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

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Complexation of copper(II) with Br^- ions has been studied by calorimetry and spectrophotometry in *N,N*-dimethylformamide (DMF) containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 as constant ionic media at 25 °C. Calorimetric titration curves obtained in each solution were well explained in terms of formation of $[CuBr_n]^{(2-n)+}$ (n=1—4) and their formation constants, enthalpies and entropies were determined. Electronic spectra of individual copper(II) bromo complexes were also determined in the $(C_2H_5)_4NClO_4$, $LiClO_4$, and NH_4ClO_4 DMF solutions over the range 260—500 nm, the spectra of each complex being kept practically unchanged in these solutions. The complexation of copper(II) with Br^- ions is considerably weaker in the $LiClO_4$ solution than in the $(C_2H_5)_4NClO_4$ one and is even more weakened in the NH_4ClO_4 solution due to the formation of LiBr and NH_4Br ion pairs in the relevant solutions. The variation of the stepwise enthalpy and entropy values suggests that the coordination structure around copper(II) ion changes from octahedral to tetrahedral at the formation of $[CuBr_3]^-$. The result for the complexation between copper(II) and bromide ions thus obtained was compared with that for the complexation between the metal and chloride ions.

Complexation of copper(II) with chloride ions has so far been studied in aqueous and nonaqueous solutions, and the formation constants and enthalpies of the mononuclear $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes have been determined.[1—6)]

On the other hand, as to the copper(II) bromo complexes, the formation constants and enthalpies have been obtained only for the mono- and dibromocopper(II) complexes,[7)] although the formation of $[CuBr_4]^{2-}$ was indicated by spectrophotometry in some aprotic solvents.[8—12)] The $[CuBr_4]^{2-}$ complex has the flattened tetrahedral D_{2d} structure in the $Cs_2[CuBr_4]$ crystal.[13)] By judging from similar electronic spectra of $[CuBr_4]^{2-}$ in solution and in the $Cs_2[CuBr_4]$ crystal,[14—15)] the flattened tetrahedral D_{2d} structure of $[CuBr_4]^{2-}$ is also expected in solution, as well as in the case of $[CuCl_4]^{2-}$.[16)] In fact, the tetrahedral $[CuBr_4]^{2-}$ complex was revealed in water by the X-ray diffraction method.[17)] Although the structure of the tetrahalogenocuprate(II) complex is thus well established both in crystal and in solution, the knowledge of the structure of the mono-, di-, and trihalogeno complexes of copper(II) ion in solution is limited because these complexes have hardly been isolatd as single crystals. We recently elucidated by the X-ray diffraction method that the mono- and trichloro complexes have the distorted octahedral $[CuCl(dmf)_5]^+$ and the distorted tetrahedral $[CuCl_3(dmf)]^-$ structures, respectively, in *N, N*-dimethylformamide (DMF).[18)] The formation of the distorted octahedral $[CuBr(H_2O)_5]^+$ complex has been also indicated.[17)] Barnes and Hume[10)] suggested the formation of the five-coordinate $[CuBr_3(solvent)_2]^-$ complex having a distorted trigonal-bipyramidal structure from measurements of electronic spectra in various aprotic solvents.

In order to throw more light on the formation and the structure of copper(II) bromo complexes in solution, we investigated the complexation between copper(II) and bromide ions in DMF containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 as constant ionic media at 25 °C by using similar calorimetric and spectrophotometric procedures to those employed previously for the copper(II) chloride system in some aprotic solvents.[1,2)]

Experimental

Reagent. All chemicals used were of reagent grade. *Lithium bromide* was once recrystallized from methanol. *Ammonium perchlorate, tetraethylammonium bromide,* and *ammonium bromide* were used without further purification. LiBr and $(C_2H_5)_4NBr$ were dried at 150 and 100 °C, respectively, in vacuum and NH_4ClO_4 and NH_4Br at 150 °C under an atmospheric pressure.

Other chemicals were prepared or purified as described elsewhere.[1)]

Measurements. Calorimetric and spectrophotometric measurements were carried out in a room thermostated at (25±0.2) °C. Test solutions contained 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$ or 1 mol dm^{-3} NH_4ClO_4 as a constant ionic medium.

