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Calorimetric and Spectrophotometric Studies of Chloro Complexes of Nickel(II) and Zinc(II) Ions in *N,N*-Dimethylformamide

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Complexation of Ni(II) and Zn(II) with Cl^- ions has been studied by calorimetry and spectrophotometry in *N,N*-dimethylformamide (DMF) containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. Calorimetric titration curves obtained in each system were well-explained in terms of formation of $[MCl_n]^{(2-n)+}$ (n=1—4 and M^{2+}=Ni^{2+} or Zn^{2+}), and their formation constants, enthalpies and entropies were determined. Formation of the nickel(II) chloro complexes in DMF was also supported by spectrophotometry. In the nickel(II) chloride system, the stepwise enthalpy ΔH°_3 and entropy ΔS°_3 values are remarkably large and positive as compared with the ΔH°_n and ΔS°_n (n=1, 2, and 4) values. Individual electronic spectra of nickel(II) ion, $[NiCl]^+$ and $[NiCl_2]$ are significantly different in both intensities and peak positions from those of $[NiCl_3]^-$ and $[NiCl_4]^{2-}$ over the range 300—850 nm. These thermodynamic and spectrophotometric results were explained in terms of formation of the octahedral $[NiCl]^+$ complex as well as $[Ni(dmf)_6]^{2+}$ and of formation of the tetrahedral $[NiCl_3]^-$ and $[NiCl_4]^{2-}$ complexes in DMF. On the other hand, in the zinc(II) chloride system, the ΔS°_n (n=1 and 2) values are large and positive, but the ΔS°_n (n=3 and 4) values are significantly small. The corresponding ΔH°_n (n=1 and 2) values are positive but the ΔH°_n (n=3 and 4) values are significantly negative. It is thus postulated that the $[ZnCl_n]^{(2-n)+}$ (n=2 and 3) complexes have the tetrahedral coordination structure as well as the $[ZnCl_4]^{2-}$ complex in DMF.

In previous papers, we reported complexation between copper(II) and chloride ions in *N,N*-dimethylformamide (DMF),[1)] acetonitrile[2)] and dimethyl sulfoxide (DMSO),[3)] and in acetonitrile-DMF mixtures[4)] by calorimetry and spectrophotometry. The complexation between copper(II) and chloride ions is markedly enhanced in these aprotic solvents as compared with that in water, which may mainly be ascribed to weaker solvent-solvent interactions in the former solvents than in the latter, as already noted by Ahrland.[5)] The coordination structure around copper(II) ion changes in the course of the complexation of the metal ion with chloride ions, and the distorted octahedral $[Cu(dmf)_6]^{2+}$ and $[CuCl(dmf)_5]^+$ complexes and the distorted tetrahedral $[CuCl_3(dmf)]^-$ and $[CuCl_4]^{2-}$ complexes are formed in DMF according to an X-ray diffraction study.[6)]

It has been established from measurements of electronic spectra of the tetrahalogenonickelate(II) complexes that they have the tetrahedral structure both in crystal and in solution.[7—9)] The tetrahedral $[NiCl_4]^{2-}$ ion is slightly distorted in $(R_4N)_2NiCl_4$ (R=CH_3 or C_2H_5) but almost regular in the triphenylmethylarsonium compound.[10,11)] The tetrahedral $[ZnCl_4]^{2-}$ entity has also been found in M_2ZnCl_4 (M^+=K^+, Rb^+ and Cs^+) crystals,[12—16)] in $ZnCl_2$-KCl melts[17)] and in a highly concentrated zinc(II) chloride aqueous solution.[18)] Complexation between nickel(II) and halide ions has so far been studied by spectrophotometry in some aprotic solvents.[19,22)] However, no quantitative result of their formation constants and enthalpies has been obtained in aprotic solvents. On the other hand, complexation of zinc(II) with halide ions has been well studied by potentiometry and calorimetry in DMSO,[23,24)] although no reliable result has been reported in other aprotic solvents.[25)]

Although the donicity of DMF and DMSO is not significantly different,[26)] we pointed out in a previous paper[3)] that the complexation of copper(II) with chloride ions is markedly weaker in DMSO than in DMF due to stronger solvent-solvent interactions in the bulk of the former. In this respect, DMF can be a better solvent than DMSO for studying weak complexation of metal ions such as nickel(II) and zinc(II) with chloride ions.

In this work, we therefore investigated complexation of Ni(II) and Zn(II) with chloride ions in DMF by calorimetry and spectrophotometry using similar procedures to those employed in previous works,[1—4)] and thermodynamic quantities of formation of the metal chloro complexes were determined. Electronic spectra of individual nickel(II) chloro complexes in DMF were also estimated. On the basis of the thermodynamic and spectrophotometric results, changes in the coordination structure around nickel(II) and zinc(II) ions in the course of the complexation in DMF are discussed.

