  Bull. Chem. Soc. Jpn., 59, 2407—2413 (1986)

Calorimetric and Spectrophotometric Studies of Copper(II) Chloro Complexes in Dimethyl Sulfoxide

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(Received March 5, 1986)

Complex formation equilibria between copper(II) and chloride ions have been studied by calorimetric and spectrophotometric titrations in dimethyl sulfoxide (DMSO) containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ or 1 mol dm^{-3} $LiClO_4$ as a constant ionic medium at 25 °C. Both calorimetric and spectrophotometric data obtained were well explained in terms of formation of $[CuCl_n]^{(2-n)+}$ (n=1—4) in each solution, and their formation constants, enthalpies and entropies were determined. It was found that the complexation at each step was appreciably suppressed in the $LiClO_4$ DMSO solution compared to that in the $(C_2H_5)_4NClO_4$ one, which was ascribed to the extensive formation of LiCl ion-pairs in the former solution. As well as in *N,N*-dimethylformamide (DMF),[1] positive values of stepwise ΔH_n° and ΔS_n° (n=1—3) and negative ΔH_4° values were observed in DMSO. However, the ΔS_n° (n=1, 2, and 4) values in DMSO were appreciably smaller than the corresponding ones in DMF. The result was interpreted in terms of stronger intermolecular interactions in the bulk DMSO than those in DMF. The entropies of transfer of $[CuCl_n]^{(2-n)+}$ (n=0—4) from DMF to DMSO were significantly positive. This result also suggested that DMSO is a highly associated solvent. Electronic spectra of individual copper(II) chloro complexes were extracted from the spectra measured by varying molar ratios of chloride to copper(II) ions in solution. In contrast to the electronic spectra of Cu^{2+}, $[CuCl]^+$ and $[CuCl_2]$, the spectra of $[CuCl_3]^-$ and $[CuCl_4]^{2-}$ in DMSO were not appreciably different from those in DMF, indicating that solvation of these complexes are rather weak in both solvents.

The complexation of copper(II) with chloride ions in dimethyl sulfoxide (DMSO) has so far been studied by spectrophotometry,[2,3] potentiometry,[3-5] and conductometry.[5] These works elucidated the formation of mononuclear copper(II) chloro complexes in the solvent. Although the formation constants of these complexes have been obtained, their enthalpies and entropies have not been determined in DMSO yet.

We previously reported the complex formation equilibria between copper(II) and chloride ions in *N,N*-dimethylformamide (DMF),[1] in acetonitrile[6] and in their mixtures[7] by calorimetric and spectrophotometric measurements. A large difference was found in the enthalpies of complexation in these solvents, so that the difference in the metal-solvent bonding energies was indicated to play a dominant role for solvent effect on the complexation. In this respect, the donicity of DMSO is only slightly larger than that of DMF.[8] However, DMSO is expected to be a highly associated liquid,[9] while DMF has so weak intermolecular interactions that it shows practically random distribution in the bulk.[10]

In this work, therefore, we investigated the complexation of copper(II) with chloride ions in DMSO and compared the thermodynamic quantities of complexation thus obtained with those in DMF. The thermodynamic quantities were determined in 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMSO solutions by the same methods as used in previous works.[1,6] In order to evaluate the enthalpies of transfer of each $[CuCl_n]^{(2-n)+}$ (n=0—4) complex from DMF to DMSO, the enthalpy of solution of neutral $CuCl_2$ was determined in DMSO, as well as in DMF. Similarly, the corresponding Gibbs energies of transfer ΔG_t° of each complex were evaluated on the basis of the ΔG_t° values of copper(II) and chloride ions from the literature.[11,12] Electronic spectra of individual copper(II) chloro complexes were extracted by resolving the spectra measured in DMSO by varying molar ratios of chloride to metal ions.

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 were recrystallized three times from water, and $Cu(ClO_4)_2\cdot 6H_2O$ crystals were then dried in a vacuum oven at 70 °C. *Copper(II) perchlorate DMSO solvates*, $Cu(ClO_4)_2\cdot x$DMSO, were prepared from $Cu(ClO_4)_2\cdot 6H_2O$ by dissolving in an ethanol-diethyl ether mixture of equal volume fractions, followed by adding DMSO to yield the DMSO solvate crystals. The crystals thus obtained were washed with acetone, recrystallized from acetone and dried in vacuum at 50 °C for several days. An electrogravimetrical analysis showed that the value of x within the crystals finally obtained was close to 5.

Dimethyl sulfoxide was refluxed over CaH_2 for about one day, then distilled twice over CaH_2 at 50 °C under a reduced pressure (260 Pa) and kept over molecular sieves 4A 1/16 in a dark bottle with a P_2O_5 drying-tube.