Calorimetric titrations were performed using a Dewar vessel in a water-bath thermostated at (25±0.007) °C. 100 cm^3 of a $Cu(ClO_4)_2$ DMF solution containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, or 1 mol dm^{-3} NH_4ClO_4 was placed in a Dewar vessel which was filled with dry nitrogen gas and isolated from moisture with a P_2O_5 drying-tube, and then it was titrated with the relevant titrant solution of 0.16 mol dm^{-3} $(C_2H_5)_4NBr$, 1 mol dm^{-3} LiBr, or 1 mol dm^{-3} NH_4Br. The concentration of metal

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ions in the initial test solution was varied over the range 5—20 mmol dm^{-3} in the $(C_2H_5)_4NClO_4$ DMF solution and 20—50 mmol dm^{-3} in the $LiClO_4$ and NH_4ClO_4 DMF solutions. Heats of complexation observed at each titration point were ranged 1—7 J in the $(C_2H_5)_4NClO_4$ and NH_4ClO_4 solutions and 1—12 J in the $LiClO_4$ solution with a certainty ±0.05 J and were corrected for heats of dilution of the titrant. Heats of dilution were measured in advance by separate experiments. All of the measurements were carried out by using a fully automatic on-line system for calorimetry developed in our laboratory.[19] Details of the data treatment have been described elsewhere.[1]

Electronic spectra were measured with a HITACHI 340 spectrophotometer (HITACHI) equipped with a PC-9801 computer (NEC) which recorded data every 2 nm over the wavelength range 260—500 nm. A flow cell with a light-path length of 0.5 cm was connected with a titration vessel through Teflon and glass tubes. 20 cm^3 of a $Cu(ClO_4)_2$ solution was placed in a vessel under a dry nitrogen atmosphere and then titrated with the relevant titrant solution.

Results and Discussion

Calorimetric Results. Calorimetric titration curves for complexation between copper(II) and bromide ions obtained in 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 DMF solutions are depicted in Figs. 1, 2, and 3, respectively. In each figure, enthalpies $\Delta H^\circ = -q/(\delta v C_{X,tit})$ were plotted against C_X/C_M, where q, δv, C_X, and C_M stand for the heat evolved, the volume of an aliquot of the titrant added and the total concentrations of bromide

Table 1. The Least-Squares Refinement of Overall Formation Constants, $\log(\beta_n/\text{mol}^{-n}\,\text{dm}^{3n})$, and Enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol^{-1}, of $[CuBr_n]^{(2-n)+}$ Using Calorimetric Data in *N*,*N*-Dimethylformamide Containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C

	(1, 3)	(1, 2, 3)	(1, 3, 4)	(1-4)
$\log \beta_1$	3.17 (0.13)	3.08 (0.14)	3.30 (0.10)	3.48 (0.08)
$\log \beta_2$	—	5.43 (0.13)	—	5.54 (0.13)
$\log \beta_3$	9.67 (0.13)	7.78 (0.12)	8.26 (0.12)	8.50 (0.09)
$\log \beta_4$	—	—	8.97 (0.38)	9.77 (0.16)
$\Delta H^\circ_{\beta 1}$	20.9 (0.5)	21.5 (0.8)	20.4 (0.3)	19.6 (0.2)
$\Delta H^\circ_{\beta 2}$	—	33.4 (0.8)	—	38.1 (1.5)
$\Delta H^\circ_{\beta 3}$	61.5 (0.4)	65.2 (0.5)	55.8 (0.5)	56.2 (0.5)
$\Delta H^\circ_{\beta 4}$	—	—	96.3 (22)	72.7 (2)
U a)	3.2	1.48	0.983	0.291
R b)	0.0522	0.0345	0.0289	0.0158

Values in parentheses refer to standard deviations. The sets (1, 4) and (1-5) gave larger U values. The number of calorimetric data points is 96. a) Error-square sum. b) The Hamilton R-factor.