Experimental

Reagent. *Nickel(II) perchlorate DMF solvate* was obtained by dissolving nickel(II) perchlorate hexahydrate crystals in DMF and then by repeatedly recrystallizing from DMF in order to remove water, and was finally isolated by recrystallizing them from a 50% v/v DMF-acetone mixture. *Zinc(II) perchlorate DMF solvate* was prepared from zinc(II) perchlorate hexahydrate crystals by the similar procedure to that used for preparing nickel(II) perchlorate DMF solvate and was finally obtained by recrystallizing them from acetone. Each of nickel(II) and zinc(II) perchlorate DMF solvates thus prepared was dried at about 40 °C in a vacuum oven for several days and kept in a desiccator over P_2O_5. The value of x within $[M(ClO_4)_2\cdot(dmf)_x]$ (M^{2+}=Ni^{2+} or Zn^{2+}) was found to be 6, as already noted by Schneider,[27)] which was confirmed by gravimetry using dimethylglyoxime and by titration with EDTA for nickel(II) and zinc(II) perchlorate DMF solvates, respectively.

Tetraethylammonium perchlorate and *tetraethylammonium chloride* of reagent grade were once recrystallized from water and dried at 100 °C.

N,N-Dimethylformamide was dried for several weeks over molecular sieves 4A 1/16 and then distilled at 40 °C under a reduced pressure (260 Pa) and stored over the molecular sieves in a dark bottle with a P_2O_5 drying-tube.

Measurements. Calorimetric and spectrophotometric measurements were carried out in a room thermostated at (25.0±0.2) °C. All test solutions prepared contained 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium.

Calorimetric measurements were performed in a thermostated water-bath controlled at (25.000±0.007) °C. 100 cm^3 of a metal perchlorate DMF solution was placed in a Dewar vessel which was filled with dry nitrogen gas and prevented from moisture with a P_2O_5 drying-tube, and then it was titrated with 0.4 mol dm^{-3} $(C_2H_5)_4NCl$ DMF solution. The concentration of metal ions in the initial test solution was varied over the range 5—15 and 5—20 mmol dm^{-3} for nickel(II) and zinc(II) ions, respectively. Heats of complexation observed at each titration point were ranged 1—5 J with a certainty ±0.05 J and were corrected for heats of dilution of the titrant which were determined in advance by separate experiments by titrating a 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution with the 0.4 mol dm^{-3} $(C_2H_5)_4NCl$ titrant solution. All of the measurements were carried out by using a fully automatic on-line system for calorimetry developed in our laboratory.[28] Details of the data treatment have been described elsewhere.[2,3]

Electronic spectra were measured with a HITACHI 340 spectrophotometer (HITACHI) equipped with a PC-9801F2 computer (NEC) which recorded data every 2 nm over the wavelength range 300—850 nm. A flow cell with a light-path length of 0.5 cm was connected with a titration vessel through Teflon and glass tubes. 20 cm^3 of a metal perchlorate solution was placed in a vessel under a dry nitrogen atmosphere and then titrated with the 0.4 mol dm^{-3} $(C_2H_5)_4NCl$ titrant solution.

Results and Discussion

Nickel(II) Chloro Complexes. Calorimetric titration curves obtained in the nickel(II) chloride system with varying concentrations of the metal ion are depicted in Fig. 1. In the figure, enthalpies $\Delta H^\circ = -q/(\delta v C_{X,tit})$ were plotted against C_X/C_M, where q, δv, C_X and C_M stand for the heat evolved, the volume of an aliquot of the titrant added and the concentrations of chloride and nickel(II) ions in solution, respectively, at each titration point, and $C_{X,tit}$ denotes the concentration of chloride ion in the titrant solution.

Complexation between nickel(II) and chloride ions in DMF is rather weak because, as seen in Fig. 1, the titration curves were strongly dependent on the concentration of nickel(II) ion in the solutions and appreciable endothermicities were still observed at $C_X/C_M > 10$. The enthalpy ΔH° in each titration curve first decreased with increasing C_X/C_M and then increased after passing through a minimum. Each titration curve showed a maximum value around $C_X/C_M = 3$—7 and then decreased to approach $\Delta H^\circ = 0$.

