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Calorimetric and Spectrophotometric Studies of Ternary Copper(II) Complexes with Bromide Ions and 2,2′-Bipyridyl in *N,N*-Dimethylformamide

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Mixed ligand complexation of copper(II) with bromide ions and 2,2′-bipyridyl (bpy) has been calorimetrically studied in *N,N*-dimethylformamide (DMF) containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Complexation of the metal ion with 2,2′-bipyridyl has been also studied in the same solution. The calorimetric titration curves obtained were satisfactorily explained in terms of formation of the mononuclear $[CuBr_p(bpy)_q]^{(2-p)+}$ (denoted as $(1pq)$) complexes such as (101), (102), (103), (111), (121), and (112), and their formation constants and enthalpies were determined. The mixed ligand (111), (112), and (121) complexes are quite stable and yielded to a large extent in the DMF solution. Electronic spectra of these complexes have been measured in DMF over the range 400—1500 nm. The thermodynamic quantities of formation and electronic spectra of the complexes thus obtained are discussed in connection with the coordination structure of the complexes in DMF. The formation of the five-coordinate $[Cu(bpy)_2(dmf)]^{2+}$ and $[CuBr(bpy)_2]^+$ complexes is suggested in the DMF solution as well as in crystal.

Complexation of bivalent transition metal ions with nitrogen-coordinating bidentate ligands such as 1,10-phenanthroline (phen) and 2,2′-bipyridyl (bpy) has so far been studied in water.[1] Mixed ligand complexes involving these ligands and a variety of amino acids (or peptides) have also been intensively studied from the biochemical point of view.[2]

As to mixed ligand complexes of copper(II) involving 2,2′-bipyridyl, Barclay et al.[3] reported the five-coordinate trigonal-bipyramidal $[CuI(bpy)_2]^+$ complex in crystal. A similar coordination structure has also been revealed for the $[CuX(bpy)_2]^+$ ($X^-=Cl^-$, Br^- and I^-) complex with varying counter anions.[4–8] The trigonal-bipyramidal $[Cu(bpy)_2(H_2O)]^{2+}$ complex has been observed in crystal,[9] as well as the corresponding $[Cu(phen)_2(H_2O)]^{2+}$ complex.[10–12] Besides, Faye[13] suggested from measurements of electronic spectra that both bis(1,10-phenanthroline)copper(II) and monochlorobis(1,10-phenanthroline)copper(II) complexes have the triginal-bipyramidal structure in acetone and nitromethane solutions.

Although the knowledge of the structure and electronic spectra of the five-coordinate copper(II) complexes has been so far accumulated, the thermodynamic behavior of these complexes in solution has not been well elucidated yet.

In the present work, we calorimetrically investigated the formation of ternary copper(II) complexes with bromide ions and 2,2′-bipyridyl in *N,N*-dimethylformamide containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. The formation of binary copper(II) complexes with 2,2′-bipyridyl has been also explored in the same ionic medium solution. The complexation of copper(II) with bromide ions has already been examined in the $(C_2H_5)_4NClO_4$ DMF solution.[14] In order to elucidate the coordination structure of the ternary copper(II) complexes in DMF, electronic spectra were measured over the range 400—1500 nm in DMF solutions in which one of the ternary complexes was predominantly formed. Electronic spectra of the 2,2′-bipyridyl complexes of copper(II) have also been measured in DMF. The thermodynamic quantities of formation and electronic spectra of the $[Cu(bpy)_n]^{2+}$ and $[CuCl_p(bpy)_q]^{(2-p)+}$ complexes thus determined will be discussed in connection with the coordination structure of the complexes in DMF.

Experimental

Reagent. All chemicals used were of reagent grade. 2,2′-*Bipyridyl* was used without further purification and dried in vacuum over P_2O_5 in a desiccator. Other chemicals were prepared or purified as described elsewhere.[14,15]

Measurements. Calorimetric measurements were carried out in a room thermostated at (25.0±0.2) °C, a Dewar vessel for calorimetric titrations being immersed in a water bath controlled at (25±0.007) °C. All test solutions contained 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium. 100 cm^3 of a DMF solution containing copper(II) perchlorate or copper(II) bromide with varying molar ratios of bromide to the metal ions 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 0.1 mol dm^{-3} 2,2′-bipyridyl DMF solution. Heats of complexation observed at each titration point were ranged 1—5 J with certainty ±0.05 J and were corrected for heats of dilution of the titrant, although the correction was very small. Heats of dilution were determined in advance by separate experiments by titrating a 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution with the 2,2′-bipyridyl solution. All of the measurements were carried out by using a fully automatic on-line system for calorimetry developed in our laboratory.[16,17]

Calorimetric data were treated with the least-squares method by taking into account the mass-balance equations for the metal and bromide ions and 2,2′-bipyridyl in solution, and the formation constants and enthalpies of assumed complexes were simultaneously optimized. The least-

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squares program having been used for the binary systems in previous works[14–16] was extended for the ternary system in this work.

