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A Calorimetric Study of Ternary Zinc(II) Complexes with Chloride Ions and 2,2′-Bipyridyl in *N*,*N*-Dimethylformamide

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Formation equilibria of ternary zinc(II) complexes with chloride ions and 2,2′-bipyridyl (bpy) have been calorimetrically studied in *N*,*N*-dimethylformamide (DMF) containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. Formation of binary (2,2′-bipyridyl)zinc(II) complexes has also been explored. The calorimetric data were satisfactorily explained in terms of formation of the ternary $[ZnCl(bpy)]^+$ and $[ZnCl_2(bpy)]$ complexes together with the binary $[Zn(bpy)_n]^{2+}$ (n=1—3) ones, and their formation constants and enthalpies were determined. The formation of the ternary $[ZnCl(bpy)]^+$ and $[ZnCl_2(bpy)]$ complexes is not so favorable in DMF. It is suggested that both $[ZnCl(bpy)]^+$ and $[ZnCl_2(bpy)]$ complexes have the four-coordinate tetrahedral structure in DMF.

Complexation of zinc(II) ion with 2,2′-bipyridyl (bpy) has so far been studied in aqueous solution and the formation of mononuclear $[Zn(bpy)_n]^{2+}$ (n=1—3) complexes has been established.[1—6)] However, the complexation equilibria in nonaqueous solvents have not been well investigated yet. In fact, the only formation of $[Zn(bpy)]^+$ was kinetically investigated in dimethyl sulfoxide.[7)]

Ternary (2,2′-bipyridyl)zinc(II) complexes with various carboxylic acids, amino acids (peptides), and amines have been extensively studied in aqueous solution.[1,8)] On the other hand, as to the (2,2′-bipyridyl)zinc(II) complexes with halide ions, their formation equilibria have not been reported in any solvent, although the $[ZnCl_2(bpy)]$ complex was isolated from acetonitrile solution and its crystal structure was determined.[9)]

In a previous paper,[10)] we reported the formation equilibria of the ternary copper(II) complexes with bromide ions and 2,2′-bipyridyl in DMF. In the present work, in order to shed more light on the formation equilibria of ternary metal(II) complexes with 2,2′-bipyridyl and halide ions in solution, we calorimetrically investigated the formation of the ternary (2,2′-bipyridyl)chlorozinc(II) complexes in DMF. As to the related binary zinc(II)-chloride system, the formation equilibria having been previously explored,[11)] the thermodynamic quantities of formation of the $[ZnCl_n]^{(2-n)+}$ (n=1—4) complexes were used as known values in the course of the analysis of calorimetric data obtained in the present study.

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.[11)]

Measurements. Calorimetric measurements were carried out in a room thermostated at (25.0±0.2) °C. All solutions prepared contained 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium. A Dewar vessel was immersed in a thermostated water-bath at (25.0±0.007) °C. 100 cm^3 of a DMF solution with varying concentrations of $Zn(ClO_4)_2$ and $(C_2H_5)_4NCl$ 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. The concentration of zinc(II) ion in the initial test solution was varied over the range 3—21 mmol dm^{-3}. Heats of complexation observed at each titration point were ranged 0.3—3 J with a certainty ±0.05 J. The measured heats of complexation were corrected for heats of dilution. Heats of dilution were determined in advance by separate experiments by titrating a 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF solution with the 2,2′-bipyridyl solution containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$. The observed heats of dilution were found to be very small. All of the measurements were carried out by using a fully automatic on-line system for calorimetry developed in our laboratory.[12,13)] The method of the data treatment was similar to that used in a previous work.[10)]

Results and Discussion

Calorimetric titration curves obtained for the binary zinc(II)-2,2′-bipyridyl system are depicted in Fig. 1. In the figure, enthalpies $\Delta H^\circ = -q/(\delta v C_{L,tit})$ are 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 total concentrations of chloride and zinc(II) ions in solution, respectively, at each titration point, and $C_{L,tit}$ denotes the concentration of 2,2′-bipyridyl in the titrant solution. The observed ΔH° values were all negative, indicating an exothermic formation of zinc(II) 2,2′-bipyridyl complexes. As well as in water,[1)] the formation of a series of mononuclear $[Zn(bpy)_n]^{2+}$ (n=1—3) complexes was expected in DMF. The calorimetric data were thus analyzed by assuming the formation of the complexes and their formation constants and enthalpies were optimized, the result being summarized in the column of "Binary" in Table 1. The solid lines in Fig. 1 show the