The calorimetric data were analyzed by assuming the formation of plausible sets of nickel(II) chloro complexes and by simultaneously optimizing their formation constants and enthalpies by the least-squares method, the results being summarized in

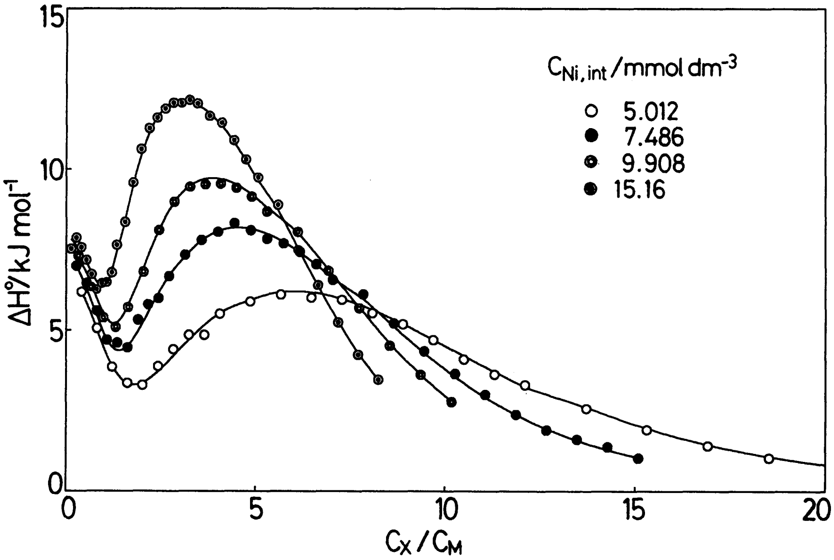

Fig. 1. Calorimetric titration curves of nickel(II) chloride DMF solutions containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25°C. Concentrations of nickel(II) ions, $C_{Ni,int}$/mmol dm^{-3}, in initial test solutions are given in the figure. The solid lines show the theoretical curves calculated by using the constants of the set (1—4) by calorimetry in Table 1.

Table 1. The Least-Squares Refinement of Overall Formation Constants, $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$, and Enthalpies, $\Delta H^\circ_{\beta n}/\mathrm{kJ\,mol}^{-1}$, of $[\mathrm{NiCl}_n]^{(2-n)+}$ in *N*,*N*-Dimethylformamide Containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C

	Calorimetry		Spectrophotometry	
	(1—4)	(1, 3, 4)	(1—4)	(1, 3, 4)
$\log\beta_1$	2.85(0.05)	2.72(0.03)	2.89(0.01)	2.97(0.01)
$\log\beta_2$	3.76(0.13)	—	3.75(0.05)	—
$\log\beta_3$	5.53(0.06)	5.56(0.04)	5.80(0.02)	5.93(0.01)
$\log\beta_4$	7.40(0.06)	7.19(0.03)	7.46(0.02)	7.54(0.01)
$\Delta H^\circ_{\beta 1}$	8.6(0.2)	9.4(0.1)	—	—
$\Delta H^\circ_{\beta 2}$	27.7(5)	—	—	—
$\Delta H^\circ_{\beta 3}$	90.6(9)	73.2(2.5)	—	—
$\Delta H^\circ_{\beta 4}$	77.2(0.8)	79.4(0.7)	—	—
$U^{a)}$	0.145	0.186	0.0165	0.0208
$R^{b)}$	0.0129	0.0146	0.0123	0.0138
$N^{c)}$	107	107	2100	2100

Values in parentheses refer to standard deviations. a) Error-square sum. b) The Hamilton *R*-factor. c) The number of data points.

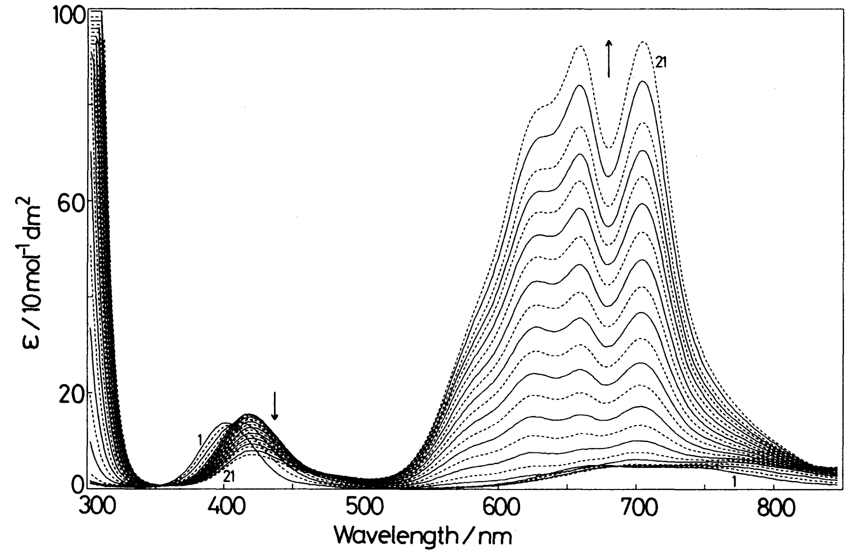

Fig. 2. Electronic spectra of nickel(II) chloride DMF solutions in the range 300—850 nm. Intensities are normalized with a unit concentration of the metal ion in solution. The spectra changed along the direction of the arrows with increasing C_X/C_M, the C_X/C_M value being varied from 0 of the solution No. 1 to 3.78 of the solution No. 21.