Other chemicals used were prepared and dried by usual procedures as described elsewhere.[1] All test solutions were prepared in a dry box over P_2O_5 under an atmosphere of nitrogen gas.

Measurements. Calorimetric and spectrophotometric measurements were carried out in a room thermostated at (25.0±0.2) °C. All test solutions prepared contained 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ or 1 mol dm^{-3} $LiClO_4$ as a constant ionic medium.

Calorimetric measurements were performed in a thermostated water-bath at (25.000±0.007) °C. 100 cm^3 of a cop-

per(II) perchlorate solution was placed in a Dewar vessel, which was filled with nitrogen gas and prevented from moisture with a P_2O_5 drying-tube, and then was titrated with either 0.2 mol dm^{-3} $(C_2H_5)_4NCl$ or 1 mol dm^{-3} LiCl DMSO solution. The concentration of copper(II) ion in the initial test solutions was varied in the range 8—40 mmol dm^{-3}. Heats of complexation at each point of titration were ranged 1—5 J with a certainty ±0.05 J and were corrected for heats of dilution of the titrant separately determined by titrating either 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ or 1 mol dm^{-3} $LiClO_4$ DMSO solution with relevant titrant solutions in advance. Details of the data treatment have been described previously.[1,13]

Electronic spectra were measured with a HITACHI 340 spectrophotometer (HITACHI) equipped with a JEC 6 electronic computer (JEOL) which recorded data at selected wavelengths. A flow cell with a light-pass length of 0.5 cm was connected with a titration vessel through teflon and glass tubes. 15 cm^3 of a $Cu(ClO_4)_2$ DMSO solution was placed in a vessel under a nitrogen atmosphere and then was titrated with either the $(C_2H_5)_4NCl$ or LiCl DMSO solution.

Analysis of Calorimetric and Spectrophotometric Data. Calorimetric data obtained were analyzed by assuming the formation of mononuclear $[CuCl_n]^{(2-n)+}$, and their formation constants and enthalpies were simultaneously determined by the least-squares method as described previously.[1,6,7,13]

The absorbance data obtained at thirty different wavelengths in the range 250—500 nm were analyzed by the same procedure as that used previously,[1,6] and the formation constants of $[CuCl_n]^{(2-n)+}$ (n=1—4) were determined together with the molar extinction coefficents of the complexes at each relevant wavelength.

Results and Discussion

Calorimetric titration curves obtained in 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMSO solutions are depicted in Figs. 1 and 2, respectively. In each solution, 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 total concentrations of chloride and copper(II) ions in a solution, respectively, at each titration point, and $C_{X,tit}$ denotes the concentration of chloride ion in the titrant solution.

The trend of variation of the titration curves was similar in both $(C_2H_5)_4NClO_4$ and $LiClO_4$ DMSO solutions over the whole range of C_X/C_M examined. In both solutions, the ΔH° values at lower $C_X/C_M<0.5$ were kept constant and were independent of the metal concentration in solutions, the $[CuCl]^+$ complex being indicated to solely form in the range. With increasing C_X/C_M up to 2, the ΔH° value then increased and changed depending on the metal concentration, so that $[CuCl_2]$ was expected to form with a more endothermicity than $[CuCl]^+$. In the range $C_X/C_M>2$, the ΔH° value gradually decreased to approach $\Delta H^\circ=0$ with an increase in C_X/C_M, the higher $[CuCl_3]^-$ and $[CuCl_4]^{2-}$ complexes being expected to form over the range.

The result of the least-squares refinement of the calorimetric and spectrophotometric data in the $(C_2H_5)_4NClO_4$ DMSO solution are summarized in Table 1.

