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Complex Formation and Solvation of $[CuCl_n]^{(2-n)+}$ in Acetonitrile and in N,N-Dimethylformamide

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Complex formation equilibria between copper(II) and chloride ions have been studied by calorimetry and spectrophotometry in acetonitrile(AN) containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25°C. Both calorimetric and spectrophotometric titration curves could be 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. Stepwise enthalpies ΔH_n° (n=1—4) were all negative, the ΔH_4° value being especially largely negative. On the other hand, the stepwise entropy ΔS_n° was largely positive for n=1—3, but largely negative for n=4. The result suggested that solvation of the $[CuCl_3]^-$ complex was extremely weak in AN and that release of solvent molecules from $[CuCl_3]^-$ was not so significant that the enthalpy and entropy of formation of $[CuCl_4]^{2-}$ were mainly attributable to those of desolvation of Cl^- followed by a bond formation between the $[CuCl_3]^-$ complex and the chloride ion. The $[CuCl_4]^{2-}$ complex might have no solvent molecules in the primary coordination sphere of the metal ion within the complex in AN. Enthalpies of solution of anhydrous $CuCl_2$ crystals were measured in AN and N,N-dimethylformamide(DMF) in order to evaluate enthalpies of transfer ΔH_t° of Cu^{2+} from water to the aprotic solvents. The ΔH_t° values well correlated with Gutmann's donor number of the solvents. The enthalpies of transfer ΔH_t° of $[CuCl_n]^{(2-n)+}$ (n=0—4) from AN to DMF were evaluated, and the enthalpy values monotonously increased with n. The $\Delta H_t^\circ(CuCl_4^{2-})$ value was only slightly positive as well as $\Delta H_t^\circ(Cl^-)$, and the result also suggested that the metal ion within the complex was not primarily solvated with solvent molecules in both AN and DMF. Electronic spectra of individual copper(II) chloride complexes were determined in AN.

In a previous paper,[1] we discussed about complex formation equilibria between copper(II) and chloride ions in N,N-dimethylformamide (DMF) studied by calorimetry and spectrophotometry.

It has already been pointed out that the formation of copper(II) chloride complexes is enhanced in aprotic solvents with either weaker (acetonitrile[2] and propylene carbonate[3]) or stronger (dimethyl sulfoxide[3] and DMF[4]) donicity than water.[5] According to Ahrland,[6] it can be explained in terms of difference in solvation of chloride ion between aprotic solvents and water. Solvation of chloride ion is more favorable in water owing to hydrogen-bonding with water molecules than in aprotic solvents.

Formation constants of copper(II) chloride complexes are largely different among aprotic solvents. Since the acceptor property of acetonitrile (AN) (the acceptor number (A_N)=19.3) is not largely different from that of DMF (A_N=16.0),[7] more favorable formation of copper(II) chloride complexes in AN than in DMF may be ascribed to weaker solvation of copper(II) ion with the former solvent (the donor number (D_N)=14.1) than with the latter (D_N=26.6).[7] Although the formation constants of copper(II) chloride complexes have been determined in AN,[2] no values of enthalpies and entropies of formation of the complexes have been reported.

In the present work, we investigated complex formation equilibria between copper(II) and chloride ions in acetonitrile by means of calorimetry and spectrophotometry as employed in a previous study[1] and determined formation constants, enthalpies and entropies of formation of the complexes. Enthalpies of solution of anhydrous $CuCl_2$ crystals were measured in AN and DMF in order to elucidate solvation phenomena of each complex species. Enthalpies of transfer of Cu^{2+} from water to the aprotic solvents were first evaluated, and then, enthalpies of transfer of individual copper(II) chloride complexes from AN to DMF were evaluated from the enthalpies of formation of the copper(II) chloride complexes obtained in both AN and DMF[1] and the enthalpies of transfer of Cu^{2+} and Cl^- from AN to DMF.

Electronic spectra of individual copper(II) chloride complexes were determined in AN and were compared with those determined in DMF, which suggested the difference in structures of the solvated neutral $[CuCl_2]$ complex in AN and DMF.

