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The Square Planar-Octahedral Equilibrium of Bismacrocyclic Ni(II)Ni(II) and Cu(II)Ni(II) Complexes with Polymethylene Bridges of Various Lengths

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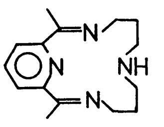
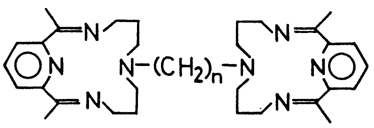
Bismacrocyclic Ni(II)Ni(II) and Cu(II)Ni(II) complexes, i.e., 7,7′-polymethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]dinickel(II) perchlorates and 7,7′-polymethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]copper(II)-nickel(II) perchlorates with polymethylene bridges 2—6-C long, were found to exist in an equilibrium between square planar and octahedral Ni(II) ions in water. The equilibrium constants and the thermodynamic parameters, ΔH and ΔS, for the Cu(II)Ni(II) complexes were evaluated on the basis of the analyses of the temperature-dependent absorption spectra. The formation of octahedral species was found to be exothermic; this reflects the predominant contribution of an exothermic change to the formation of Ni(II)-water bonds. The absolute values of ΔS corresponding to those expected for the liberation of two molecules of water are not in conflict with the equilibrium proposed. For both the Ni(II)Ni(II) and Cu(II)Ni(II) complexes, the equilibrium shifts toward the octahedral side as the polymethylene bridge is shortened.

The proximate effect of two metal ions is a very interesting problem and has been investigated by the use of chelation with bismacrocyclic ligands in which two macrocycles are linked with a C-C bond or a series of polymethylene bridges. For example, binuclear Cu(II)Cu(II)[1–5] and Ni(II)Ni(II)[4–7] complexes were synthesized and characterized by ESR spectroscopic,[1,3–5] magnetic,[1] X-ray diffraction,[2] and electrochemical methods.[3–7] Our electrochemical study[7] of the Ni(II)Ni(II) complexes with L^2—L^6 revealed that the half-wave potentials of $[\mathrm{Ni^{II}Ni^{II}}]/[\mathrm{Ni^{II}Ni^{III}}]$ and $[\mathrm{Ni^{II}Ni^{III}}]/[\mathrm{Ni^{III}Ni^{III}}]$ shift toward the positive side as the polymethylene bridge becomes short.



L¹



L² : n=2
L³ : n=3
L⁴ : n=4
L⁵ : n=5
L⁶ : n=6

In this paper we will show that the length of the polymethylene bridge affects the square planar-octahedral equilibrium of the bismacrocyclic Ni(II)Ni(II) and Cu(II)Ni(II) complexes.

The spectrophotometric studies of the monomacrocyclic Ni(II) complex with the L^1 ligand showed that the equilibrium between the diamagnetic square planar (low-spin) and paramagnetic pseudo octahedral (high-spin) species in water, as is shown in Equilibrium 1:

$$[\mathrm{Ni^{II}}(L^1)]^{2+} + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Ni^{II}}(L^1)(\mathrm{OH_2})_2]^{2+}, \qquad (1)$$

was influenced by various factors, e.g., the temperature, the addition of salts, and the lack of saturation of the ligand.[8,9]

We expected that homobinuclear Ni(II)Ni(II) complexes with L^2—L^6 would enable us to clarify the effects of the polymethylene bridge length on the square planar-octahedral equilibrium and that the heterobinuclear Cu(II)Ni(II) complexes, having one Ni(II) ion, would facilitate the evaluation of the equilibrium constant and/or the thermodynamic parameters, as will be discussed in the text.

These expectations were indeed realized by means of visible absorption spectroscopy and by detailed analyses of the temperature-dependent absorption spectra, as will be described below.

Experimental

Materials. The syntheses of Ni(II)Ni(II)[7] and Cu(II)-Ni(II)[10] complexes with L^2—L^6 were reported previously. The Cu(II)Cu(II) complexes with L^2—L^6 were synthesized according to the method by Murase and his co-workers.[1] The water used was purified by the use of a Millipore Milli-Q system.

Measurements. The absorption spectra were measured with a Hitachi recording spectrophotometer, model 340, equipped with a data printer, the absorbance being recorded within ±0.001. The temperature was determined with a thermistor digital thermometer, Takara model D621, with a Teflon coated sensor, Takara DXK-67, directly inserted into the tightly sealed cell. The readings of the temperature were corrected within ±0.1 K by the use of a standard thermometer.