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titration curves calculated by using the constants in Table 1, which satisfactorily reproduce the experimental points over the whole range of C_L/C_M examined. Therefore, the formation of the $[Zn(bpy)_n]^{2+}$ (n=1—3) complexes was concluded in DMF.

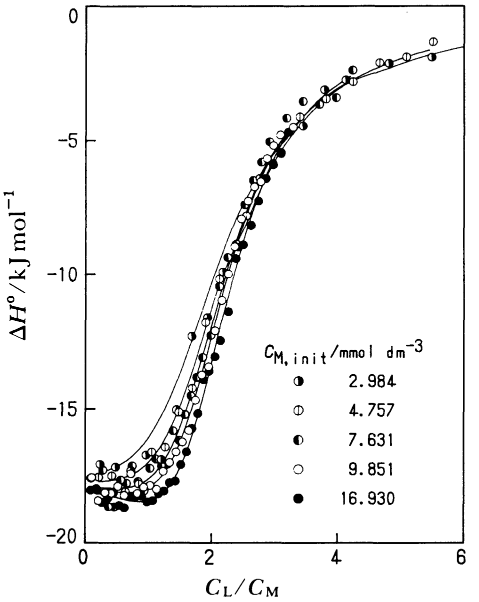

Fig. 1. Calorimetric titration curves of zinc(II) 2,2′-bipyridyl DMF solutions containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of zinc(II) ions, $C_{M,init}$/mol dm^{-3}, in the initial test solutions are given in the figure. The solid lines show the curves calculated by using the constants in the column of "Combined" in Table 1.

Table 1. The Least-Squares Refinement of Overall Formation Constants, $\log(\beta_{1pq}/\mathrm{mol}^{-(p+q)}\mathrm{dm}^{3(p+q)})$, and Enthalpies, $\Delta H^\circ_{\beta 1pq}$/kJ mol^{-1}, of $[ZnCl_p(bpy)_q]^{(2-p)+}$ (bpy=2,2′-bipyridyl) in N,N-Dimethylformamide Containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C

	Binary	Ternary	Combined
$\log\beta_{101}$	3.95(0.38)	—	3.88(0.22)
$\log\beta_{102}$	7.07(0.41)	—	6.87(0.23)
$\log\beta_{103}$	8.94(0.50)	—	8.73(0.30)
$\log\beta_{111}$	—	9.31(0.22)	9.24(0.19)
$\log\beta_{121}$	—	14.55(0.10)	14.54(0.08)
$\Delta H^\circ_{\beta 101}$	−18.3(0.3)	—	−18.2(0.3)
$\Delta H^\circ_{\beta 102}$	−38.1(0.8)	—	−39.1(1.0)
$\Delta H^\circ_{\beta 103}$	−56.4(3.0)	—	−55.9(3.2)
$\Delta H^\circ_{\beta 111}$	—	−7.0(3.1)	−7.9(4.3)
$\Delta H^\circ_{\beta 121}$	—	−15.6(1.9)	−16.2(1.5)
U[a)]	0.207	0.490	0.649
R[b)]	0.0251	0.0486	0.0348
N[c)]	135	75	210

Values in parentheses refer to three standard deviations. Values of $\log\beta_{1p0}$ and $\Delta H^\circ_{\beta 1p0}$ of formation of $[ZnCl_p]^{(2-p)+}$ (p=1—4) were fixed. a) Error-square sum. b) The Hamilton R-factor. c) The number of data points.