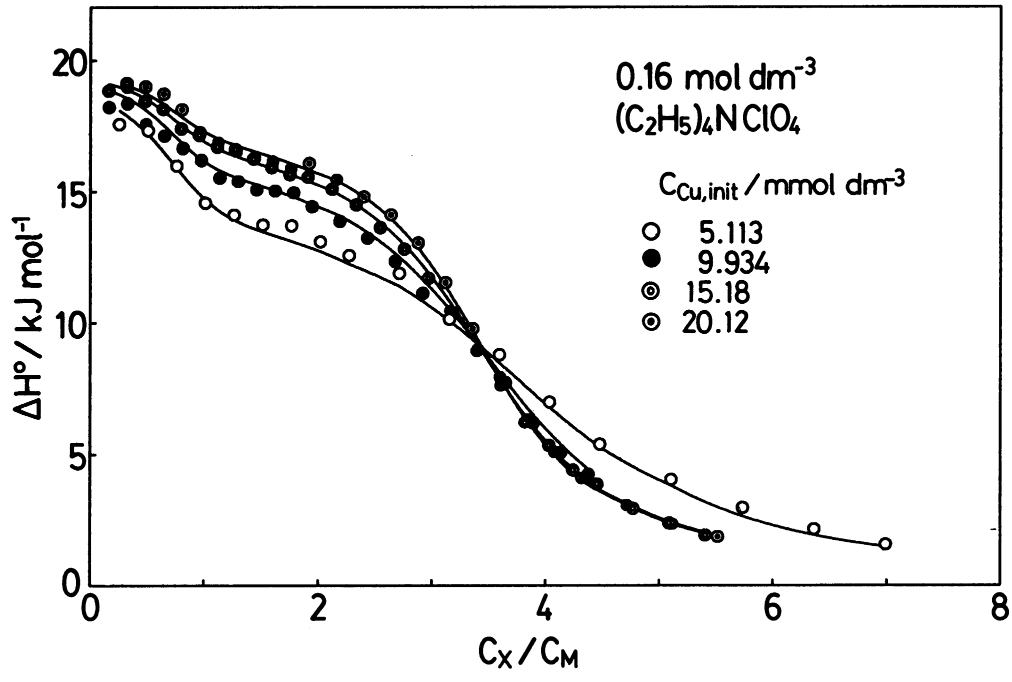

Fig. 1. Calorimetric titration curves of copper(II) bromide DMF solutions containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of copper(II) ions, $C_{Cu,init}$/mmol dm^{-3}, in initial test solutions are given in the figure. The solid lines show the curves calculated by using the constants of the set (1—4) by calorimetry in Table 2.

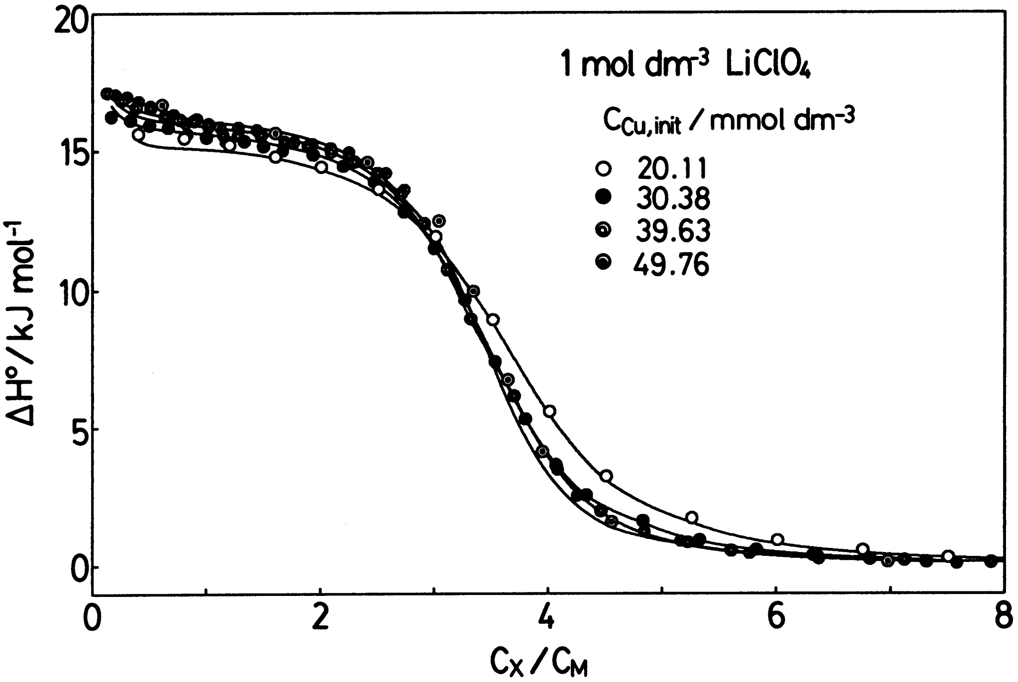

Fig. 2. Calorimetric titration curves of copper(II) bromide DMF solutions containing 1 mol dm^{-3} LiClO$_4$ at 25 °C. Concentrations of copper(II) ions, $C_{\mathrm{Cu,init}}$/mmol dm^{-3}, in initial test solutions are given in the figure. The solid lines show the curves calculated by using the constants of the set (1—4) by calorimetry in Table 2.