Electronic spectra were measured using a Cary 2300 spectrophotometer (Varian) over the range 400—1500 nm.

Results and Discussion

Calorimetric titration curves for the complexation of copper(II) ion with 2,2′-bipyridyl are depicted in Fig. 1. The corresponding curves in the ternary system are depicted in Fig. 2. In both figures, enthalpies $\Delta H^\circ = -q/(\delta v C_{L,tit})$ were plotted against C_L/C_M, where q, δv, C_L, and C_M stand for the heat evolved, the volume of an aliquot of the titrant added and the concentrations of 2,2′-bipyridyl and copper(II) ion in solution, respectively, at each titration point, and $C_{L,tit}$ denotes the concentration of 2,2′-bipyridyl in the titrant soluton.

In Fig. 1 the ΔH° values are negative and kept practically constant in the range $C_L/C_M<1$, indicating a formation of $[Cu(bpy)]^{2+}$ complex. The ΔH° values drastically change at $C_L/C_M=1$ and are slightly dependent on the concentration of the metal ion over the range $C_L/C_M=1$—4, rather weak $[Cu(bpy)_2]^{2+}$ and $[Cu(bpy)_3]^{2+}$ complexes being expected to be formed in the range. As expected, the calorimetric data were well explained in terms of the formation of $[Cu(bpy)_n]^{2+}$ ($n=1$—3), and their formation constants and enthalpies were optimized by the least-squares method. The overall formation constants and enthalpies of formation of the complexes thus obtained are summarized in Table 1. As seen in Fig. 1, the solid lines, the titration curves calculated by using the constants in Table 1, satisfactorily reproduce the experimental points over the whole range of C_L/C_M examined.

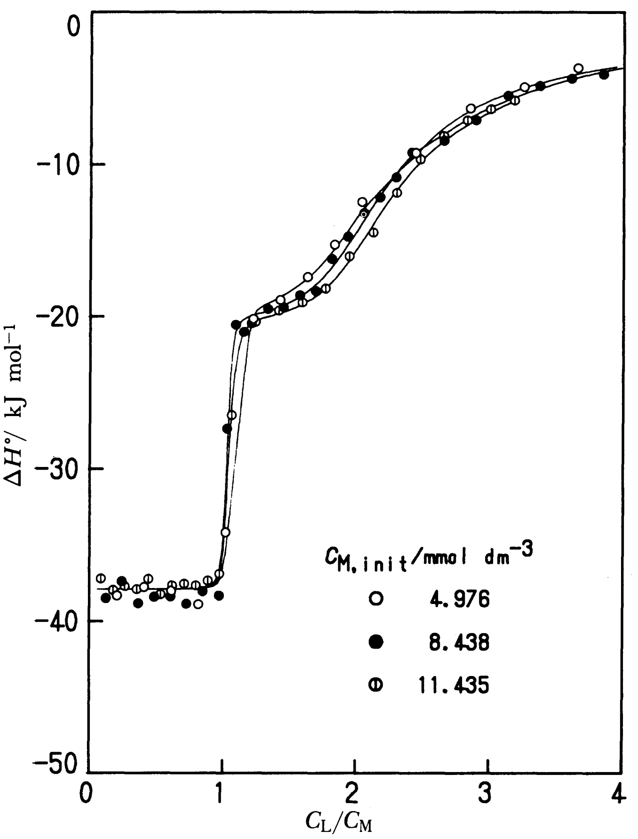

Fig. 1. Calorimetric titration curves of copper(II) 2,2′-bipyridyl DMF solutions containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of copper(II) ions, $C_{M,init}$/mmol dm^{-3}, in the initial test solutions are given in the figure. The solid lines show the curves calculated by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

