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Calorimetric and Spectrophotometric Studies on Formation of Copper(II) Chloride Complexes in *N,N*-Dimethylformamide

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Formation of copper(II) chloride complexes has been studied by calorimetric and spectrophotometric titrations in *N,N*-dimethylformamide (DMF) containing different ionic media, 0.1 and 0.2 mol dm^{-3}$(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ at 25 °C. In all the DMF solutions examined, calorimetric and spectrophotometric titration curves were well explained in terms of formation of a series of four mononuclear complexes, $[CuCl_n]^{(2-n)+}$(n=1—4), and formation constants, enthalpies and entropies of formation of the complexes were determined. Formation constants were determined by both calorimetry and spectrophotometry and most of the values obtained by the different methods were in good agreement each other. Calorimetric titration curves obtained in 0.1 and 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic media were practically the same, but they significantly differed from those obtained in 1 mol dm^{-3} $LiClO_4$ ionic medium, the result indicating that the formation of copper(II) chloride complexes was more favored in the former ionic media than in the latter. Stepwise enthalpies of formation were positive for $[CuCl]^+$, $[CuCl_2]$, and $[CuCl_3]^-$, but negative for $[CuCl_4]^{2-}$ in the $(C_2H_5)_4NClO_4$ DMF solutions, while the values in the 1 mol dm^{-3} $LiClO_4$ DMF solution were more negative by 6—8 kJ mol^{-1} than the respective values in the $(C_2H_5)_4NClO_4$ solutions. A significant difference was also found for stepwise entropies of formation of copper(II) chloride complexes between the ionic media. The ionic medium effect on the formation of the complexes found was ascribed to ion pairing of LiCl in the 1 mol dm^{-3} $LiClO_4$ DMF solution, ion pairing of $(C_2H_5)_4NCl$ being insignificant in the $(C_2H_5)_4NClO_4$ DMF solutions used. A largely negative ΔH_4° and a small ΔS_4° values in the $(C_2H_5)_4NClO_4$ DMF solutions suggested that solvation of the $[CuCl_3]^-$ complex was not strong, and thus, release of solvent molecules from the $[CuCl_3]^-$ complex did not play an important role for the formation of $[CuCl_4]^{2-}$. Therefore, the enthalpy and entropy of formation of $[CuCl_4]^{2-}$ were mainly attributable to those of desolvation of chloride ions and of bond formation between Cl^- and $[CuCl_3]^-$. The $[CuCl_4]^{2-}$ complex may have no DMF molecules in the primary coordination sphere of the central metal ion within the complex. Electronic spectra of individual copper(II) chloride complexes were determined from spectra at various concentrations of chloride ions by using the formation constants obtained.

Although a number of studies have so far been carried out for electronic spectra of copper(II) chloride complexes in both crystalline and solution states, only a few quantitative investigations were examined for the formation of the complexes in solutions. Khan and Schwing-Weill[1)] reported the formation constants and electronic spectra of $[CuCl_n]^{(2-n)+}$ (n=1—4) in aqueous solution containing 5 mol dm^{-3} $Na(ClO_4,Cl)$ as a constant ionic medium. Ellev *et al.*[2,3)] also spectrophotometrically studied the complex formation reactions in *N,N*-dimethylformamide (DMF) and dimethyl sulfoxide (DMSO) containing 1 mol dm^{-3} $LiClO_4$ and in propylene carbonate containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$. Manahan and Iwamoto[4)] investigated the formation and electronic spectra of the copper(II) chloride complexes in acetonitrile by a combination of spectrophotometric and electrochemical methods. In weaker donor solvents such as acetonitrile and propylene carbonate, a series of four mononuclear complexes, $[CuCl_n]^{(2-n)+}$ (n=1—4), were found. However, the only formation of $[CuCl]^+$, $[CuCl_3]^-$, and $[CuCl_4]^{2-}$ were concluded in stronger donor solvents such as DMSO and DMF.

The formation of copper(II) chloride complexes was more favorable in aprotic solvents than in water, and it was more enhanced in weaker donor solvents. Although the formation constants of the $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes have been determined by some authers,[1-4)] no values of enthalpy and entropy of formation of the complexes have been reported.

The aim of our present study is to elucidate interactions between copper(II) and chloride ions and between the ions and solvent molecules in *N,N*-dimethylformamide from enthalpic and entropic points of view. The complex formation reactions of copper(II) with chloride ions in DMF containing various inert ionic media were investigated by calorimetry and formation constants, and enthalpies and entropies of formation of the complexes were determined. Spectrophotometric measurements were also carried out to determine the formation constants and electronic spectra of the individual copper(II) chloride complexes.