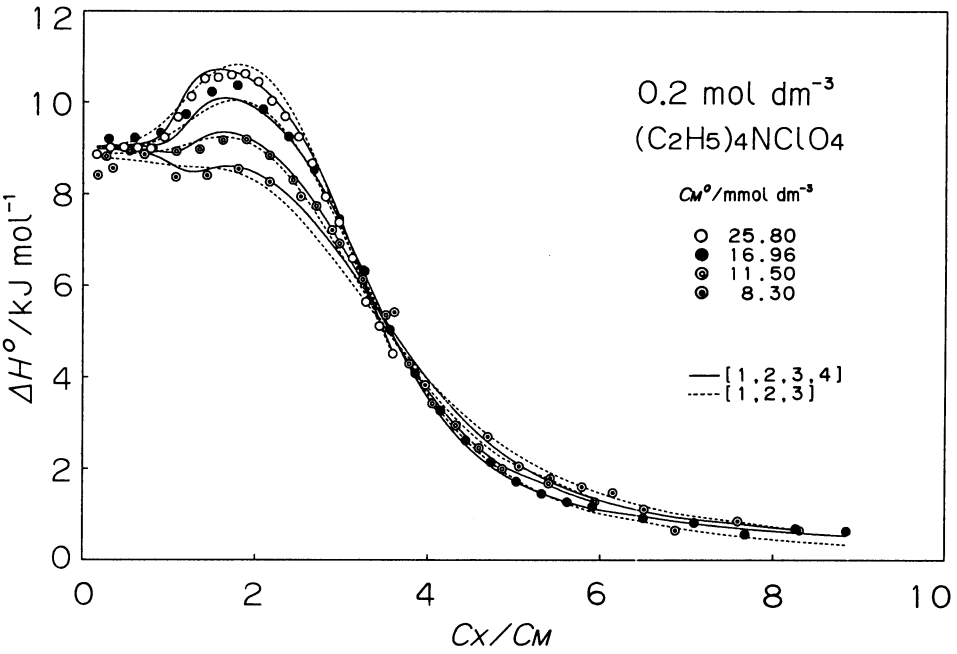

Fig. 1. Calorimetric titration curves of copper(II) chloride DMSO solutions containing 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Initial concentrations of copper(II) perchlorate (C_M°/mmol dm^{-3}) are given in the figure. The solid and broken lines show the theoretical curves calculated by using the constants of the sets (1—4) and (1—3), respectively, in Table 1.

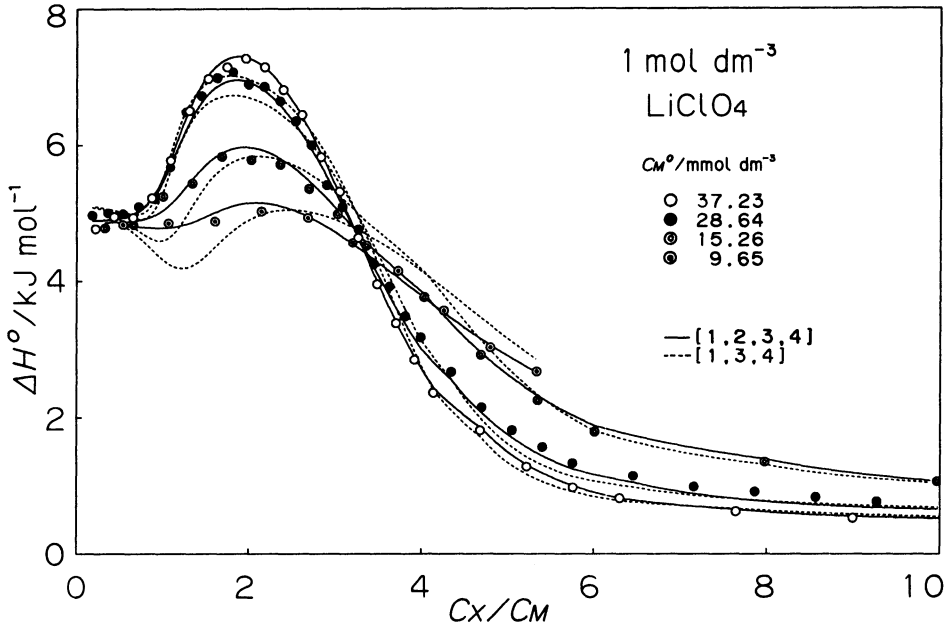

Fig. 2. Calorimetric titration curves of copper(II) chloride DMSO solutions containing 1 mol dm^{-3} $LiClO_4$ at 25 °C. Initial concentrations of copper(II) perchlorate (C°_M/mmol dm^{-3}) are given in the figure. The solid and broken lines show the theoretical curves calculated by using the constants of the sets (1—4) in Table 2 and the set (1, 3, 4), respectively.

Table 1. The Least-Squares Refinement of Overall Formation Constants, β_n/mol^{-n} dm^{3n}, and Enthalpies, $\Delta H^{\circ}_{\beta n}$/kJ mol^{-1}, of Formaion of Copper(II) Chloro Complexes in Dimethyl Sulfoxide Containing 0.2 mol dm^{-3} $(C_2H_5)_4ClO_4$ as a Constant Ionic Medium at 25 °C