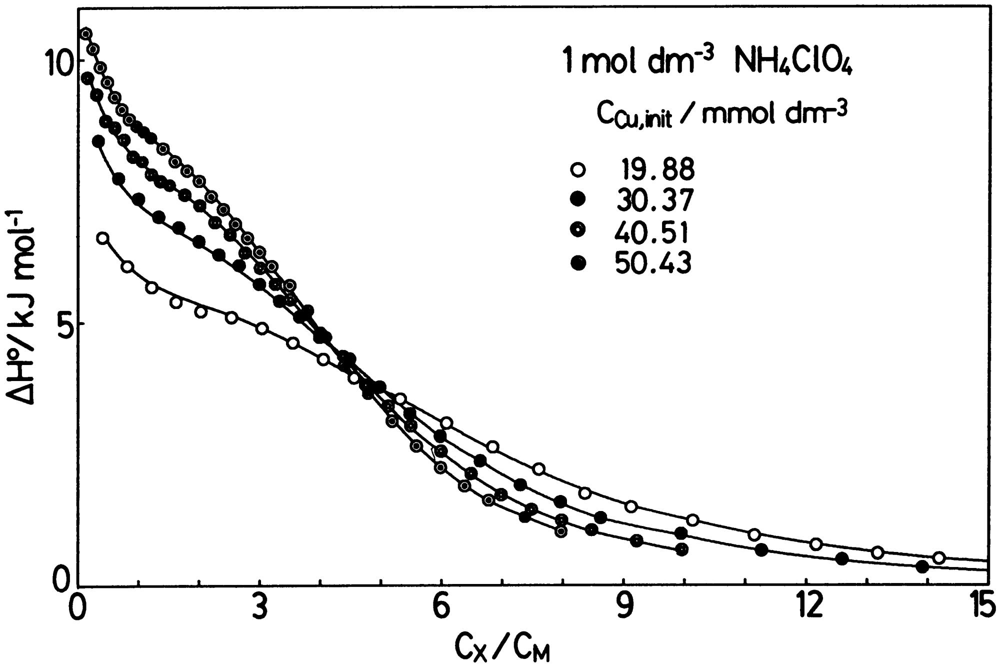

Fig. 3. Calorimetric titration curves of copper(II) bromide DMF solutions containing 1 mol dm^{-3} NH$_4$ClO$_4$ at 25 °C. Concentrations of copper(II) ions, $C_{\mathrm{Cu,init}}$/mmol dm^{-3}, in initial test solutions are given in the figure. The solid lines show the curves calculated by using the constants of the set (1—4) by calorimetry in Table 2.

and copper(II) ions in solution, respectively, at each titration point, and $C_{\mathrm{X,tit}}$ denotes the concentration of bromide ion in the titrant solution.

The calorimetric data obtained in each solution were analyzed by assuming the formation of plausible copper(II) bromo complexes and by simultaneously optimizing their formation constants and enthalpies by the least-squares method, the typical results obtained in the $(C_2H_5)_4NClO_4$ DMF solution being listed in Table 1. As seen in Table 1, among various sets examined the set (1—4) assuming the formation of $[CuBr_n]^{(2-n)+}$ (n=1—4) shows the minimal error-square sum U. The calorimetric data obtained in the $LiClO_4$ and NH_4ClO_4 DMF solutions were also

Table 2. Final Results of the Least-Squares Refinement of Overall Formation Constants, $\log(\beta_n/\mathrm{mol^{-n}\,dm^{3n}})$, and Enthalpies, $\Delta H^\circ_{\beta n}/\mathrm{kJ\ mol^{-1}}$, of $[CuBr_n]^{(2-n)+}$ in N,N-Dimethylformamide at 25 °C

	0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$	1 mol dm^{-3} $LiClO_4$	1 mol dm^{-3} NH_4ClO_4
$\log\beta_1$	3.48 (0.08)	2.29 (0.10)	1.58 (0.02)
$\log\beta_2$	5.54 (0.13)	4.53 (0.06)	2.57 (0.04)
$\log\beta_3$	8.50 (0.09)	7.03 (0.07)	4.00 (0.02)
$\log\beta_4$	9.77 (0.16)	8.22 (0.10)	4.29 (0.08)
$\Delta H^\circ_{\beta 1}$	19.6 (0.2)	20.1 (0.8)	16.5 (0.4)
$\Delta H^\circ_{\beta 2}$	38.1 (1.5)	30.0 (0.4)	27.3 (1.3)
$\Delta H^\circ_{\beta 3}$	56.2 (0.5)	53.5 (0.2)	43.5 (0.7)
$\Delta H^\circ_{\beta 4}$	72.7 (2)	54.4 (0.1)	42.5 (0.8)
$U^{a)}$	0.219	1.60	0.292
$R^{b)}$	0.0158	0.0146	0.0096
$N^{c)}$	96	119	121