Experimental

Reagents. *Copper(II) perchlorate* was prepared from copper(II) oxide and perchloric acid of super special reagent grade. The copper(II) perchlorate thus prepared was recrystallized three times from water. The copper(II) perchlorate hexahydrate, $Cu(ClO_4)_2 \cdot 6H_2O$, thus obtained were dried in a vacuum oven at 70 °C for 48 hours.

Copper(II) perchlorate DMF solvates, $Cu(ClO_4)_2(DMF)_x$, were prepared by dissolving copper(II) perchlorate hexahydrate crystals in DMF and recrystallized six times from DMF and finally from a DMF-acetone mixture. The crystals thus obtained involved four to six DMF molecules per copper(II) ion, as already noted by Schneider,[5)] and were dried at 40 °C in a vacuum oven for several days and kept in a vacuum desiccator over P_2O_5. Electrogravimetrical analysis showed that the copper(II) perchlorate DMF solvate crystals finally obtained were $Cu(ClO_4)_2(DMF)_4$.

Lithium perchlorate and *lithium chloride* were recrystallized from water and dried as described elsewhere.[6)]

Tetraethylammonium perchlorate and *tetraethylammonium chloride* of reagent grade were used without further purification 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 (2 mmHg) and stored over the molecular sieves in a dark bottle with a P_2O_5 guard-tube. The residual water determined by Karl Fisher tests was less than 220 ppm.

As *N*,*N*-dimethylformamide is hygroscopic, all test solutions were prepared in a dry box over P_2O_5 and under an atmosphere of dried nitrogen gas.

Measurements. Calorimetric measurements were carried out in a thermostated bath controlled at (25.000±0.007) °C placed in a room thermostated at (25.0±0.2) °C. Throughout the calorimetric titrations, an ionic medium was kept constant by using either $(C_2H_5)_4NClO_4$ (0.1 and 0.2 mol dm^{-3}) or $LiClO_4$ (1 mol dm^{-3}). A 100 cm^3 of copper(II) perchlorate solution was first placed in a Dewar vessel, which was filled with nitrogen gas and prevented from moisture with a P_2O_5 guard-tube, and then titrated with a relevant chloride solution. The titrants employed were $(C_2H_5)_4NCl$ (0.1 and 0.2 mol dm^{-3}) and LiCl (1 mol dm^{-3}) solutions. The heat of dilution of chloride ions was separately determined by titrating either $(C_2H_5)_4NClO_4$ or $LiClO_4$ solution without copper(II) perchlorate with the relevant titrant solutions. The values were 0.06, 0.08, and 0.28 J cm^{-3} per the addition of a unit volume of the titrants, 0.1 and 0.2 mol dm^{-3} $(C_2H_5)_4NCl$ and 1 mol dm^{-3} LiCl, respectively. A heat q of reaction evolved at each point of titration was ranged −5 to 5 J with a certainty ±0.05 J. Calorimetric measurements were carried out by using a fully automatic on-line system as described in a previous paper.[6]

Spectrophotometric measurements were carried out in DMF solutions containing the same ionic media as those employed in calorimetric measurements. A flow cell with a light-path length of 0.5 cm was connected with a titration vessel through teflon and glass tubes. A 15 cm^3 of $Cu(ClO_4)_2$ DMF solution was placed in a vessel under a nitrogen atmosphere and then titrated with either a tetraethylammonium or a lithium chloride solution. Electronic spectra were measured with a HITACHI 340 spectrophotometer (HITACHI) equipped with a JEC 6 electronic computer (JEOL) which recorded data at selected wavelengths.

Analysis of Calorimetric and Spectrophotometric Data. A heat q_i evolved at a titration point i is represented by Eq. 1 by using formation constants β_n and overall enthalpies $\Delta H^\circ_{\beta_n}$ of formation of the $[CuCl_n]^{(2-n)+}$ complexes.

$$q_i = -(V_i\sum_n\beta_n\Delta H^\circ_{\beta_n}m_ix_i^n - V_{i-1}\sum_n\beta_n\Delta H^\circ_{\beta_n}m_{i-1}x_{i-1}^n), \quad (1)$$

where V denotes the volume of a test solution, and m and x stand for concentrations of free copper(II) and chloride ions, respectively, which are related to their total concentrations C_M and C_X according to the mass-balance equations 2 and 3:

$$C_M = \sum_n\beta_nm_ix_i^n + m \quad (2)$$

$$C_X = \sum_n n\beta_nm_ix_i^n + x. \quad (3)$$

The formation constants and enthalpies were determined by minimizing the error-square sum, $U=\sum_i(q_{i,\text{obsd}}-q_{i,\text{calcd}})^2$ by using the program KALORI.[7]