	Cal (1—3)[a]	Cal (1—4)[a]	Spec (1—4)[a]
$\log\beta_1$	3.61(0.19)	4.23(0.23)	4.66(0.08)
$\log\beta_2$	6.07(0.19)	6.48(0.25)	7.30(0.11)
$\log\beta_3$	8.13(0.19)	8.95(0.26)	9.56(0.10)
$\log\beta_4$	—	9.55(0.46)	10.59(0.12)
$\Delta H^{\circ}_{\beta 1}$	9.08(0.09)	9.06(0.05)	—
$\Delta H^{\circ}_{\beta 2}$	20.4(0.3)	21.4(0.4)	—
$\Delta H^{\circ}_{\beta 3}$	39.9(0.3)	34.9(0.5)	—
$\Delta H^{\circ}_{\beta 4}$	—	55(9)	—
N[b]	90	90	2370
U[c]	0.728	0.348	0.114
R[d]	0.0323	0.0223	0.0099

Values in parentheses refer to standard deviations. a) The numbers indicate the n values of the $[CuCl_n]^{(2-n)+}$ complexes assumed in the course of the refinements. b) The number of data points. c) The error-square sum. d) The Hamilton R-factor.

The calorimetric data were analyzed by assuming several sets of mononuclear complexes. Among these sets examined, the set (1—4) assuming the formation of $[CuCl_n]^{(2-n)+}$ (n=1, 2, 3, and 4) gave the minimum error-square sum. However, since the $\Delta H^{\circ}_{\beta 4}$ value showed a rather large standard deviation, the $[CuCl_4]^{2-}$ complex may not appreciably form in the solution. Therefore, the set (1—3) eliminating $[CuCl_4]^{2-}$ was also examined for comparison. As seen in Fig. 1 by the broken lines, the theoretical curves calculated by using the constants of the set (1—3) in Table 1 ill fitted the experimental points, and thus it was concluded that the $[CuCl_4]^{2-}$ complex must not be neglected. In fact, as seen in Fig. 1 by the solid lines, the experimental points well fell on the theoretical curves when the four $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes were taken into account. Electronic spectra measured in the solution were also indicated the formation of the four complexes and their formation constants evaluated were similar to those obtained by calorimetry.

The result of the least-squares refinement of the calorimetric and spectrophotometric data in the $LiClO_4$ DMSO solution are summarized in Table 2. In the solution, the formation constants and enthalpies of all the $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes were determined with sufficient accuracy by both calorimetry and spectrophotometry. According to the result obtained by Elleb et al.[2] in the same solution by spectrophotometry, the formation of $[CuCl_2]$ was not conclusive. In fact, the distribution of species calculated by using the formation constants of the complexes in Table 2 indicated that the degree of formation of $[CuCl_2]$ was rather small. Thus, the refinement of the calorimetric data was also carried out for the set (1, 3, and 4) by eliminating the neutral complex. However, as seen in Fig. 2, the theoretical curves for the set (1—4) given by the solid lines well reproduced the experimental points, while those for the set (1, 3, and 4) shown by the broken lines ill

Table 2. The Least-Squares Refinement of Overall Formation Constants, β_n/mol^{-n}dm^{3n}, Enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, of Formation of Copper(II) Chloro Complexes in Dimethyl Sulfoxide Containing 1 mol dm^{-3} $LiClO_4$ as a Constant Ionic Medium at 25 °C

	Cal	Spec	Cal[a]	Spec[a]
$\log\beta_1$	3.63(0.16)	3.35(0.02)	4.11(0.17)	3.79(0.02)
$\log\beta_2$	5.67(0.19)	5.11(0.08)	6.56(0.19)	6.01(0.08)
$\log\beta_3$	7.49(0.17)	7.21(0.07)	8.85(0.17)	8.55(0.07)
$\log\beta_4$	8.19(0.20)	7.78(0.09)	9.64(0.19)	9.59(0.09)
$\Delta H^\circ_{\beta 1}$	3.56(0.06)	—	8.99(0.06)	—
$\Delta H^\circ_{\beta 2}$	9.6(0.2)	—	20.5(0.2)	—
$\Delta H^\circ_{\beta 3}$	22.5(0.5)	—	37.9(0.4)	—
$\Delta H^\circ_{\beta 4}$	11.9(0.6)	—	23.5(1.1)	—
N[b]	104	2160	104	2160
U[c]	1.16	0.113	1.09	0.113
R[d]	0.0503	0.0126	0.0332	0.0126

Values in parentheses refer to standard deviations. a) The formation of LiCl ion-pairs is taken into consideration: $\log K_{ip}=0.25$, $\Delta H^\circ_{ip}=8.5$ kJ mol^{-1}. b) The number of data points. The formation constants by spectrophotometry were obtained by using absorbance data at 30 different wavelengths. c) The error-square sum. d) The Hamilton R-factor.

fitted the experimental points, implying that the $[CuCl_2]$ complex should not be neglected. The formation constants were also evaluated from the spectrophotometric data, which were similar to those obtained by calorimetry as well.

