26.8 (t), 27.5 (t), 46.6 (t), 52.0 (t), 52.3 (t), 53.6 (t), 120.9 (d), 137.0 (d), 157.9 (s).

$[Ni^{II}_2(L^5)](ClO_4)_4$: Yield: 10.6%. Found: C, 35.16; H, 4.96; N, 10.49%. Calcd for $C_{31}H_{52}N_8Ni_2Cl_4O_{16}$: C, 35.39; H, 4.98; N, 10.65%. $^{13}$C NMR ($CF_3COOD$, TMS) $\delta$=21.1 (t), 24.7 (t), 26.3 (t), 52.0 (t), 53.3 (t), 56.8 (t), 62.8 (t), 121.1 (d), 143.8 (d), 160.6 (s).

$L^5$: $^{13}$C NMR ($CDCl_3$, TMS) $\delta$=25.2 (t), 25.4 (t), 26.8 (t), 46.5 (t), 52.0 (t), 52.4 (t), 53.6 (t), 120.9 (d), 136.9 (d), 158.0 (s).

$[Ni^{II}_2(L^4)](ClO_4)_4$: Yield: 13.3%. Found: C, 34.40; H, 4.81; N, 10.67%. Calcd for $C_{30}H_{50}N_8Ni_2Cl_4O_{16}$: C, 34.71; H, 4.86; N, 10.80%. $^{13}$C NMR ($CF_3COOD$, TMS) $\delta$=18.8 (t), 24.9 (t), 52.0 (t), 53.3 (t), 56.5 (t), 63.0 (t), 121.1 (d), 143.9 (d), 160.9 (s).

$L^4$: $^{13}$C NMR ($CDCl_3$,, TMS) $\delta$=23.3 (t), 27.4 (t), 46.6 (t), 52.0 (t), 52.7 (t), 54.2 (t), 120.6 (d), 136.4 (d), 159.3 (s).

$[Ni^{II}_2(L^2)](ClO_4)_4$: Yield 6.7%. Found: C, 33.46; H, 3.94; N, 11.10%. Calcd for $C_{28}H_{46}N_8Ni_2Cl_4O_{16}$: C, 33.57; H, 3.82; N, 11.18%.

$L^2$: $^{13}$C NMR ($CDCl_3$, TMS) $\delta$=27.0 (t), 46.2 (t), 49.1 (t), 52.4 (t), 53.5 (t), 120.8 (d), 136.8 (d), 158.0 (s).

**Measurements.** Water used was purified by Milli-Q system.

Infrared spectra were measured with Hitachi 260-10 spectrophotometer. The measurements of the absorption spectra and the computational analysis of the temperature-dependent spectra were performed according to the same methods as described in our previous papers.[3]

## Results and Discussion

**Synthesis of Dinickel(II) Complexes.** As shown in Scheme 1, the template condensations between 2,6-diformylpyridine and the branched polyamines using $Ni^{2+}$ ions gave bismacrocyclic dinickel(II) complexes with C=N bonds. The dinickel(II) complex with a trimethylene bridge isolated[5] shows a band assigned to $\nu_{C=N}$ at 1640 cm$^{-1}$ in its IR spectrum. The elemental analysis and $^{13}$C NMR spectrum {5 triplets (methylene including the bridge), 2 doublets (pyridine), and 2 singlets (pyridine and C=N)} indicated the formation of a bismacrocyclic complex. The C=N bonds in the complexes, thus formed, could be reduced to C–N bonds by the use of sodium borohydride in an aqueous methanolic solution. The IR spectra of the reduced products showed an absorption band due to the skeletal vibration of pyridine ring but not the band corresponding to the $\nu_{C=N}$ around 1550—1700 cm$^{-1}$. The absorption spectra also confirmed reduction of the C=N bonds. As shown in Fig. 1, an unreduced complex shows a strong absorption band around 400 nm of charge transfer from the C=N bonds to Ni(II) ions.