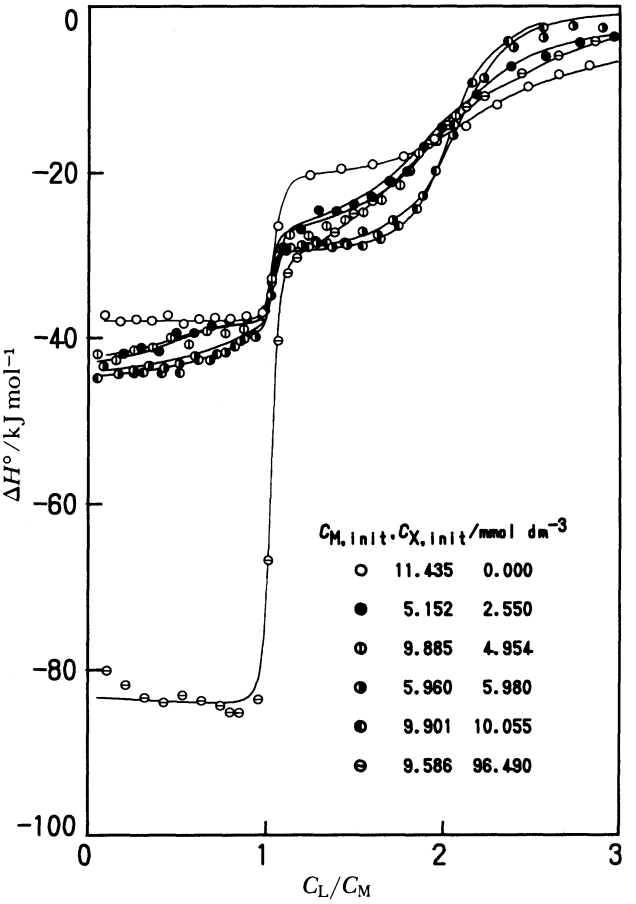

Fig. 2. Calorimetric titration curves in the ternary system obtained by titrating copper(II) bromide DMF solutions with a 2,2′-bipyridyl DMF solution, each containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of copper(II) and bromide ions, $C_{M,init}$ and $C_{X,init}$/mmol dm^{-3}, in initial test solutions are given in the figure. The solid lines show the curves calculated by using the constants in Table 1.

In Fig. 2 the calorimetric titration curves are strongly dependent on the molar ratio of bromide to copper(II) ions in the solution. The curves calculated by using the only known formation constants and enthalpies of $[CuBr_n]^{(2-n)+}$ ($n=1$—4)[14] and those of $[Cu(bpy)_n]^{2+}$ ($n=1$—3) determined above hardly reproduce the experimental points, and thus the formation of ternary $[CuBr_p(bpy)_q]^{(2-p)+}$ (denoted as $(1pq)$) complexes must be considered. Ternary $(1pq)$ complexes with $p+2q\leq 6$ may be plausibly formed by taking into

Table 1. The Least-Squares Refinement of Overall Formation Constants, $\log(\beta_{1pq}/\mathrm{mol}^{-(p+q)}\mathrm{dm}^{3(p+q)})$, and Enthalpies, $\Delta H^\circ_{\beta 1pq}/\mathrm{kJ\,mol^{-1}}$, of $[\mathrm{CuBr}_p(\mathrm{bpy})_q]^{(2-p)+}$ (bpy=2,2′-bipyridyl) in *N*,*N*-Dimethylformamide Containing 0.16 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ at 25 °C

	$[\mathrm{Cu(bpy)}_q]^{2+}$	$[\mathrm{CuBr}_p(\mathrm{bpy})_q]^{(2-p)+}$
$\log\beta_{101}$	7.04(0.41)	7.20(0.33)
$\log\beta_{102}$	10.55(0.45)	10.74(0.35)
$\log\beta_{103}$	12.34(0.48)	12.56(0.37)
$\log\beta_{111}$	—	11.90(0.26)
$\log\beta_{121}$	—	14.12(0.22)
$\log\beta_{112}$	—	15.87(0.23)
$\Delta H^\circ_{\beta 101}$	−37.9(0.3)	−37.9(0.3)
$\Delta H^\circ_{\beta 102}$	−58.7(0.8)	−58.7(0.6)
$\Delta H^\circ_{\beta 103}$	−86.2(3.9)	−85.7(3.7)
$\Delta H^\circ_{\beta 111}$	—	−24.0(0.5)
$\Delta H^\circ_{\beta 121}$	—	−18.7(0.7)
$\Delta H^\circ_{\beta 112}$	—	−54.5(0.7)
U[a)]	0.178	0.520
R[b)]	0.0197	0.0210
N[c)]	84	220

Values in parentheses refer to three standard deviations. The formation constants and enthalpies of formation of $[\mathrm{CuBr}_n]^{(2-n)+}$ (n=1—4)[14] were fixed in the course of the least-squares analysis. a) Error-square sum. b) The Hamilton R-factor. c) The number of data points.

account the six-coordinate about the metal ion, together with the mono- and bidentate coordinations of bromide ion and 2,2′-bipyridyl, respectively. The possible compositions of the ternary complexes are thus (111), (121), (131), (141), (112), and (122). However, the formation of the (131), (141), and (122) complexes were eliminated in the course of the least-squares analysis. The formation constants and enthalpies of these ternary complexes were finally optimized together with those of the binary $[\mathrm{Cu(bpy)}_n]^{2+}$ (n=1—3) complexes by using the whole set of data shown in Figs. 1 and 2, the results being also listed in Table 1. The Hamilton R-factor was 2.10% and the thermodynamic quantities of each complex was obtained with relatively small standard deviations. As seen in Fig. 2, the solid lines calculated by using the constants in Table 1 and those for the $[\mathrm{CuBr}_n]^{(2-n)+}$ (n=1—4) previously determined,[14] satisfactorily reproduce the experimental points. The $\log\beta_{10q}$ (q=1—3) values thus obtained in the mixed ligand ternary system were in satisfactorily good agreement with those in the binary system without bromide ions.