Analyses of the Data. The physical data, including the molar absorption coefficients of the component species, the equilibrium constants, and the thermodynamic parameters, were derived as follows.

The equilibrium constant according to Equilibrium 1 is defined at an arbitrary temperature T_j as:

$$K_j = [\text{octahedral species}]/[\text{square planar species}]. \quad (2)$$

At an arbitrary wavelength λ_i and temperature T_j, this equation is transformed into Eq. 3 by introducing the apparent molar absorption coefficient, $\varepsilon_{\text{obs}ij}$, and the molar absorption coefficients, $\varepsilon_{\text{s}i}$ and $\varepsilon_{\text{o}i}$, for the square planar and octahedral species respectively:[11]

$$K_{ij} = (\varepsilon_{\text{s}i} - \varepsilon_{\text{obs}ij})/(\varepsilon_{\text{obs}ij} - \varepsilon_{\text{o}i}). \quad (3)$$

The following relationship is then readily derived by transforming Eq. 3:

$$(K_{ij}+1)\varepsilon_{\text{obs}ij} = \varepsilon_{\text{o}i}K_{ij} + \varepsilon_{\text{s}i}. \quad (4)$$

The temperature-dependent equilibrium constant K_{ij} is given by Eq. 5:

$$K_{ij} = \exp(\Delta S/R - \Delta H/RT_j). \quad (5)$$

Actual calculations were performed according to the following procedure by means of a computer program written by the present authors for this study.

(1) Set the initial values of ΔH and ΔS and calculate the values of K_{ij} at various temperatures T_j by means of Eq. 5.

(2) Plot the values of $(K_{ij}+1)\varepsilon_{\text{obs}ij}$ against K_{ij} at various wavelength λ_i according to Eq. 4, and then evaluate the values of $\varepsilon_{\text{o}i}$, the slope, and $\varepsilon_{\text{s}i}$, the intercept, at various λ_i values by means of the least-square fit.

(3) Calculate the values of K_{ij} at various T_j and λ_i values with the values of $\varepsilon_{\text{o}i}$ and $\varepsilon_{\text{s}i}$ derived in (2) by means of Eq. 3. Call the equilibrium constants thus obtained K_{ij}', thus distinguishing them from the K_{ij} values derived in (1).

(4) Calculate the value of $\sum_i\sum_j(K_{ij} - K_{ij}')^2$.

(5) After changing the initial values of ΔH and ΔS, repeat the operations from (1) to (4), until the value of $\sum_i\sum_j(K_{ij} - K_{ij}')^2$ reaches the minimum. A set of optimum values of ΔH and ΔS can then be obtained, as well as $\varepsilon_{\text{o}i}$ and $\varepsilon_{\text{s}i}$; the Simplex method[12] is employed for the optimization. Confirm the coincidence of the calculated values of $\varepsilon_{\text{calc}ij}$ with those of $\varepsilon_{\text{obs}ij}$ measured at various T_j and λ_i values.

The calculations were carried out on a NEC personal computer, model VX4, equipped with a numeric data coprocessor (80287, 8 MHz).

Results and Discussion

The monomacrocyclic Ni(II) complex with L^1 shows three absorption bands strong, medium, and weak around 400, 480, and 700—800 nm respectively in an aqueous solution.[8] These bands are ascribed to the charge-transfer from C=N bonds to the Ni(II) ion, to the d-d transition of square planar Ni(II) ions, and to that of octahedral Ni(II) ions respectively.[13] All the bismacrocyclic Ni(II)Ni(II) complexes investigated also showed these three bands in aqueous solutions, indicating the presence of a square planar-octahedral equilibrium. It is well-known that, in the monomacrocyclic Ni(II) complex, the square planar form increases with an increase in the temperature: that is, the equilibrium shifts to the left side of Equilibrium 1. Figure 1(a) shows the temperature-dependent absorption spectra of the bismacrocyclic complex, $[\text{Ni}^{\text{II}}{}_2(\text{L}^2)]^{4+}$. The reversible spectral change observed herein is very similar to that observed in the corresponding monomacrocyclic Ni(II) complex with L^1.[8,9] The formation of other species. e.g., the 5-coordinate species, can be excluded because of the observation of an isosbestic point at 628 nm. Similar temperature-dependent spectra were observed for other Ni(II)Ni(II) complexes with L^3—L^6.

