lattices. The nonradiative decay rates depend on both the chemical composition and the site geometry of the host lattice. Chemical variation has a bigger effect than structural variation. The observed decrease of the quenching temperature in the series chloride, fluoride, oxide can be simply explained by the energy gap law:[35] The number of vibrational quanta p needed to bridge the energy gap between the emitting state and the ground state decreases in this series as a result of increasing vibrational energies. A quantitative discussion of this dependence on the parameter p is given in ref 11. The degree of distortion at the V^{3+} site is mainly responsible for the variations observed within the chloride elpasolite lattices in Figures 7 and 8. We found that this distortion is also reflected in the Huang–Rhys parameter S, and the quenching temperatures could be correlated with S.[11]

In conclusion we find that by variation of the chemical composition and the site symmetry and geometry of V^{3+} in a number

of elpasolite host lattices we obtain a great deal of insight into the nature of the first excited states, the radiative and nonradiative relaxation processes. This insight cannot be obtained by the study of one compound alone, the trends within the series being very important for spectroscopic assignments as well as a physical understanding of the effects. High-resolution optical luminescence spectroscopy in the near-IR region at low temperatures with its extremely high information content is an essential experimental technique for the study of V^{3+} and Ti^{2+} ions.

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Formation of Binary and Ternary Complexes of Cadmium(II) with Halide Ions and 2,2'-Bipyridine in *N,N*-Dimethylformamide

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The formation of binary and ternary complexes of cadmium(II) with halide ions (X) and 2,2'-bipyridine (bpy) has been studied by calorimetry in *N,N*-dimethylformamide (DMF) containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ as an ionic medium at 25 °C. The formation of ternary $[CdX(bpy)]^+$, $[CdX_2(bpy)]$, $[CdX_3(bpy)]^-$, $[CdX(bpy)_2]^+$, and $[CdX_2(bpy)_2]$ complexes is proposed, together with binary halogeno $[CdX_n]^{(2-n)+}$ ($n = 1$–4; X = Cl, Br, I) and 2,2'-bipyridine $[Cd(bpy)_n]^{2+}$ ($n = 1$–3) ones, and their formation constants, enthalpies, and entropies are obtained. The coordination geometry is suggested to be six-coordination for $[CdX(DMF)_5]^+$ and four-coordination for $[CdX_2(DMF)_2]$, $[CdX_3(DMF)]^-$, and $[CdX_4]^{2-}$; i.e., the change from octahedral to tetrahedral occurs at the formation of $[CdX_2]$. The ternary complexes are six-coordinated, except for $[CdX_3(bpy)]^-$, which is five-coordinated. The $[CdX_3(bpy)]^-$ complex is formed as the dominant species in the chloride and bromide systems, while the formation of the corresponding iodide complex is practically negligible. Affinities of halide ions with Cd^{2+}, $[Cd(bpy)]^{2+}$, or $[Cd(bpy)_2]^{2+}$ are compared in view of the effect of bound 2,2'-bipyridine molecules on the Cd^{II}–X interactions.

Introduction

A number of studies have been carried out so far on the complexation of cadmium(II) with halide ions in not only water but also nonaqueous solvents,[1–8] and the formation of a series of mononuclear $[CdX]^+$, $[CdX_2]$, $[CdX_3]^-$, and $[CdX_4]^{2-}$ complexes has been elucidated. The coordination geometry of the solvated cadmium(II) ion in water,[9,10] dimethyl sulfoxide (DMSO),[11] and *N,N*-dimethylformamide (DMF),[12] which is octahedral with six solvent molecules solvating the central metal ion through oxygen atoms, has been established by X-ray diffraction. The coordination geometry in solution may be essentially the same as that in the crystal, as in the case for DMSO.[13] With the $[CdX_n]^{(2-n)+}$ complexes, the $[CdI_4]^{2-}$ geometry of an almost regular tetrahedron has been revealed by X-ray diffraction in water[14] and DMSO.[15] Also, six-coordination for $[CdI(H_2O)_5]^+$ and $[CdI(DMSO)_5]^+$ and four-coordination for $[CdI_3(DMSO)]^-$ have been revealed in relevant solutions.[16] Ahrland discussed the variation of thermodynamic parameters of the formation of $[CdX_n]^{(2-n)+}$ ($n = 1$–4) in water and DMSO in relation to changes in their coordination structure,[2] suggesting that the change from octahedral to tetrahedral occurs at the formation of $[CdX_3]^-$ in water but at the formation of $[CdX_2]$ in DMSO. It is also noteworthy that the log K_1 value of $[CdX]^+$ increases in the order Cl < Br < I in water, while the reverse is the case in DMSO.[2] With regard

to the relative order of stabilities an extended work including fluoride ion has recently been made in some binary solvent mixtures.[8]