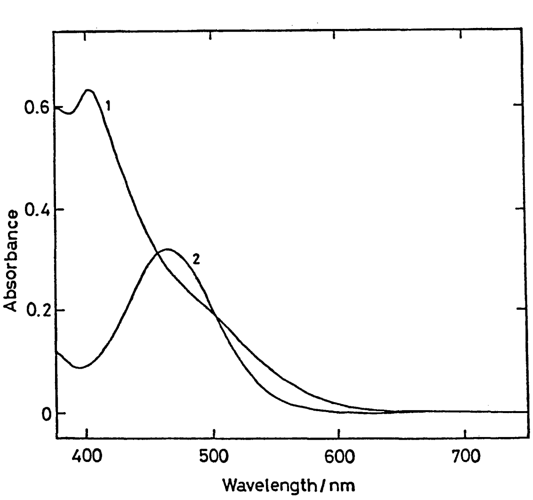
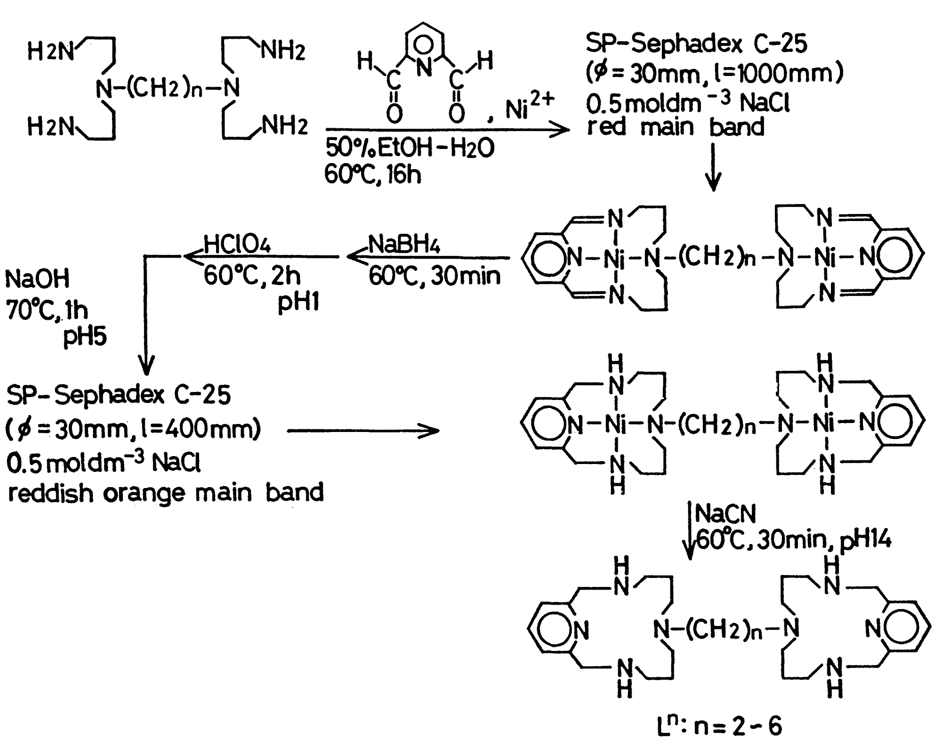


Fig. 1. Absorption spectra of 1.0×10$^{-3}$ mol dm$^{-3}$ unreduced (1) and reduced (2) dinickel(II) complexes with a trimethylene bridge in nitromethane solutions.



Scheme 1.

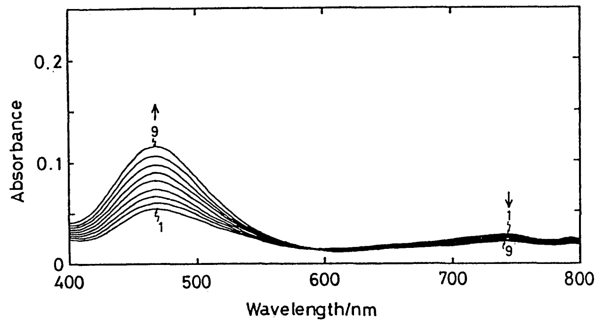


Fig. 2. Absorption spectra of 1.00×10$^{-3}$ mol dm$^{-3}$ [Ni$^{II}_2$(L$^2$)]$^{4+}$ in aqueous solution at 275.3 (1), 281.2 (2), 286.2 (3), 291.9 (4), 298.3 (5), 303.5 (6), 309.9 (7), 315.4 (8), 321.2 K (9).

