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A Spectrophotometric Study of the Formation and Thermochromism of the Nickel(II)-Piperidine Complexes in *N*,*N*-Dimethylformamide Solutions

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The transition energy between the pair of coordination states in a nickel(II) complex is sometimes low. In such a case, the state changes only upon a slight heating, so its solution shows a characteristic thermochromism. Such kinds of thermochromism of nickel(II) complexes have already been reported by several authors. Sone and Kato have studied the thermochromism of the ethylenediamine chelate of nickel(II),[1] Cotton and others studied the thermal change of bis(acetylacetonato)-nickel(II) in solution,[2] and several authors have reported about the formation of the $[NiCl_4]^{2-}$ ion at high temperatures.[3-5] Recently we have found that the nickel(II) chloride - piperidine complex formed in the *N*,*N*-dimethylformamide (DMF) solution containing a large excess (with a mole ratio of about 10 to 30 : 1) of piperidine is remarkably thermochromic. The solution which was yellow at room temperature became violet at high temperatures, and the color change was quite reversible. These observations led us to study the complex species formed in such solutions.

Experimental

The visible absorption spectra at 25°C were obtained with a Hitachi EPS-2 type automatic recording spectrophotometer. The spectra at high temperature were obtained with an Ito Model QU-3 spectrophotometer, with heated paraffin oil being circulated around the cell chamber. The reagents used were all GR grade, the $Ni(ClO_4)_2 \cdot 6DMF$ was made by the method reported by Gutmann.[6]

The Preparation of the Sample Solution. In general, a mixed solution of nickel(II) chloride and amine in DMF was stable for about 6 hours, and practically no spectral change could be observed in it. However, a gradual spectral change then appeared as a result of the aging of the solution. Consequently, the spectral measurements at 25°C were carried out within five hours after the preparation of the sample. The concentration of the nickel ion in the sample solutions was 0.04 M. The optical path length of the cell was 5.5 mm. The absorption coefficient of the solution showed a little deviation from Beer's law even at the concentration of 0.01 M. When the concentration of the nickel salt was higher, precipitation occurred when much amine was added.

Results and Discussion

The visible absorption spectra of the DMF solutions containing piperidine and nickel(II) chloride, where the mole ratio of the former to the latter was 0 to 101, were examined. Typical results are shown in Fig. 1. Many peaks which are considerably overlapping are observed, but no exact isosbestic points can be detected.

The relation between the absorption coefficients at various wave numbers and the mole ratio of amine to nickel are shown in Fig. 2. These curves seem to have a bending point at the mole ratio of 1 : 1, and probably another at about 2 : 1.

The DMF solution of nickel(II) chloride (curve a, Fig. 1) shows one low peak at 23800 cm^{-1}, a high peak at 16100 cm^{-1} with two shoulders at 17200 cm^{-1} and 15400—14300 cm^{-1} at its sides, and a small peak at 8050 cm^{-1}. The application of the band assignments proposed by Gutmann[6] for the DMF solution of the nickel(II) perchlorate-tetramethylammonium chloride system to our data

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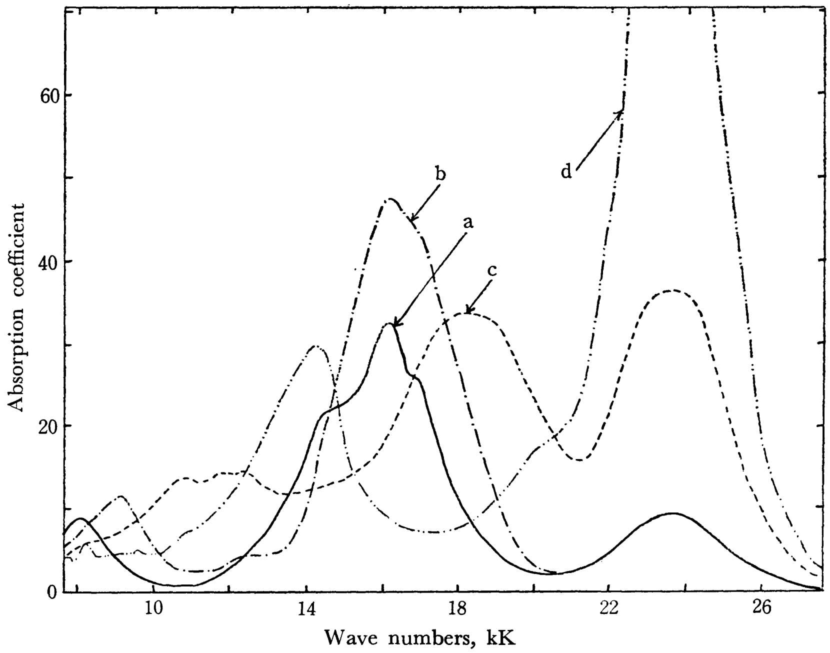

Fig. 1. Spectra of nickel(II) chloride - piperidine - DMF system. Ni^{2+} = 0.04 M, at 25°C. Piperidine/Ni^{2+}(M/M) are a) —— 0, b) —·— 0.45, c) ---- 6.0, d) —··— 101.