We have so far reported ternary complexation equilibria of the divalent transition-metal ions[17–19] Cu^{2+}, Zn^{2+}, and Ni^{2+}, using

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‡Institute for Molecular Science.

halide ions and 2,2′-bipyridine as ligands in N,N-dimethylform-amide (DMF). In addition to the normal binary mononuclear complexes $[MX_n]^{(2-n)+}$ and $[M(bpy)_n]^{2+}$, we observed the formation of such ternary complexes as $[MX(bpy)]^+$, $[MX_2(bpy)]$, $[MX(bpy)_2]^+$, and $[MX_2(bpy)_2]$. It has been demonstrated, however, that the types and stabilities of the ternary complexes strongly depend on the metal ion. Indeed, all of the four types are observed in the Ni^{II}–Cl–bpy system, while the formation of $[CuBr_2(bpy)_2]$, $[ZnCl_2(bpy)_2]$, and $[ZnCl(bpy)_2]^+$ is weak and practically negligible.
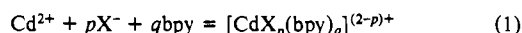
On the other hand, it has been pointed out that relative stabilities among halogeno complexes of a metal(II) ion strongly depend on the solvent.[2] Similarly, the relative stabilities might be influenced by ligating molecules such as 2,2′-bipyridine, rather than solvents, to the metal(II) ion. In comparison with ternary 2,2′-bipyridine halogeno complexes of transition-metal(II) ions, systems involving the rather soft cadmium(II) ion may be of particular interest. Therefore, as an extension of the studies of the ternary systems, we have now examined the Cd^{II}–X–bpy (X = Cl, Br, I) systems in DMF. Although no thermodynamic investigation has been made into the systems so far, limited information on the coordination structure has been obtained for the bis(2,2′-bipyridine)cadmium(II) nitrate hemihydrate crystal,[20] which shows a composite structure of six-coordinate [Cd-(NO$_3$)$_2$(bpy)$_2$] and [Cd(H$_2$O)(NO$_3$)(bpy)$_2$]$^+$, both with a cis arrangement. We employed an on-line controlled titration calorimetry system for studying solution equilibria, and its advantage and validity, in comparison with spectrophotometry, have been established for various metal systems in our previous papers.
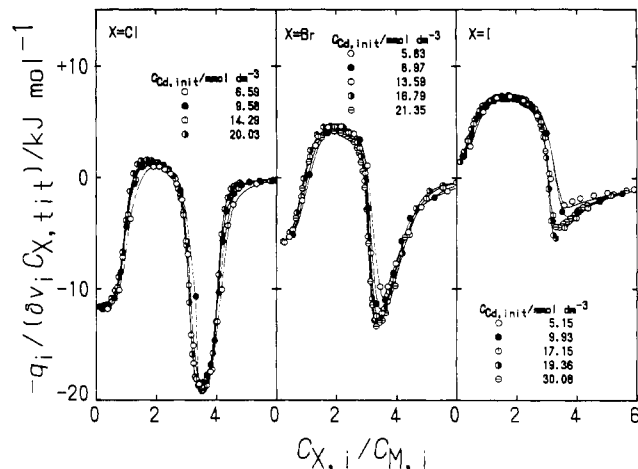
Experimental Section

Reagents. All chemicals used were of reagent grade. The DMF solvate of cadmium(II) perchlorate was prepared by dissolution of Cd-(ClO$_4$)$_2$·6H$_2$O crystals in DMF and then by recrystallization three times from DMF. The DMF solvate thus obtained was finally recrystallized from acetone, washed with ether, and dried at 40 °C in a vacuum oven for several days. It was kept in a desiccator over P$_2$O$_5$. The value of x in Cd(ClO$_4$)$_2$·xDMF was found to be 6 from the analysis of metal ions by EDTA titration. Tetraethylammonium perchlorate, tetraethylammonium chloride, tetraethylammonium bromide, and tetraethylammonium iodide were recrystallized once from water and dried in vacuo at 100 °C. 2,2′-Bipyridine was used without further purification and dried in vacuo in a desiccator over P$_2$O$_5$. N,N-Dimethylformamide was dried for several weeks over molecular sieve 4A 1/16 and then distilled under reduced pressure and stored with molecular sieve in a dark bottle with a P$_2$O$_5$ drying tube.