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

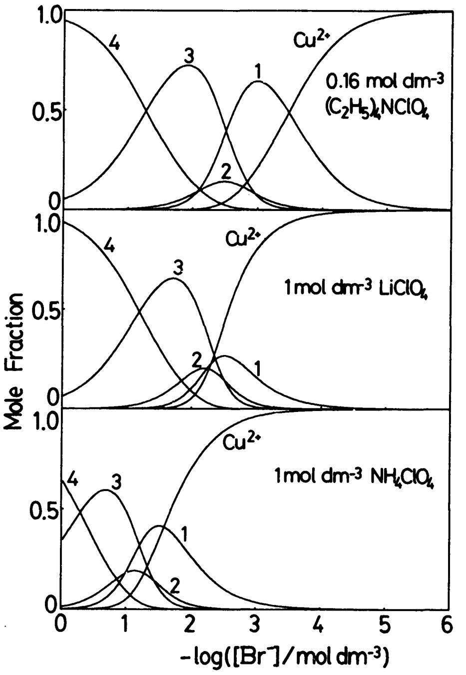

Fig. 4. Distribution of the copper(II) bromo complexes in 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 DMF solutions. The numbers represent n within $[CuBr_n]^{(2-n)+}$.

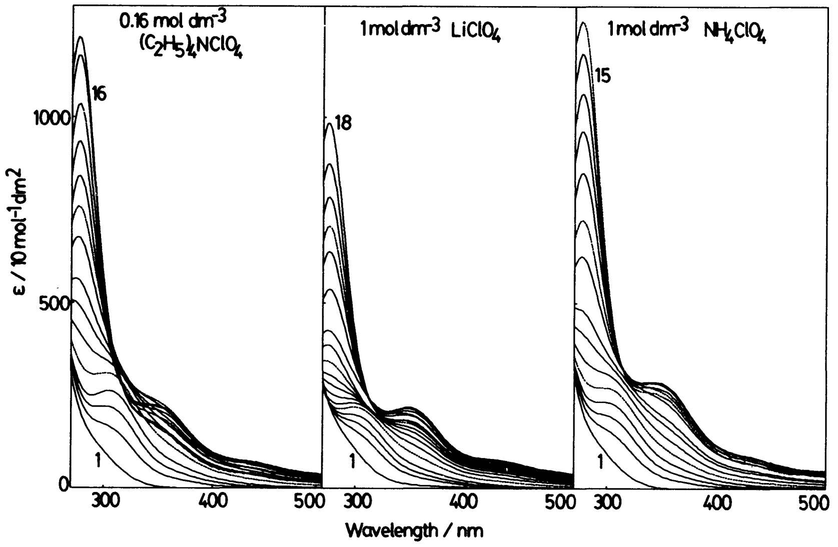

Fig. 5. Electronic spectra of copper(II) bromide DMF solutions in the range 260—500 nm. Intensities are normalized with the unit concentration of the metal ion in solution. Electronic spectra were obtained at various C_X/C_M, the value being varied from 0 (the solution No. 1) to 413 (No. 16), 318 (No. 18) and 2051 (No. 15) in the $(C_2H_5)_4NClO_4$, $LiClO_4$ and NH_4ClO_4 DMF solutions, respectively.

satisfactorily explained by the set (1—4). The overall formation constants and enthalpies of the $[CuBr_n]^{(2-n)+}$ (n=1—4) complexes thus obtained in the DMF solutions are summarized in Table 2. As seen in Figs. 1—3 the solid lines, the titration curves calculated using the constants in Table 2, well reproduce the experimental points over the whole range of C_X/C_M examined in each solution, and thus we conclude the formation of a series of four mononuclear copper(II) bromo complexes in all the solutions examined.

The complexation is weaker in the $LiClO_4$ solution than in the $(C_2H_5)_4NClO_4$ one and is even more weakened in the NH_4ClO_4 solution, as seen in the distribution of the copper(II) bromo complexes in Fig. 4. It is noted that the formation of $[CuBr_2]$ is strongly suppressed in any DMF solution examined. It is also noted that the formation of $[CuBr]^+$ is extensive in the $(C_2H_5)_4NClO_4$ DMF solution but is strongly suppressed in the $LiClO_4$ and NH_4ClO_4 DMF solutions.