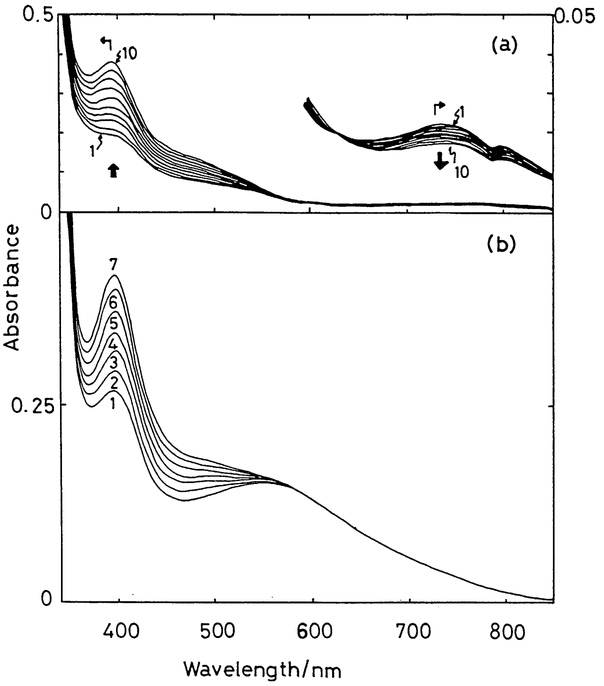


Fig. 1. (a) Absorption spectra of 4.00×10⁻⁴ mol dm⁻³ $[\text{Ni}^{\text{II}}{}_2(\text{L}^2)]^{4+}$ in aqueous solution at 281.0 (1), 285.6 (2), 290.4 (3), 294.4 (4), 298.6 (5), 303.0 (6), 308.6 (7), 313.8 (8), 318.6 (9), 323.2 K (10). (b) Absorption spectra of 5.00×10⁻⁴ mol dm⁻³ $[\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}(\text{L}^3)]^{4+}$ in aqueous solution at 277.9 (1), 284.3 (2), 291.1 (3), 297.0 (4), 304.2 (5), 312.2 (6), 317.2 K (7).

The temperature-dependent absorption spectrum of the heterobinuclear complex, $[\text{Cu}^{\text{II}}\text{Ni}^{\text{II}}(\text{L}^3)]^{4+}$, in water shows absorption bands at ca. 400 nm and around 560—570 nm ascribable to the charge-transfer from C=N bonds to the Ni(II) ion and to the d-d transition of the Cu(II) ion respectively (Fig. 1(b)).[1,10] As the temperature rises, the absorption band at 400 nm increases remarkably: however, that around 560—570 nm increases only slightly. Thus, the temperature-dependency of the absorption band is significant on the Ni(II) ring, but not on the Cu(II) ring. Similar temperature-dependent absorption spectra were obtained in other Cu(II)Ni(II) complexes with L^2 and L^4—L^6. These results suggest that, on the Ni(II) ion, the square planar-octahedral equilibrium is also attained in the heterobinuclear Cu(II)Ni(II) complexes.