Measurements. Calorimetric measurements were carried out by using a fully automatic on-line calorimetry system,[21] in a room thermostated at 25 ± 0.2 °C. All cadmium(II) perchlorate and 2,2′-bipyridine solutions contained 0.1 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ as an ionic medium. In binary systems, cadmium(II) perchlorate solutions were titrated with either 0.1 mol dm^{-3} (C$_2$H$_5$)$_4$NX (X = Cl, Br, I) or 0.2 mol dm^{-3} 2,2′-bipyridine solution. In ternary systems, solutions of varying concentration ratios of halide to cadmium(II) ions were titrated with the 2,2′-bipyridine solution. A solution (40 cm^3) containing cadmium(II) ions was placed in a stainless steel vessel, the inside wall of which was coated with Teflon. The vessel, filled with dry nitrogen gas and isolated from moisture with a P$_2$O$_5$ drying tube, was inserted in an aluminum block thermostated at 25.0 ± 0.0001 °C in an air bath. Portions of a 2,2′-bipyridine solution were added to this solution from an autoburet (APB-118, Kyoto Electronics). Heats of complexation at each titration point were measured with a certainty of ±0.02 J and corrected for heat of dilution of the titrant. The heat of dilution had been determined in advance by separate experiments and was found to be very small.

Data Analysis. If the formation of only mononuclear complexes is assumed, the overall formation of the $[CdX_p(bpy)_q]^{(2-p)+}$ complex can be defined as in eq 1 and 2. The heat q_i measured at the ith titration point

$$Cd^{2+} + pX^- + qbpy = [CdX_p(bpy)_q]^{(2-p)+} \quad (1)$$

$$\beta_{1pq} = [CdX_p(bpy)_q^{(2-p)+}]/[Cd^{2+}][X^-]^p[bpy]^q \quad (2)$$

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Figure 1. Calorimetric titration curves for the Cd^{II}–X (X = Cl, Br, I) systems obtained in N,N-dimethylformamide containing 0.1 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ at 25 °C. Concentrations of Cd^{II} ion in initial test solutions, $C_{Cd,init}$/(mmol dm^{-3}), are given. The solid lines are calculated by using constants in Table I.

Table I. Least-Squares Refinement of Overall Formation Constants log $(\beta_{1pq}/(\text{mol}^{-(p+q)} \text{dm}^{3(p+q)}))$ and Reaction Enthalpies $\Delta H^\circ{}_{\beta_{1pq}}/(\text{kJ mol}^{-1})$ of $[CdX_p]^{(2-p)+}$ (X = Cl, Br, I) and $[Cd(bpy)_q]^{2+}$ (bpy = 2,2′-Bipyridine) in N,N-Dimethylformamide Containing 0.1 mol dm^{-3} (C$_2$H$_5$)$_4$NClO$_4$ as an Ionic Medium at 25 °C

	Cl	Br	I		bpy
log β_{110}	6.9 (0.1)[a]	5.9 (0.1)	4.5 (0.1)	log β_{101}	2.84 (0.05)
log β_{120}	12.0 (0.3)	10.5 (0.4)	8.0 (0.3)	log β_{102}	5.17 (0.05)
log β_{130}	17.8 (0.3)	15.8 (0.4)	12.6 (0.2)	log β_{103}	6.0 (0.1)
log β_{140}	21.7 (0.4)	18.8 (0.4)	14.6 (0.3)		
$\Delta H^\circ{}_{\beta_{110}}$	-12.0 (0.2)	-6.0 (0.4)	1.3 (0.3)	$\Delta H^\circ{}_{\beta_{101}}$	-13.6 (0.2)
$\Delta H^\circ{}_{\beta_{120}}$	-4 (1)	7 (2)	23 (5)	$\Delta H^\circ{}_{\beta_{102}}$	-31.1 (0.5)
$\Delta H^\circ{}_{\beta_{130}}$	-7.6 (0.3)	4.9 (0.3)	18.2 (0.2)	$\Delta H^\circ{}_{\beta_{103}}$	-47 (2)
$\Delta H^\circ{}_{\beta_{140}}$	-28.6 (0.4)	-11.1 (0.4)	6.6 (0.7)		
U^b	0.127	0.108	0.046	U^b	0.027
R^c	0.034	0.042	0.030	R^c	0.012
N^d	128	102	123	N^d	151

