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Solvent Effects on the Formation of Copper(II) Chloro Complexes in Acetonitrile-Dimethyl Sulfoxide Mixtures

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Complexation of copper(II) with chloride ions has been calorimetrically and spectrophotometrically studied in various acetonitrile (AN)-dimethyl sulfoxide (DMSO) mixtures at 25 °C. Complexation of copper(II) ion with DMSO as a ligand in AN has also been investigated calorimetrically. It is indicated that the solvent effect on the thermodynamic parameters of the complexation is dominated by two factors, (1) the preferential solvation of copper(II) ion with DMSO that mainly affects the enthalpies, and (2) the change in solvent-solvent interactions in the bulk that strongly affects the corresponding entropies.

Complexation of copper(II) with chloride ions is enhanced in *N*,*N*-dimethylformamide (DMF),1) dimethyl sulfoxide (DMSO)2) and acetonitrile (AN)3) over water, although the donicity of DMF or DMSO is stronger than that of water,4) i.e. an energy to break copper(II)-solvent bonds is larger in DMSO or DMF than in water. The enhanced complexation in these aprotic solvents is generally due to large and positive entropies, in contrast to small or even negative entropies in water. It is also found that the difference in the complexation of copper(II) with chloride ions is significant even in these aprotic donor solvents. Although the donicities of DMSO and DMF are not largely different, the complexation of copper(II) ions is weaker in the former solvent than in the latter. The difference is also mainly ascribed to the entropies. These facts suggest that the solvent-solvent interaction in the bulk solvent molecules plays an important role for the complexation, as the entropy difference may reflect that solvent molecules coordinating to metal and ligand ions are liberated and enter the bulk solvent of different structures.5)

In order to throw more light on the role of solvent structure in the bulk for complexation reactions, we have examined the complexation in AN-DMF mixtures.6) Both AN and DMF solvents have so weak solvent-solvent interactions that they distribute practically at random in the liquid phase.7) In contrast to DMF, DMSO is a strongly self-associated donor solvent in the liquid at room temperature.8–10) Then, in this work we further investigated the complex formation of the same copper(II)-chloride system in AN-DMSO mixtures. The complexation of copper(II) ion with DMSO as a ligand in AN was also explored to elucidate preferential solvation of copper(II) ion with DMSO molecules in the mixtures.

Experimental

Reagents. All chemicals used were of reagent grade and were prepared or purified as described previously.1–3)

Measurements. Calorimetric measurements were carried out in a room thermostated at 25±0.5 °C by using a computer assisted titration calorimetry system. In the copper(II) chloride system, acetonitrile-dimethyl sulfoxide mixtures of 0.05 and 0.1 mole fraction DMSO were used as solvents. The ionic strength of test solutions was kept constant at 0.2 mol dm^{-3} by using $(C_2H_5)_4NClO_4$ throughout measurements. A copper(II) perchlorate solution (100 cm^3) was placed in a Dewar vessel kept at 25.0±0.0001 °C, filled with dry nitrogen gas and isolated from moisture with a P_2O_5 drying-tube, and was titrated with a 0.2 mol dm^{-3} $(C_2H_5)_4NCl$ solution. The concentration of copper(II) ions in the initial test solution was varied over the range 10—30 mmol dm^{-3} in the mixtures. In the copper(II) DMSO system, an AN solution of copper(II) perchlorate (50 cm^3) was titrated with DMSO (0.5 mol dm^{-3}) in AN in which the ionic strength was kept at 0.1 mol dm^{-3} with $(C_2H_5)_4NClO_4$. In both systems, heats observed at each titration point were corrected for heat of dilution of the titrant, which had been determined by separate experiments and found to be very small in all the solutions examined.