Experimental

Reagents. *Copper(II) perchlorate acetonitrile solution* was prepared according to Hathaway and Underhill[8] by the reaction of metallic copper with nitrosyl perchlorate, $Cu+2NOClO_4=Cu(ClO_4)_2+2NO$, in acetonitrile under a reduced pressure. Nitrosyl perchlorate was prepared by passing nitrogen oxides, which was obtained by dropwise adding concentrated nitric acid to sodium nitrate crystals, into 70% perchloric acid, and nitrosyl perchlorate thus obtained were filtered and then sucked under a dry atmosphere. About 10 g of nitrosyl perchlorate thus prepared was repeatedly washed with acetonitrile on a glass filter with a P_2O_5 guard-tube and finally a free-flowing powder was obtained. The dry nitrosyl perchlorate was reacted with metallic copper in *ca.* 100 cm^3 of dry acetonitrile within a round-bottle flask, which was evacuated through a P_2O_5 guard-tube with a water pump. The reaction was continued for several hours and then the solution was filtered under a nitrogen atmosphere through a G4 glass filter to remove residual nitrosyl perchlorate and copper metals. The concentration of copper(II) perchlorate in the stock solution was determined electrogravimetrically.

Tetraethylammonium perchlorate and *tetraethylammonium chloride* of reagent grade were used without further purification and dried at 100 °C in a vacuum oven. Impurities of halide ions in the tetraethylammonium perchlorate was negligibly small because no precipitate of silver halide was found by titrating the aqueous solution of the salt with a silver nitrate solution.

Acetonitrile was dried with calcium hydride, and then distilled under an atmospheric pressure and stored over 4A 1/16 molecular sieves in a bottle closed with a P_2O_5 guard-tube. The residual water determined by a Karl-Fisher test was less than 50 ppm.

All test solutions were prepared in a dry box over P_2O_5 under an atmosphere of dried nitrogen gas.

Measurements. All calorimetric and spectrophotometric titrations were carried out in acetonitrile containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium.

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. 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 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ solution. The heat of dilution of chloride ions was separately determined by titrating a 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ solution without copper(II) perchlorate with the $(C_2H_5)_4NCl$ solution, and was 0.065 J cm^{-3} per the addition of a unit volume of the titrant. A heat of reaction evolved at each point of titration was ranged 0—5 J with certainty ±0.05 J. Calorimetric measurements were carried out by using a fully automatic on-line system as described elsewhere.[9)]

Enthalpies of solution of anhydrous $CuCl_2$ crystals in a solvent were measured by using an MPS-11 calorimeter (Tokyo Riko, Tokyo) equipped with a PC-8801 computer (NEC, Tokyo) by breaking an ampoule containing a given amount of the salt in 50 cm^3 of the solvent without any ionic medium in a tefron vessel. Detailed procedure of measurement and analysis of heat evolved were described previously.[10)]

Spectrophotometric measurements were carried out in acetonitrile solutions with a flow cell of a light-pass length of 0.5 cm which was connected with a titration vessel through tefron and glass tubes. A 15 cm^3 of $Cu(ClO_4)_2$ acetonitrile solution was placed in a vessel under a nitrogen atmosphere and then titrated with a 0.1 mol dm^{-3} $(C_2H_5)_4NCl$ solution. Electronic spectra were measured with a HITACHI 340 spectrophotometer (Hitachi, Tokyo) equipped with a JEC 6 electronic computer (JEOL) which recorded data at selected wavelengths at every 2 nm in the range 240—520 nm. The formation constants of copper(II) chloride complexes were determined spectrophotometrically by using absorbances obtained at 10 different wavelengths, 254, 278, 294, 304, 310, 330, 406, 420, 460, and 480 nm.

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

$$q_i = -(V_i\sum_n \beta_n \Delta H^\circ_{\beta n} m_i x_i^n - V_{i-1}\sum_n \beta_n \Delta H^\circ_{\beta n} m_{i-1} x_{i-1}^n), \tag{1}$$

where V denotes the volume of the 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 Eqs. 2 and 3:

$$C_M = m_i + \sum_n \beta_n m_i x_i^n, \tag{2}$$

$$C_X = x_i + \sum_n n\beta_n m_i x_i^n. \tag{3}$$

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.[11)]

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

$$A_{ij} = \sum_n \varepsilon_n(\lambda_j)\beta_n m_i x_i^n \quad (\beta_0=1). \tag{4}$$