[a] Values in parentheses refer to 3 standard deviations. [b] Error-square sum. [c] The Hamilton R factor. [d] The number of calorimetric data points.

is expressed by formation constants β_{1pq} and overall enthalpies $\Delta H^\circ{}_{\beta_{1pq}}$ (eq 3) where V_i denotes the volume of the test solution. The concen-

$$q_i = -(V_i \sum\sum \beta_{1pq} \Delta H^\circ{}_{\beta_{1pq}}[Cd^{2+}]_i[X^-]_i^p[bpy]_i^q - V_{i-1}\sum\sum\beta_{1pq}\Delta H^\circ{}_{\beta_{1pq}}[Cd^{2+}]_{i-1}[X^-]_{i-1}^p[bpy]_{i-1}^q) \quad (3)$$

trations of free Cd^{2+} and X$^-$ ions and 2,2′-bipyridine are related to their total concentrations, $C_{M,i}$, $C_{X,i}$, and $C_{L,i}$, respectively, according to the mass balance equations (4)–(6).

$$C_{M,i} = [Cd^{2+}]_i + \sum\sum\beta_{1pq}[Cd^{2+}]_i[X^-]_i^p[bpy]_i^q \quad (4)$$

$$C_{X,i} = [X^-]_i + \sum\sum p\beta_{1pq}[Cd^{2+}]_i[X^-]_i^p[bpy]_i^q \quad (5)$$

$$C_{L,i} = [bpy]_i + \sum\sum q\beta_{1pq}[Cd^{2+}]_i[X^-]_i^p[bpy]_i^q \quad (6)$$

Formation constants and enthalpies were determined simultaneously by minimizing $U = \sum(q_{i,\text{obsd}} - q_{i,\text{calcd}})^2$, and a nonlinear least-squares program according to an algorithm proposed by Marquardt[22] was used.

Results

The calorimetric titration curves obtained in the binary cadmium(II) chloride, bromide, and iodide systems are depicted in Figure 1. The heat of reaction q_i measured at each titration point is normalized with the volume of the titrant added δv_i and the concentration of the ligand ions in the titrant $C_{X,\text{tit}}$, and the term $-q_i/[(\delta v_i)C_{X,\text{tit}}]$ is plotted against $C_{X,i}/C_{M,i}$, where $C_{X,i}$ and $C_{M,i}$

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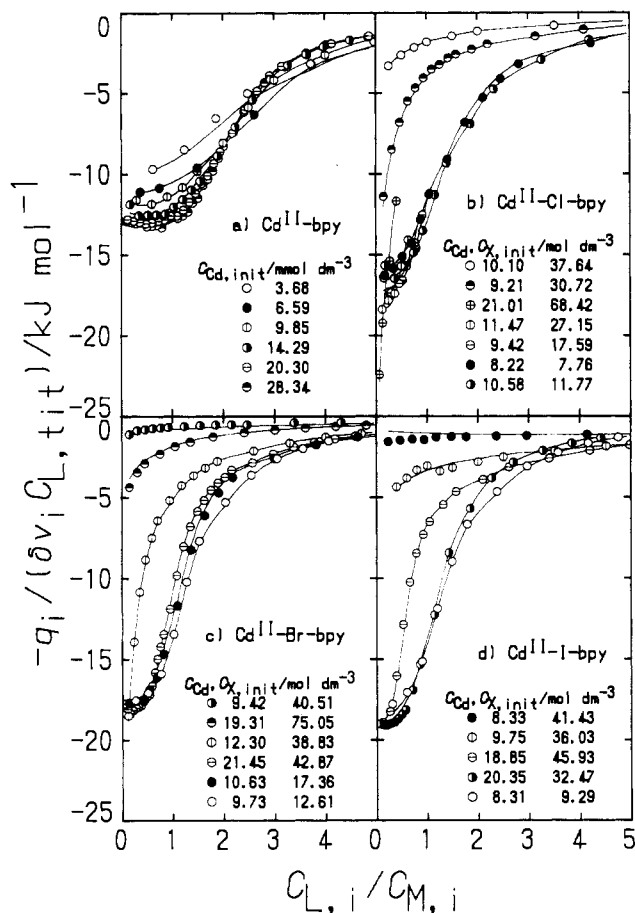
Figure 2. Calorimetric titration curves for the Cd^{II}-bpy and Cd^{II}-X-bpy systems obtained in N,N-dimethylformamide containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C. Concentrations of Cd^{II} and X^- ions in initial test solutions, $C_{Cd,init}/(mmol\ dm^{-3})$ and $C_{X,init}/(mmol\ cm^{-3})$, are given. The solid lines are calculated by using constants in Tables I and II.