Table 1.

Among various sets examined, the set (1—4) assuming the formation of $[\mathrm{NiCl}_n]^{(2-n)+}$ (n=1—4) and the set (1,3,4) eliminating $[\mathrm{NiCl}_2]$ from the set (1—4) gave relatively small Hamilton *R*-factors (calculated by $\{\sum(q_{i,\mathrm{obsd}}-q_{i,\mathrm{calcd}})^2/\sum(q_{i,\mathrm{obsd}})^2\}^{1/2}$), 0.0129 and 0.0146, respectively. Other sets such as (1, 2), (1, 3), (1, 4), (1, 2, 3), and (1, 2, 4) gave much larger values of the Hamilton *R*-factor. As seen in Fig. 1 by the solid lines, theoretical titration curves calculated by using the constants of the set (1—4) in Table 1 well reproduced the experimental points over the whole range of C_X/C_M examined. However, the set (1, 3, 4) could also reproduce the experimental points rather satisfactorily because the Hamilton *R*-factor of the set (1, 3, 4) was close to that of the set (1—4), and therefore, the $\Delta H^\circ_{\beta 2}$ and $\Delta H^\circ_{\beta 3}$ values evaluated from the calculation by using the set (1—4) contained relatively large uncertainties.

Electronic spectra of nickel(II) chloride DMF solutions measured with varying concentrations of the ligand ion are depicted in Fig. 2. Each spectrum should be represented as the sum of electronic spectra of individual nickel(II) chloro complexes by taking into account the distribution of species in solution. Therefore, absorbance data obtained at selected 30 wavelengths in the range 300—850 nm were analyzed by assuming the formation of plausible sets of nickel(II) chloro complexes and their formation constants and molar extincition coefficients of each complex at relevant wavelengths were optimized by the least-squares method. Among various sets of complexes examined, again the sets (1—4) and (1, 3, 4), as seen in Table 1, gave relatively small Hamilton R-factors, 0.0123 and 0.0138, respectively. The same analysis was performed by using absorbance data at differently chosen 30 wavelengths in the range 300—850 nm in order to check the reproducibility of the formation constants thus evaluated, and the formation constants of each complex obtained by using the second set of data gave practically the same values as those evaluated by using the first set of absorbance data.

Since the formation constant log β_2 of the [NiCl$_2$] complex, as well as the log β_n (n=1, 3, and 4) values of the other three nickel(II) chloro complexes obtained by calorimetry and spectrophotometry is in very good agreement with each other, as seen in Table 1, we concluded that the formation of the [NiCl$_2$] complex should be taken into account together with the other three complexes in DMF. Consequently, we finally propose the formation of $[\mathrm{NiCl}_n]^{(2-n)+}$ (n=1—4) in DMF. Distribution of the nickel(II) chloro complexes in DMF is depicted in Fig. 3, which was calculated by using the formation constants of the set (1—4) by calorimetry in Table 1.

Zinc(II) Chloro Complexes. Calorimetric titration curves for the zinc(II) chloride system obtained by using similar procedure to that employed in the previous section are depicted in Fig. 4. In contrast to the nickel(II) chloride system, the titration curves showed only a slight dependence on the concentration of zinc(II) ion in solution. In addition, the ΔH° values approached zero at $C_X/C_M>4$, indicating that the zinc(II) chloro complexes are more stable than the nickel(II) chloro complexes in DMF.

The calorimetric data were analyzed by assuming the formation of plausible sets of mononuclear $[\mathrm{ZnCl}_n]^{(2-n)+}$($n\leq4$) complexes, and their formation constants and enthalpies were simultaneously refined. Among them, the sets (1—4) and (2—4) gave relatively small Hamilton R-factors, 0.0359 and 0.0500, respectively. The results of overall formation constants and enthalpies thus optimized for both sets are summarized

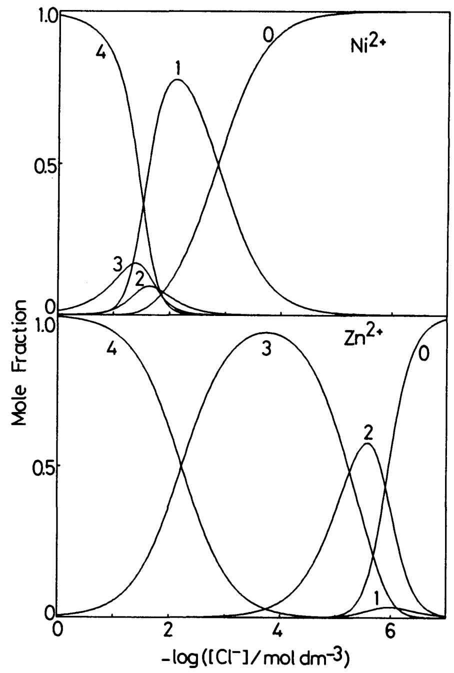

Fig. 3. Distribution of species of the chloro complexes of nickel(II) and zinc(II) ions in 0.4 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ DMF solution. The numbers represent n within $[\mathrm{MCl}_n]^{(2-n)+}$ ($\mathrm{M}^{2+}=\mathrm{Ni}^{2+}$ and Zn^{2+}).