In Fig. 3 the distribution of species is shown as the function of $-\log([\mathrm{bpy}]/\mathrm{mol\,dm^{-3}})$ in solution with varying $R(=C_\mathrm{X}/C_\mathrm{M})$ values, which is calculated by using the formation constants of the ternary copper(II) complexes with 2,2′-bipyridyl and bromide ions, together with those of relevant binary copper(II) complexes. It is indicated from the figure that the (111) and (112) complexes are predominantly formed in solution containing equimolar amounts of copper(II) and bromide ions (R=1). With increasing R, the formation of the ternary copper(II) complexes is suppressed for the (111) complex but is enhanced for the (121) one. The (112) complex is formed in all the solutions. In Fig. 4 the distribution of species is represented as the function of $-\log([\mathrm{Br}^-]/\mathrm{mol\,dm^{-3}})$ in solution with varying R' $(=C_\mathrm{L}/C_\mathrm{M})$ ratios of 2,2′-bipyridyl to copper(II) ion, for comparison.

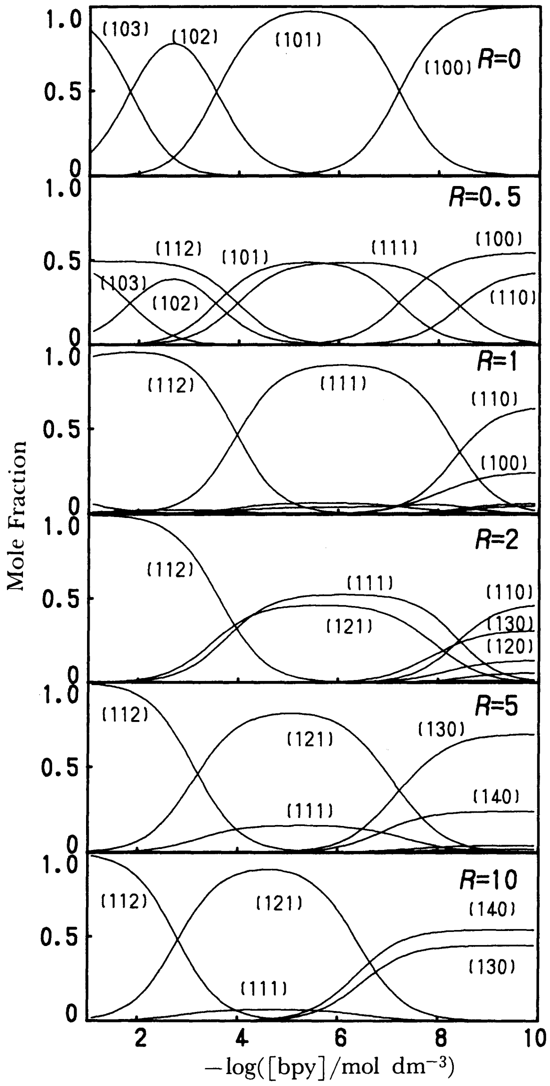

Fig. 3. Distribution of the $[\mathrm{CuBr}_p(\mathrm{bpy})_q]^{(2-p)+}$ (denoted as $(1pq)$) complexes as the function of $-\log([\mathrm{bpy}]/\mathrm{mol\,dm^{-3}})$ in DMF containing 0.16 mol dm^{-3} $(\mathrm{C_2H_5})_4\mathrm{NClO_4}$ at 25 °C. The R value stands for the molar ratio of bromide to copper(II) ions in solution.

The distribution of species in Figs. 3 and 4 indicates that each of the (101), (102), (103), (111), (112), and (121) complexes is yielded as a main species in a DMF solution with a suitable composition of the ligands to copper(II) ion. Electronic spectra of DMF solutions in which each of the $[\mathrm{Cu(bpy)}_n]^{2+}$ (n=0—3) complex is predominantly formed are depicted in Fig. 5. As well, electronic spectra of the $[\mathrm{CuBr(bpy)}]^+$, $[\mathrm{CuBr(bpy)_2}]^+$ and $[\mathrm{CuBr_2(bpy)}]$ complexes are shown in Fig. 6.