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 acetonitrile (AN) are depicted in Fig. 1. The enthalpy ΔH/kJ mol^{-1} of reaction per a unit mole addition of chloride ions at each titration point was plotted against the ratio C_X/C_M, where C_X and C_M denote the total cocentrations of chloride and copper(II) ions, respectively, in a solution. As seen in Fig. 1, remarkable changes in ΔH were observed at C_X/C_M=1 and 3, which indicate the formation of a series of four copper(II) chloride complexes having significantly different enthalpies of formation between $[CuCl]^+$ and $[CuCl_2]$ and between $[CuCl_3]^-$ and $[CuCl_4]^{2-}$, but inappreciable different ones between $[CuCl_2]$ and $[CuCl_3]^-$. Therefore, calorimetric data obtained were analyzed by assuming the formation of $[CuCl_n]^{(2-n)+}$ (n=1—4) by the least-squares method

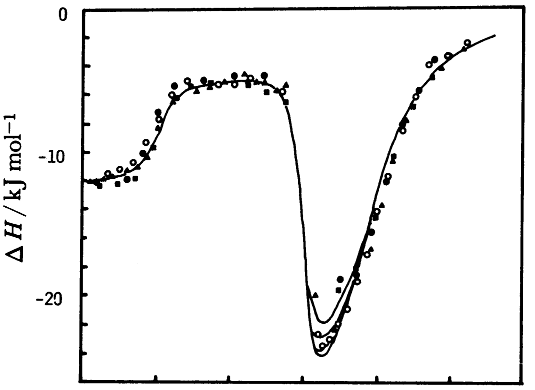

Fig. 1. Calorimetric titration curves of copper(II) chloride acetonitrile solutions containing 0.1 mol dm^{-2} $(C_2H_5)_4NClO_4$. Initial concentrations of copper(II) perchlorate (C_M/mmol dm^{-3}): 16.06 (○), 11.66 (▲), 9.67 (●), and 6.282 (■). The solid lines were calculated by using the constants in Table 1.

TABLE 1. OVERALL FORMATION CONSTANTS, $\beta_n/\text{mol}^{-n}\text{dm}^{3n}$ AND ENTHALPIES, $\Delta H^\circ_{\beta n}/\text{kJ mol}^{-1}$, FOR THE REACTION, $Cu^{2+}+nCl^-=CuCl_n^{(2-n)+}$ (n=1—4), IN ACETONITRILE CONTAINING 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ AS A CONSTANT IONIC MEDIUM AT 25 °C

	Calorimetry	Spectrophotometry
log β_1	9.69	9.76
log β_2	17.64	17.36
log β_3	22.58	22.50
log β_4	25.43	25.44
$\Delta H^\circ_{\beta 1}$	−11.66	−12.61 (0.2)
$\Delta H^\circ_{\beta 2}$	−16.66	−16.62 (0.2)
$\Delta H^\circ_{\beta 3}$	−21.09	−21.10 (0.3)
$\Delta H^\circ_{\beta 4}$	−55.39	−54.54 (0.4)
U[a)]	2.91	0.374
NP[b)]	129	250

a) Least-squares sum, b) The number of data points. The values in parentheses refer to standard deviations.

to determine both formation constants and enthalpies of formation of the complexes. The theoretical curves calculated by using the constants thus optimized are illustrated by the solid lines in Fig. 1, and they well reproduced the experimental curves over the whole range of C_X/C_M examined. The formation constants and enthalpies of formation of the copper(II) chloride complexes finally obtained are summarized in Table 1. The formation constants determined by spectrophotometry are also listed in Table 1. $\Delta H^\circ_{\beta n}$ values given in the column of "Spectrophotometry" in Table 1 were those estimated by inserting the formation constants thus evaluated from the spectrophotometric data to the calorimetric data in Fig. 1. A reasonable agreement was obtained between the formation constants and enthalpies of formation determined by calorimetry and spectrophotometry, although standard deviations for each constant determined by calorimetry were not well evaluated.