Absorbance A_{ij} at a titration point i and a selected wavelength λ_j is represented by Eq. 4 by using the formation constants and molar extinction coefficients $\varepsilon_n(\lambda_j)$ of the $[CuCl_n]^{(2-n)+}$ complexes.

$$A_{ij} = \sum_n\varepsilon_n(\lambda_j)\beta_nm_ix_i^n \quad (\beta_0=1), \quad (4)$$

where the wavelengths λ_j selected in the present work were 262, 270, 280, 290, 300, 310, 320, 370, 410, and 440 nm. The formation constants and molar extinction coefficients were determined by minimizing the error-square sum, $U=\sum_i\sum_j(A_{ij,\text{obsd}}-A_{ij,\text{calcd}})^2$ by using the program SPEC.

Results and Discussion

Calorimetric titration curves obtained in 1 mol dm^{-3} $LiClO_4$ ionic medium are depicted in Fig. 1. The enthalpy ΔH°/kJ mol^{-1} per the addition of a unit mole of chloride ions at each titration point was plotted against the ratio C_X/C_M, where C_X and C_M denote total concentrations of chloride and copper(II) ions, respectively, in a solution. In DMF solution with the same ionic medium, Ellev *et al.*[2] reported the only formation of $[CuCl]^+$, $[CuCl_3]^-$, and $[CuCl_4]^{2-}$ from spectrophotometric measurements. Therefore, the formation constants and enthalpies were first optimized by assuming the formation of the three copper(II) chloride complexes. The theoretical curves calculated by using the constants thus obtained are illustrated by broken lines in Fig. 1, which appreciably deviated from experimental curves, especially in the range C_X/C_M=0.5—2. This indicated that the formation of the $[CuCl_2]$ complex can not be neglected in the DMF solution. Subsequently, we assumed the formation of four complexes, $[CuCl_n]^{(2-n)+}$ (n=1—4), and then the experimental points fit well the curves (solid lines) calculated by using the constants of the four complexes. A comparison for the formation constants and enthalpies obtained by different assumptions of three (case 1, n=1, 3, and 4) and four (case 2, n=1, 2, 3, and

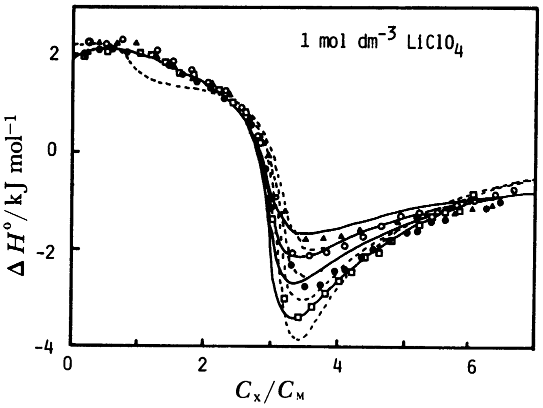

Fig. 1. Calorimetric titration curves of copper(II) chloride DMF solutions containing 1 mol dm^{-3} $LiClO_4$. Initial concentrations of copper(II) perchlorate (C_M/mmol dm^{-3}): 25.40 (▲), 35.63 (○), 48.36 (●) and 74.73 (□).

TABLE 1. THE LEAST-SQUARES REFINEMENT OF FORMATION CONSTANTS, β_n/mol^{-n}dm^{3n} AND ENTHALPIES, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, OF COPPER(II) CHLORIDE COMPLEXES IN DMF CONTAINING 1 mol dm^{-3} LiClO$_4$ AT 25 °C

	Case 1	Case 2
β_1	$(1.86\pm1.5)\times10^4$	$(6.20\pm1.3)\times10^3$
β_2	—	$(1.25\pm0.01)\times10^7$
β_3	$(1.85\pm1.6)\times10^{10}$	$(3.54\pm0.5)\times10^{10}$
β_4	$(2.66\pm2.4)\times10^{11}$	$(2.60\pm0.3)\times10^{11}$
$\Delta H^\circ_{\beta_1}$	(2.2 ± 0.1)	(1.84 ± 0.05)
$\Delta H^\circ_{\beta_2}$	—	(5.41 ± 0.25)
$\Delta H^\circ_{\beta_3}$	(4.8 ± 0.2)	(4.42 ± 0.06)
$\Delta H^\circ_{\beta_4}$	$-(6.5\pm0.9)$	$-(9.90\pm0.6)$
U[a)]	13.1	1.1
N[b)]	92	92

a) Error-square sum, b) The number of calorimetric data points.