Calorimetric titration curves for the ternary zinc(II)-Cl^--2,2′-bipyridyl system are depicted in Fig. 2. In the figure, the titration curves remarkably shift to lower C_L/C_M region as the molar ratio of chloride to metal ions in solution is increased. The titration curves calculated with the only known formation constants and enthalpies of $[ZnCl_n]^{(2-n)+}$ (n=1—4) and those of $[Zn(bpy)_n]^{2+}$ (n=1—3) determined above hardly reproduced the experimental points, and thus the formation of ternary $[ZnCl_p(bpy)_q]^{(2-p)+}$ (denoted as ($1pq$)) complexes must be taken into account. At the first step of approach, a plausible set of the ternary complexes such as (111), (121), and (112) were assumed. Their formation constants and enthalpies were obtained with a satisfactorily small Hamilton R-factor of 0.0437. However, the formation constant of the (112) complex thus obtained was rather small with a relatively large uncertainty, and thus the formation of the complex was ambiguous. The least-squares analysis was then carried out by eliminating the (112) complex from the first set of complexes, the R-factor in this case being 0.0439. In both cases with and without the (112) complex, the R-factor remained practically unchanged, and thus the formation of $[ZnCl(bpy)_2]^+$ may be insignificant in DMF. Subsequent least-squares analyses were performed by assuming the only formation of either (111) or (121) complex, together with the binary chloro and 2,2′-bipyridyl complexes. The Hamilton R-factors in both cases were relatively large, indicating that the formation of both complexes must be taken

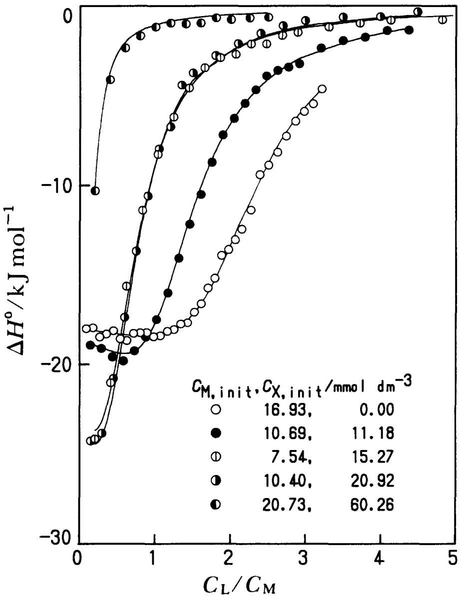

Fig. 2. Calorimetric titration curves of the ternary zinc(II) system obtained by titrating zinc(II) chloride DMF solutions with a 2,2′-bipyridyl DMF solution, each containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of zinc(II) and chloride ions, $C_{M,init}$/mol dm^{-3} and $C_{X,init}$/mol dm^{-3}, in the initial test solutions are given in the figure. The solid lines show the curves calculated by using the constants in the column of "Combined" in Table 1.

into account in DMF. The thermodynamic quantities of the (111) and (121) complexes are summarized in the column of "Ternary" in Table 1. Finally the whole calorimetric data obtained for the binary and ternary systems were analyzed altogether to simultaneously optimize the thermodynamic quantities of the binary $[Zn(bpy)_n]^{2+}$ (n=1—3) and ternary $[ZnCl(bpy)]^+$ and $[ZnCl_2(bpy)]$ complexes with the fixed values of the $[ZnCl_n]^{(2-n)+}$ (n=1—4) complexes, the result being listed in the column of "Combined" in Table 1. The values are in satisfactory agreement with the corresponding ones in the columns of "Binary" and "Ternary". As seen in Fig. 2, the solid lines, calculated by using the constants of the binary and ternary zinc(II) complexes in the column of "Combined" in Table 1 and with those of $[ZnCl_n]^{(2-n)+}$ (n=1—4),[11] well reproduce the experimental points over the whole range of C_L/C_M examined.

