CHEMISTRY LETTERS, pp. 1823-1826, 1988.

Square Planar-Octahedral Equilibrium of Bismacrocyclic Ni(II)Ni(II) Complexes with a Polymethylene Bridge of Various Lengths

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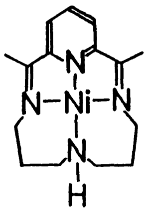
Bismacrocyclic Ni(II)Ni(II) complexes, i.e., 7,7'-polymethylenebis[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]dinickel(II) perchlorates with polymethylene bridges of 2-6-C length, exist in the equilibrium between square planar and octahedral forms in water. The equilibrium shifts toward the octahedral side as the polymethylene bridge is shortened.

Recently binuclear Cu(II)Cu(II)[1-5] and Ni(II)Ni(II)[4-6] complexes with bis(tetraazamacrocycle) have been actively synthesized and characterized by ESR spectroscopic,[1,3-5] magnetic,[1] X-ray diffraction,[2] and electrochemical[3-6] methods. We reported the synthesis and electrochemical properties of a series of Ni(II)Ni(II) complexes with bis(tetraazamacrocycle), 7,7'-polymethylene[2,12-dimethyl-3,7,11,17-tetraazabicyclo[11.3.1]heptadeca-1(17),2,11,13,15-pentaene]-dinickel(II) perchlorates, where the polymethylene is ethylene (**2**), trimethylene (**3**), tetramethylene (**4**), pentamethylene (**5**), and hexamethylene (**6**).[7] This electrochemical study[7] revealed that the half-wave potentials of the $[\mathrm{Ni^{II}Ni^{II}}]/[\mathrm{Ni^{II}Ni^{III}}]$ and $[\mathrm{Ni^{II}Ni^{III}}]/[\mathrm{Ni^{III}Ni^{III}}]$ couples shift toward the positive side as the polymethylene bridge becomes short.



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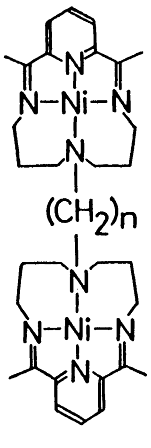

n = 2 : **2**
n = 3 : **3**
n = 4 : **4**
n = 5 : **5**
n = 6 : **6**

In the present spectrophotometric study, we show that the polymethylene bridge length affects the square planar-octahedral equilibrium. To our best knowledge, such a finding is unprecedented in the literature.

The equilibrium between diamagnetic square planar (singlet low-spin) and paramagnetic pseudo octahedral (triplet high-spin) species in water, shown as Eq. 1, has been studied for the monocyclic Ni(II) complex **1**.[8,9]

$$[\mathrm{NiL}]^{2+} + 2\mathrm{H_2O} \rightleftharpoons [\mathrm{NiL(OH_2)_2}]^{2+} \qquad (1)$$

The square planar-octahedral equilibrium is affected by various factors, including temperature, solvent, addition of salts, and unsaturation of a ligand.[8,9] We expected that the Ni(II)Ni(II) complexes **2**-**6** enable us to clarify the effects of the polymethylene bridge length on the square planar-octahedral equilibrium. The expectation was indeed realized by measurement of visible absorption spectra as described herein.

In aqueous solutions all Ni(II)Ni(II) complexes investigated were found to exist in the square planar-octahedral equilibrium. The absorption spectra of all complexes show a large absorption band at 395 nm having a shoulder at 480 nm, ascribable to square planar Ni(II) ions, and a small absorption band around 700-800 nm, due to d-d transition of octahedral ones. It is well known that the higher the temperature, the more the amount of square planar form, that is, the equilibrium shifts to the left side. Figure 1 shows the temperature-dependent absorption spectra of **2**.[10] Actually, as the temperature is raised, the absorption band around 400-500 nm, associated with 4-coordinate form, increases, and that around 700-800 nm, which is characteristic of 6-coordinate form, decreases. The absence of another form, e.g., 5-coordinate species, is supported by the presence of an isosbestic point at 628 nm.[11] The reversible spectral change observed here is just very similar to that observed in the corresponding monocyclic Ni(II) complex **1**.[8,9] Similar temperature dependent spectra were observed for **3**-**6**.

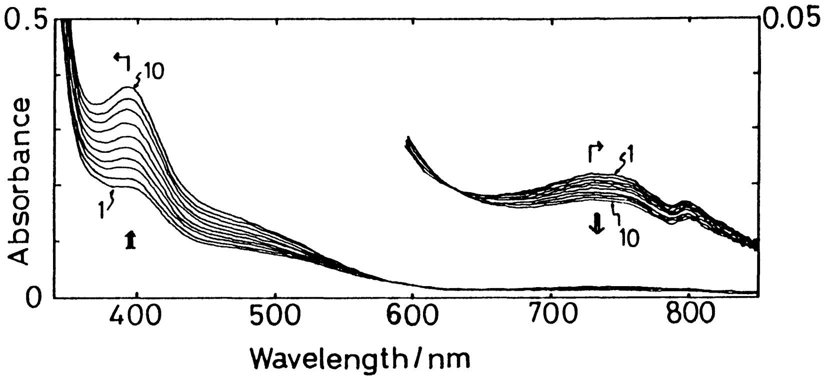

Fig. 1. Absorption spectra of aqueous solution of 4.00 x 10^{-4} mol dm^{-3} **2** at 281.0 (1), 285.6 (2), 290.4 (3), 294.4 (4), 298.6 (5), 303.0 (6), 308.6 (7), 313.8 (8), 318.6 (9), 323.2 K (10).