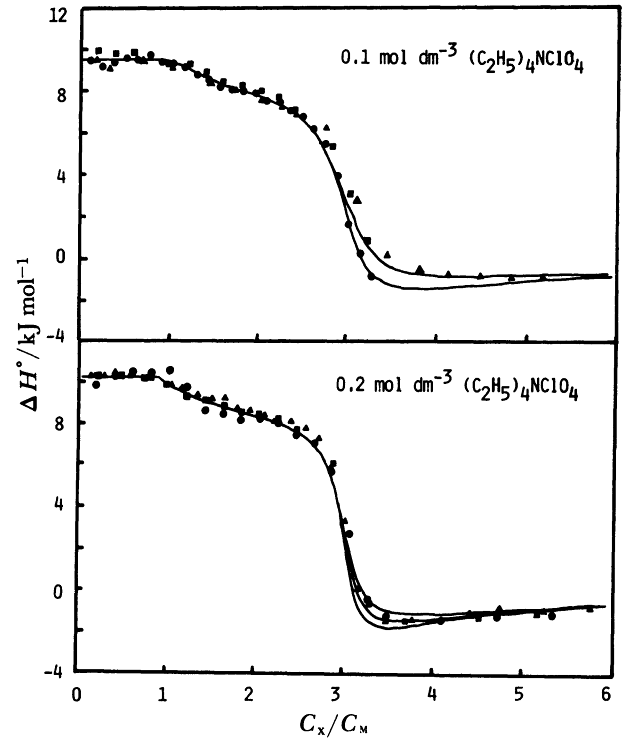

Fig. 2. Calorimetric titration curves of copper(II) chloride DMF solutions containing 0.1 and 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$. Initial concentrations of copper(II) perchlorate (C_M/mmol dm^{-3}): 7.30 (■), 15.20 (▲) and 20.25 (●) in 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution, and 9.80 (●), 14.66 (■) and 19.93 (▲) in 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution.

4) copper(II) chloride complexes is shown in Table 1. The error-square sum U and standard deviations were much smaller in case 2 than in case 1. Thus, we concluded that a series of four mononuclear complexes, $[CuCl_n]^{(2-n)+}$ (n=1—4), were formed in the 1 mol dm^{-3} LiClO$_4$ DMF solution.

Calorimetric titration curves obtained in DMF solutions containing 0.1 and 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ are depicted in Fig. 2. Experimental points well fell on the curves (solid lines) calculated by using the formation constants in Table 2 and the enthalpies in Table 3 of the four mononuclear copper(II) chloride complexes in each $(C_2H_5)_4NClO_4$ DMF solution.

The stepwise formation constants obtained by calorimetry and spectrophotometry in each ionic medium are compared in Table 2. In all cases, the error-square sum U became small enough to explain experimental data in terms of the formation of $[CuCl_n]^{(2-n)+}$ (n=1—4). Standard deviations for each constant were not well evaluated because the product of diagonal elements of the error matrix exceeded 10^{-75}, which was the lowest limit of the computer ability employed. However, a reasonable agreement was obtained between the formation constants determined by calorimetry and spectrophotometry.

The overall enthalpies of formation of the complexes obtained by calorimetry are listed in Table 3, together with the enthalpy values obtained by employing the formation constants determined by spectrophotometry for the analysis of the calorimetric data. Except for the $\Delta H^\circ_{\beta_4}$ value in the 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium, all enthalpy values obtained by the both estimations were in good agreement. In the 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium, test solutions were titrated with a 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ solution, and thus, the formation of the $[CuCl_4]^{2-}$ complex might be insufficient even after the addition of a large volume of the titrant. Therefore, the $\Delta H^\circ_{\beta_4}$ value thus estimated may involve a rather large uncertainty.

Formation of Copper(II) Chloride Complexes in $(C_2H_5)_4NClO_4$ Ionic Media. It is obvious from similar calorimetric titration curves in Fig. 2 that thermodynamic quantities in the 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium were not appreciably different from those in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium.

Thermodynamic quantities, ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1}, and ΔS°_n/J K^{-1}mol^{-1}, for stepwise reactions, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4), in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ ionic medium are summarized in Table 4, together with those in the 1 mol dm^{-3} LiClO$_4$ ionic medium.