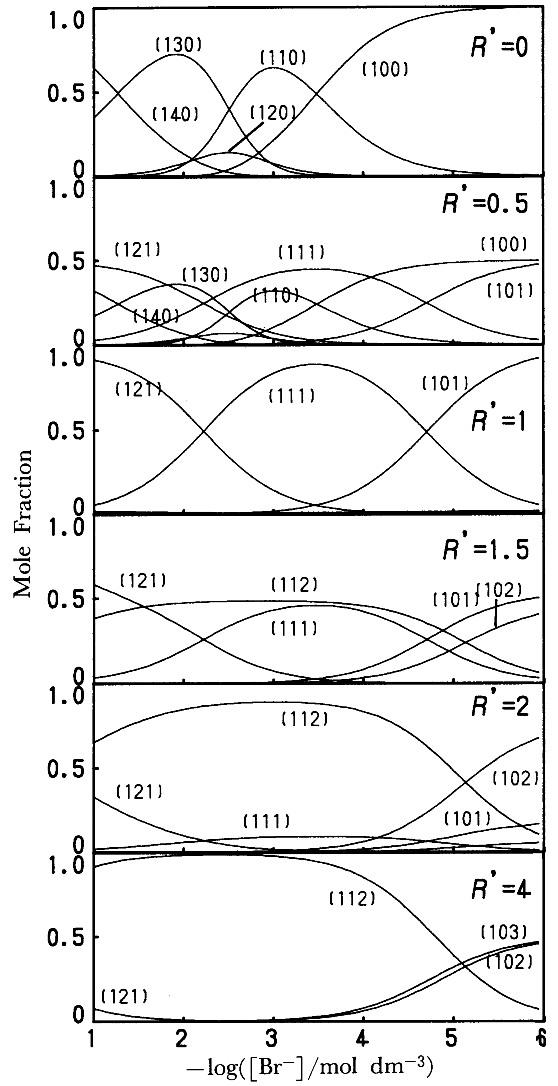

Fig. 4. Distribution of the $[CuBr_p(bpy)_q]^{(2-p)+}$ (denoted as ($1pq$)) complexes as the function of $-\log([Br^-]/mol\ dm^{-3})$ in DMF containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. The R' value stands for the molar ratio of 2,2′-bipyridyl to copper(II) ion in solution.

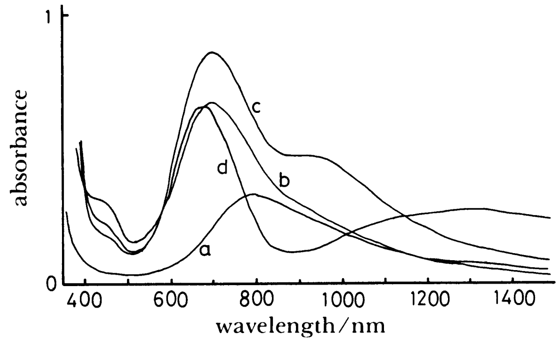

Fig. 5. Electronic spectra of various copper(II) 2,2′-bipyridyl DMF solutions. Concentrations of metal ions and ligands, C_M and C_L/mmol dm^{-3}: 9.69, 0.0 (spectrum a for $[Cu(dmf)_6]^{2+}$); 10.17, 11.60 (b for $[Cu(bpy)]^{2+}$); 9.92, 21.2 (c for $[Cu(bpy)_2]^{2+}$); 10.67, 100. (d for $[Cu(bpy)_3]^{2+}$).

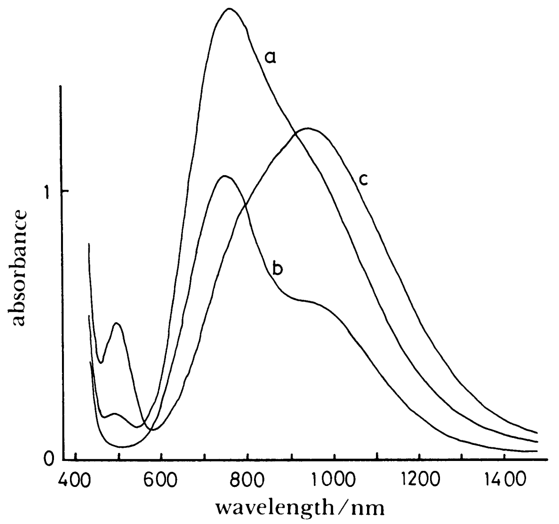

Fig. 6. Electronic spectra of the ternary copper(II) complexes with bromide ions and 2,2′-bipyridyl in DMF. Concentrations of metal and bromide ions and 2,2′-bipyridyl, C_M, C_X and C_L/mmol dm^{-3}: 10.15, 11.01, 9.97 (spectrum a for $[CuBr(bpy)]^+$); 9.87, 10.47, 20.35 (b for $[CuBr(bpy)_2]^+$); 4.00, 16.0, 4.25 (c for $[CuBr_2(bpy)]$).