Heats of solution of anhydrous $CuCl_2$ crystals were measured in the AN-DMSO mixtures of the same composition as that used for titration calorimetry. Details of the measurements were described elsewhere.3)

Electronic spectra were measured with an MPS-2000 spectrophotometer (Shimadzu) equipped with a PC-9801 VM computer (NEC) which recorded data at 1 nm intervals over the wavelength range 250—500 nm. A flow-cell with the pathlength of 0.5 cm was connected with a titration vessel through Teflon and glass tubes. A copper(II) perchlorate solution (20 cm^3) was placed in the vessel under a dry nitrogen atmosphere and was titrated with a 0.2 mol dm^{-3} $(C_2H_5)_4NCl$ solution. The measurements were carried out in AN-DMSO mixtures of 0.025, 0.05, 0.10, and 0.5 mole fraction DMSO. Absorbance data at selected 50 wavelengths over the range 250—500 nm were used for a least-squares calculation of formation constants.

Data Analysis. Calorimetric and spectrophotometric data obtained were analyzed by the same method described

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previously.[11]

Results and Discussion

Copper(II) Chloride Complexes. Calorimetric titration curves obtained in AN-DMSO mixtures of 0.05 and 0.1 mole fraction DMSO are depicted in Fig. 1. As the heat of reaction q at each titration point depends on the volume of an aliquot of the titrant added δv and the concentration of ligand ions in the titrant $C_{\mathrm{X,tit}}$, the $-q/(\delta v C_{\mathrm{X,tit}})$ values are plotted against the ratio of the total concentrations of the ligand to the metal ion in solution $C_{\mathrm{X}}/C_{\mathrm{M}}$. The titration curves are well explained in terms of the formation of mononuclear $[\mathrm{CuCl}_n]^{(2-n)+}$ (n=1—4) complexes in these mixtures, as well as in pure DMSO[2] and AN.[3] In Table 1 their formation constants and enthalpies simultaneously determined are summarized. The solid lines in Fig. 1 are calculated by using the constants in relevant mixtures in Table 1 and they well reproduce the experimental points over the whole range of $C_{\mathrm{X}}/C_{\mathrm{M}}$ examined.

In Fig. 2 are shown typical electronic spectra measured in the AN-DMSO mixture of 0.025 mole fraction DMSO. The spectral changes with the concentration of chloride ions in the solution are similar in all the AN-DMSO mixtures examined. According to the analysis by the matrix rank method,[12] the number of species formed is five including the solvated copper(II) ion, each having appreciably different electronic spectra. The absorbance data are in fact satisfactorily explained in terms of the formation of $[\mathrm{CuCl}_n]^{(2-n)+}$ (n=1—4) and their

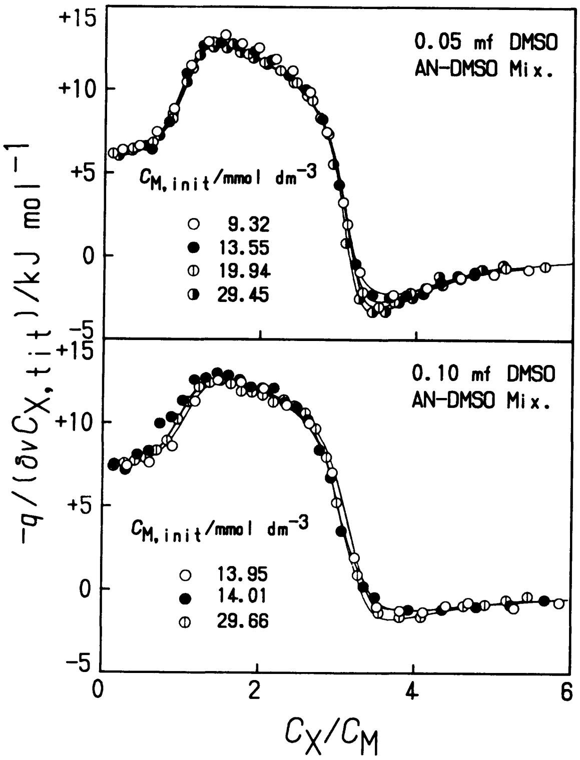

Fig. 1. Calorimetric titration curves for the copper(II) chloride system obtained in AN-DMSO mixtures at 25 °C. Concentrations of copper(II) ions in the initial solutions $C_{\mathrm{M,init}}$/mmol dm^{-3} are given. The solid lines show the curves calculated by using the constants in Table 1.