Copper(II) ions are more strongly solvated in DMF than in water,[8)] as is expected from a stronger donor property of DMF (the donor number (D_N)=26.6) than that of water (D_N=18.0).[9)] On the other hand, chloride ions are less strongly solvated in DMF than in water.[10)] The change in enthalpy of solvation of Cl$^-$ between the solvents is much less significant than that of Cu^{2+}. Therefore, the formation of copper(II) chloride complexes should be less favored in DMF than in water from the enthalpic point of view. However, the reverse was the case, that is, the formation of copper(II) chloride complexes was more favorable in DMF than in water. The facts indicated that the formation of the complexes was more favored by the entropy term in DMF than in water, although the enthalpies and entropies of formation of the complexes in water have not been known.

According to Ahrland,[11)] such a more favorable en-

Table 2. Stepwise formation constants, K_n/mol^{-1} dm^3, for the reactions, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4), obtained in N,N-dimethylformamide containing various ionic media at 25 °C

	0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$		0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$		1 mol dm^{-3} $LiClO_4$	
	Cal[a)]	Spec[b)]	Cal[a)]	Spec[b)]	Cal[a)]	Spec[b)]
$\log K_1$	7.60	7.16	6.79	5.72	3.79	4.26
$\log K_2$	3.95	4.15	4.54	4.19	3.31	3.44
$\log K_3$	3.67	3.92	4.00	4.02	3.45	4.14
$\log K_4$	1.12	1.35	1.52	1.60	0.86	0.98
U[c)]	0.25	0.238	0.52	0.084	1.13	0.131
N[d)]	56	210	73	210	92	340

a) Calorimetry, b) Spectrophotometry, c) Error-square sum, d) The number of data points.

Table 3. The overall enthalpies, $\Delta H^\circ_{\beta n}$/ kJ mol^{-1}, for the reactions, $Cu^{2+}+nCl^-=CuCl_n^{(2-n)+}$ (n=1—4), obtained in N,N-dimetylformamide containing various ionic media at 25 °C

	0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$		0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$		1 mol dm^{-3} $LiClO_4$	
	Cal[a)]	Spec[b)]	Cal[a)]	Spec[b)]	Cal[a)]	Spec[b)]
$\Delta H^\circ_{\beta 1}$	9.5	9.6(0.07)	10.3	10.3(0.1)	1.84	1.99(0.04)
$\Delta H^\circ_{\beta 2}$	19.3	19.4(0.15)	20.0	20.4(0.2)	5.41	4.32(0.07)
$\Delta H^\circ_{\beta 3}$	25.4	25.1(0.13)	27.3	27.4(0.1)	4.42	4.67(0.05)
$\Delta H^\circ_{\beta 4}$	6.5	15.0(0.9)	19.7	19.8(0.2)	−9.89	−8.60(0.11)

Values in parentheses refer to standard deviations. a) Calorimetry, b) Enthalpy values evaluated by using formation constants obtained by spectrophotometry in Table 2.

Table 4. Thermodynamic quantities, ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1} and ΔS°_n/J K^{-1} mol^{-1}, for stepwise reactions, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4), in N,N-dimethylformamide solution at 25 °C

	0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$	1 mol dm^{-3} $LiClO_4$
ΔG°_1	−38.8	−21.6
ΔG°_2	−25.9	−18.9
ΔG°_3	−22.8	−19.7
ΔG°_4	−8.7	−5.0
ΔH°_1	10.3	1.8
ΔH°_2	9.7	3.6
ΔH°_3	7.3	−1.0
ΔH°_4	−8.1	−14.3
ΔS°_1	165	79
ΔS°_2	120	75
ΔS°_3	101	63
ΔS°_4	2	−31

tropy of complex formation reactions of metal ions in DMF than in water is not unexpected and it can be interpreted in terms of both different solvation structure of metal ions and different solvent structure between solvent molecules in DMF from those in water. In water, water molecules leave a hydrate structure and then enter another fairly well-ordered structure of bulk water. The entropy changes at the two stages compensate each other to yield a modest entropy gain, or even a net loss if the entropy change connected with the coordination of the ligand is not so favorable. In DMF, solvent molecules leave a solvate structure which may be more strictly ordered than the corresponding hydrate and then enter a bulk solvent that is fairly unstructured. Thus, a very large entropy gain may result.

Largely positive entropies ΔS°_n of formation were observed for the formation reactions of the $[CuCl_n]^{(2-n)+}$ (n=1—3) complexes in DMF containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$, which therefore suggested that the metal and chloride ions in the solution were extensively desolvated in the course of the formation of the complexes.