Distribution of Species. In Fig. 3 the distribution of species in solutions with varying R_c ($=C_X/C_M$) values is shown as a function of $-\log([bpy]/mol\ dm^{-3})$, which was calculated by using the formation constants given in the column of "Combined" in Table 1, together with those of the zinc(II) chloro complexes.[11] In solutions involving chloride ions ($R_c>0$), the ternary (111) and (121) complsxes are formed, the formation of these complexes being strongly suppressed, however. It is indicated that the formation of the ternary complexes is very much unfavorable in solution of $R_c>3$ in which the tri- and tetrachlorozincate(II) complexes are predominated. In Fig. 4 the distribution of species in solutions with varying R_c' ($=C_L/C_M$) values is shown as a function of $-\log([Cl^-]/mol\ dm^{-3})$ for comparison. It is seen in Fig. 4 that the ternary complexes are only formed in a range $-\log([Cl^-]/mol\ dm^{-3})$=3—6 and they disappear in solution of a higher chloride concentration where the $[ZnCl_3]^-$ and $[ZnCl_4]^{2-}$ complexes are mainly yielded.

Binary (2,2′-Bipyridyl)zinc(II) Complexes. The thermodynamic quantities of stepwise formation of the $[Zn(bpy)_n]^{2+}$ (n=1—3) complexes obtained in DMF are listed in Table 2 together with those in water.

The stepwise formation constants of each $[Zn(bpy)_n]^{2+}$ complex in DMF are smaller than those in water, and the smaller values in DMF are mainly due

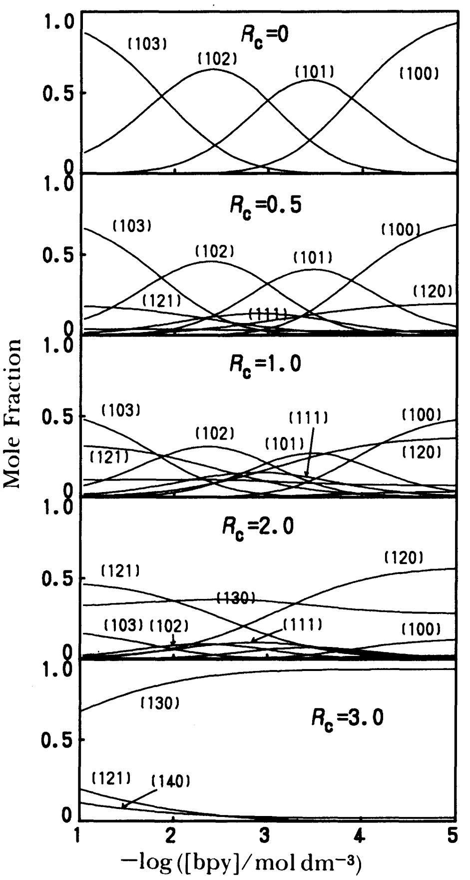

Fig. 3. Distribution of the $[ZnCl_p(bpy)_q]^{(2-p)+}$ (denoted as ($1pq$)) complexes as a function of $-\log([bpy]/mol\ dm^{-3})$ at the total zinc(II) ion concentration of 0.01 mol dm^{-3} in DMF. The R_c value stands for the molar ratio of chloride to zinc(II) ions in solution.

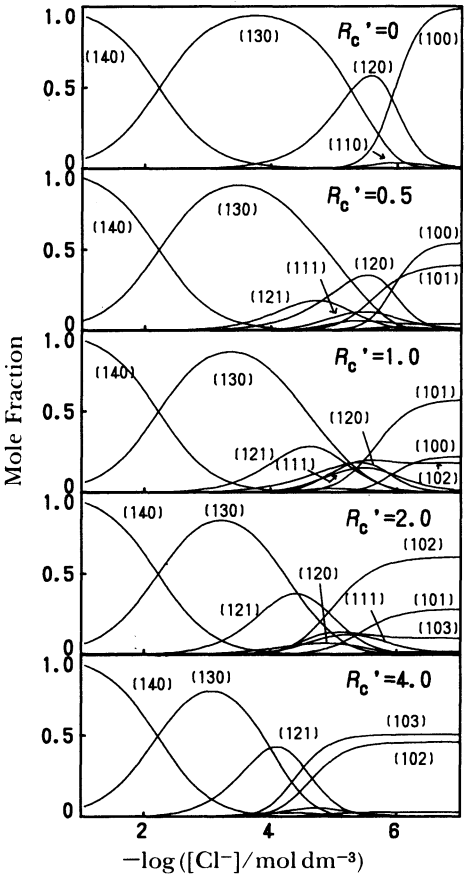

Fig. 4. Distribution of the $[ZnCl_p(bpy)_q]^{(2-p)+}$ (denoted as ($1pq$)) complexes as a function of $-\log([Cl^-]/mol\ dm^{-3})$ at the total zinc(II) ion concentration of 0.01 mol dm^{-3} in DMF. The R_c' value stands for the molar ratio of 2,2′-bipyridyl to zinc(II) ion in solution.