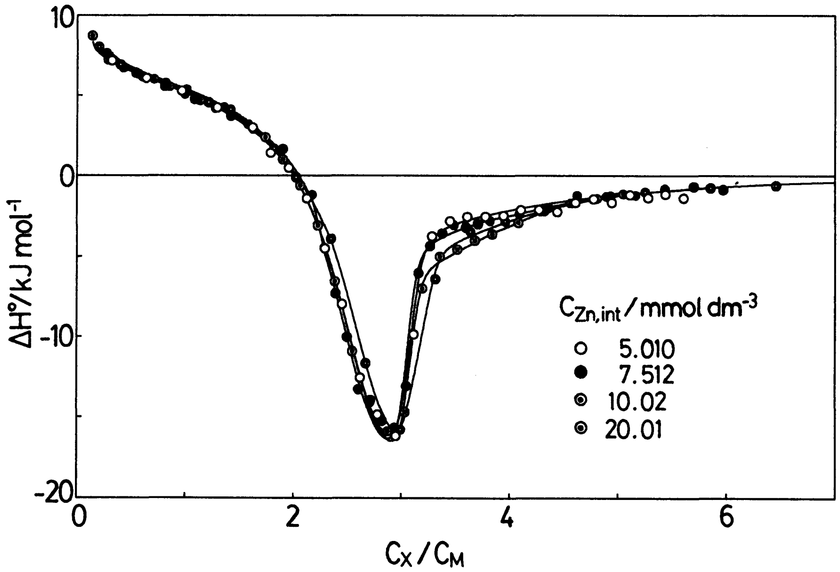

Fig. 4. Calorimetric titration curves of zinc(II) chloride DMF solutions containing 0.4 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ at 25°C. Concentrations of zinc(II) ions, $C_{\mathrm{Zn,int}}$/mmol dm^{-3}, in initial test solutions are given in the figure. The solid lines show the theoretical curves calculated by using the constants of the set (1—4) in Table 2.

Table 2. The Least-Squares Refinement of Overall Formation Constants, $\log(\beta_n/\text{mol}^{-n}\,\text{dm}^{3n})$, and Enthalpies, $\Delta H^\circ_{\beta n}/\text{kJ mol}^{-1}$, of $[\text{NiCl}_n]^{(2-n)+}$ in *N*,*N*-Dimethylforamide Containing $0.4\,\text{mol dm}^{-3}$ $(C_2H_5)_4NClO_4$ at 25 °C

	(1—4)	(2—4)
$\log\beta_1$	4.81(0.14)	—
$\log\beta_2$	11.80(0.16)	11.66(0.20)
$\log\beta_3$	17.06(0.24)	16.56(0.29)
$\log\beta_4$	19.28(0.26)	18.77(0.32)
$\Delta H^\circ_{\beta 1}$	14.7(2.9)	—
$\Delta H^\circ_{\beta 2}$	16.1(0.1)	16.4(0.2)
$\Delta H^\circ_{\beta 3}$	−1.5(0.1)	−1.6(0.1)
$\Delta H^\circ_{\beta 4}$	−9.4(0.2)	−9.4(0.2)
U[a]	0.287	0.558
R[b]	0.0359	0.0500
N[c]	118	118

Values in parentheses refer to standard deviations. a) Error-square sum. b) The Hamilton *R*-factor. c) The number of data points.

Table 3. Thermodynamic Quantities, $\log(K_n/\text{mol}^{-1}\,\text{dm}^3)$, $\Delta G^\circ_n/\text{kJ mol}^{-1}$, $\Delta H^\circ_n/\text{kJ mol}^{-1}$, and $\Delta S^\circ_n/\text{J K}^{-1}\,\text{mol}^{-1}$, for the Stepwise Formation of $[\text{NiCl}_n]^{(2-n)+}$ and $[\text{ZnCl}_n]^{(2-n)+}$ in *N*,*N*-Dimethylformamide (DMF) and Dimethyl Sulfoxide (DMSO) at 25 °C