On the other hand, the ΔS°_4 value for the reaction, $CuCl_3^-+Cl^-=CuCl_4^{2-}$, was almost zero and remarkably smaller than the ΔS°_n (n=1—3) values in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution, indicating that the entropy gain due to desolvation of the $[CuCl_3]^-$ complex in the course of the formation of $[CuCl_4]^{2-}$ may not be significant if the extent of entropy loss accompaning the coordination of the ligand is similar at each consecutive step of the formation reactions, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4).

A large difference between the enthalpies of formation of the copper(II) chloride complexes was also observed. The ΔH°_4 value was negative in contrast to the ΔH°_n (n=1—3) values which were all positive. The $[CuCl_3]^-$ complex may not be strongly solvated in DMF, and thus, DMF molecules weakly solvating the complex may be exothermically replaced with a chloride ion in the course of the formation of the $[CuCl_4]^{2-}$ complex. Consequently, it was suggested that the $[CuCl_4]^{2-}$ complex has no solvent molecules in the primary coordination sphere of copper(II) ion within the complex.

Formation of Copper(II) Chloride Complexes in $LiClO_4$ Ionic Medium. In the 1 mol dm^{-3} $LiClO_4$ DMF solution, the ΔH°_n value of formation of the $[CuCl_n]^{(2-n)+}$

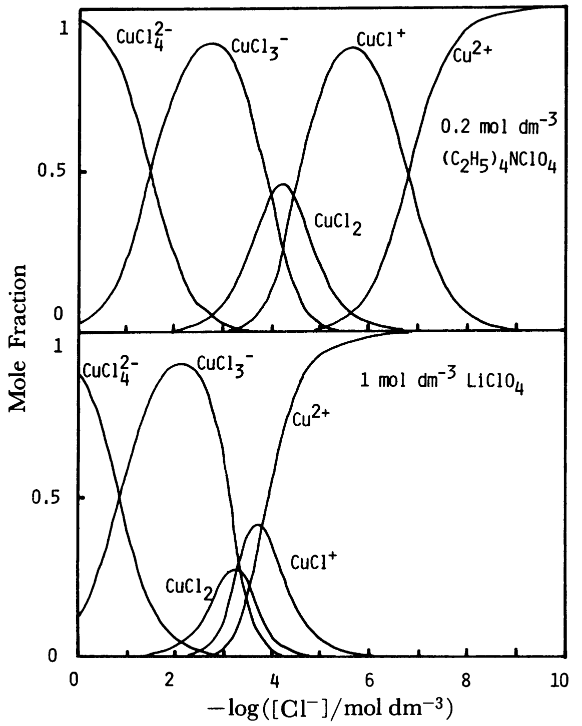

Fig. 3. Distribution of the copper(II) chloride complexes in 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMF solutions, calculated by using the formation constants obtained by calorimetry.

complex was slightly positive for $n=1$ and 2, slightly negative for $n=3$ and largely negative for $n=4$, all the enthalpy values being more negative by 6—8 kJ mol^{-1} than the respective values in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution. As to the entropy of formation of $[CuCl_n]^{(2-n)+}$ in the 1 mol dm^{-3} $LiClO_4$ DMF solution, the ΔS°_n value was positive for $n=1$—3, but was negative for $n=4$, and all the values were significantly smaller than the respective entropy values in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution. Consequently, the formation of copper(II) chloride complexes was less favored in the 1 mol dm^{-3} $LiClO_4$ than in the $(C_2H_5)_4NClO_4$ DMF solutions as illustrated by the distribution curves in Fig. 3.

It has been reported that lithium ions associate with perchlorate[12] and chloride[13—15] ions to form solvent-shared and contact ion pairs in DMF solutions. Since it is expected that lithium ions are strongly solvated with DMF molecules,[16] ionic association of $LiClO_4$ may not be significant in solutions less than 2 mol dm^{-3} of the salt.[12] However, LiCl forms ion pairs even in relatively dilute solutions, the K_1 value for the formation of the ion pairs being reported to be 35 by conductivity[14] and 4 by emf measurements.[15] From these constants, we can estimate that 25—85% of chloride ions in the 1 mol dm^{-3} LiCl DMF solution may form ion pairs.