These electronic spectra observed in the wavelength range 400—1500 nm may be ascribed to the d-d transition bands of copper(II) ion within the complexes.

Binary (2,2′-Bipyridyl)copper(II) Complexes. In DMF, copper(II) ion is present as $[Cu(dmf)_6]^{2+}$ with the distorted octahedral structure according to X-ray diffraction measurements.[19] The DMF molecules coordinating to copper(II) ion are stepwise replaced with 2,2′-bipyridyl molecules and the $[Cu(bpy)_3]^{2+}$ complex is finally formed in the solution. The $[Cu(bpy)_3]^{2+}$ complex may have the distorted octahedral structure in DMF because its electronic spectrum in DMF is very similar to that in crystals,[20] and the distorted octahedral $[Cu(bpy)_3]^{2+}$ complex has been revealed in the $[Cu(bpy)_3](ClO_4)_2$ crystal.[21] Similarly, the mono(2,2′-bipyridyl) complex may have the distorted octahedral structure as represented by $[Cu(bpy)(dmf)_4]^{2+}$ with two DMF molecules at the equatorial position and the others at the axial position, because its electronic spectrum shows a similar single peak to that of the $[Cu(dmf)_6]^{2+}$ complex, although the peak position of the former complex is shifted to shorter wavelength by ca. 100 nm than that of the latter.

The bis(2,2′-bipyridyl)copper(II) complex exhibits two absorption bands at ca. 690 and 950 nm in DMF as well as in water,[22] suggesting a similar coordination structure of the complex in both solutions. It is noted that the electronic spectrum of the bis(2,2′-bipyridyl) complex in solution is also very similar to that (with peaks at 708 and 930 nm) arising from the five-coordinate $[Cu(bpy)_2(H_2O)]^{2+}$ moiety in the $[Cu(bpy)_2(H_2O)]S_5O_6$ crystal.[9] Therefore, the five-coordinate $[Cu(bpy)_2(dmf)]^{2+}$ complex is plausibly formed in

Table 2. Thermodynamic Quantities, $\log(K_n/\mathrm{mol^{-1}\,dm^3})$, $\Delta G_n^\circ/\mathrm{kJ\,mol^{-1}}$, $\Delta H_n^\circ/\mathrm{kJ\,mol^{-1}}$, and $\Delta S_n^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$, for the Stepwise Formation of the 2,2′-Bipyridyl and Ethylenediamine Complexes of Copper(II)

	2,2′-Bipyridyl DMF[a)]	2,2′-Bipyridyl Water[b)]	Ethylenediamine Water[c)]
$\log K_1$	7.20	7.81	11.38
$\log K_2$	3.54	4.64	9.97
$\log K_3$	1.82	4.17	
ΔG_1°	−41.1	−44.6	−65.0
ΔG_2°	−20.2	−26.5	−56.9
ΔG_3°	−10.4	−23.8	
ΔH_1°	−37.9	−49.7	−67.7
ΔH_2°	−20.8	−22.6	−71.0
ΔH_3°	−27.0	−27.7	
ΔS_1°	11	−17	−9
ΔS_2°	−2	13	−47
ΔS_3°	−56	−13	

a) This work in *N,N*-dimethylformamide containing 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$. b) Ref. 1, in 0.1 mol dm^{-3} $NaClO_4$ aqueous solution. c) Ref. 18, in 3 mol dm^{-3} $LiClO_4$ aqueous solution.

DMF.