Figure 2(a) shows the absorption spectra of

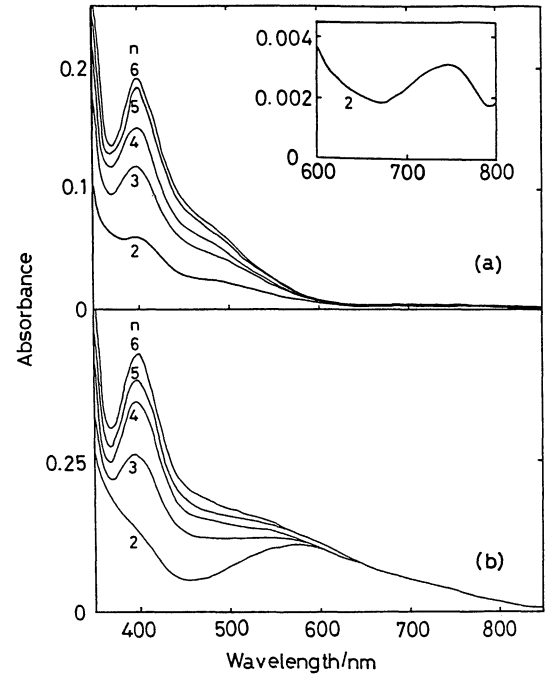


Fig. 2. (a) Absorption spectra of 1.0×10^{-4} mol dm^{-3} [$Ni^{II}_2(L^n)$]$^{4+}$ (n=2—6) in aqueous solutions at 298.2±0.2 K. (b) Absorption spectra of 4.0×10^{-4} mol dm^{-3} [$Cu^{II}Ni^{II}(L^n)$]$^{4+}$ (n=2—6) in aqueous solutions at 298.2±0.2 K.

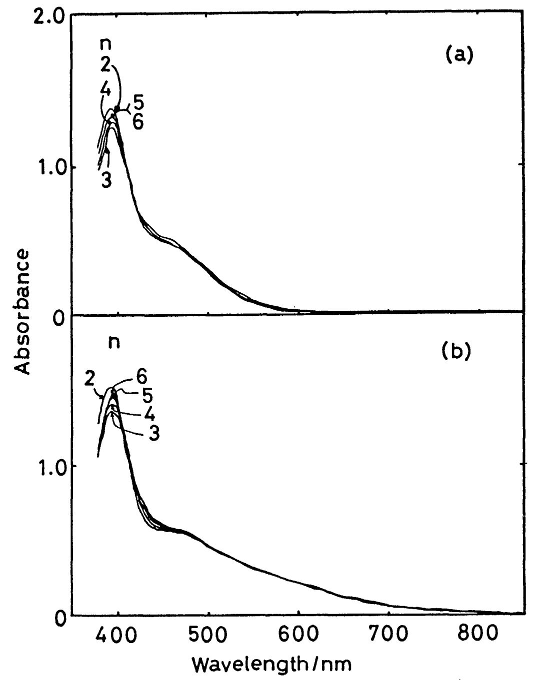


Fig. 3. (a) Absorption spectra of 4.0×10^{-4} mol dm^{-3} [$Ni^{II}_2(L^n)$]$^{4+}$ (n=2—6) in nitromethane solutions at 298.2±0.2 K. (b) Absorption spectra of 4.0×10^{-4} mol dm^{-3} [$Cu^{II}Ni^{II}(L^n)$]$^{4+}$ (n=2—6) in nitromethane solutions at 298.2±0.2 K.

Ni(II)Ni(II) complexes with L^2—L^6 in aqueous solutions. Although the spectra were taken under the same conditions, the apparent molar absorption coefficients ε are undoubtedly affected by the length of the polymethylene chains (see Table 1); as the bridge becomes shorter, the intensity of the absorption band at 400—500 nm decreases, whereas that at 700—800 nm increases. A remarkable difference is observed between [$Ni^{II}_2(L^2)$]$^{4+}$ and [$Ni^{II}_2(L^3)$]$^{4+}$.[14)]

Figure 2(b) shows the absorption spectra of an aqueous solution of the Cu(II)Ni(II) complexes. As was observed in Ni(II)Ni(II) complexes, the intensity of the absorption band due to the Ni(II) ring decreases remarkably along with the sequence of the polymethylene bridge. On the other hand, the absorption band based on the Cu(II) ring depends scarcely at all on the length of the methylene chain.[15)]

Thus, shortening the polymethylene bridge has the same effect as lowering the temperature for both the homo and hetero binuclear complexes.

In nitromethane or sulfolane, the square planar species should predominate over the octahedral ones, because these solvents have a much poorer coordinating ability than water.[9)] Indeed, in these solvents, the Ni(II)Ni(II) complexes showed the absorption band not around 700—800 nm, but around 400—500 nm, indicating the presence of only square planar species. The spectral features and intensities were independent