TABLE 5. ENTHALPIES OF SOLUTION OF $(C_2H_5)_4NCl$ CRYSTALS IN *N,N*-DIMETHYLFORMAMIDE SOLUTION AT 25 °C

Ionic Medium	ΔH°_S/kJ mol^{-1}
Pure DMF	7.3
0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$	9.7
0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$	10.3
1 mol dm^{-3} $LiClO_4$	18.7

Enthalpies of solution of $(C_2H_5)_4NCl$ crystals measured in DMF solutions of various ionic media are listed in Table 5. The enthalpy of solution of $(C_2H_5)_4NCl$ in 1 mol dm^{-3} $LiClO_4$ DMF solution was more positive by 8—9 kJ mol^{-1} than the values in 0.1 and 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solutions. The difference may be mainly attributable to the enthalpy of formation of ion pairs between lithium and chloride ions in the 1 mol dm^{-3} $LiClO_4$ DMF solution, although enthalpies of solution of the crystals may vary depending on ionic media of the solutions examined. In fact, the enthalpy of solution of $(C_2H_5)_4NCl$ in the 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution was slightly more positive than that in pure DMF solution, but was practically the same as that in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution. The positive enthalpy of formation of the LiCl ion pair has also been suggested from concentration dependence of heat of solution of LiCl in DMF.[13]

Considering that $K_1>1$ and $\Delta H^\circ_{ip}>0$ for the formation of ion pairs between lithium and chloride ions in DMF, we can expect the relations between the thermodynamic quantities, ΔG°_{ip}, ΔH°_{ip}, and ΔS°_{ip}, for the ion pairs formation reaction, $Li^+ + Cl^- = LiCl$, in DMF as follows: $\Delta G^\circ_{ip}<0$ and $T\Delta S^\circ_{ip}>\Delta H^\circ_{ip}>0$. Therefore, the entropy of formation which may be mainly owing to desolvation of DMF molecules from lithium ions plays an important role for the formation of LiCl ion pairs in DMF.

Accordingly, the complex formation reactions between copper(II) and chloride ions should be accompanied by dissociation of LiCl ion pairs in 1 mol dm^{-3} $LiClO_4$ DMF solution. The enthalpy of dissociation of LiCl was negative, which led to more negative ΔH°_n ($n=1$—4) values of formation of $[CuCl_n]^{(2-n)+}$ in the 1 mol dm^{-3} $LiClO_4$ than in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ where $(C_2H_5)_4NCl$ does not appreciably form ion pairs. The smaller entropies ΔS°_n of formation of $[CuCl_n]^{(2-n)+}$ ($n=1$—4) in the 1 mol dm^{-3} $LiClO_4$ than in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ may be also ascribed to the ion pairing of LiCl in the former DMF solution.

Electronic Spectra of Copper(II) Chloride Complexes. Electronic spectra of copper(II) chloride at various concentrations of chloride ions were measured in 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMF solutions. Each spectrum obtained was resolved into spectra of individual copper(II) chloride complexes by knowing the formation constants of the complexes in the solutions. Molar extinction coefficients of individual copper(II) chloride complexes at various wavelengths thus obtained in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMF solutions are depicted in Fig. 4.

The calculated spectra of the $[CuCl]^+$, $[CuCl_3]^-$, and $[CuCl_4]^{2-}$ complexes in the 1 mol dm^{-3} $LiClO_4$ DMF solu-

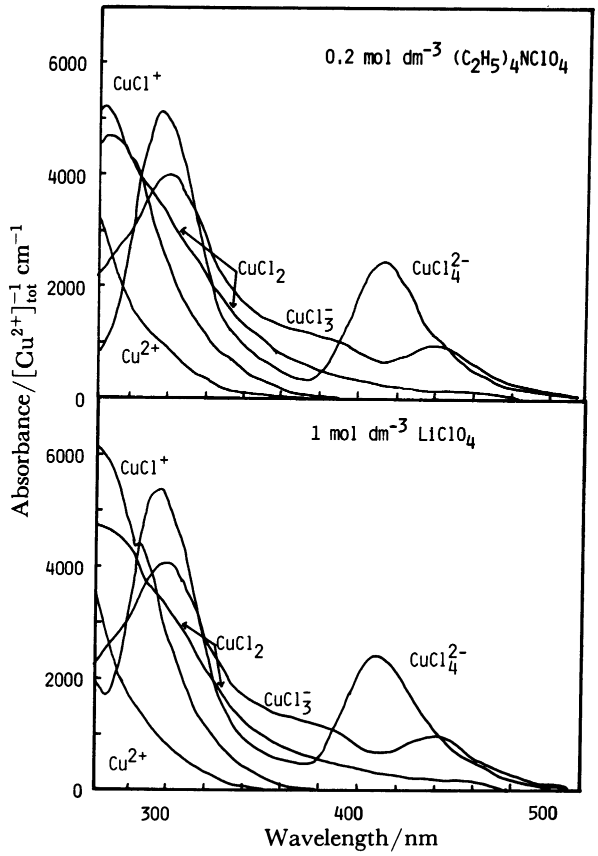

Fig. 4. Molar extinction coefficients of individual copper(II) chloride complexes at various wavelengths in 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMF solutions.