The thermodynamic quantities of stepwise formation of $[Cu(bpy)_n]^{2+}$ (n=1—3) in DMF are summarized in Table 2, together with those of $[Cu(bpy)_n]^{2+}$ (n=1—3)[1)] and $[Cu(en)_n]^{2+}$ (n=1 and 2)[18)] in water. The ΔH_1° value for the formation of the $[Cu(bpy)]^{2+}$ complex is large and negative and the corresponding ΔS_1° value is slightly positive in DMF. It is noted that the ΔH_2° value is significantly less negative than the ΔH_1° value in the copper(II)-2,2′-bipyridyl system both in DMF and in water. On the other hand, the ΔH_2° value is even more negative than the ΔH_1° value in the copper(II)-ethylenediamine system in water. According to X-ray diffraction measurements,[23)] the bis(ethylenediamine) complex has the distorted octahedral (or practically the square planar) $[Cu(en)_2(H_2O)_{ax}(H_2O)_{ax}]^{2+}$ structure with extremely elongated two axial water molecules in water. Therefore, the significant difference observed for the ΔH_2° values in the 2,2′-bipyridyl and ethylenediamine systems may be ascribable to the difference in the coordination structure of the bis(2,2′-bipyridyl) and bis(ethylenediamine) complexes of copper(II). It is also noted that the ΔH_3° and ΔS_3° values are more negative than the corresponding ΔH_2° and ΔS_2° values in the copper(II)-2,2′-bipyridyl system. Considering the five-coordinate $[Cu(bpy)_2(dmf)]^{2+}$ complex as discussed in a preceding section, we expect that the more negative ΔH_3° and ΔS_3° values than the corresponding ΔH_2° and ΔS_2° ones may be explained in terms of the liberation of only one DMF molecule within the five-coordinate $[Cu(bpy)_2(dmf)]^{2+}$ complex followed by the formation of the six-coordinate $[Cu(bpy)_3]^{2+}$ complex.

Table 3. Thermodynamic Quantities, $\Delta G^\circ/\mathrm{kJ\,mol^{-1}}$, $\Delta H^\circ/\mathrm{kJ\,mol^{-1}}$, and $\Delta G^\circ/\mathrm{J\,K^{-1}\,mol^{-1}}$, of Stepwise Formation of $[CuBr_p(bpy)_q]^{(2-p)+}$ (bpy=2,2′-bipyridyl), Together with Those of Stepwise Formation of $[CuBr_n]^{(2-p)+}$ (n=1—4) in *N,N*-Dimethylformamide at 25 °C

Reaction	ΔG°	ΔH°	ΔS°
$[CuBr(bpy)]^+ + bpy = [CuBr(bpy)_2]^+$	−22.7	−30.5	−26
$[Cu(bpy)_2]^{2+} + Br^- = [CuBr(bpy)_2]^+$	−29.3	4.2	112
$[CuBr]^+ + bpy = [CuBr(bpy)]^+$	−48.1	−43.6	15
$[Cu(bpy)]^{2+} + Br^- = [CuBr(bpy)]^+$	−26.8	13.9	137
$[CuBr_2] + bpy = [CuBr_2(bpy)]$	−49.0	−56.7	−26
$[CuBr(bpy)]^+ + Br^- = [CuBr_2(bpy)]$	−12.7	5.3	64
$Cu^{2+} + Br^- = [CuBr]^+$[a)]	−19.9	19.6	132
$[CuBr]^+ + Br^- = [CuBr_2]$[a)]	−11.8	18.5	101
$[CuBr_2] + Br^- = [CuBr_3]^-$[a)]	−16.9	18.1	117
$[CuBr_3]^- + Br^- = [CuBr_4]^{2-}$[a)]	−7.3	16.5	80

a) Ref. 14, in 0.16 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution.

Ternary (2,2′-Bipyridyl)bromocopper(II) Complexes. The thermodynamic quantities of stepwise formation of ternary copper(II) complexes with bromide ions and 2,2′-bipyridyl, together with those of binary copper(II) bromo complexes, in DMF are summerized in Table 3.

As seen in Table 3, the coordination of a bromide ion to the $[Cu(bpy)_2]^{2+}$ complex is endothermic with a large and positive entropy change. Such a result can not be expected from a simple addition of bromide ion tó the $[Cu(bpy)_2(dmf)]^{2+}$ complex to form a six-coordinate $[CuBr(bpy)_2(dmf)]^+$ complex. We thus expect the rupture of a Cu-dmf bond within $[Cu(bpy)_2(dmf)]^{2+}$ followed by the formation of the five-coordinate $[CuBr(bpy)_2]^+$ complex without any DMF molecule coordinating to the central metal ion, as having already been found in crystal.[7,8)] The conclusion may be supported by the electronic spectra of the bis(2,2′-bipyridyl)monobromocopper(II) complex in DMF because it exhibits peaks at ca. 750 and 950 nm, and a similar spectrum with peaks at 755 and 955 nm has been observed for the five-coordinate $[CuCl(bpy)_2]^{2+}$ moiety within the $[CuCl(bpy)_2]_2S_5O_6 \cdot 6H_2O$ crystal.[9)] The monobromocopper(II) complex may exist as $[CuBr(dmf)_5]^+$ in DMF, as well as $[CuCl(dmf)_5]^+$.[19)] DMF molecules coordinating to the $[CuBr(dmf)_5]^+$ complex are replaced with 2,2′-bipyridyl molecules and the five-coordinate $[CuBr(bpy)_2]^+$ complex may be finally formed in DNF. As seen in Table 3, in the course of the successive reactions of $[CuBr]^+$ with 2,2′-bipyridyl molecules in DMF, the formation of the $[CuBr(bpy)]^+$ complex exhibits a positive ΔS° value and the subsequent formation of $[CuBr(bpy)_2]^+$ a negative ΔS° one. Since a relatively large ΔS° value may be associated with the change from the six- to five-coordinate structure in the course of a complexation reaction, the coordination structure may be changed at the formation of the $[CuBr(bpy)]^+$ complex. As seen in Fig. 6, the electronic spectrum of the $[CuBr(bpy)]^+$ complex shows a