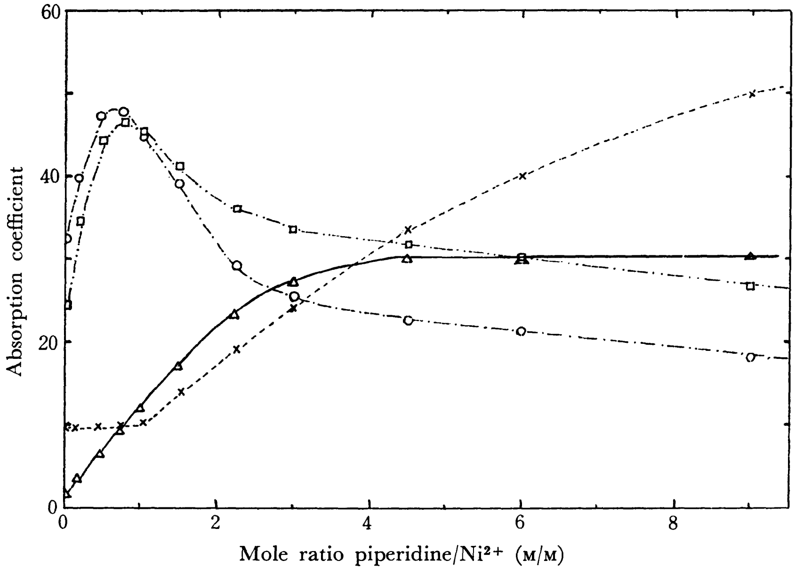

Fig. 2. The relation between the absorption coefficients at various wave numbers and the ratio of piperidine to nickel chloride in the DMF solutions. Ni^{2+} = 0.04 M, at 25°C.
a) --×-- 23800 cm^{-1}, b) —△— 19200 cm^{-1}, c) —··—□—··— 17200 cm^{-1} and
d) —·—○—·— 16100 cm^{-1}

indicates that the main peak at 16100 cm^{-1} and the shoulder at 17200 cm^{-1} are the $^3T_1(F) \rightarrow {}^3T_1(P)$ absorptions of the tetrahedral $[Ni(DMF)Cl_3]^-$ and $[Ni(DMF)_3Cl]^+$, while the smaller peak at 23800 cm^{-1} is the $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ absorption of such coexisting octahedral species as $[Ni(DMF)_4Cl_2]^0$ and $[Ni(DMF)_6]^{2+}$. Among these, the intensities of the peaks at about 16000—17000 cm^{-1} are far lower than the values to be expected from the $^3T_1(F) \rightarrow {}^3T_1(P)$ band of the pure tetrahedral species. This is probably due to the fact that a considerable amount of nickel is in the form of octahedral species in the solution.[7–15]

When lithium chloride was added to the solution, the intensity of the shoulder at 15400—14300 cm^{-1} increased very rapidly and the other peaks disappeared. Consequently, it can be inferred that this peak corresponds to the $^3T_1(F) \rightarrow {}^3T_1(P)$ transition band of the tetrahedral $[NiCl_4]^{2-}$.

The results shown in Fig. 2 indicate that the dominant complex species in the solution containing a little amine have the amine : nickel composition of 1 : 1. They are probably such slightly distored tetrahedral species as $[Ni(DMF)_2(pip)Cl]^+$ and $[Ni(DMF)(pip)Cl_2]^0$. When the concentration of amine in the solution is increased, the species with the amine : nickel composition of 2 : 1 begins to appear, and in the concentrated amine solution, this diamine complex becomes predominant. Therefore the original tetrahedral species change into pentacoordinate species; probably they are such distorted square-pyramidal species as $[NiCl_2(DMF)(pip)_2]^0$ or $[NiCl(DMF)_2(pip)_2]^+$. This fact also seems to be proved by the spectral data. The spectra of the penta-coordinate bis(diethyldithiophosphate)diethylamine nickel(II) complex, for example, shows main peaks at about 6500 cm^{-1} (12), 9500 cm^{-1} (26), 12700 cm^{-1} (131), 17400 cm^{-1} (30) and 21500 cm^{-1} (250) (where the approximate ε's are shown in parentheses).[16] As is shown in Fig. 1, the spectra of the sample solutions in this study, especially those of the solutions containing a large excess of amine, show peaks at 14300, 19200 and 23800 cm^{-1} (curve d, Fig. 1.), and their general features resemble those of the penta-coordinate species.

The precipitate obtained from the concentrated DMF solution containing nickel(II) chloride and piperidine was always $NiCl_2(pip)_2 \cdot \frac{1}{2}DMF$, even if a large excess of amine was added. Moreover, the morpholine adduct of nickel sulfate was found to be $Ni(morph)_2SO_4$ (where morph means morpholine).[17] Therefore, it may be concluded that at most two molecules of amine can coordinate to one central nickel ion. The solid $NiCl_2(pip)_2 \cdot \frac{1}{2}DMF$ and the complex solutions always show their magnetic moments between 3.0 and 3.3 B.M. Therefore, the possibility of the presence of the square-planar complex species can be rejected.