As seen in Tables 1 and 2, a significant difference was found between the corresponding quantities in the $(C_2H_5)_4NClO_4$ and $LiClO_4$ solutions. It has been so far suggested that lithium chloride forms contact ion-pairs in DMSO,[14-16] although it is ambiguous.[17] Besides, in contrast to the $(C_2H_5)_4NClO_4$ DMSO solution, significant heats of dilution were observed when the LiCl DMSO solution was added to a DMSO solution of the relevant ionic medium. Therefore, it was expected that the LiCl contact ion-pairs appreciably formed in the LiCl titrant solution, and its formation constant and enthalpy, $\log(K_{ip}/\text{mol}^{-1}\text{dm}^3)=(0.25\pm0.07)$ and $\Delta H^\circ_{ip}=(8.5\pm0.6)$ kJ mol^{-1} (the uncertainties refer to standard deviations), respectively, were estimated by analyzing the heats of dilution of the LiCl titrant solution. Then, a further analysis of the calorimetric and spectrophotometric data obtained in the $LiClO_4$ DMSO solution was performed by knowing amount of LiCl ion-pairs formed in the solution. The formation constants and enthalpies of formation of $[CuCl_n]^{(2-n)+}$ (n=1—4) thus corrected for the formation of LiCl ion pairs are also listed in Table 2, the stepwise $\log(\beta_n/\beta_{n-1})$ values being practically the same as the corresponding values in the $(C_2H_5)_4NClO_4$ DMSO solution. Thus, it is concluded that an extensive formation of LiCl ion-pairs reduces the concentration of free chloride ions, which reflects on the unfavorable complexation of copper(II) with chloride ions in the $LiClO_4$ DMSO solution compared to that in the $(C_2H_5)_4NClO_4$ DMSO solution.

Figure 3 shows the distribution of species of the copper(II) chloro complexes in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMSO solution (the upper figure by the solid lines) and 1 mol dm^{-3} $LiClO_4$ DMSO solution (the lower figure). The distribution of species corrected for the formation of LiCl ion-pairs in the $LiClO_4$ solution is also depicted (the upper figure by the broken lines), which is similar to that in the $(C_2H_5)_4NClO_4$ solution.

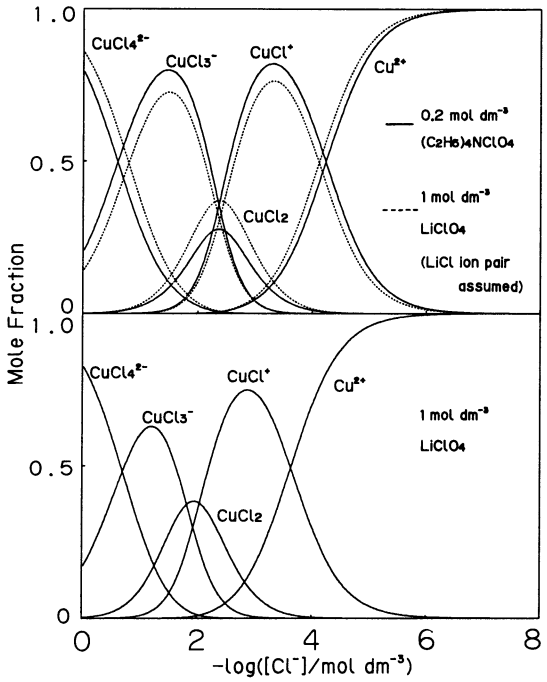

Fig. 3. Distribution of species of the copper(II) chloro complexes in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMSO solutions. The distribution of species in the $LiClO_4$ DMSO solution corrected for the formation of LiCl ion-pairs is depicted by the broken lines.

Thermodynamic quantities, $\log(K_n/\text{mol}^{-1}\text{dm}^3)$, ΔG°_n/kJ mol^{-1}, ΔH°_n/kJ mol^{-1} and ΔS°_n/J K^{-1} mol^{-1}, for the stepwise formation of $[CuCl_n]^{(2-n)+}$ in DMSO are summarized in Table 3, together with those in DMF for comparison.[1]

Table 3. Thermodynamic Quantities, $\log(K_n/\text{mol}^{-1}\,\text{dm}^3)$, $\Delta G_n^\circ/\text{kJ mol}^{-1}$, $\Delta H_n^\circ/\text{kJ mol}^{-1}$, and $\Delta S_n^\circ/\text{J K}^{-1}\,\text{mol}^{-1}$, for the Stepwise Formation of $[CuCl_n]^{(2-n)+}$ in Dimethyl Sulfoxide at 25 °C