denote the total concentrations of the ligand and metal ions, respectively, in solution. The titration curves are all well explained in terms of the formation of $[CdX]^+$, $[CdX_2]$, $[CdX_3]^-$, and $[CdX_4]^{2-}$ (X = Cl, Br, I). The overall formation constants log β_n and enthalpies $\Delta H^\circ_{\beta_n}$ of these complexes are summarized in Table I. The solid lines in Figure 1, calculated by using the constants in Table I, well reproduce the experimental points.

Similarly, calorimetric titration curves obtained in the binary Cd^{II}-bpy system and in the ternary Cd^{II}-X-bpy systems are depicted in Figure 2. In the binary Cd^{II}-bpy system the data are well explained in terms of the formation of $[Cd(bpy)]^{2+}$, $[Cd(bpy)_2]^{2+}$, and $[Cd(bpy)_3]^{3+}$, and their thermodynamic parameters are also listed in Table I.

The thermodynamic parameters thus obtained in the binary Cd^{II}-X and Cd^{II}-bpy systems were fixed as known parameters in the analysis of ternary Cd^{II}-X-bpy systems. Since the cadmium(II) ion possesses six-coordination geometry in DMF,[12] and 2,2'-bipyridine behaves as a bidentate chelating ligand, we first assumed the formation of only four types of complexes, [CdX(bpy)]$^+$, [CdX$_2$(bpy)], [CdX(bpy)$_2$]$^+$, and [CdX$_2$(bpy)$_2$], as in the Ni^{II}-Cl-bpy system.[19] The least-squares refinement of formation constants and enthalpies of these complexes was successful in the iodide system, while it failed in the chloride and bromide systems. This implies that another type of ternary complex is present, in addition to the above four, in the last two systems. In fact, the introduction of [CdX$_3$(bpy)]$^-$ led to a drastic reduction of the R factors in both chloride and bromide systems, while no improvement was brought about by assuming any other species. We therefore propose the formation of [CdCl$_3$(bpy)]$^-$ and [CdBr$_3$(bpy)]$^-$. Thermodynamic parameters of formation of the ternary complexes are listed in Table II. All the solid lines in Figure 2, calculated by using the constants in Table II, reproduce well the experimental points.

Table II. Least-Squares Refinement of Overall Formation Constants log $(\beta_{1pq}/(mol^{-(p+q)}\ dm^{3(p+q)}))$ and Reaction Enthalpies $\Delta H^\circ_{\beta_{1pq}}/(kJ\ mol^{-1})$ of $[CdX_p(bpy)_q]^{(2-p)+}$ (X = Cl, Br, I; bpy = 2,2'-Bipyridine) in N,N-Dimethylformamide Containing 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$ as an Ionic Medium at 25 °C

	Cl	Br	I
log β_{111}	10.5 (0.2)^a	9.5 (0.2)	8.1 (0.1)
log β_{121}	15.6 (0.1)	14.22 (0.07)	11.78 (0.07)
log β_{131}	19.4 (0.1)	17.29 (0.08)	
log β_{112}	12.5 (0.2)	11.6 (0.2)	10.1 (0.2)
log β_{122}	17.1 (0.3)	14.9 (0.3)	12.82 (0.08)
$\Delta H^\circ_{\beta_{111}}$	-26.5 (0.7)	-22.1 (0.7)	-16.7 (1)
$\Delta H^\circ_{\beta_{121}}$	-31 (2)	-17.9 (0.7)	-5.6 (0.8)
$\Delta H^\circ_{\beta_{131}}$	-33 (4)	-24 (2)	
$\Delta H^\circ_{\beta_{112}}$	-43.6 (0.8)	-40.3 (1)	-35 (1)
$\Delta H^\circ_{\beta_{122}}$	-60 (10)	-72 (27)	-31 (3)
U^b	0.023	0.041	0.048
R^c	0.023	0.023	0.022
N^d	83	133	103