Formation of Copper(II) Chloride Complexes in AN. Thermodynamic quantities, log(K_n/mol^{-1}dm^3), ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1} and ΔS°_n/J K^{-1}mol^{-1}, for the stepwise reaction, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4), in the 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ AN solution are summarized in Table 2, together with those in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution.[1)]

TABLE 2. THERMODYNAMIC QUANTITIES, log(K_n/mol^{-1}dm^3), ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1} AND ΔS°_n/J K^{-1}mol^{-1}, FOR STEPWISE REACTION, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4), IN ACETONITRILE AND IN *N,N*-DIMETHYLFORMAMIDE AT 25 °C

	AN	DMF[a)]
log K_1	9.69	6.79
log K_2	7.95	4.54
log K_3	4.94	4.00
log K_4	2.85	1.52
ΔG°_1	−55.3	−38.8
ΔG°_2	−45.4	−25.9
ΔG°_3	−28.2	−22.8
ΔG°_4	−16.3	−8.7
ΔH°_1	−11.7	10.3
ΔH°_2	−5.0	9.7
ΔH°_3	−4.4	7.3
ΔH°_4	−34.3	−8.1
ΔS°_1	147	165
ΔS°_2	135	120
ΔS°_3	80	101
ΔS°_4	−61	2

a) Ref. 1.

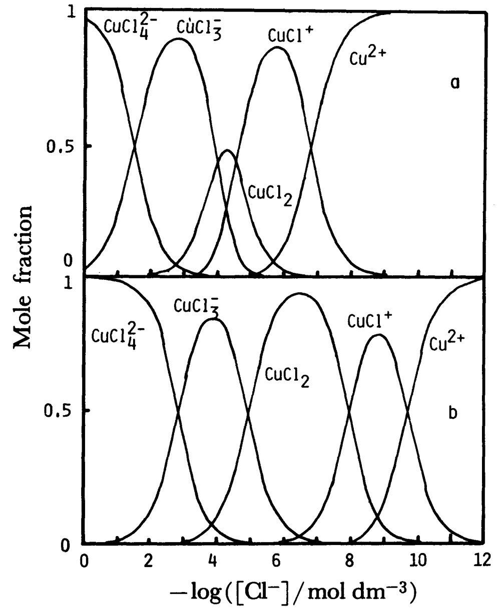

Fig. 2. Distribution curves of the copper(II) chloride complexes in the 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ (a) *N,N*-dimethylformamide and (b) acetonitrile solutions.

Formation of the copper(II) chloride complexes was more favorable in AN than in DMF, as visualized in Fig. 2 by the distribution curves of the complexes in the solvents. The more enhanced formation of the complexes in AN than in DMF was mainly owing to the more negative enthalpy values in the former solvent than in the latter, since the entropy values of formation of the complexes were not largely different at each consecutive step n=1—3 in these solvents, and the formation of the $[CuCl_4]^{2-}$ complex was entropically less favorable in the former solvent than in the latter. The favorable enthalpies of formation of copper(II) chloride complexes in AN than in DMF may be ascribed to weaker solvation of the metal ion in the former solvent, as is expected from the smaller donor number of AN.[7)] The difference in solvation of copper(II) ions in AN and DMF will be discussed in the following section.

The ΔH°_4 value was much more negative than other ΔH°_n (n=1—3) values in AN, the trend being more significant in AN than in DMF. Formation of a complex in a solution is accompanied by desolvation of both metal ion and ligand. Since the desolvation reactions are endothermic, the stronger the solvation of metal ion, the less negative enthalpy of formation of a complex would result. Therefore, the largely negative

ΔH_4° value than the ΔH_n° (n=1—3) values should be ascribed to the difference in solvation between $[CuCl_3]^-$ and $[CuCl_n]^{(2-n)+}$ (n=0—2) in AN, because the metal-ligand bond within a complex is usually weaker in a complex formed at a higher consecutive step. The metal-solvent interactions within $[CuCl_3]^-$ may be much weaker than those within $[CuCl_n]^{(2-n)+}$ (n=0—2) in AN, and thus, a relatively less energy for removing solvent molecules from the coordination sphere of the $[CuCl_3]^-$ complex might be needed in the course of formation of $[CuCl_4]^{2-}$.

As described in a previous paper,[1] a largely positive ΔS_n° (n=1—3) value indicated that desolvation of solvent molecules also played an important role in the course of the formation of $[CuCl_n]^{(2-n)+}$ in AN. On the other hand, a negative ΔS_4° value suggested that desolvation of the $[CuCl_3]^-$ complex did not play an essential role, and thus, the complex might not be strongly solvated. Thus, we concluded that the $[CuCl_4]^{2-}$ complex may practically have no solvent molecules in the primary coordination sphere of the metal ion within the complex in AN.