Table 1. Overall Formation Constants, $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$, and Enthalpies, $\Delta H^{\circ}_{\beta n}$/kJ mol^{-1}, of $[\mathrm{CuCl}_n]^{(2-n)+}$ (n=1—4) Obtained by Using Calorimetric Data in Acetonitrile-Dimethyl Sulfoxide Mixtures at 25 °C

	DMSO content/mole fraction 0.05	0.1
$\log\beta_1$	6.0(0.3)	5.5(0.4)
$\log\beta_2$	10.5(0.6)	9.6(0.9)
$\log\beta_3$	15.0(0.7)	13.4(0.9)
$\log\beta_4$	17.2(0.8)	15.2(0.9)
$\Delta H^{\circ}_{\beta 1}$	5.9(0.3)	7.4(0.4)
$\Delta H^{\circ}_{\beta 2}$	24.2(1.4)	22.8(1.5)
$\Delta H^{\circ}_{\beta 3}$	29.4(0.3)	31.6(0.5)
$\Delta H^{\circ}_{\beta 4}$	23.5(0.3)	25.7(0.5)
U[a]	0.685	0.863
R[b]	0.0276	0.0362
N[c]	91	81

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

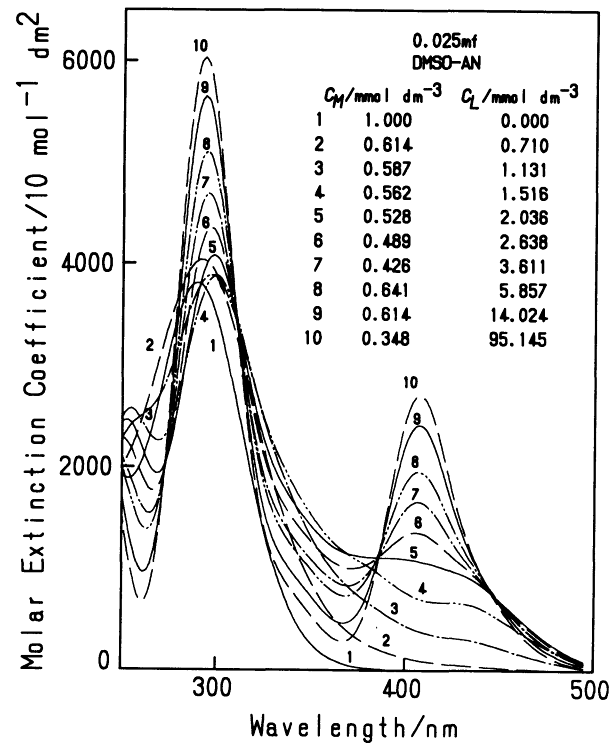

Fig. 2. Measured electronic spectra of copper(II) chloride solutions in the AN-DMSO mixture of 0.025 mole fraction DMSO. Intensities are normalized with the concentration of copper(II) ion in solution.

Table 2. Overall Formation Constants, $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$, of $[\mathrm{CuCl}_n]^{(2-n)+}$ (n=1—4) Obtained by Using Spectrophotometric Data in Acetonitrile-Dimethyl Sulfoxide Mixtures at 25 °C

	DMSO content/mole fraction			
	0.025	0.05	0.1	0.5
$\log\beta_1$	6.5(0.1)	6.06(0.07)	5.87(0.10)	4.67(0.09)
$\log\beta_2$	11.2(0.2)	10.4(0.1)	9.8(0.1)	7.4(0.1)
$\log\beta_3$	15.9(0.2)	14.6(0.1)	13.6(0.1)	10.1(0.1)
$\log\beta_4$	18.4(0.2)	16.9(0.1)	15.6(0.1)	11.3(0.1)
U[a]	0.0572	0.0270	0.0310	0.0503
R[b]	0.0056	0.0038	0.0042	0.0055
N[c]	3800	3850	3750	3800