Spectrophotometric Results. Electronic spectra of copper(II) bromide DMF solutions in the 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 DMF solutions are depicted in Fig. 5 over the wavelength range 260—500 nm, absorbance being normalized with the metal concentration in solution. Absorption bands observed are not simply assignable to each coppar(II) bromo complex, because absorbance monotonously increases with increasing concentration of bromide ion in the solutions over the wavelength range measured. Since each measured spectrum should be represented as the sum of electronic spectra of individual copper(II) bromo complexes by taking into account the distribution of species in solution, absorbance data obtained at selected 28 wavelengths in the range 260—500 nm were analyzed by assuming the formation of a series of mononuclear copper(II) bromo complexes, and their formation constants and molar extinction coefficients of each complex at relevant wavelengths were optimized by the least-squares method. The formation constants thus obtained are summarized in Table 3, the values, as a whole, being in satisfactory agreement with those calorimetrically determined.

In the $LiClO_4$ DMF solution, the variation in the measured electronic spectra with C_X/C_M is well explained in terms of the formation of $[CuBr_n]^{(2-n)+}$ (n=1—4). On the other hand, in the $(C_2H_5)_4NClO_4$ and NH_4ClO_4 DMF solutions the corresponding

Table 3. Final Results of the Least-Squares Refinement of Overall Formation Constants, $\log(\beta_n/\text{mol}^{-n}\,\text{dm}^{3n})$ of $[CuBr_n]^{(2-n)+}$ using Spectrophotometric Data in *N*,*N*-Dimethylformamide at 25 °C

	0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ (1, 3, 4)	1 mol dm^{-3} $LiClO_4$ (1—4)	1 mol dm^{-3} NH_4ClO_4 (1, 3, 4)
$\log\beta_1$	3.12 (0.06)	2.48 (0.36)	1.83 (0.05)
$\log\beta_2$	—	4.61 (0.47)	—
$\log\beta_3$	8.72 (0.08)	7.04 (0.29)	4.44 (0.09)
$\log\beta_4$	10.59 (0.11)	8.54 (0.82)	5.18 (0.16)
$U^{a)}$	0.264	0.913	0.494
$R^{b)}$	0.0248	0.0465	0.0330
$N^{c)}$	1876	1932	1876

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

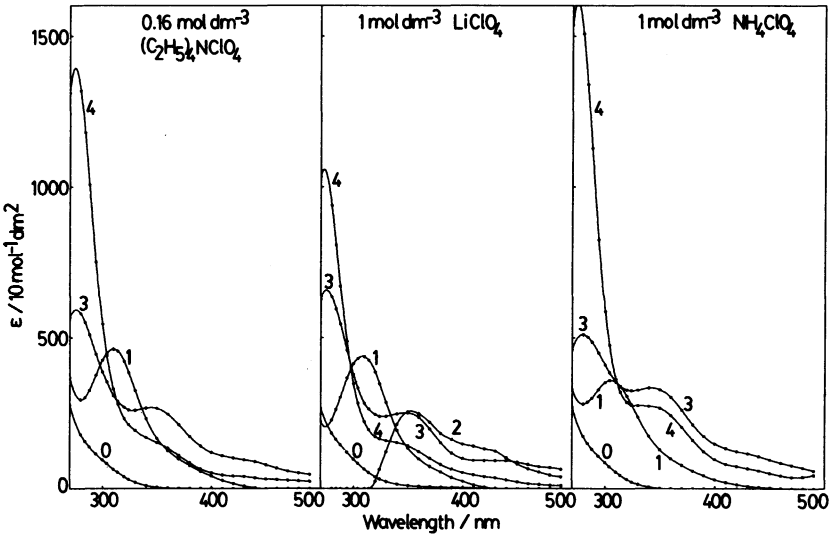

Fig. 6. Electronic spectra of individual copper(II) bromo complexes in the range 260—500 nm obtained in 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 DMF solutions. The numbers represent n within $[CuBr_n]^{(2-n)+}$.

spectral changes can be explained even without taking the formation of [CuBr$_2$] into account. The degree of the formation of [CuBr$_2$] might be too small to extract its characteristic electronic spectrum from the measured spectra in the DMF solutions.