	Nickel(II)	Zinc(II)	
	DMF	DMF	DMSO[a]
$\log K_1$	2.85	4.81	1.94
$\log K_2$	0.91	6.99	3.90
$\log K_3$	1.77	5.26	2.25
$\log K_4$	1.87	2.22	—
ΔG°_1	−16.3	−27.5	−11.1
ΔG°_2	−5.2	−39.9	−22.3
ΔG°_3	−10.1	−30.0	−12.0
ΔG°_4	−10.7	−12.7	—
ΔH°_1	8.6	14.7	22.3
ΔH°_2	19.1	1.4	0.8
ΔH°_3	62.9	−17.6	−10.2
ΔH°_4	−13.4	−7.9	—
ΔS°_1	84	142	112
ΔS°_2	82	139	77
ΔS°_3	245	42	9
ΔS°_4	−9	16	—
$\Delta G^\circ_{\beta 4}$[b]	−42.2	−110.0	—
$\Delta H^\circ_{\beta 4}$[b]	77.2	−9.4	—
$\Delta S^\circ_{\beta 4}$[b]	401	338	—

a) Ref. 24. b) Values of the overall formation of $[\text{MCl}_4]^{2-}$ ($M^{2+}=Ni^{2+}$ and Zn^{2+}).

in Table 2. Considering the appreciably smaller Hamilton *R*-factor of the set (1—4) than that of the set (2—4), we finally propose the formation of $[\text{ZnCl}_n]^{(2-n)+}$ (n=1—4) in DMF. Distribution of species of the zinc(II) chloro complexes in DMF calculated by using the formation constants of the set (1—4) in Table 2 is also depicted in Fig. 3. As seen in Fig. 3, the formation of $[\text{ZnCl}]^+$ is so weak that the $\Delta H^\circ_{\beta 1}$ value evaluated involves a rather large uncertainty.

Stepwise Thermodynamic Quantities. Stepwise formation constants, $\log(K_n/\text{mol}^{-1}\,\text{dm}^3)$, Gibbs energies, $\Delta G^\circ_n/\text{kJ mol}^{-1}$, enthalpies, $\Delta H^\circ_n/\text{kJ mol}^{-1}$, and entropies, $\Delta S^\circ_n/\text{J K}^{-1}\,\text{mol}^{-1}$, were then calculated, the results being summarized in Table 3.

Nickel(II) ion may be primarily coordinated with six DMF molecules in DMF as has been observed within the $\text{Ni(ClO}_4)_2\cdot(\text{dmf})_6$ solvate crystal,[27] because the absorption spectrum of nickel(II) perchlorate DMF solutions showed practically the same spectral profile as the reflectance spectrum of the solvate crystal. Zinc(II) ion is suggested to be coordinated with six solvent molecules in zinc(II) perchlorate DMSO solutions and in the $\text{Zn(ClO}_4)_2\cdot(\text{dmso})_6$ crystal.[29,30] Similarly, zinc(II) ion may be coordinated with six DMF molecules in zinc(II) perchlorate DMF solution as well as in the $\text{Zn(ClO}_4)_2\cdot(\text{dmf})_6$ crystal.[27] Chloride ions stepwise coordinate to Ni(II) or Zn(II) ion to yield the tetrahedral $[\text{MCl}_4]^{2-}$ ($M^{2+}=Ni^{2+}$ or Zn^{2+}) complex in the solutions[7,8] and thus all solvent molecules coordinating to the metal ions are liberated at the formation of the $[\text{MCl}_4]^{2-}$ complex. The structural change around Ni(II) and Zn(II) ions from octahedral to tetrahedral must thus take place at a certain step of complexation between the metal and chloride ions.

DMF molecules coordinating to metal ions lose their freedom of motion to a great extent. On the contrary, as the result of complexation between a metal and ligand ions, DMF molecules coordinating to the ions are liberated, the process being accompanied by an increase in the degree of freedom of the DMF molecules, i.e., the entropy change associated with the liberation of solvent molecules must be large and positive.

As seen in Table 3, the ΔH°_3 and ΔS°_3 values of stepwise formation of $[\text{NiCl}_3]^-$ are extremely large and positive as compared with the corresponding values of the $[\text{NiCl}_n]^{(2-n)+}$ (n=1, 2, and 4). Thus, DMF molecules coordinating to nickel(II) ion must be extensively liberated and the coordination number around the metal ion may be decreased at the formation of $[\text{NiCl}_3]^-$. Individual electronic spectra of $[\text{NiCl}_3]^-$ and $[\text{NiCl}_4]^{2-}$ in DMF show strong absorption bands over the range 550—750 nm which are not observed in the spectra of $[\text{NiCl}_n]^{(2-n)+}$ (n=0—2) as will be discussed in a later section. Thus, we propose the tetrahedral structure for the $[\text{NiCl}_3]^-$ complex as well as the tetrahedral $[\text{NiCl}_4]^{2-}$ complex. The trichloronickelate(II) complex may thus involve one DMF molecule within the coordination shell of the metal ion as represented by $[\text{NiCl}_3(\text{dmf})]^-$. The metal-solvent bond within the complex may be weak because the subsequent stepwise formation of $[\text{NiCl}_4]^{2-}$ shows even negative enthalpy and entropy changes.