^{a} Values in parentheses refer to 3 standard deviations. ^{b} Error-square sum. ^{c} The Hamilton R factor. ^{d} The number of calorimetric data points.
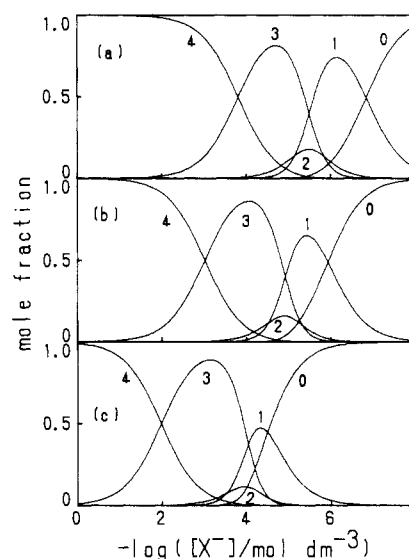
Figure 3. Distribution of species in N,N-dimethylformamide at 25 °C: (a) Cd^{II}-Cl; (b) Cd^{II}-Br; (c) Cd^{II}-I. The number n represents $[CdX_n]^{(2-n)+}$.

Discussion

Binary Cadmium(II) Halogeno Complexes. The distribution of species for the binary cadmium(II) halide systems is shown in Figure 3. The formation of the mono-, di-, tri-, and tetrahalogeno complexes of cadmium(II) ion is indicated in DMF, as in DMSO.[2] It is found that the formation constants are larger in DMF than in DMSO. The same applies also for the copper(II) chloride system.[23,24] The enhanced complexation in DMF over that in DMSO may be partly due to weaker solvation of the metal ions in DMF. However, the generally larger reaction entropies in DMF than in DMSO suggest that the difference in solvent-solvent interactions in the bulk also plays an important role in the solvent effect.[23,24]

Thermodynamic parameters for the stepwise formation of halogeno complexes of cadmium(II) ions are listed in Table III. In the chloride system we notice the remarkable feature that the ΔH°_2 value is large and positive compared with the ΔH°_1, ΔH°_3, and ΔH°_4 values and that the ΔS°_n values are all large and positive except for ΔS°_4. A similar result is also obtained in the bromide and iodide systems. Cadmium(II) ion is present as an octahedrally

(23) Ishiguro, S.; Suzuki, H.; Jeliazkova, B. G.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2407.
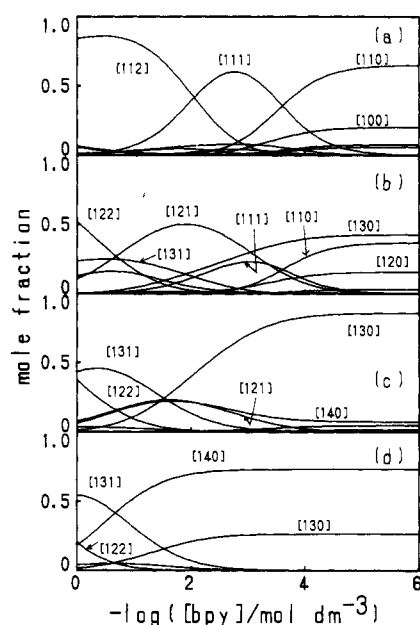(24) Ishiguro, S.; Suzuki, H.; Jeliazkova, B. G.; Ohtaki, H. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 39.

Table III. Stepwise Formation Constants log $(K_n/(\text{mol}^{-1}\ \text{dm}^3))$ and Reaction Enthalpies $\Delta H°_n/(\text{kJ mol}^{-1})$ and Entropies $\Delta S°_n/(\text{J mol}^{-1}\ \text{K}^{-1})$ for the Reaction $[MX_{n-1}]^{(3-n)+} + X^- = [MX_n]^{(2-n)+}$ (X = Cl, Br, I; M^{2+} = Cd^{2+}, $[Cd(bpy)]^{2+}$, $[Cd(bpy)_2]^{2+}$; bpy = 2,2′-Bipyridine) in N,N-Dimethylformamide at 25 °C