Table 1. Absorption Spectral Data at 298.2±0.2 K

Complex	Water			Nitromethane			Sulfolane		
	λ_{max}	(ε)	$\varepsilon^{480\,nm}$	λ_{max}	(ε)	$\varepsilon^{480\,nm}$	λ_{max}	(ε)	$\varepsilon^{480\,nm}$
	nm	mol^{-1} dm^3 cm^{-1}	mol^{-1} dm^3 cm^{-1}	nm	mol^{-1} dm^3 cm^{-1}	mol^{-1} dm^3 cm^{-1}	nm	mol^{-1} dm^3 cm^{-1}	mol^{-1} dm^3 cm^{-1}
[Ni^{II}_2 (L^2)]$^{4+}$	396	(590)	230	395	(3400)	1000	398	(3500)	1200
[Ni^{II}_2 (L^3)]$^{4+}$	398	(1200)	480	395	(3100)	990	400	(3000)	1200
[Ni^{II}_2 (L^4)]$^{4+}$	398	(1500)	560	395	(3200)	980	400	(3300)	1200
[Ni^{II}_2 (L^5)]$^{4+}$	399	(1800)	660	395	(3300)	1000	400	(3100)	1100
[Ni^{II}_2 (L^6)]$^{4+}$	399	(1900)	680	395	(3300)	1000	400	(3100)	1100
[$Cu^{II}Ni^{II}$ (L^2)]$^{4+}$	396	(350)	160	395	(1900)	650	398	(1800)	710
[$Cu^{II}Ni^{II}$ (L^3)]$^{4+}$	398	(700)	340	395	(1700)	650	402	(1600)	760
[$Cu^{II}Ni^{II}$ (L^4)]$^{4+}$	398	(910)	400	395	(1800)	660	402	(1800)	750
[$Cu^{II}Ni^{II}$ (L^5)]$^{4+}$	399	(970)	430	395	(1700)	650	401	(1700)	700
[$Cu^{II}Ni^{II}$ (L^6)]$^{4+}$	399	(1100)	470	395	(1800)	670	402	(1700)	740

of the temperature and the length of the methylene chain of both the Ni(II)Ni(II) and Cu(II)Ni(II) complexes (see Fig. 3(a)(b) and Table 1).

It is known that the molar absorption coefficients around 400 nm of the octahedral species are much smaller than those of square planar species for the monomacrocyclic $[\mathrm{Ni^{II}(L^1)}]^{2+}$.[8] As a similar relation of ε can be expected for the bismacrocyclic complexes, the absorbance values around 400 nm enable us to estimate the ratio of [square planar form]/[octahedral form] ($\simeq\varepsilon_{\mathrm{obs}ij}/(\varepsilon_{\mathrm{s}i}-\varepsilon_{\mathrm{obs}ij})$) roughly; the larger the absorbance, the more amount of the square planar form. The amount of the square planar form in water increases according to the sequence of $\mathrm{L^2 \ll L^3 < L^4 < L^5 < L^6}$, which clearly indicates that, as the polymethylene bridge is shortened, the equilibrium is shifted to the side of the octahedral species.

In order to estimate the exact ratio of [square planar form]/[octahedral form], it is necessary to know the equilibrium constants and/or the thermodynamic parameters, ΔH and ΔS. For this purpose, it is necessary to record the spectra of the pure square planar and pure octahedral species. However, such spectra might not be obtained, because the square planar-octahedral equilibrium occurs immediately after the Ni(II) complexes have been dissolved in water. In these cases, the conventional method involving the use of a large excess of sodium perchlorate has often been employed.[16–18] This method was used in the monomacrocyclic Ni(II) complex with cyclam,[16,17] but it could not be used for the present bismacrocyclic Ni(II) complexes because the complexes were precipitated by the addition of an excess of sodium perchlorate. This might be attributable to the large positive charge (+4) in the binuclear complexes. Although the addition of an excess of calcium chloride[17] was examined, the intended spectra could not be obtained because new absorption bands appeared. This might be caused by the coordination of chloride ions to the bismacrocyclic Ni(II)Ni(II) complexes.