	Dimethyl Sulfoxide			*N,N*-Dimethylformamide
	0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$	1 mol dm^{-3} $LiClO_4$	1 mol dm^{-3} $LiClO_4$[a]	0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$[c]
$\log K_1$	4.23	3.63	4.11	6.79
$\log K_2$	2.25	2.04	2.45	4.54
$\log K_3$	2.47	1.82	2.29	4.00
$\log K_4$	0.60	0.70	0.79	1.52
ΔG_1°	−24.1	−20.7	−23.5	−38.8
ΔG_2°	−12.8	−11.6	−14.0	−25.9
ΔG_3°	−14.1	−10.4	−13.1	−22.8
ΔG_4°	−3.4	−4.0	−4.5	−8.7
ΔH_1°	9.1	3.6	9.0	10.3
ΔH_2°	12.3	6.0	11.5	9.7
ΔH_3°	13.5	13.0	17.5	7.3
ΔH_4°		−10.6	−14.5	−8.1
ΔS_1°	111	81	109	165
ΔS_2°	84	59	85	120
ΔS_3°	93	78	103	101
ΔS_4°		−22	−33	2
$\Delta G_{\beta 4}^\circ$[b]		−46.7	−55.0	−96.2
$\Delta H_{\beta 4}^\circ$[b]		11.9	23.5	19.2
$\Delta S_{\beta 4}^\circ$[b]		197	263	387

a) The formation of LiCl ion-pairs was taken into account. b) For the overall formation of $[CuCl_4]^{2-}$. c) Ref. 1.

Formation of Copper(II) Chloro Complexes. As seen in Table 3, the thermodynamic quantities of formation of the copper(II) chloro complexes in DMSO are, in general, similar to those in DMF, as expected from strong donicities and relatively weak acceptor abilities of both solvents.[8] As well as in DMF, the positive ΔH_n° (n=1—3) values were observed in DMSO, indicating that copper(II) ion is strongly solvated in these solvents. It was found that the ΔH_n° (n=1—3) values changed in the sequence $\Delta H_1^\circ<\Delta H_2^\circ<\Delta H_3^\circ$ in DMSO but in the sequence $\Delta H_1^\circ>\Delta H_2^\circ>\Delta H_3^\circ$ in DMF. The Cu-Cl bonds are weaken within a higher $[CuCl_n]^{(2-n)+}$ complex and solvation energies of $[CuCl_n]^{(2-n)+}$ (n=1—3) become weaker with n due to an electron donation from chloride ions to the metal ion. The different trend of ΔH_n° (n=1—3) in DMSO and DMF suggests that weakening of the metal-solvent bonds within $[CuCl_n]^{(2-n)+}$ (n=1—3) with n occurs in a different manner in these solvents. The negative ΔH_4° value observed in DMSO suggests that the metal-solvent bond is very weak within $[CuCl_3(dmso)]^-$, and $[CuCl_4]^{2-}$ is not solvated in the first coordination sphere of the metal ion, the structure of the complexes being discussed in the later section.

In previous papers,[1,6] we discussed the entropies of formation of the copper(II) chloro complexes in DMF and acetonitrile in relation to the solvent-solvent interactions in the bulk. The positive and large ΔS_n° (n=1—3) values observed in DMSO suggests that DMSO molecules solvating copper(II) and chloride ions are liberated from the coordination shells of the ions, and enter the bulk solvent with a relatively high freedom.[18] However, comparing the entropy changes in DMSO (corrected for the formation of LiCl ion-pairs) with those in DMF, the ΔS_n° (n=1 and 2) values, as well as $\Delta S_{\beta 4}^\circ$, in DMSO are appreciably smaller than the corresponding ones in DMF. This suggests that the solvent-solvent interaction in DMSO is significantly different from that in DMF. It has been so far pointed out that DMSO is a highly associated liquid,[9] and DMSO oligomers are formed even in dilute DMSO solutions of benzene,[19] while DMF has only weak intermolecular interactions in the liquid state.[10] Therefore, less entropies of formation of the complexes in DMSO are attributable to larger entropy losses of the solvent molecules at entering the structured bulk phase from the coordination sphere as compared with the case of DMF which has a random intermolecular structure in the bulk. In contrast to large difference in $\Delta S_{\beta 4}^\circ$ in DMSO and DMF, the $\Delta H_{\beta 4}^\circ$ value in DMSO was even more positive than that in DMF. Thus, we propose that the effect of solvent-solvent interactions in the bulk on the thermodynamic quantities of formation of complexes in aprotic solvents reflects mainly on the entropy changes.