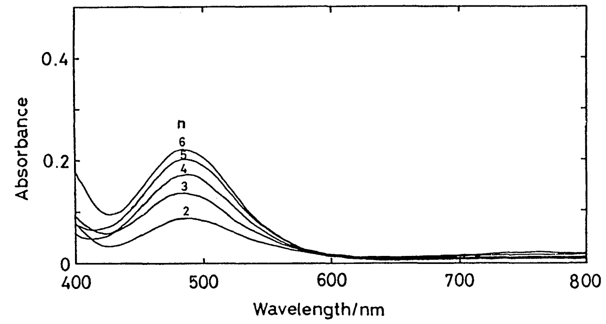


Fig. 3. Absorption spectra of 1.0×10$^{-3}$ mol dm$^{-3}$ [Ni$^{II}_2$(L$^n$)]$^{4+}$ ($n$=2—6) in aqueous solutions at 298.2±0.2 K.

However, the reduced complex does not show such a band but, rather, a moderately intense band at ca. 470 nm. Furthermore, $^{13}$C NMR spectra of the free ligands, prepared by removing metals from the reduced dinickel(II) complexes with sodium cyanide, agreed with those expected for the free ligand, L$^2$—L$^6$: they show 4 triplets (methylene), 2 doublets (pyridine), 1 singlet (pyridine), and some triplets (methylene bridge). In the $^{13}$C NMR spectra of the reduced dinickel(II) complexes in CF$_3$COOD, no splitting of signals[4] was observed except for the one set of signals expected, suggesting that only one species should be present.

**Square Planar-Octahedral Equilibrium.** The new series of complexes, [Ni$^{II}_2$(L$^n$)]$^{4+}$ ($n$=2—6) , in aqueous solutions showed a moderately intense band at ca. 470 nm and a weak band around 700—800 nm, which revealed that dinickel(II) complexes exist in square planar-octahedral equilibrium. It is well known for the square planar-octahedral equilibria of tetraazamacrocyclic nickel(II) complexes in aqueous media that the higher temperature causes a larger number to exist in the square planar form; that is, the equilibrium shifts to the left side in Equilibrium 1. Figure 2 shows the temperature-dependent absorption spectra of [Ni$^{II}_2$(L$^2$)]$^{4+}$.[6] Actually, as the temperature is raised, the absorption band around 400—500 nm, associated with the square planar form, increases, and that at 700—800 nm, which is characteristic of octahedral form, decreases. The absence of other forms, e.g., 5-coordinate species, is supported by the observation of an isosbestic point at 590 nm. The reversible spectral change observed herein is very similar to that observed in the Ni(II) complex with a

Table 1. Absorption Spectral Data

| Complex | Water[a)] | | Nitromethane[a)] | | Sulfolane[b)] | |
|---|---|---|---|---|---|---|
| | $\lambda_{max}$ | $(\varepsilon)$ | $\lambda_{max}$ | $(\varepsilon)$ | $\lambda_{max}$ | $(\varepsilon)$ |
| | nm | $mol^{-1} dm^3 cm^{-1}$ | nm | $mol^{-1} dm^3 cm^{-1}$ | nm | $mol^{-1} dm^3 cm^{-1}$ |
| $[Ni^{II}_2(L^2)]^{4+}$ | 469 | (90) | —[c)] | | 473 | (350) |
| $[Ni^{II}_2(L^3)]^{4+}$ | 466 | (130) | 466 | (320) | 468 | (320) |
| $[Ni^{II}_2(L^4)]^{4+}$ | 466 | (170) | 466 | (320) | 469 | (330) |
| $[Ni^{II}_2(L^5)]^{4+}$ | 466 | (200) | 466 | (350) | 469 | (340) |
| $[Ni^{II}_2(L^6)]^{4+}$ | 466 | (220) | 466 | (350) | 468 | (350) |

a) At 298.2 K. b) At 303.2 K. c) Insoluble.