Enthalpies of Transfer of Cu^{2+}. Enthalpies of transfer of Cu^{2+} from water to AN and to DMF were determined by measuring enthalpies of solution of anhydrous $CuCl_2$ crystals in the solvents. Copper(II) chloride dissolved was expected to be completely dissociated into copper(II) and chloride ions in water,[5,10] but it was mostly associated in AN and in DMF.

Enthalpies of solution of $CuCl_2$ crystals for the following processes were determined in AN and DMF:

$$CuCl_2(c) = Cu^{2+}(s) + 2Cl^-(s);\ \Delta H_s^\circ(Cu^{2+}, 2Cl^-), \tag{5}$$

$$CuCl_2(c) = CuCl_2(s);\ \Delta H_s^\circ(CuCl_2), \tag{6}$$

by measuring the enthalpy of solution $\Delta H_{s,obsd}^\circ$ and by using Eqs. 7 and 8:

$$\Delta H_s^\circ(Cu^{2+}, 2Cl^-) = \Delta H_{s.obsd}^\circ - \sum_n \alpha_n \Delta H_{\beta n}^\circ, \tag{7}$$

$$\Delta H_s^\circ(CuCl_2) = \Delta H_s^\circ(Cu^{2+}, 2Cl^-) - \Delta H_{\beta 2}^\circ, \tag{8}$$

where c and s stand for crystalline and solution states, respectively, and α_n denotes the mole fraction of the $[CuCl_n]^{(2-n)+}$ complex. The α_n values were calculated in each measurement by knowing the formation constants of the copper(II) chloride complexes and the total concentration of $CuCl_2$ in a solvent. The results are listed in Table 3.

The enthalpy of transfer $\Delta H_t^\circ(Cu^{2+}, 2Cl^-)$ from water to another solvent (S) was represented as the sum of enthalpies of transfer of each ionic component as follows:

$$\Delta H_t^\circ(Cu^{2+}, 2Cl^-) = \Delta H_{s.S}^\circ(Cu^{2+}, 2Cl^-) - \Delta H_{s.W}^\circ(Cu^{2+}, 2Cl^-), \tag{9}$$

$$= \Delta H_t^\circ(Cu^{2+}) + 2\Delta H_t^\circ(Cl^-). \tag{10}$$

Table 3. Enthalpies of solution ΔH_s° of anhydrous $CuCl_2$ and enthalpies of transfer ΔH_t° of copper(II) and chloride ions from water to acetonitrile and to N,N-dimethylformamide at 25 °C

	ΔH°/kJ mol^{-1}		
	Water[a)]	AN	DMF
$\Delta H_{s,obsd}^\circ$	−56.3	−15.9	−55.3
$\Delta H_s^\circ(CuCl_2)$	—	−15.9	−54.7
$\Delta H_s^\circ(Cu^{2+}, 2Cl^-)$	−56.3	0.6	−74.5
$\Delta H_t^\circ(Cl^-)$	—	19.0[b)]	21.3[b)]
$\Delta H_t^\circ(Cu^{2+})$	—	18.9	−60.8

a) Ref. 10, b)Ref. 12.

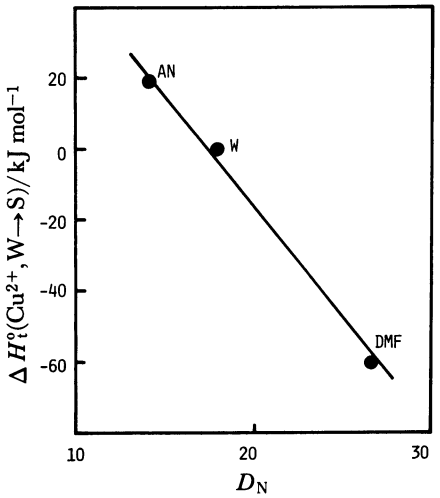

Fig. 3. Enthalpies of transfer of Cu^{2+} from water to AN and to DMF plotted against the donor number D_N of the solvents.

The $\Delta H_t^\circ(Cl^-)$ values from water to AN and to DMF have been reported by Cox *et al.*[12] on the basis of the extrathermodynamic assumption, $\Delta H_t^\circ(Ph_4As^+) = \Delta H_t^\circ(BPh_4^-)$, and thus, the $\Delta H_t^\circ(Cu^{2+})$ values from water to the aprotic solvents were calculated by subtracting the contribution of Cl^- ions from $\Delta H_t^\circ(Cu^{2+}, 2Cl^-)$. The results are also given in Table 3. The $\Delta H_t^\circ(Cu^{2+})$ values thus obtained were plotted against the donor number[7] of the solvents in Fig. 3, which showed a very good linear relationship. Figure 3 indicates that copper(II) ion is more strongly solvated in DMF than in water, and much more than in AN.