Thermodynamic Quantities of Transfer from *N,N*-Dimethylformamide to Dimethyl Sulfoxide. By measuring heats of solution of anhydrous $CuCl_2$ in DMSO, the enthalpies of solution for the following processes were evaluated:[6]

$$CuCl_2(c) = Cu^{2+}(s) + 2Cl^-(s);\ \Delta H_s^\circ(Cu^{2+}, 2Cl^-), \quad (1)$$

$$CuCl_2(c) = CuCl_2(s);\ \Delta H_s^\circ([CuCl_2]), \quad (2)$$

where c and s stand for the crystalline and solution states, respectively. Since the $\Delta H_s^\circ(Cu^{2+}, 2Cl^-)$ and $\Delta H_s^\circ([CuCl_2])$ values have been determined in DMF,[6] the enthalpy of transfer of copper(II) ion from DMF to DMSO, $\Delta H_t^\circ(Cu^{2+})$, was evaluated by knowing the $\Delta H_t^\circ(Cl^-)$ value from the literature:[20]

$$\Delta H^\circ_{s,DMSO}(Cu^{2+},2Cl^-) - \Delta H^\circ_{s,DMF}(Cu^{2+},2Cl^-) = \Delta H_t^\circ(Cu^{2+}) + 2\Delta H_t^\circ(Cl^-). \quad (3)$$

Similarly, the enthalpies of transfer of $[CuCl_n]^{(2-n)+}$ from DMF to DMSO, $\Delta H_t^\circ([CuCl_n]^{(2-n)+})$, were obtained from the relation:

$$\Delta H^\circ_{\beta n,DMSO} - \Delta H^\circ_{\beta n,DMF} = \Delta H_t^\circ([CuCl_n]^{(2-n)+}) - \Delta H_t^\circ(Cu^{2+}) - n\Delta H_t^\circ(Cl^-), \quad (4)$$

since all the values except for $\Delta H_t^\circ([CuCl_n]^{(2-n)+})$ have been known.

The Gibbs energies of transfer, $\Delta G_t^\circ([CuCl_n]^{(2-n)+})$ from DMF to DMSO were calculated by using the relation similar to Eq. 4 on the basis of the known $\Delta G_t^\circ(Cu^{2+})$ and $\Delta G_t^\circ(Cl^-)$ values from the literature.[11,12] The results are summarized in Table 4, together with the corresponding ΔS_t° values calculated from the ΔG_t° and ΔH_t° values.

The negative $\Delta H_t^\circ(Cu^{2+})$ value from DMF to DMSO may be attributable to the slightly larger donicity of DMSO than that of DMF.[8] Since the $\Delta H_t^\circ(Cl^-)$ value is also negative, the negative $\Delta H_t^\circ([CuCl_n]^{(2-n)+})$ values are expected from the view-point of both metal-solvent and ligand-solvent interactions of each complex.

The $\Delta G_t^\circ(Cu^{2+})$ value is more negative than $\Delta H_t^\circ(Cu^{2+})$ due to the largely positive $\Delta S_t^\circ(Cu^{2+})$ value. The ΔS_t° values of all the $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes are positive. However, such positive ΔS_t° value from DMF to DMSO can hardly be explained in terms of the solely different donicities of these solvents, because the ΔS_t° values of the $[CuCl_n]^{(2-n)+}$ complex from acetonitrile to DMF, these solvents having largely different donicities, are close to zero.[6] The significantly positive $\Delta S_t^\circ([CuCl_n]^{(2-n)+})$ (n=1—4) values from DMF to DMSO may be ascribed to the difference in their intermolecular interactions in the bulk. When we consider the process of solvation of an ion which is transferred from vacuum to a solvent, the entropy of solvation of an ion, ΔS°_{solv}, should be negative as the result of formation of the solvation sphere. The stronger the metal-solvent bonds, the more negative value of ΔS°_{solv} may result. However, at the formation of solvation shell, solvent-solvent interactions in the bulk must be partially broken, and this process gives a positive value of entropy change. The more the association of solvent molecules in the bulk, the larger the positive entropy change is at the breaking of intermolecular interactions. Accordingly, the ΔS_t° value of an ion may be largely positive when the ion is transferred from a solvent randomly distributed to that associated, as such a case of transferring ions from acetonitrile to water.[21] Since DMSO has a long range intermolecular interactions,[9] and easily associates,[19] the large and positive ΔS_t° values of transfer of $[CuCl_n]^{(2-n)+}$ (n=0—4), as well as $\Delta S_t^\circ(Cl^-)$, from DMF to DMSO can be explained in terms of the different intermolecular interactions in the bulk phase.