Table 2. 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 $[\text{Zn(bpy)}_n]^{2+}$ (n=1—3 and bpy=2,2′-bipyridyl)

	0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ DMF[d)]	0.1 mol dm^{-3} KNO_3[a)] Water	0.1 mol dm^{-3} $NaClO_4$[b)] Water	1 mol dm^{-3} KNO_3[c)] Water
	25 °C	25 °C	20 °C	30 °C
log K_1	3.95	5.16	5.30	5.26
log K_2	3.12	4.44	4.53	4.55
log K_3	1.87	3.74	3.80	3.96
ΔG_1°	−22.5	−29.5	−30.3	−30.0
ΔG_2°	−17.8	−25.3	−25.9	−26.0
ΔG_3°	−10.7	−21.3	−21.7	−22.6
ΔH_1°	−18.3	−29.0	−30.0	−26.2
ΔH_2°	−19.9	−28.4	−22.3	−22.9
ΔH_3°	−18.3	−24.1	−20.9	−17.4
ΔS_1°	14	0	0	15
ΔS_2°	−7	−9	10	11
ΔS_3°	−26	−10	1	18

a) Ref. 2. b) Ref. 4. c) Ref. 5. d) *N,N*-Dimethylformamide.

Table 3. Thermodynamic Quantities, $\Delta G^\circ/\text{kJ mol}^{-1}$, $\Delta H^\circ/\text{kJ mol}^{-1}$, and $\Delta S^\circ/\text{J K}^{-1}\,\text{mol}^{-1}$, of Stepwise Formation of the $[\text{ZnCl}_n(\text{bpy})]^{(2-n)+}$ (n=0—2, bpy=2,2′-bipyridyl) Complexes, Together with Those of Stepwise Formation of $[\text{ZnCl}_n]^{(2-n)+}$ (n=1—4) in *N,N*-Dimethylformamide at 25 °C

Reaction	ΔG°	ΔH°	ΔS°
$Zn^{2+}+bpy=[Zn(bpy)]^{2+}$	−22.5	−18.3	14
$[ZnCl]^{+}+bpy=[ZnCl(bpy)]^{+}$	−25.7	−21.6	13
$[ZnCl_2]+bpy=[ZnCl_2(bpy)]$	−15.7	−31.7	−54
$[Zn(bpy)]^{2+}+Cl^{-}=[ZnCl(bpy)]^{+}$	−30.6	11.4	141
$[ZnCl(bpy)]^{+}+Cl^{-}=[ZnCl_2(bpy)]$	−19.9	−8.6	70
$Zn^{2+}+Cl^{-}=[ZnCl]^{+}$	−27.5	14.7	142
$[ZnCl]^{+}+Cl^{-}=[ZnCl_2]$	−39.9	1.4	139
$[ZnCl_2]+Cl^{-}=[ZnCl_3]^{-}$	−30.0	−17.6	42
$[ZnCl_3]^{-}+Cl^{-}=[ZnCl_4]^{2-}$	−12.7	−7.9	16

to the less negative enthalpy values in the solvent than those in water. Since the donicity of DMF (the donor number D_N=26.6) is stronger than that (D_N=14.8) of water,[14)] the less negative enthalpy values of the zinc(II) 2,2′-bipyridyl complexes in DMF than those in water may be mainly ascribed to a stronger solvation of the metal ion in the former solvent than in the latter.