Table 2. Thermodynamic Parameters and Molar Absorption Coefficients

Complex	$-\Delta H$ 10^4 J mol^{-1}	$-\Delta S$ J K^{-1} mol^{-1}	$\varepsilon_{\mathrm{s}}^{400\ \mathrm{nm}}$ 10^3mol^{-1} dm^3 cm^{-1}	$\varepsilon_{\mathrm{o}}^{400\ \mathrm{nm}}$ 10^2mol^{-1} dm^3 cm^{-1}
$[\mathrm{Ni^{II}(L^1)}]^{2+}$[a]	2.12	59.4	1.17	—
$[\mathrm{Cu^{II}Ni^{II}(L^2)}]^{4+}$	2.6_4	$66._9$	1.4_0	1.6_0
$[\mathrm{Cu^{II}Ni^{II}(L^3)}]^{4+}$	1.6_8	$55._6$	1.3_2	0.4_5
$[\mathrm{Cu^{II}Ni^{II}(L^4)}]^{4+}$	1.9_2	$69._0$	1.3_8	0.9_4
$[\mathrm{Cu^{II}Ni^{II}(L^5)}]^{4+}$	2.0_8	$75._3$	1.2_9	1.3_0
$[\mathrm{Cu^{II}Ni^{II}(L^6)}]^{4+}$	2.0_4	$74._9$	1.3_3	1.3_4
$[\mathrm{Ni^{II}(cyclam)}]^{2+}$	1.9_7	$71._1$	0.062[d]	—
	2.3[b]	84[b]	0.0645[e]	—
	1.9[c]	71[c]	0.063[f]	—

a) Ref. 8. b) The units of the values in Ref. 16 are changed (×4.184). c) The values in Ref. 17 are also changed. d) ε_{s} at 450 nm. e) ε_{s} at 445 nm in Ref. 16. f) ε_{s} at 451 nm in Ref. 17.

Therefore, we used the computational method which enabled us to determine the equilibrium constants and the thermodynamic parameters in which detailed analyses of the temperature-dependent absorption spectra for the square planar-octahedral equilibrium are included (see Experimental section).

This method was applied to the square planar-octahedral equilibrium of an aqueous solution of monomacrocyclic $[\mathrm{Ni^{II}(cyclam)}]^{2+}$. The values of ΔH, ΔS, and ε of the square planar species at 450 nm thus obtained are in good agreement with those reported previously[16,17] (Table 2). Encouraged by the satisfactory results, we next applied the computational method to the bismacrocyclic complexes.

For the homobinuclear Ni(II)Ni(II) complexes, both Ni(II) ions attain the square planar-octahedral equilibrium; thus, the following two equilibria should exist;

$$[\mathrm{Ni^{II}Ni^{II}(L}^n\mathrm{)}]^{4+} + 4\mathrm{H_2O} \rightleftarrows [\mathrm{Ni^{II}Ni^{II}(L}^n\mathrm{)(OH_2)_2}]^{4+} + 2\mathrm{H_2O} \rightleftarrows [\mathrm{Ni^{II}Ni^{II}(L}^n\mathrm{)(OH_2)_4}]^{4+}. \qquad (6)$$

In this case, the evaluation of thermodynamic parameters is difficult, because seven unknown parameters, three spectra of the components, and two sets of ΔH and ΔS are present. On the other hand, for the heterobinuclear Cu(II)Ni(II) complexes, the situation becomes simpler because only one equilibrium for the Ni(II) ion needs to be taken into consideration.[19] Thus, an analysis similar to that done for $[\mathrm{Ni^{II}(cyclam)}]^{2+}$ should be applied to the Cu(II)Ni(II) complexes (see Analyses of the data).

The thermodynamic parameters thus evaluated are given in Table 2. The values of ΔH are comparable to those for $[\mathrm{Ni^{II}(cyclam)}]^{2+}$ [16,17] and for monomacrocyclic $[\mathrm{Ni^{II}(L^1)}]^{2+}$.[8] For some monomacrocyclic Ni(II) complexes, the Ni-N bond length has been reported to be $(2.07-2.10)\times10^{-8}$ cm in the octahedral complexes and $(1.88-1.91)\times10^{-8}$ cm in the square planar complexes.[20] Therefore, if only the Ni-N bond is considered, the formation of the octahedral species should be endothermic, because the bond strength of Ni-N is weakened in the octahedral species. The ΔH values for all the Cu(II)Ni(II) complexes, however, were negative, indicating that the formation of octahedral species is exothermic. These results might show that the exothermic contribution to the formation of Ni-water bonds exceeds the endothermic contribution attributable to the Ni-N bonds.