The electronic spectra of individual copper(II) bromo complexes are shown in Fig. 6. In the LiClO$_4$ DMF solution, the electronic spectrum of [CuBr]$^+$ shows a single peak at 310 nm, and the spectrum of [CuBr$_2$] shows a peak at 350 nm and a weak absorption at ca. 430 nm, over the range measured. On the other hand, the [CuBr$_3$]$^-$ complex has two peaks at 275 and 350 nm and a weak absorption at ca. 450 nm. It is noted that the absorption band of the [CuBr$_2$] complex overlaps that of [CuBr$_3$]$^-$, and thus it is difficult to extract the individual spectrum of the former complex at the coexistence of the [CuBr$_2$] and [CuBr$_3$]$^-$ complexes in solution. The [CuBr$_4$]$^{2-}$ complex shows a peak at 275 nm and a broad peak at ca. 350 nm. The peak positions thus determined for each copper(II) bromo complex are in accordance with those of the ligand to metal charge transfer bands reported by Howard and Keeton.[11] Similar electronic spectra were obtained for each [CuBr$_n$]$^{(2-n)+}$ (n=1,3, or 4) complex in the (C$_2$H$_5$)$_4$NClO$_4$, LiClO$_4$, and NH$_4$ClO$_4$ DMF solutions as seen in Fig. 6, so that the coordination structure of each [CuBr$_n$]$^{(2-n)+}$ (n=1, 3, or 4) complex may be essentially the same in these ionic medium solutions.

Ion-Pair Formation of Bromide Ions. As noted in a preceding section, the complexation of copper(II) with bromide ions is considerably weaker in the 1 mol dm^{-3} LiClO$_4$ solution than in the 0.16 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ one, and is even more weakened in the 1 mol dm^{-3} NH$_4$ClO$_4$ solution. A similar trend has been observed for the comlexation of copper(II) with chloride ions in the 0.2 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ and 1 mol dm^{-3} LiClO$_4$ DMF solutions.[1] The ion-pair formation of chloride ion with medium cations

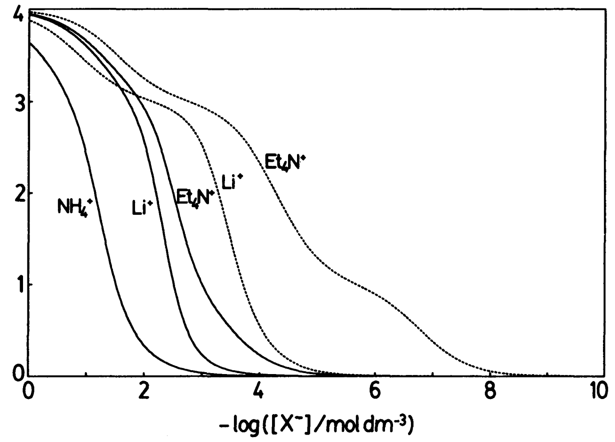

Fig. 7. Formation functions $\bar{n}$ of the copper(II) bromide (the solid lines) and copper(II) chloride (the dotted lines) systems in *N,N*-dimethylformamide containing (C$_2$H$_5$)$_4$NClO$_4$ (Et$_4$N$^+$), LiClO$_4$ (Li$^+$), and NH$_4$ClO$_4$ (NH$_4^+$) at 25 °C.

Table 4. 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 [CuX$_n$]$^{(2-n)+}$ in *N,N*-Dimethylformamide at 25 °C

	0.16 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ X=Br	1 mol dm^{-3} LiClO$_4$ X=Br	1 mol dm^{-3} NH$_4$ClO$_4$ X=Br	0.2 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$[a] X=Cl
$\log K_1$	3.48	2.29	1.58	6.79
$\log K_2$	2.06	2.24	0.99	4.54
$\log K_3$	2.96	2.50	1.43	4.00
$\log K_4$	1.27	1.19	0.29	1.52
ΔG°_1	−19.9	−13.1	−9.0	−38.8
ΔG°_2	−11.8	−12.8	−5.7	−25.9
ΔG°_3	−16.9	−14.3	−8.2	−22.8
ΔG°_4	−7.3	−6.8	−1.6	−8.7
ΔH°_1	19.6	20.1	16.5	10.3
ΔH°_2	18.5	9.9	10.8	9.7
ΔH°_3	18.1	23.6	16.1	7.3
ΔH°_4	16.5	0.8	−1.0	−8.1
ΔS°_1	132	111	86	165
ΔS°_2	101	76	55	120
ΔS°_3	117	127	82	101
ΔS°_4	80	26	2	2
$\Delta G^\circ_{\beta 4}$[b]	−55.8	−46.9	−24.5	−96.2
$\Delta H^\circ_{\beta 4}$[b]	72.7	54.4	42.5	19.2
$\Delta S^\circ_{\beta 4}$[b]	431	340	225	387

a) Ref. 1. b) For the overall formation of [CuBr$_4$]$^{2-}$.