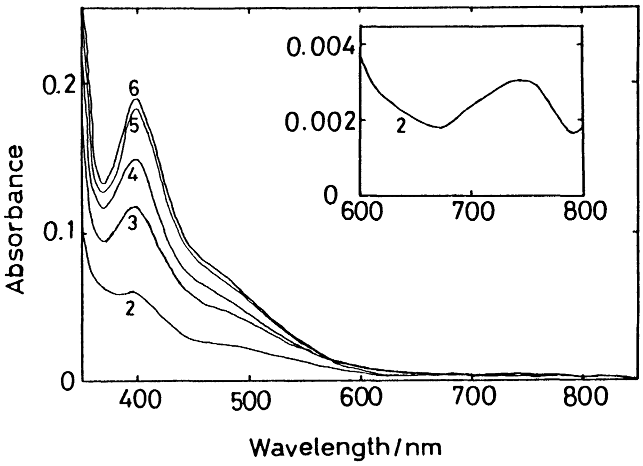

Fig. 2. Absorption spectra of aqueous solutions of 1.00 x 10^{-4} mol dm^{-3} Ni(II)Ni(II) complexes at 298.0 K.

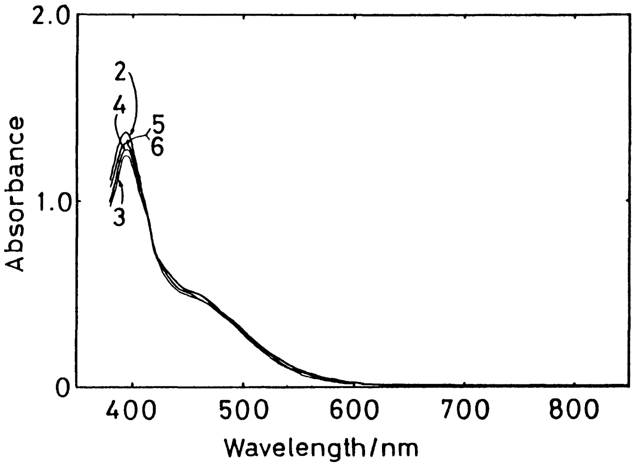

Fig. 3. Absorption spectra of nitromethane solutions of 4.00 x 10^{-4} mol dm^{-3} Ni(II)Ni(II) complexes at 298.0 K.

Figure 2 shows the absorption spectra of **2**-**6** in aqueous solutions. Although the spectra were taken under the same conditions, apparent molar absorption coefficients ε are quite different among the Ni(II)Ni(II) complexes (see Table 1); as the bridge becomes shorter, the absorption band around 400-500 nm decreases, whereas, that around 700-800 nm increases. A remarkable difference is observed between **2** and **3**.12) Shortening the polymethylene bridge gives 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 Ni(II)Ni(II) complexes, i.e., equilibrium between square planar and octahedral forms depends on length of the polymethylene bridge.

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 absorption band around 700-800 nm is not observed, indicating that only square planar species is present. The spectral features and intensities are independent of temperature and species of these Ni(II)Ni(II) complexes (see Fig. 3 and Table 1).

As the ε of the 6-coordinate species should be much smaller than those of 4-coordinate species around 400-500 nm,8) the absorbance values enable us to estimate the ratio of [4-coordinate form]/[6-coordinate form] roughly; the larger absorbance the larger amount of 4-coordinate form. The amount of 4-coordinate form in water increases according to the sequence of **2**<<**3**<**4**<**5**<**6**, which clearly indicates that the equilibrium is shifted to the side of 6-coordinate species, as the polymethylene bridge is shortened.

Table 1. Absorption Spectral Data at 298.0 K

Complex	Water		Nitromethane		Sulfolane	
	λ_{max} (ε)	ε_{480nm}	λ_{max} (ε)	ε_{480nm}	λ_{max} (ε)	ε_{480nm}
	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}
2	396 (590)	230	395 (3400)	1000	398 (3500)	1200
3	398 (1200)	480	395 (3100)	990	400 (3000)	1200
4	398 (1500)	560	395 (3200)	980	400 (3300)	1200
5	399 (1800)	660	395 (3300)	1000	400 (3100)	1100
6	399 (1900)	680	395 (3300)	1000	400 (3100)	1100

The present work is partially supported by a Grant-in-Aid for Scientific Research No. 62740352 from the Ministry of Education, Science and Culture.

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10) The addition of $NaClO_4$ also increases the amount of 4-coordinate species. However, precipitation occurs over the concentration of 10^{-1} mol dm^{-3}. The addition of $CaCl_2$ causes the coordination of chloride ions to the Ni(II) ions.

11) We consider that three species, ([4-coordinate form]$_2$), ([4-coordinate form][6-coordinate form]), ([6-coordinate form]$_2$), are present in the equilibrium, and that the spectrum of the middle complex may be almost a half of the sum of that for the former one and that for the later one.

12) Thus observed differences in absorption spectra were confirmed not to be due to the dissociation of Ni(II) ions from the complexes or due to the hydrolysis of the Ni(II) ions from the following results. (1) Treatment of an aqueous solution of the complex **2** with dimethylglyoxime produced no red products, indicating that demetallation does not occur. (2) The spectrum of $[Ni^{II}_2(\mathbf{2})]^{4+}$ in water did not change between pH 3-7; pH was always kept at ca. 5.6-6.2 in the present experiments.

(Received July 6, 1988)