The values of ΔS are also comparable to those for $[\mathrm{Ni^{II}(cyclam)}]^{2+}$ [16,17] and $[\mathrm{Ni^{II}(L^1)}]^{2+}$.[8] The absolute values of ΔS correspond to those expected for the effective liberation of two water molecules from the complexes in an aqueous solution, viz., $(30-40)\times2$ J K^{-1} mol^{-1}.[21] Thus, the entropy change agrees with that to be expected for the square planar-octahedral equilibrium of one Ni(II) ion, indicating that it is acceptable to take only one equilibrium into consider-

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

Complex	K	[square planar]	[octahedral]
		%	%
$[\mathrm{Cu^{II}Ni^{II}}(\mathrm{L^2})]^{4+}$	13.$_2$	7	93
$[\mathrm{Cu^{II}Ni^{II}}(\mathrm{L^3})]^{4+}$	1.0$_8$	48	52
$[\mathrm{Cu^{II}Ni^{II}}(\mathrm{L^4})]^{4+}$	0.58$_8$	63	37
$[\mathrm{Cu^{II}Ni^{II}}(\mathrm{L^5})]^{4+}$	0.52$_0$	66	34
$[\mathrm{Cu^{II}Ni^{II}}(\mathrm{L^6})]^{4+}$	0.38$_7$	72	28

a) At 298.2 K.

ation in the analyses of the Cu(II)Ni(II) complexes.

The molar absorption coefficients at 400 nm for the square planar species, $\varepsilon_s^{400\,\mathrm{nm}}$ are almost constant (1300—1400), regardless of the polymethylene bridge length (Table 2). Therefore, the change in the absorption band at $\varepsilon_s^{400\,\mathrm{nm}}$ attributable to the length of the polymethylene bridge should directly reflect the [square planar form]/[octahedral form] ratio. In fact, the equilibrium constants, K, at 298.2 K and the [square planar form]/[octahedral form] ratios calculated by the use of the ΔH and ΔS values depended on the length of the polymethylene bridge; the amounts of the square planar species monotonically decrease with the decrease in the length of the polymethylene chain. The amounts of the square planar form in water increase according to the sequence of: $\mathrm{L^2} \ll \mathrm{L^3} < \mathrm{L^4} < \mathrm{L^5} < \mathrm{L^6}$ (Table 3).

Thus, all the data obtained herewith clearly indicate that the equilibrium is shifted to the side of the octahedral species as the polymethylene bridge is shortened. On the basis of our previous conclusion that the electrostatic repulsion between two Ni(II) ions increases as the polymethylene chain becomes short,[7)] the present results might be explained in the following manner. In the Ni(II)Ni(II) complexes with a short methylene chain, the octahedral form should be favored, because the electron-donating coordination of water reduces the electrostatic repulsion between the Ni(II) ions.

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18) The spectrum, i.e., ε_{si}, of the square planar species can be obtained by shifting the equilibrium to the square planar side by adding a large excess of sodium perchlorate or of another non-coordinating electrolyte. Then, the equilibrium constant can be deduced from Eq. 3 by the use of the ε_{si}, in which the absorption band due to octahedral species is ignored, i.e., $\varepsilon_{oi} \simeq 0$.

19) In order to get some information about the temperature-dependence of the absorption bands assigned to the d-d transition of the Cu(II) ring, the temperature-dependent spectra of the corresponding Cu(II)Cu(II) complexes were also investigated. Compared with the cases of the Cu(II)Ni(II) complexes, very small changes in the absorbance were observed in the Cu(II)Cu(II) complexes in the range of 6—50 °C; the maximum change in absorbance observed in 350—800 nm was ca. 0.012 for 1.0×10^{-3} mol dm^{-3} Cu(II)Cu(II) complexes. In the analysis, provided

that a similar temperature-dependence in the spectra occurs on the side of the Cu(II) ion of the Cu(II)Ni(II) complexes, the small absorbance change ascribed to the Cu(II) ring was corrected by using the absorbance change observed for the Cu(II)Cu(II) complexes.

20) For a detailed discussion, see L. Y. Martin, C. R. Seperati, and D. H. Busch, *J. Am. Chem. Soc.*, **99**, 2968 (1977); P. O. Whimp, M. F. Bailey, and N. F. Curtis, *J. Chem. Soc. A*, **1970**, 1956; L. N. Swink and M. Atoji, *Acta Crystallogr.*, **13**, 639 (1960); J. M. Waters and K. R. Whittle, *J. Inorg. Nucl. Chem.*, **34**, 155 (1972): T. Ito and K. Toriumi, *Chem. Lett.*, **1978**, 1395.

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