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 $[CuCl_n]^{(2-n)+}$ from *N,N*-Dimethylformamide to Dimethyl Sulfoxide at 25 °C

	ΔG_t°	ΔH_t°	ΔS_t°
Cu^{2+}	−30.5[a]	−3.6	90
$[CuCl]^+$	−21.2	−7.4	46
$[CuCl_2]$	−15.3	−8.1	24
$[CuCl_3]^-$	−11.6	−0.4	38
$[CuCl_4]^{2-}$	−13.4	−9.3	14
Cl^-	−6.0[b]	−2.5[c]	12

a) Ref. 11. b) Ref. 12. c) Ref. 20.

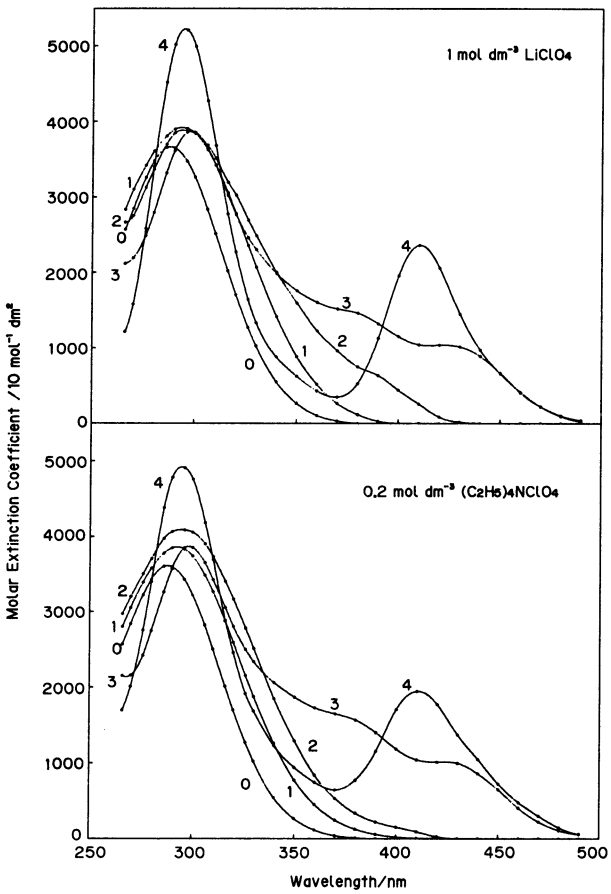

Fig. 4. Electronic spectra of individual copper(II) chloro complexes in the range 250—500 nm obtained in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMSO solutions. The numbers represent n within $[CuCl_n]^{(2-n)+}$.

Electronic Spectra of Copper(II) Chloro Complexes. Together with the formation constants, electronic spectra of individual copper(II) chloro complex-

es were extracted by resolving the spectra measured at various C_X/C_M ratios in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ and 1 mol dm^{-3} $LiClO_4$ DMSO solutions and represented in Fig. 4 over the range 250—500 nm.

As well as in DMF,[1] electronic spectra of each $[CuCl_n]^{(2-n)+}$ complex obtained are practically independent of ionic media, indicating that the structures of each complex obtained are not influenced by the medium salts.

As to Cu^{2+}, $[CuCl]^+$ and $[CuCl_2]$, the absorption maximum of each species in DMSO is appreciably shifted to a longer wavelength than that in DMF, suggesting that these species are differently solvated with DMSO and with DMF. In contrast, the electronic spectra of $[CuCl_3]^-$ and $[CuCl_4]^{2-}$ in DMSO are very similar to those of relevant species in DMF,[1] and thus the metal-solvent interaction in these solvent may be very weak. According to X-ray diffraction measurements for DMF solutions of copper(II) chloride,[22] the $[CuCl_4]^{2-}$ complex has a distorted tetrahedral structure and no solvent molecule is directly coordinated to the central metal ion, and the $[CuCl_3]^-$ complex has an additional DMF molecule to form a distorted tetrahedral structure and thus the complex should be described as $[CuCl_3(dmf)]^-$. The Cu–dmf bond within $[CuCl_3(dmf)]^-$ is weaker as indicated by its longer bond-length (230 pm) than the Cu–dmf(eq) bond (201 pm) within $[Cu(dmf)_6]^{2+}$. The similar electronic spectra of $[CuCl_3]^-$ and $[CuCl_4]^{2-}$ in DMSO and in DMF suggest that these complexes have practically the same structures in both solvents and the Cu–dmso bond within $[CuCl_3(dmso)]^-$ may be as weak as the Cu–dmf bond within $[CuCl_3(dmf)]^-$.

The present work has been financially supported by the Grant-in-Aid for Special Project Research No. 60129031 and partly by the Grant-in-Aid for Scientific Research No. 60540389 from the Ministry of Education, Science and Culture.

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