The $\Delta H_t^\circ(Cu^{2+})$ value from water to AN obtained was 18.9 kJ mol^{-1}, which was more positive than the value (11.5 kJ mol^{-1}) obtained by Libuš *et al.*[13] by employing a thermodynamic cycle different from that employed in the present work.

Enthalpies of Transfer of $[CuCl_n]^{(2-n)+}$ from AN to DMF. The differences in overall enthalpies of formation of the copper(II) chloride complexes in AN and in DMF are related to enthalpies of transfer of species pertaining to the complex formation reactions as follows:

$$\Delta H_{\beta n}^\circ(DMF) - \Delta H_{\beta n}^\circ(AN) = \Delta H_t^\circ(CuCl_n^{(2-n)+}) - \Delta H_t^\circ(Cu^{2+}) - n\Delta H_t^\circ(Cl^-). \tag{11}$$

Table 4. Thermodynamic quantities of transfer, ΔG°_t/kJ mol^{-1}, ΔH°_t/kJ mol^{-1} and ΔS°_t/J K^{-1} mol^{-1}, of copper(II) chloride complexes from acetonitrile to N,N-dimethylformamide at 25 °C

Species	ΔG°_t	ΔH°_t	ΔS°_t	$\Delta\Delta G^{\circ\,a)}_n$	$\Delta\Delta H^{\circ\,a)}_n$	$\Delta\Delta S^{\circ\,a)}_n$
Cu^{2+}	$-77.4^{b)}$	-79.7	-8			
Cl^-	$3.7^{c)}$	$2.3^{c)}$	$-5^{c)}$			
$[CuCl]^+$	-57.2	-55.4	6	16.5	22.0	18
$[CuCl_2]$	-34.0	-38.4	-15	19.5	14.7	-15
$[CuCl_3]^-$	-25.3	-24.4	3	5.0	11.7	21
$[CuCl_4]^{2-}$	-14.0	4.1	61	7.6	26.2	63

a) $\Delta\Delta G^\circ_n=\Delta G^\circ_n(\mathrm{DMF})-\Delta G^\circ_n(\mathrm{AN})$, $\Delta\Delta H^\circ_n=\Delta H^\circ_n(\mathrm{DMF})-\Delta H^\circ_n(\mathrm{AN})$, $\Delta\Delta S^\circ_n=\Delta S^\circ_n(\mathrm{DMF})-\Delta S^\circ_n(\mathrm{AN})$, for the reaction, $CuCl_{n-1}^{(3-n)+}+Cl^-=CuCl_n^{(2-n)+}$ (n=1—4). b) Ref. 15. c) Ref. 12.

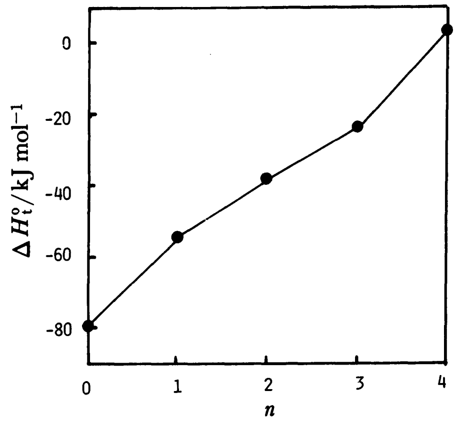

Fig. 4. Enthalpies of transfer of the $[CuCl_n]^{(2-n)+}$ (n=0—4) complexes plotted against n, the number of chloride ions bound per metal ion within a complex.

The $\Delta H^\circ_t(CuCl_n^{(2-n)+})$ value can be calculated, since all the values in Eq. 11 except for $\Delta H^\circ_t(CuCl_n^{(2-n)+})$ have been determined. The $\Delta H^\circ_t(CuCl_n^{(2-n)+})$ (n=1—4) values thus calculated are summarized in Table 4, and are also plotted against n in Fig. 4.