|	Cd^{2+}			$[Cd(bpy)]^{2+}$			$[Cd(bpy)_2]^{2+}$		
	Cl	Br	I	Cl	Br	I	Cl	Br	I
log K_1	6.9	5.9	4.5	7.6	6.7	5.2	7.3	6.4	4.9
log K_2	5.2	4.5	3.5	5.2	4.7	3.7	4.6	3.3	2.7
log K_3	5.8	5.3	4.6	3.8	3.1				
log K_4	3.8	3.0	2.0						
$\Delta H°_1$	−12.0	−6.1	1.3	−12.9	−8.5	−3.1	−12.6	−9.3	−4.0
$\Delta H°_2$	7.7	13.1	21.6	−4.0	4.2	11.1	<0	<0	4.3
$\Delta H°_3$	−3.3	−2.1	−4.7	−2.6	−6.5				
$\Delta H°_4$	−20.9	−16.1	−11.7						
$\Delta S°_1$	91	93	90	102	100	89	98	91	80
$\Delta S°_2$	124	130	140	86	104	108	>0	>0	67
$\Delta S°_3$	101	95	71	63	39				
$\Delta S°_4$	3	4	−1						
$\Delta H°_2 + \Delta H°_3$	4.4	11.0	16.9	−6.6	−2.3				
$\Delta S°_2 + \Delta S°_3$	225	225	211	149	143				
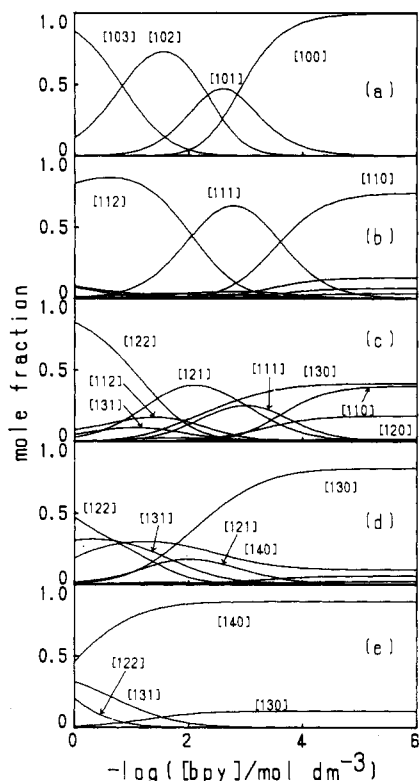
Figure 4. Distribution of species in the Cd^{II}–Cl–bpy system in N,N-dimethylformamide at 25 °C calculated at $C_M/(\text{mol dm}^{-3})$ and $C_X/(\text{mol dm}^{-3})$: (a) 0.01, 0 (b) 0.01, 0.01; (c) 0.01, 0.02; (d) 0.01, 0.03; (e) 0.01, 0.04. The symbol $[1pq]$ represents $[CdCl_p(bpy)_q]^{(2-p)+}$.

Figure 5. Distribution of species in the Cd^{II}–Br–bpy system in N,N-dimethylformamide at 25 °C calculated at $C_M/(\text{mol dm}^{-3})$ and $C_X/(\text{mol dm}^{-3})$: (a) 0.01, 0.01; (b) 0.01, 0.02; (c) 0.01, 0.03; (d) 0.01, 0.04. The symbol $[1pq]$ represents $[CdBr_p(bpy)_q]^{(2-p)+}$.

solvated $[Cd(DMF)_6]^{2+}$ ion in DMF,[12] and $[CdX_4]^{2-}$ may be tetrahedral in DMF as well as in water[13] and DMSO.[14] As a consequence, the coordination geometry of the solvated cadmium(II) ion must be changed upon complexation. Endothermicity observed at the second consecutive step suggests that the change takes place, and more than one metal–solvent bond is ruptured, on the formation of $[CdX_2]$. Relatively large and positive $\Delta S°_2$ values, consistent with an extensive libration of solvent molecules from the coordination sphere of the cadmium(II) ion, provide further evidence for the structure change at this step. From these considerations, we propose the formation of six-coordinate $[CdX(DMF)_5]^+$ and four-coordinate $[CdX_2(DMF)_2]$, $[CdX_3(DMF)]^-$, and $[CdX_4]^{2-}$ complexes as the main species. However, looking at the entropy values in detail, we notice that, although $\Delta S°_2 > \Delta S°_3$, their difference becomes gradually larger along the series Cl < Br < I, while the $\Delta S°_1$ and $\Delta S°_4$ values and the sum of $\Delta S°_2 + \Delta S°_3$ are almost the same among the halogeno complexes. This might be explained in terms of the presence of six-coordinate $[CdX_2(DMF)_4]$, though only to a minor extent,

leading to an octahedral (O_h)–tetrahedral (T_d) equilibrium (eq 7), which shifts toward the T_d side in the sequence Cl < Br < I.