tion were similar to those obtained in the same DMF solution by Ellev *et al.*[2] who neglected the formation of the $[CuCl_2]$ complex in the solution. Although the formation of the $[CuCl_2]$ complex was less significant in the 1 mol dm^{-3} $LiClO_4$ DMF solution than in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution as seen in Fig. 3, the formation of the complex was still appreciable even in the former solution. Thus, the spectrum of the $[CuCl_2]$ complex could be determined in both the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMF solutions, the spectra of the complex thus obtained in the solutions being practically the same. No absorption peak in the range of wavelength 300—500 nm was observed for the $[CuCl_2]$ complex as well as the $[CuCl]^+$ complex.

Molar extinction coefficients of individual copper(II) chloride complexes calculated were not appreciably different between the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMF solutions over the whole range of wavelengths measured, and therefore, structures of the copper(II) chloride complexes formed in the solutions might not essentially be affected by the inert ionic medium salts within the concentration range examined in the present study.

From electronic spectra measured in various nonaqueous solvents and in crystals, Furlani and Morpurgo[17] suggested a flattened tetrahedral structure with D_{2d} symmetry for the $[CuCl_4]^{2-}$ complex. However, structures of the copper(II) chloride complexes in DMF have not been directly determined by a diffraction method. Fergusson[18] suggested that the presence of an absorption peak between 435 and 455 nm of a copper(II) chloride complex was indicative of the D_{2d} form of the complex. If the consideration by Fergusson would be acceptable for the $[CuCl_3]^-$ complex in DMF, the complex should have the D_{2d} form with a DMF molecule solvating copper(II) ion within the complex, since the spectrum of the $[CuCl_3]^-$ complex showed an absorption peak at *ca.* 440 nm. However, the copper(II)-DMF bond within the $[CuCl_3]^-$ complex may not be so strong, as already discussed in a previous section. On the other hand, the spectrum of the $[CuCl]^+$ and also that of the $[CuCl_2]$ complex did not show any peak at the region of wavelength 435—455 nm.

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References

1) M. A. Khan and M. J. Schwing-Weill, *Inorg. Chem.*, **15**, 2202 (1976).

2) M. Ellev, J. Meullemeestre, M. J. Schwing-Weill, and F. Vierling, *Inorg.Chem.*, **19**, 2699 (1980).

3) M. Ellev, J. Meullemeestre, M. J. Schwing-Weill, and F. Vierling, *Inorg. Chem.*, **21**, 1477 (1982).

4) S. E. Manahan and R. T. Iwamoto, *Inorg. Chem.*, **4**, 1409 (1965).

5) W. Schneider, *Helv. Chim. Acta*, **46**, 1842 (1963).

6) S. Ishiguro, Y. Oka, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, **56**, 2426 (1983).

7) R. Karlsson and L. Kullberg, *Chem. Scr.*, **9**, 54 (1976).

8) S. Ishiguro, B. G. Jeliazkova, and H. Ohtaki, *Bull. Chem. Soc. Jpn.*, in press.

9) V. Gutmann, "The Donor-Acceptor Approach to Molecular Interactions," Prenum, New York and London (1978).

10) Y. Marcus, *Pure & Appl. Chem.*, **55**, 977 (1983).

11) S. Ahrland, *Pure & Appl. Chem.*, **51**, 2019 (1979).

12) D. W. James and R. E. Mayes, *J. Phys. Chem.*, **88**, 637 (1984).

13) R. P. Held and C. M. Criss, *J. Phys. Chem.*, **71**, 2487 (1967).

14) J. E. Prue and P. J. Sherrington, *Trans. Faraday Soc.*, **57**, 1795 (1961).

15) J. N. Bulter and J. C. Synnott, *J. Am. Chem. Soc.*, **92**, 2602 (1970).

16) C. V. Krishnan and H. L. Friedman, *J. Phys. Chem.*, **75**, 3606 (1971).

17) C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, **1**, 102 (1963).

18) J. Fergusson, *J. Chem. Phys.*, **40**, 3406 (1964).