On the other hand, in the zinc(II) chloride system, an extensive liberation of solvent molecules may take place at the formation of the $[\text{ZnCl}]^+$ complex because both ΔS_1° and ΔH_1° values shown in Table 3 are large and positive, and thus the coordination number around zinc(II) ion might be decreased within the $[ZnCl]^+$ complex. However, it is hard to conclude the coordination structure of $[ZnCl]^+$ (four-, five- or six-coordination) because the ΔS_n° (n=1 and 2) values involve rather large uncertainties due to the weak formation of the $[ZnCl]^+$ complex in DMF. The formation of $[ZnCl(dmso)_3]^+$ in DMSO[23,24] and of $[ZnCl(CH_3OH)_5]^+$ in methanol[31] has been suggested.

In contrast to large and positive ΔS_n° (n=1 and 2) values of formation of the $[ZnCl]^+$ and $[ZnCl_2]$ complexes, the ΔS_n° (n=3 and 4) values of $[ZnCl_3]^-$ and $[ZnCl_4]^{2-}$ are significantly small. The corresponding ΔH_n° (n=1 and 2) values are positive but the ΔH_n° (n=3 and 4) values are negative. The result indicates that the liberation of DMF molecules takes place to a great extent at each consecutive step of the formation of $[ZnCl]^+$ and $[ZnCl_2]$ but only to a small extent at the formation of $[ZnCl_3]^-$ and $[ZnCl_4]^{2-}$. It is thus expected that the $[ZnCl_2]$ and $[ZnCl_3]^-$ complexes may have a smaller coordination number than the $[Zn(dmf)_6]^{2+}$ and $[ZnCl]^+$ complexes in DMF. We therefore propose that the di- and trichloro complexes of Zn(II) have the tetrahedral four-coordinate structure in DMF, as represented by $[ZnCl_2(dmf)_2]$ and $[ZnCl_3(dmf)]^-$, respectively, which are similar to the tetrahedral $[ZnCl_4]^{2-}$ complex.

The metal-solvent interaction may be very weak within the $[ZnCl_n]^{(2-n)+}$ (n=2 and 3) complexes as indicated by negative ΔH_n° (n=3 and 4) values in spite of weaker metal-chloride bonds within higher complexes. The negative ΔH_n° value has also been observed at the stepwise formation of $[CuCl_4]^{2-}$,[1-4] as well as $[NiCl_4]^{2-}$ as discussed in a preceding section. The weakening of metal-solvent interactions may lead to an elongation of metal-solvent bonds within a metal complex. Structural evidence of elongation of a metal-solvent bond with an increase in the number of a ligand atom in the coordination shell which has a larger electron donicity than the solvent molecules has been obtained for the copper(II) chloro complexes in DMF[6] and the copper(II) and nickel(II) glycinato complexes in water[32-34] by means of X-ray diffraction.

Comparison between Formation of $[ZnCl_n]^{(2-n)+}$ in DMF and in DMSO. Complexation of zinc(II) with chloride ions has been studied in DMSO by Ahrland et al.,[23,24] and the formation of $[ZnCl_n]^{(2-n)+}$ (n=1—3) was indicated. According to their formation constants, the formation of $[ZnCl]^+$ is suppressed in DMSO as well as in DMF. It is noted that, as seen in Table 3, the formation constants of the zinc(II) chloro complexes in DMSO are markedly smaller than those in DMF, the result being mainly ascribed to smaller entropy changes in the former solvent than in the latter. When solvent molecules are liberated from the coordination sphere of an ion to enter the bulk solvent in the course of complexation, it is expected that the entropy of formation of a complex is positive. However, the positive entropy at the liberation of solvent molecules may be compensated for the structure formation of the solvent molecules in the bulk, if the solvent has rather strong solvent-solvent interactions. Since the donicity of DMF and DMSO is not largely different, the entropy increase at the liberation of solvent molecules from zinc(II) ion may be to a similar extent in both solvents. However, as described in a preceding paper,[3] DMSO has a long-range solvent-solvent interactions in the bulk than DMF has. Therefore, when solvent molecules subsequently enter the bulk phase, their degrees of freedom decrease more extensively in DMSO than in DMF, and thus, a less net entropy change of formation of a zinc(II) chloro complex results.

Electronic Spectra of Individual $[NiCl_n]^{(2-n)+}$ Complexes. Electronic spectra of individual nickel(II) chloro complexes were extracted from measured electronic spectra at varying concentrations of chloride ion in nickel(II) chloride DMF solutions over the wavelength range 300—850 nm, and the result is depicted in Fig. 5.