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

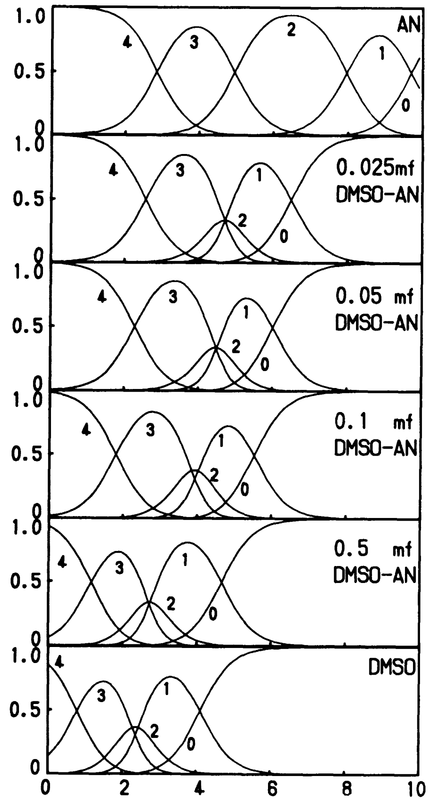

Fig. 3. Distribution of the copper(II) chloro complexes. The number represents n within $[\mathrm{CuCl}_n]^{(2-n)+}$.

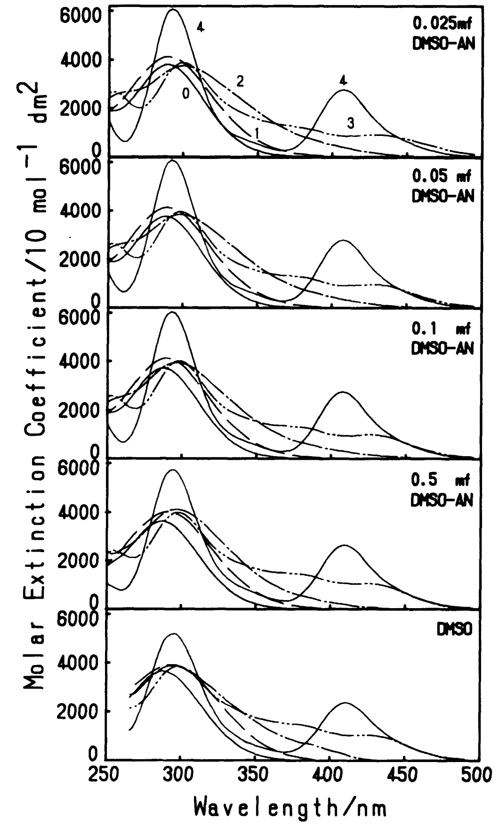

Fig. 4. Extracted electronic spectra of individual copper(II) chloro complexes. The number represents n within $[\mathrm{CuCl}_n]^{(2-n)+}$.

formation constants were determined. The result is summarized in Table 2. The formation constants thus obtained by spectrophotometry in the 0.05 and 0.1 mole fraction DMSO mixtures are reasonably agreed with the respective values obtained by calorimetry in these solvents. The distribution of the species in these solutions, together with that in pure AN and DMSO, is shown in Fig. 3.

Extracted electronic spectra of the individual $[\mathrm{CuCl}_n]^{(2-n)+}$ (n=1—4) complexes are depicted in Fig. 4. The electronic spectra of each species in all the AN-DMSO mixtures examined are practically the same as those in DMSO[2] and in DMF.[1] In DMF the structure of the distorted octahedral $[\mathrm{CuCl(dmf)_5}]^+$ and the distorted tetrahedral $[\mathrm{CuCl_3(dmf)}]^-$ and $[\mathrm{CuCl_4}]^{2-}$ complexes has been determined by X-ray diffraction.[13] It is therefore expected that the corresponding chloro complexes of copper(II) ion in DMSO and in the AN-DMSO mixtures have essentially the same coordination structures as those in DMF.