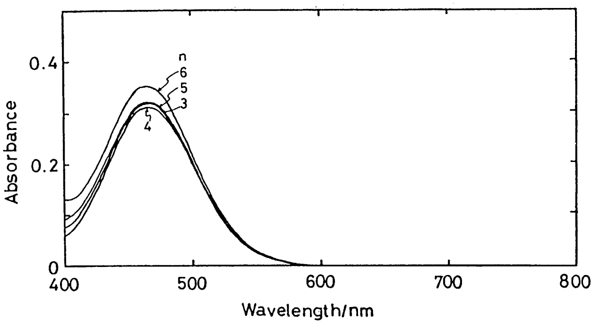


Fig. 4. Absorption spectra of $1.0\times10^{-3}$ mol dm$^{-3}$ $[Ni^{II}_2(L^n)]^{4+}$ ($n$=3—6) in nitromethane solutions at 298.2±0.2 K.

similar monomacrocyclic ligand.[7)] Similar temperature dependent spectra were observed for other dinickel(II) complexes with $L^3$—$L^6$.

Figure 3 shows the absorption spectra of the dinickel(II) complexes with $L^2$—$L^6$ in aqueous solutions. Although the spectra were taken under the same conditions, the apparent molar absorption coefficients $\varepsilon$ are quite different in the dinickel(II) complexes (see Table 1); Since the bridge becomes shorter the absorption band around 450—550 nm decreases, whereas that around 700—800 nm increases. Shortening the polymethylene bridge thus has the same effect as lowering the temperature. The differences, thus observed, in absorption spectra are attributable to the different ratios of [square planar form]/[octahedral form] among these dinickel(II) complexes, i.e., the equilibrium between square planar and octahedral forms depends on the length of the polymethylene bridge.

In nitromethane or sulfolane, the square planar species should predominate over the octahedral ones, since these solvents have a much poorer coordinating ability than water.[8)] Indeed, in these solvents, no absorption band was observed around 700—800 nm, but was observed around 450—550 nm, indicating that only the square planar species was present. Furthermore, the spectral features and intensities were independent of the temperature and species of these dinickel(II) complexes (see Fig. 4 and Table 1); thus, in nitromethane or sulfolane these complexes always exist in the square planar species, regardless of the temperature and length of the polymethylene chain.

The following equilibria should be taken into consideration for the dinickel(II) complexes, because both two Ni(II) ions can be involved in the square planar-octahedral equilibrium;

$$[Ni^{II}Ni^{II}(L^n)]^{4+} + 4H_2O \leftrightarrows [Ni^{II}(OH_2)_2Ni^{II}(L^n)]^{4+} + 2H_2O \leftrightarrows [Ni^{II}(OH_2)_2Ni^{II}(OH_2)_2(L^n)]^{4+}. \quad (2)$$

If this is the case, a determination of the thermodynamic parameters is not facile because of the presence of seven unknown parameters. On the basis of the assumption that two Ni(II) sites in one dinickel(II) complex attain equilibrium independently, i.e., total amounts of octahedral Ni(II) ion and square planar Ni(II) ion is equal to that of two times of a dinickel(II) complex, the computational analysis[3)] of temperature-dependent absorption spectra enabled us to evaluate the equilibrium constants for one Ni(II) ion, defined by

$$K=[\text{octahedral Ni(II) ion}]/[\text{square planar Ni(II) ion}]. \quad (3)$$

Table 2 lists the thermodynamic parameters thus calculated. For all complexes negative values of $\Delta H$ and $\Delta S$ were obtained. The negative values of $\Delta H$ show that the formation of the octahedral species is exothermic. The values of $\Delta H$ and $\Delta S$ are close to those of similar monocyclic Ni(II) complexes[7)]: 2.02—$2.32\times10^4$ J mol$^{-1}$ for $\Delta H$ and 59.4—77.0 J K$^{-1}$ mol$^{-1}$ for $\Delta S$, respectively.