Although the absolute values of formal charges of the $[CuCl_n]^{(2-n)+}$ (n=0—4) complexes vary with n from 2 (n=0) to 0 (n=2) and then again 2 (n=4), the $\Delta H^\circ_t(CuCl_n^{(2-n)+})$ values monotonously changed with n from the $\Delta H^\circ_t(Cu^{2+})$ value of −79.7 kJ mol^{-1} to the $\Delta H^\circ_t(CuCl_4^{2-})$ value of 4.1 kJ mol^{-1}. Since the relative dielectric constant of AN (36.0) is not different from that of DMF (36.7), it is obvious that simple electrostatic theories (such as Born's equation and its derivatives with respect to temperature) are not applicable to explain the change in enthalpies of transfer of the complexes between the solvents. Such a monotonous variation of ΔH°_t values has also been observed for enthalpies of transfer of mercury(II) halide complexes $[HgX_n]^{(2-n)+}$ (n=1—4) from dimethyl sulfoxide to pyridine,[14] the solvents having largely different dielectric constants.

Accordingly, the enthalpy of transfer of $[CuCl_n]^{(2-n)+}$ from AN to DMF should be ascribed to different solvation of the both metal and ligand ions within the complex between the solvents. It is expected that solvation of Cl^- ion within $[CuCl_n]^{(2-n)+}$ may not be significantly different between AN and DMF, since the $\Delta H^\circ_t(Cl^-)$ value from AN to DMF is only slightly positive. The enthalpy of transfer of $[CuCl_n]^{(2-n)+}$ should thus be mainly attributed to the difference in solvation of the metal ion within the complex in the solvents.

The $\Delta H^\circ_t(CuCl_n^{(2-n)+})$ (n=1—3) values from AN to DMF were negative as well as $\Delta H^\circ_t(Cu^{2+})$, indicating that the metal ion within $[CuCl_n]^{(2-n)+}$ (n=1—3) was more strongly solvated with DMF than with AN. The ΔH°_t values increased in the sequence $[CuCl]^+<[CuCl_2]<[CuCl_3]^-$, which may be due, probably, to the decrease in the solvation number of the complexes with an increase in the number of chloride ions within the complexes, although the numbers of solvent molecules coordinating to the metal ion within the complexes have not been known.

The $\Delta H^\circ_t(CuCl_4^{2-})$ value was only slightly positive as well as $\Delta H^\circ_t(Cl^-)$, indicating that the metal ion within the complex was probably not primarily solvated with solvent molecules in both AN and DMF, and thus, the enthalpy of transfer of the $[CuCl_4]^{2-}$ complex was mainly determined by the change in solvation of chloride ions within the complex between the solvents.

Gibbs Energies and Entropies of Transfer of $[CuCl_n]^{(2-n)+}$ *from AN to DMF.* The Gibbs energy of transfer ΔG°_t of Cu^{2+} has been reported by Coetzee and Istone[15] to be 59.4 and −18.0 kJ mol^{-1} from water to AN and to DMF, respectively, and thus, the $\Delta G^\circ_t(Cu^{2+})$ value from AN to DMF is −77.4 kJ mol^{-1}. The $\Delta G^\circ_t(Cl^-)$ value has also been reported to be 3.7 kJ mol^{-1} from AN to DMF.[12]

By using the ΔG°_t values of copper(II) and chloride ions from AN to DMF, we calculated the Gibbs energies of transfer of $[CuCl_n]^{(2-n)+}$ (n=1—4) by the same procedure as used for evaluation of ΔH°_t of the complexes in a previous section.

The entropies of transfer ΔS°_t of $[CuCl_n]^{(2-n)+}$ (n=1—4) from AN to DMF could thus be calculated from the Gibbs energies and enthalpies of transfer of the complexes. The results are summarized in Table 4.

All the $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes were more stable in DMF than in AN, as indicated by negative ΔG°_t values of the complexes, which were predominantly contributed by the enthalpy term except for the $[CuCl_4]^{2-}$ complex. As to the $[CuCl_4]^{2-}$ complex, the largely positive ΔS°_t value led to the negative ΔG°_t value, the ΔH°_t value being even slightly positive.

However, the reason why the $\Delta S^\circ_t(\mathrm{CuCl_4^{2-}})$ value was so largely positive compared with the $\Delta S^\circ_t(\mathrm{CuCl}_n^{(2-n)+})$ (n=1—3) values still remained unknown.