It is expected that the equilibrium of the system under consideration is affected by the nature of the chloride ion, piperidine, and DMF. When the nickel perchlorate, $Ni(ClO_4)_2 \cdot 6DMF$, was used in place of nickel chloride, the intensities of

TABLE 1. THE THERMAL CHANGE OF THE ABSORPTION SPECTRA OF NICKEL(II) CHLORIDE- PIPERIDINE-DMF SOLUTIONS

The concentration of nickel(II) ion is 0.04 M.

The numbers in the table are apparent molar extinction coefficients (ε), and the wave numbers of the maxima of the respective peaks (kK) are given in parentheses.

Piperidine/Ni^{2+} (M/M)	I			II			III		
	25°C	50°C	75°C	25°C	50°C	75°C	25°C	50°C	75°C
0	11.6	10.4 (23.8)	12.3	23.7	34.5 (17.2 sh)	43.2	31.4	41.4 (16.1)	50.0
0.45	10.0	10.3 (23.8)	9.10	36.8	42.5 (17.2 sh)	42.8	39.0	45.5 (16.1)	49.6
2.25	18.2	14.3 (23.8)	13.2	22.3	29.0 (17.2)	35.0	19.1	27.8 (15.9 sh)	33.2
6.0	37.4	27.5 (23.8)	21.6	18.0 (18.9)	23.4 (17.9)	28.6 (17.7)			
12.0	51.1	46.9 (23.7)	39.2	14.8 (20.0)	20.5 (19.1)	34.5 (18.5)	19.5	13.4 (14.3)	10.6
30	72.7	57.8 (23.7)	45.5	12.1 (20.0)	20.5 (19.3)	28.1 (17.8)	21.1	16.5 (14.3)	14.5
101	82.4	78.7 (23.7)	49.2	10.9	14.3 (20.0 sh)	12.3	26.3	23.9 (14.1)	13.6

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the peaks were extensively lowered. The change in the spectra according to the variation of the amine concentration is small, and the thermochromism phenomenon was not observed. Probably it is due to the high stability of the [Ni-$(DMF)_6]^{2+}$ ion.

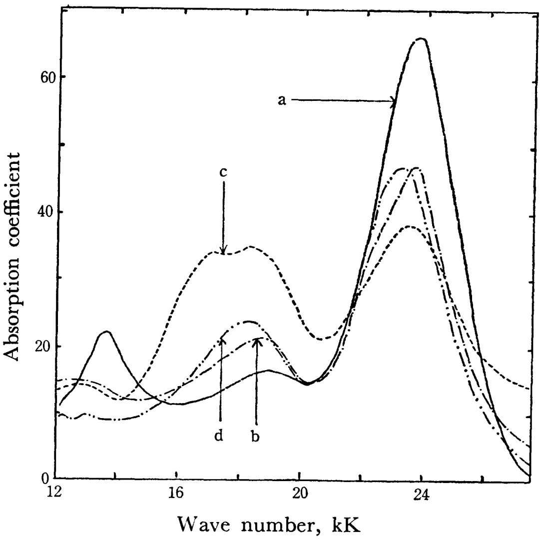

Fig. 3. The thermal change of the spectra of $NiCl_2$-piperidine-DMF system. The mole ratio of piperidine to nickel ion is 18.0, Ni^{2+}=0.04 M. a) —— 25°C, b) —·— 50°C, c) ---- 75°C and d) —··— 25°C, with 0.456 M LiCl.

Second, dimethylsulfoxide (DMSO) was used in place of DMF. The spectral change caused by the variation in the piperidine-nickel chloride mole ratio was examined. Although some spectral change according to the variation in the amine concentration was observed, it was not very remarkable, probably because of the high stability of the $[Ni(DMSO)_6]^{2+}$ ion which was dominant in the solution.

Third, various amines were added in place of piperidine to the DMF solution of nickel(II) chloride. When morpholine or pyrrolidine was used, the spectral change depending on the amine concentration was almost the same as when piperidine was used. On the other hand, in the case of using aniline, benzylamine or pyridine the change in the spectra depending on the amine concentration was not much. When diethylamine, di-*n*-butylamine, or isopropylamine was used, the spectral change and its dependence on the amine concentration were intermediate between these extremes. These results show that the amines which show the thermochromism are those which have a relatively high base dissociation constant, K_b, of about 10^{-3}. The K_b values of the amines which do not caused the thermochromism are much lower. The change in the spectra of nickel(II) chloride-DMF-piperidine solution with the variation in the temperature was then investigated; the results are shown in Fig. 3 and Table 1. The experimental results show that the spectra of a mixed sample at a high temperature resembles one which contains less amine, or one containing the same concentration of amine and an excess of chloride.

Therefore, the mechanism of the thermochromism of these complexes is explained the amine molecule in the complex species is replaced by a chloride ion or by a DMF molecule when the temperature is raised.

The enthalpy change of the reaction obtained from the relation between the $1/T$ of the solution and the absorption coefficients of the main peaks of the spectra are about 3 kcal/M, far lower than those of the tetrahedral$\rightleftarrows$octahedral or tetrahedral$\rightleftarrows$square planar change described in the literature.[2,4)]

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