Copper(II) DMSO Complexes. Calorimetric titration curves obtained by titrating copper(II) perchlorate with DMSO in AN are depicted in Fig. 5, in which the values $-q/(\delta v C_{\mathrm{L,tit}})$ are plotted against $C_\mathrm{L}/C_\mathrm{M}$, where L denotes DMSO. The calorimetric data were

Table 3. Overall Formation Constants, $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$, and Enthalpies, $\Delta H^\circ_{\beta n}/\mathrm{kJ\,mol}^{-1}$, of $[\mathrm{Cu(dmso)}_n]^{2+}$ in Acetonitrile at 25 °C

	(1—4)	(1—5)	(1—4,6)	(1—6)
$\log\beta_1$	3.2(0.3)	3.1(0.2)	3.0(0.2)	3.1(0.2)
$\log\beta_2$	3.9(2)	5.3(0.2)	5.1(0.2)	5.2(0.2)
$\log\beta_3$	7.4(0.3)	7.4(0.2)	7.3(0.2)	7.4(0.2)
$\log\beta_4$	8.7(0.3)	9.2(0.2)	8.9(0.2)	9.1(0.2)
$\log\beta_5$	—	9.6(0.3)	—	9.5(0.8)
$\log\beta_6$	—	—	9.9(0.3)	10.0(1.7)
$\Delta H^\circ_{\beta 1}$	−14.5(0.5)	−14.5(0.4)	−14.4(0.4)	−14.4(0.4)
$\Delta H^\circ_{\beta 2}$	uncertain	−31(2)	−34(3)	−32(2)
$\Delta H^\circ_{\beta 3}$	−42(2)	−45(2)	−42(1)	−43(2)
$\Delta H^\circ_{\beta 4}$	−70.8(0.8)	−59(2)	−65(1)	−61(3)
$\Delta H^\circ_{\beta 5}$	—	−77(1)	—	−71(32)
$\Delta H^\circ_{\beta 6}$	—	—	−73.1(0.8)	−75(4)
U[a]	1.27	0.346	0.364	0.335
R[b]	0.0301	0.0157	0.0161	0.0155

Values in parentheses refer to three standard deviations. The number of data point is 244 including those obtained by back titrations. a) Error-square sum. b) The Hamilton R factor.

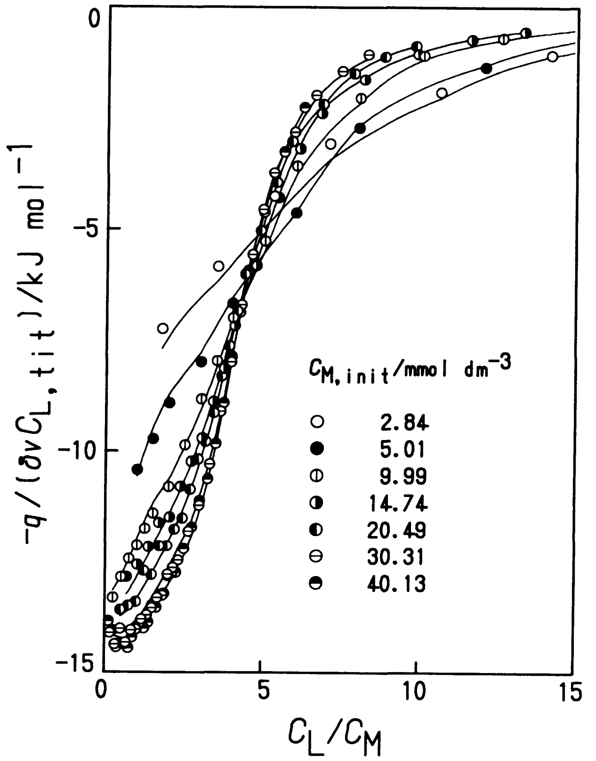

Fig. 5. Calorimetric titration curves for the copper(II) DMSO system in AN at 25 °C. Concentrations of copper(II) ions in the initial solutions $C_{\mathrm{M,init}}$/mmol dm^{-3} are given. The solid lines show the curves calculated by using the constants for the set (1—6) in Table 3.