The nickel(II) DMF solvate complex shows an absorption peak at about 400 nm and very broad and very weak bands at 500—800 nm. The monochloronickel(II) complex shows a spectrum similar to that of the solvate complex, but the absorption peak at ca. 400 nm slightly shifted to a longer wavelength by ca. 20 nm than that of the solvate complex. The electronic spectra of these species are significantly different from the spectrum of $[NiCl_4]^{2-}$ which has the tetrahedral structure. Therefore, the $[NiCl]^+$ complex may have the octahedral type structure as well as $[Ni(dmf)_6]^{2+}$. The distorted octahedral structure of $[NiCl]^+$ in water has been suggested by X-ray diffraction.[35]

Although the spectrum of the dichloronickel(II) complex obtained is rather uncertain due to the weak formation of the complex in DMF, weak absorption bands ranging 400—600 nm are attributed to the complex, the spectrum being even slightly different from the spectra of $[Ni(dmf)_6]^{2+}$ or $[NiCl]^+$. It may be difficult to conclude the structure of the $[NiCl_2]$ complex from the spectral profile obtained here, but the different shape of the spectrum of the $[NiCl_2]$ complex suggests a different structure (a largely distorted six-coordinate or even a five-coordinate structure) of the complex from that of $[Ni(dmf)_6]^{2+}$ or $[NiCl(dmf)_5]^+$.

In the spectra of the tri- and tetrachloronickelate(II) complexes, absorption peaks appearing at 400—500 nm in the spectra of $[Ni(dmf)_6]^{2+}$, $[NiCl]^+$, and $[NiCl_2]$ almost disappear, while intense absorption peaks appear in the range 500—800 nm. The electronic spectrum of $[NiCl_4]^{2-}$ obtained has been ascribed to the absorption bands arising from the complex with the tetrahedral structure.[7-9] On the other hand, the electronic spectrum of trichloronickelate(II) complex has not been discussed in detail because overlapped spectra

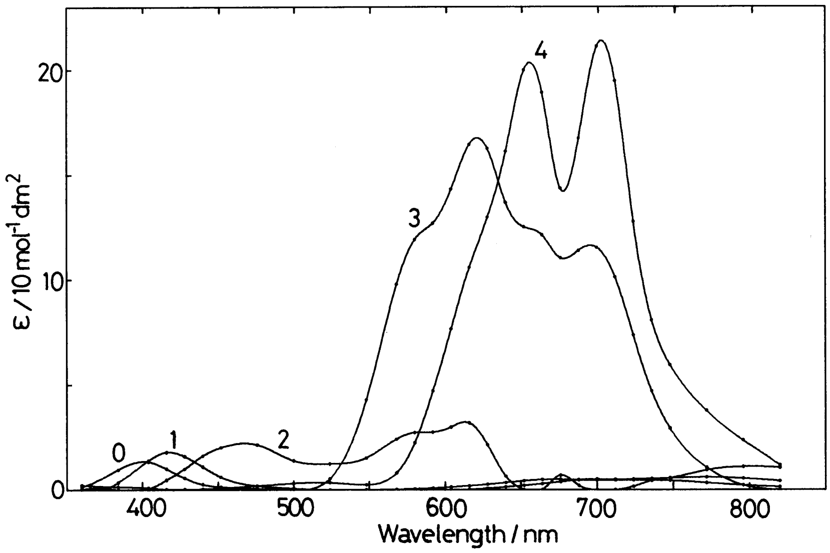

Fig. 5. Electronic spectra of individual nickel(II) chloro complexes in the range 350–850 nm obtained in 0.4 mol dm^{-2} $(C_2H_5)_4NClO_4$ DMF solution. The numbers represent n within $[NiCl_n]^{(2-n)+}$.

of $[NiCl_3]^-$ and $[NiCl_4]^{2-}$ are usually obtained in solution and it is difficult to extract the sole spectrum of $[NiCl_3]^-$. The electronic spectrum of $[NiCl_3]^-$ extracted in this work shows two peaks (ca. 620 and 695 nm) and two shoulders (ca. 575 and 660 nm). The similar intensities and peak positions of the bands of $[NiCl_3]^-$ to those of $[NiCl_4]^{2-}$ indicate that these complexes have the same type of coordination structure, i.e., the tetrahedral type structure, around the metal ion.

The similar spectrum to that of $[NiCl_3]^-$ in DMF has been observed for a nickel(II) chloride acetonitrile solution with the C_X/C_M ratio of 4,[21] the $[NiCl_3]^-$ complex probably being present as the main species in the acetonitrile solution. Similar electronic spectra of $[NiCl_3]^-$ observed in DMF and in acetonitrile in spite of a stronger donicity of DMF than that of acetonitrile suggest that the metal-solvent bonds within the $[NiCl_3(dmf)]^-$ and $[NiCl_3(acetonitrile)]^-$ complexes are so weak that the electronic spectra of the complex may not be appreciably influenced by the difference of the solvent molecules. Similar electronic spectra have also been obtained for the $[CuCl_3]^-$ complex in DMF and in acetonitrile.[1,2]

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