It is noteworthy that the molar absorption coefficient, $\varepsilon_s^{470\,nm}$, of the square planar Ni(II) ion, thus derived, is independent of the polymethylene bridge length. Furthermore, the value of $\varepsilon_s^{470\,nm}$, thus calcu-

Table 2. Thermodynamic Parameters and Molar Absorption Coefficient at 470 nm[a)]

| Complex | $-\Delta H$ | $-\Delta S$ | $\varepsilon_s^{470\,nm}$ |
|---|---|---|---|
| | $10^4$ J mol$^{-1}$ | J K$^{-1}$ mol$^{-1}$ | $10^2$ mol$^{-1}$ dm$^3$ cm$^{-1}$ |
| $[Ni^{II}_2(L^2)]^{4+}$ | $1.9_2$ | $54._4$ | 1.5 |
| $[Ni^{II}_2(L^3)]^{4+}$ | $1.8_8$ | $58._6$ | 1.6 |
| $[Ni^{II}_2(L^4)]^{4+}$ | $1.9_2$ | $62._8$ | 1.7 |
| $[Ni^{II}_2(L^5)]^{4+}$ | $1.6_7$ | $58._6$ | 1.7 |
| $[Ni^{II}_2(L^6)]^{4+}$ | $1.7_2$ | $62._8$ | 1.7 |

a) For one Ni(II) ion.

Table 3. Equilibrium Constants and the Ratios of the Species[a)]

| Complex | $K$ | [Square planar Ni(II) ion] % | [Octahedral Ni(II) ion] % |
|---|---|---|---|
| $[Ni^{II}_2(L^2)]^{4+}$ | $3.3_9$ | 23 | 77 |
| $[Ni^{II}_2(L^3)]^{4+}$ | $1.7_3$ | 37 | 63 |
| $[Ni^{II}_2(L^4)]^{4+}$ | $1.2_4$ | 45 | 55 |
| $[Ni^{II}_2(L^5)]^{4+}$ | $0.74_4$ | 57 | 43 |
| $[Ni^{II}_2(L^6)]^{4+}$ | $0.53_3$ | 65 | 35 |

a) At 298.2 K.

lated, is almost the same of the half value of $\varepsilon^{470\,\mathrm{nm}}$ obtained from the dinickel(II) complexes in nitromethane and sulfolane.

Table 3 lists the ratio of [square planar Ni(II) ion]/[octahedral Ni(II) ion] at 298.2 K calculated from the thermodynamic parameters listed in Table 2. The amount of the square planar Ni(II) ions in water decreases according to the sequence of $[Ni^{II}_2(L^6)]^{4+} > [Ni^{II}_2(L^5)]^{4+} > [Ni^{II}_2(L^4)]^{4+} > [Ni^{II}_2(L^3)]^{4+} > [Ni^{II}_2(L^2)]^{4+}$, which clearly indicates that the equilibrium is shifted to the side of octahedral species, since the polymethylene bridge is short. This same trend was observed in the square planar-octahedral equilibrium of aqueous solutions of the previously reported dinickel(II) complexes with the ligands, $L^7$—$L^{11}$.[2,3)]

Thus, a new series of bismacrocyclic complexes, $[Ni^{II}_2(L^n)](ClO_4)_4$ ($n$=2—6), was successfully prepared. The effect of the length of the polymehtylene bridge on the square planar-octahedral equilibrium could be observed along with a change in d-d bands of Ni(II) ions.

## References

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3) K. Mochizuki, A. Iijima, Y. Endoh, and Y. Ikeda, *Bull. Chem. Soc. Jpn.*, **63**, 565 (1990).

4) K. Mochizuki, unpublished data. The free ligand liberated from the reduced product of dinickel(II) complex with $L^8$ shows two set of signals in methyl, methylene, and aromatic resions of $^{13}$C NMR spectrum, indicating the presence of at least two isomers. The separation of the isomers is now in progress.

5) Some other dinickel(II) complexes as the products of the condensation were also isolated. Details will be reported elsewhere.

6) Although the ratio of the square planar species increased upon the addition of $NaClO_4$, precipitation occurred if the concentration was over $10^{-1}$ mol dm$^{-3}$.

7) K. Mochizuki, M. Fujimoto, H. Ito, and T. Ito, *Bull. Chem. Soc. Jpn.*, **53**, 2535 (1980).

8) K. Mochizuki and M. Kaneko, 36th Annual Meeting on Coordination Chemistry Nagoya, October 1986, Abstr., No. 1C18.