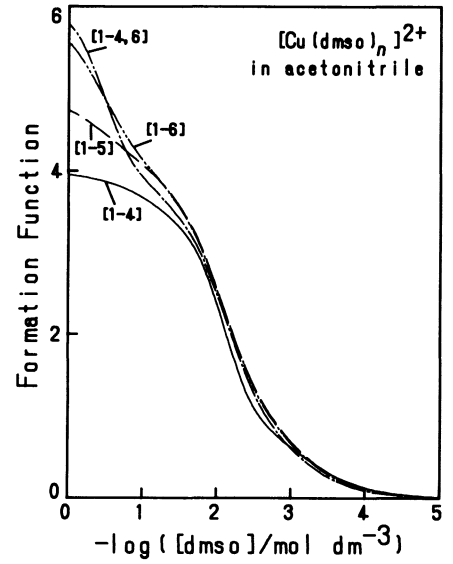

Fig. 6. Formation functions of $[\mathrm{Cu(dmso)}_n]^{2+}$ for the various combinations of n's.

analyzed by assuming the formation of $[\mathrm{Cu(dmso)}_n]^{2+}$ ($n \leqq 6$) complexes with various combinations of n's. The results of the least-squares analysis are summarized in Table 3. The Hamilton R factor for the set (1—4) assuming $[\mathrm{Cu(dmso)}]^{2+}$, $[\mathrm{Cu(dmso)}_2]^{2+}$, $[\mathrm{Cu(dmso)}_3]^{2+}$ and $[\mathrm{Cu(dmso)}_4]^{2+}$ only is appreciably larger than the values for the sets (1—5), (1—6) and (1—4,6). This evidently indicates that not only $[\mathrm{Cu(dmso)}_n]^{2+}$ (n=1—4) but also higher species, $[\mathrm{Cu(dmso)}_5]^{2+}$ and/or $[\mathrm{Cu(dmso)}_6]^{2+}$, are formed in the solutions examined. The formation functions $\bar{n}$ calculated according to Eq. 1

$$\bar{n} = \Sigma n\beta_n[\mathrm{dmso}]^n/(1 + \Sigma\beta_n[\mathrm{dmso}]^n) \tag{1}$$

are shown in Fig. 6. The highest $\bar{n}$ reached in the present measurements is ca. 4.5, i.e., the formation of $[\mathrm{Cu(dmso)}_5]^{2+}$ and/or $[\mathrm{Cu(dmso)}_6]^{2+}$ is not extensive. In addition, the $\bar{n}$ curves for these sets are similar in the range $-\log([\mathrm{dmso}]/\mathrm{mol\ dm}^{-3})>1$, and thus it is hard to draw a unique conclusion for the formation of the pentakis- and/or hexakis(dimethyl sulfoxide) copper(II) complexes under the experimental conditions employed.

Enthalpies of Solution of Anhydrous $CuCl_2$ Crystal. By using the procedure described previously,[3] the enthalpies of solution for the following processes

$$CuCl_2(c) = Cu^{2+}(s) + 2Cl^- (s);\ \Delta H^\circ_s (Cu^{2+}, 2Cl^-) \quad (2)$$
$$CuCl_2(c) = [CuCl_2] (s);\ \Delta H^\circ_s (CuCl_2) \quad (3)$$

where c and s stand for the crystalline and solution states, respectively, were determined in the AN-DMSO mixtures of 0.05 and 0.1 mole fraction DMSO. The result is given in Table 4. The ΔH°_s (Cu^{2+}, $2Cl^-$) values in the mixtures are significantly more negative than the value in AN, the fact also indicating that copper(II) ion is preferentially solvated with DMSO even in AN rich AN-DMSO mixtures. A similar trend, though much less marked, was found for the ΔH°_s ($CuCl_2$) values.

Solvent Effects on the Formation of $[CuCl_4]^{2-}$. As seen in Table 5, the overall Gibbs energy value $\Delta G^\circ_{\beta 4}$ becomes less negative with an increase in the mole fraction of DMSO in the AN-DMSO mixtures. The $\Delta H^\circ_{\beta 4}$ value in any mixture is close to that in DMSO, but largely different from that in AN. The difference may be due to the preferential solvation of copper(II) ion with DMSO in the mixtures, i.e., an energy is needed to break Cu(II)-dmso bonds in the course of the reaction