Electronic Spectra of Copper(II) Chloride Complexes. Electronic spectra of copper(II) chloride solutions at various concentrations of chloride ions were measured in the 0.1 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ AN solution. Each spectrum obtained was resolved into spectra of individual copper(II) chloride complexes by knowing the formation constants of the copper(II) chloride complexes in the solution. Molar extinction coefficients of individual copper(II) chloride complexes at various wavelengths thus obtained in the 0.1 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ AN solution are depicted in Fig. 5.

The absorption maxima of the individual copper(II) chloride complexes obtained in AN are given in Table 5, together with those obtained in DMF.[1] An absorption maximum of $[\mathrm{CuCl}]^+$ was found at slightly longer wavelength by *ca.* 35 nm in AN than in DMF. Remarkably different spectra were observed for the $[\mathrm{CuCl_2}]$ complex between AN and DMF. Three absorption maxima of the complex were found at *ca.* 255, 308, and 406 nm in AN, while only one absorption maximum was found at *ca.* 265 nm in DMF. The $[\mathrm{CuCl_3}]^-$ complex showed three absorption maxima at almost the same wavelengths as those of $[\mathrm{CuCl_2}]$ in AN, but only two maxima were found in DMF within the wavelength region examined here. The absorption spectrum of the $[\mathrm{CuCl_4}]^{2-}$ complex with two absorption maxima at *ca.* 290 and 405 nm in AN was very similar to that in DMF.

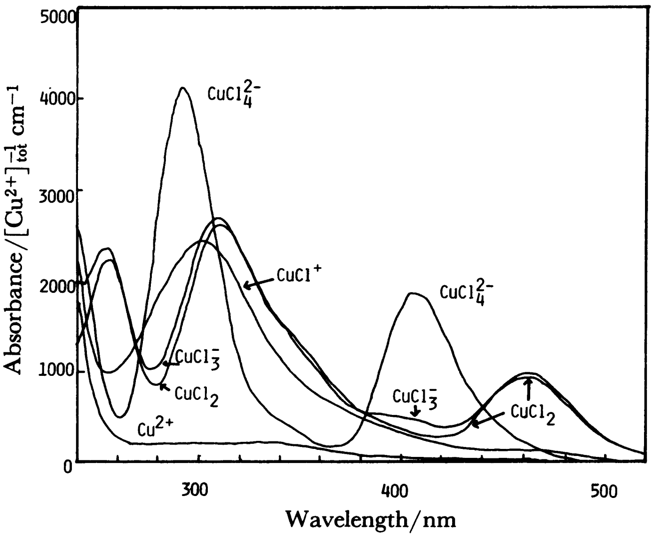

Fig. 5. Molar extinction coefficients of individual copper(II) chloride complexes at various wavelengths in the 0.1 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ AN solution.

TABLE 5. ABSORPTION MAXIMA, $\lambda_{\max}$/nm, OF ELECTRONIC SPECTRA OF COPPER(II) CHLORIDE COMPLEXES IN ACETONITRILE AND IN *N,N*-DIMETHYLFORMAMIDE

	AN	DMF[a]
$[\mathrm{CuCl}]^+$	300	265
$[\mathrm{CuCl_2}]$	255	265
	308	
	460	
$[\mathrm{CuCl_3}]^-$	255	
	308	300
	460	440
$[\mathrm{CuCl_4}]^{2-}$	290	296
	405	410

a) Ref. 1 in the 0.2 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ DMF solution.

It has been indicated from thermodynamic quantities of formation and of transfer of $[\mathrm{CuCl_4}]^{2-}$ in previous sections that the complex may have no solvent molecules in the primary coordination sphere of the metal ion within the complex. The structure of the $[\mathrm{CuCl_4}]^{2-}$ complex in AN should be the same as that in DMF,[1] as indicated by the similar absorption spectra in both the solvents.

According to Fergusson,[16] as mentioned in a previous paper,[1] the presence of an absorption maximum between 435 and 455 nm of a copper(II) chloride complex was indicative of the D_{2d} form of the complex. Therefore, it is plausible that the $[\mathrm{CuCl_2}]$ and $[\mathrm{CuCl_3}]^-$ complexes have the D_{2d} form in AN, since their spectra have an absorption maximum at *ca.* 460 nm. On the other hand, the $[\mathrm{CuCl_2}]$ complex in DMF has no maximum in the wavelength region 400—500 nm, and thus, the different solvate structures of the $[\mathrm{CuCl_2}]$ complex in AN and in DMF were expected.

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