Table 4. Thermodynamic Quantities, $\log K$, $\Delta G^\circ/\mathrm{kJ\ mol^{-1}}$, $\Delta H^\circ/\mathrm{kJ\ mol^{-1}}$, and $\Delta S^\circ/\mathrm{J\ K^{-1}\ mol^{-1}}$, of Reaction, $[\mathrm{CuBr}_p]^{(2-p)+}+[\mathrm{Cu(bpy)}_q]^{2+}=[\mathrm{CuBr}_p\mathrm{(bpy)}_q]^{(2-p)+}+\mathrm{Cu}^{2+}$ (bpy=2,2′-bipyridyl), in *N*,*N*-dimethylformamide at 25 °C

Complex formed	$\log K$	ΔG°	ΔH°	ΔS°
$[\mathrm{CuBr(bpy)}]^+$	1.23	−7.0	−5.7	4
$[\mathrm{CuBr(bpy)_2}]^+$	1.65	−9.4	−15.4	−20
$[\mathrm{CuBr_2(bpy)}]$	1.38	−7.9	−18.9	−37

peak at 750 nm and a shoulder at ca. 950 nm, these bands being also observed in the spectrum of the five-coordinate $[\mathrm{CuBr(bpy)_2}]^+$ complex. Therefore, we expect the formation of the five-coordinate $[\mathrm{CuBr(bpy)(dmf)_2}]^+$ complex in DMF.

The electronic spectrum of the mono(2,2′-bipyridyl)dibromocopper(II) complex exhibits a peak at 950 nm and a shoulder at ca. 750 nm, these peak positions being similar to that observed for the $[\mathrm{CuBr(bpy)_2}]^+$ and $[\mathrm{CuBr(bpy)}]^+$ complexes, while the relative intensity of the 950 nm band to the 750 nm one is significantly strong in the $[\mathrm{CuBr_2(bpy)}]$ complex. It seems thus difficult to conclude whether the $[\mathrm{CuBr_2(bpy)}]$ complex has the four- or five-coordinate structure in DMF.

The thermodynamic quantities of formation of the ternary $[\mathrm{CuBr(bpy)}]^+$, $[\mathrm{CuBr(bpy)_2}]^+$, and $[\mathrm{CuBr_2(bpy)}]$ complexes according to the reaction, $[\mathrm{CuBr}_p]^{(2-p)+}+[\mathrm{Cu(bpy)}_q]^{2+}=[\mathrm{CuBr}_p\mathrm{(bpy)}_q]^{(2-p)+}+\mathrm{Cu}^{2+}$, are summarized in Table 4. The ΔG° values are all appreciably negative, indicating the favorable formation of each ternary complex with respect to the relevant binary bromo and 2,2′-bipyridyl complexes of copper(II) ion in DMF. It should be noted that the corresponding ΔH° values are significantly large and negative.

The formation reactions of the $[\mathrm{CuBr(bpy)}]^+$ and $[\mathrm{CuBr(bpy)_2}]^+$ complexes may be represented as $[\mathrm{CuBr(dmf)_5}]^+ + [\mathrm{Cu(bpy)(dmf)_4}]^{2+} = [\mathrm{CuBr(bpy)(dmf)_2}]^+ + [\mathrm{Cu(dmf)_6}]^{2+} + \mathrm{dmf}$ and $[\mathrm{CuBr(dmf)_5}]^+ + [\mathrm{Cu(bpy)_2(dmf)}]^{2+} = [\mathrm{CuBr(bpy)_2}]^+ + [\mathrm{Cu(dmf)_6}]^{2+}$, respectively, by taking into account the coordination of DMF molecules within the relevant complex species. We note that one DMF molecule may be liberated at the formation of the $[\mathrm{CuBr(bpy)}]^+$ complex but no DMF molecule at the formation of $[\mathrm{CuBr(bpy)_2}]^+$. In Table 4 the ΔH° and ΔS° values for the formation of $[\mathrm{CuBr(bpy)}]^+$ are appreciably less negative than those for the formation of $[\mathrm{CyBr(bpy)_2}]$, the result might be thus ascribed to the rupture of the metal-dmf bond at the formation of the former complex.

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