is practically negligible in a 0.1—0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution, and thus the weaker complexation between copper(II) and chloride ions in the $LiClO_4$ solution than that in the $(C_2H_5)_4NClO_4$ one is ascribed to the formation of LiCl ion pairs in the former solution.[1)] It is expected that the ion-pair formation of bromide ion with medium cations is also negligible in the $(C_2H_5)_4NClO_4$ DMF solution but is appreciably enhanced in the $LiClO_4$ and NH_4ClO_4 solutions. Therefore, the formation of LiBr and NH_4Br ion pairs may be responsible for the weaker complexation of copper(II) with Br^- ions in the $LiClO_4$ and NH_4ClO_4 DMF solutions, respectively. It is noted that, since the complexation between copper(II) and bromide ions in the NH_4ClO_4 solution is weaker than that in the $LiClO_4$ solution, the ion-pair formation of bromide ion should occur more extensively in the former solution than in the latter.

In Fig. 7, the formation functions $\bar{n}$ calculated for the copper(II) chloride and bromide systems in the $LiClO_4$ solution are compared with those in the $(C_2H_5)_4NClO_4$ solution, the shift is larger for the chloride system than for the bromide one, the result suggesting that the LiCl ion pairs are more extensively formed than the LiBr ones in DMF. This is reasonable because hard Li^+ ion prefers hard and small Cl^- to Br^- ion.

As seen in Table 4, the $\Delta H^\circ_{\beta4}$ and $\Delta S^\circ_{\beta4}$ values for the overall formation of the $[CuBr_4]^{2-}$ complex in the $LiClO_4$ solution are smaller than those in the $(C_2H_5)_4NClO_4$ one, the values in the NH_4ClO_4 solution being even smaller than those in the $LiClO_4$ one. The result suggests that both enthalpy and entropy values associated with the formation of LiBr and NH_4Br ion pairs are positive. Since the formation of ion pairs may be accompanied by an extensive desolvation of both cation and anion, a positive enthalpy entropy change may be ascribed to the rupture of the M^+-dmf (M^+=Li^+ and NH_4^+) and Br^--dmf bonds and a positive entropy change to the liberation of DMF molecules from the coordination shells of M^+ and Br^- ions. The entropy increase of the ion-pair formation may be especially large in DMF because DMF molecules are randomly distributed in the bulk,[20)] and thus the increased entropy due to the liberation of DMF molecules coordinating to the ions may not be compensated with the entropy decrease due to the intermolecular interactions in the bulk solution. A similar result has also been observed for the complexation of cadmium(II) with bromide ions in dimethyl sulfoxide containing various ionic media.[21)]

Stepwise Thermodynamic Quantities. Stepwise formation constants, Gibbs energies, enthalpies and entropies of formation of the $[CuBr_n]^{(2-n)+}$ (n=1—4) complexes in the 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$, 1 mol dm^{-3} $LiClO_4$, and 1 mol dm^{-3} NH_4ClO_4 DMF solutions are summarized in Table 4, together with those of the $[CuCl_n]^{(2-n)+}$ (n=1—4) complexes in the 0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution.[1)]

Copper(II) ion is coordinated with six DMF molecules and the $[Cu(dmf)_6]^{2+}$ solvate species has the distorted octahedral structure in DMF[18)] as well as in water.[22)] On the other hand, the flattened tetrahedral $[CuBr_4]^{2-}$ complex is formed in a solution of a high concentration of Br^- ion in DMF. Thus, the coordination structure around copper(II) ion changes from the six- to four-coordinate in the course of the complexation with bromide ions. In any ionic medium examined, a relatively large and positive stepwise entropy value is observed at the third step, indicating an extensive liberation of DMF molecules from the primary solvation shell of the metal ion. It is thus suggested that the coordination structure about copper(II) ion changes at the third consecutive step and the $[CuBr_3(dmf)]^-$ complex with the tetrahedral structure is yielded. Relatively large endothermicities are also observed at the third step in the 1 mol dm^{-3} $LiClO_4$ and NH_4ClO_4 DMF solutions, and the result may be reasonably explained in terms of the breaking of more than two metal-solvent bonds accompanying the structure change from the five- or six-coordinate $[CuBr_2]$ complex to the four-coordinate $[CuBr_3]^-$ complex at this step.

In 0.1—0.2 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solutions where the fomation of $(C_2H_5)_4NX$ (X^-=Cl^- or Br^-) ion pairs is practically negligible, the formation constants of the copper(II) bromo complexes are significantly smaller than those of the copper(II) chloro complexes,[1)] due mainly to more positive ΔH°_n values for the bromide system than those for the chloride one. The result evidently indicates the weaker Cu–Br bond than the Cu–Cl bond as expected from the larger size of Br^- ion.[23)]

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