We note that the ΔS_n° (n=1—3) values of the zinc(II) 2,2′-bipyridyl complexes are practically the same as those of the nickel(II)-2,2′-bipyridyl ones with octahedral structure in DMF.[15)] The stepwise ΔH_n° (n=1—3) values are practically kept constant and the corresponding entropy values stepwise decreased by ca. 20 J K^{-1} mol^{-1} in the zinc(II)-2,2′-bipyridyl system in DMF. Such changes in the stepwise enthalpy and entropy values may hardly be expected provided that the $[\text{Zn(bpy)}_2]^{2+}$ complex has the four-coordinate tetrahedral structure, because the formation of $[\text{Zn(bpy)}_3]^{2+}$ may be very much unfavorable owing to the change from tetrahedral to octahedral structure. Therefore, we suggest an octahedral structure for the bis(2,2′-bipyridyl)zinc(II) complex. It is also suggested that the bis(2,2′-bipyridyl)zinc(II) complex may have the cis-configulation as expressed by $[\text{Zn(bpy)}_2(\text{dmf})_{\text{eq}}(\text{dmf})_{\text{ax}}]^{2+}$ because the trans-configulation is sterically unfavorable.[16)]

Ternary (2,2′-Bipyridyl)chlorozinc(II) Complexes. The thermodynamic quantities of the stepwise formation of the $[\text{ZnCl}_n(\text{bpy})]^{(2-n)+}$ (n=0—2) in DMF are summarized in Table 3, which can be calculated from the values in Table 1. The thermodynamic quantities of the stepwise formation of the zinc(II) chloro complexes[11)] are also listed in Table 3 for comparison. Comparing the enthalpy and entropy values for the reactions:

$$Zn^{2+}+bpy=[Zn(bpy)]^{2+}, \tag{1}$$

$$[ZnCl]^{+}+bpy=[ZnCl(bpy)]^{+}, \tag{2}$$

$$[ZnCl_2]+bpy=[ZnCl_2(bpy)], \tag{3}$$

in Table 3, we see that the ΔH° and ΔS° values for Reaction 3 are significantly negative compared with those for Reactions 1 and 2, the result suggesting that solvation of the $[\text{ZnCl}_2]$ complex is weaker than that of Zn^{2+}, as well as $[\text{ZnCl}]^+$ in DMF. As noted in a previous paper,[11)] the dichlorozinc(II) complex may have the four-coordinate $[\text{ZnCl}_2(\text{dmf})_2]$ structure with weak metal-dmf bonds in DMF, and thus it is plausible that the DMF molecules within the $[\text{ZnCl}_2(\text{dmf})_2]$ complex are replaced to 2,2′-bipyridyl and the four-coordinate $[\text{ZnCl}_2(\text{bpy})]$ complex is formed in DMF. It has in fact been revealed that the $[\text{ZnCl}_2(\text{bpy})]$ complex has the four-coordinate tetrahedral structure in crystal.[9)] Similarly, the $[\text{ZnCl}_2(\text{phen})]$ (phen=1,10-phenanthroline)[17)] and $(\text{ZnX}_2(\text{py})_2]$ (X=Cl, Br, and I, and py=pyridine)[18,19)] complexes have the tetrahedral structure in crystal.

We subsequently compare the enthalpy and entropy values for the reactions:

$$[\mathrm{Zn(bpy)}]^{2+} + \mathrm{Cl}^- = [\mathrm{ZnCl(bpy)}]^+, \quad (4)$$

$$[\mathrm{ZnCl(bpy)}]^+ + \mathrm{Cl}^- = [\mathrm{ZnCl_2(bpy)}]. \quad (5)$$

The $[\mathrm{Zn(bpy)}]^{2+}$ complex may have the octahedral structure with four DMF molecules coordinating to the metal ion, and the DMF molecules are stepwise liberated in the course of Reactions 4 and 5. As seen in Table 3, the ΔH° value for Reaction 4 is positive, while that for Reaction 5 is negative. The ΔS° value for Reaction 4 is much more positive than that of Reaction 5. The result suggests that liberation of DMF molecules from the central metal ion takes place relatively extensively in Reaction 4. Therefore, it is plausible that the $[\mathrm{ZnCl(bpy)}]^+$ complex has the four-coordinate structure with one DMF molecule within the first coordination sphere of the metal ion.

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