$$[Cu(dmso)_6]^{2+} + 4Cl^- = [CuCl_4]^{2-} + 6dmso \quad (4)$$

in the mixtures. The values of $(\Delta H^\circ_{\beta 4}(AN) - \Delta H^\circ_{\beta 4}(mix))$ are −78.9 and −81.1 kJ mol^{-1} in the mixtures of 0.05 and 0.1 mole fraction DMSO, respectively, which are in fact close to the enthalpy of formation of $[Cu(dmso)_n]^{2+}$ (n=5 or 6) in AN. The result also implies that the solvation enthalpy of chloride ion may not be appreciably different in AN, DMSO, and their mixtures, as expected from the similar acceptor property of the solvents (the acceptor numbers are 19.3 for both DMSO and AN),[4] and the small enthalpy of transfer of chloride ion from AN to DMSO (−1.7 kJ mol^{-1}).[14]

Table 4. Enthalpies of Solution, ΔH°_s/kJ mol^{-1}, of Anhydrous $CuCl_2$ in Acetonitrile–Dimethyl Sulfoxide Mixtures

y[a]	$\Delta H^\circ_s(CuCl_2)$	$\Delta H^\circ_s(Cu^{2+}, 2Cl^-)$
0	−15.9	0.6
0.05	−40.3	−64.5
0.1	−45.1	−67.9
1	−62.8	−83.3

a) DMSO content/mole fraction.

It is known that DMSO molecules are associated in the liquid state at room temperature.[8–10] This is due to interactions between exposed dipoles at the molecular surface of DMSO[8] in contrast to embedded dipoles of AN, although these solvent molecules have similar dipole moments (μ_{AN}=12.9×10^{-30} C m, μ_{DMSO}= 13×10^{-30} C m). A smaller molecular weight, or in other words, a smaller dispersion force, of AN than DMSO may also contribute to a weaker intermolecular interaction of the former. Donor–acceptor interactions between molecules may also be weaker in AN (the donor number D_N=14.1 and the acceptor number A_N=19.3) than in DMSO (D_N=29.8 and A_N=19.3). Consequently, AN is an unordered solvent with respect to pure DMSO. Dilute AN solutions of DMSO may be also unordered, i.e., DMSO-DMSO interactions are practically broken.

DMSO molecules solvate preferentially copper(II) ion to form $[Cu(dmso)_6]^{2+}$ in the AN-DMSO mixtures. The solvent molecules are liberated in the course of the complexation and enter the bulk solvent. As seen in Table 5 the $\Delta S^\circ_{\beta 4}$ values are all large and positive but significantly different. In AN, solvent molecules leave a relatively weak solvate structure for an unordered solvent, $\Delta S^\circ_{\beta 4}$ relatively low; in AN-DMSO mixtures, DMSO molecules leave a strong solvate structure for an unordered solvent, $\Delta S^\circ_{\beta 4}$ much larger; in DMSO, solvent molecules leave a strong solvate for an ordered solvent, again a low value of $\Delta S^\circ_{\beta 4}$, even lower than in AN. Thus, both solvate and solvent structures are responsible for the entropies of complexation.

Liberation of solvent molecules solvating chloride ion also occurs in the course of the complexation. However, the contribution of desolvation of chloride ion to the $\Delta S^\circ_{\beta 4}$ values may be small because of weak solvation of the ion in AN, DMSO, and their mixtures, as noted in a previous section.

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Table 5. Gibbs Energies, $\Delta G^\circ_{\beta 4}$/kJ mol^{-1}, Enthalpies, $\Delta H^\circ_{\beta 4}$/kJ mol^{-1}, and Entropies, $\Delta S^\circ_{\beta 4}$/J K^{-1} mol^{-1}, for the Reaction $Cu^{2+}+4Cl^-=[CuCl_4]^{2-}$, in Acetonitrile–Dimethyl Sulfoxide Mixtures at 25 °C

	DMSO content/mole fraction					
	0	0.025	0.05	0.1	0.5	1.0
$\Delta G^\circ_{\beta 4}$	−145.1	−105.2	−98.4	−86.9	−64.5	−54.6
$\Delta H^\circ_{\beta 4}$	−55.4	—	23.5	25.7	—	23.5
$\Delta S^\circ_{\beta 4}$	300	—	409	377	—	263

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