$$[CdX_2(DMF)_4] = [CdX_2(DMF)_2] + 2DMF \qquad (7)$$
$$\quad\ O_h \qquad\qquad\qquad\ T_d$$
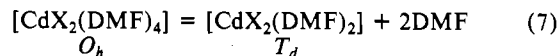
Evidently, the formation of either $[CdX_2(DMF)_4]$ or $[CdX_2(DMF)_2]$ may be followed by the formation of four-coordinate $[CdX_3(DMF)]^-$ and $[CdX_4]^{2-}$. In all halide systems examined a remarkably exothermic $\Delta H°_4$ value coupled with a relatively small $\Delta S°_4$ value is observed, implying that the DMF molecule is very weakly bonded to the metal ion in $[CdX_3(DMF)]^-$. Similar enthalpy and entropy relationships are seen also in other divalent transition-metal–halide systems in DMF.[25] Especially for Cu^{II}, an elongation of the Cu–solvent bond in $[CuCl_3(\text{solvent})]^-$ as compared with the equatorial bond in $[Cu(\text{solvent})_6]^{2+}$ has been observed in DMF[26] and acetonitrile,[27] providing evidence of weakened metal–solvent interactions.

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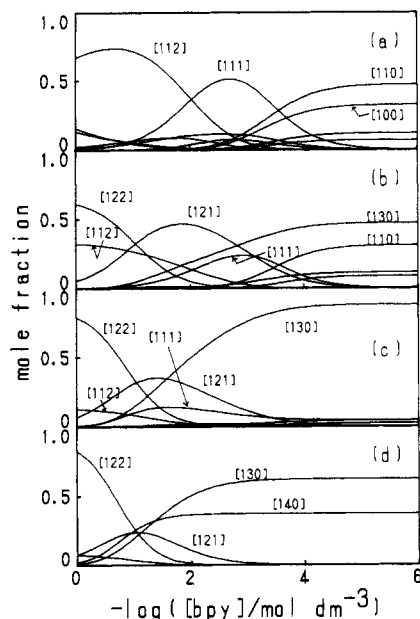
Figure 6. Distribution of species in the Cd^{II}–I–bpy systems in N,N-dimethylformamide at 25 °C calculated at $C_M/$(mol dm^{-3}) and $C_X/$(mol dm^{-3}): (a) 0.01, 0.01; (b) 0.01, 0.02; (c) 0.01, 0.03; (d) 0.01, 0.04. The symbol [1pq] represents [CdI$_p$(bpy)$_q$]$^{(2-p)+}$.

Binary Cadmium(II) 2,2′-Bipyridine Complexes. Thermodynamic parameters for the binary 2,2′-bipyridine complexes of cadmium(II) ion indicate that the formation of the complexes in DMF is unfavorable compared with that in water. The stepwise enthalpies $\Delta H°_n$ in DMF are –13.6, –16.5, and –16 kJ mol^{-1} for n = 1, 2, and 3, respectively. The values are appreciably less negative than those in water, as reasonably expected from the stronger donicity of DMF

Ternary Cadmium(II) 2,2′-Bipyridine Halogeno Complexes. Figures 4–6 show the distribution of ternary (2,2′-bipyridine) halogenocadmium(II) complexes, calculated by using the formation constants of the complexes in Tables I and II. The formation of [CdX(bpy)]$^+$ (denoted as [111]), [CdX$_2$(bpy)] [(121]), [CdX(bpy)$_2$]$^+$ ([112]), and [CdX$_2$(bpy)$_2$] ([122]) is found in all the cadmium(II) halide systems, as in the corresponding nickel(II) chloride system. In addition, the [CdX$_3$(bpy)]$^-$ ([131]) complex is found in the chloride and bromide systems. The stepwise thermodynamic parameters of formation of these ternary halogeno complexes are summarized in Table III for the reaction [MX$_{n-1}$]$^{(3-n)+}$ + X$^-$ = [MX$_n$]$^{(2-n)+}$, where M^{2+} = [Cd(bpy)]$^{2+}$ and [Cd(bpy)$_2$]$^{2+}$.

The formation of the [CdCl$_3$(bpy)]$^-$ and [CdBr$_3$(bpy)]$^-$ complexes is of particular interest because the cadmium(II) ion may be five-coordinated with a chelating 2,2′-bipyridine molecule in the complexes. Six-coordination of the complexes, with a solvent molecule bound to the cadmium(II) ion, is hardly expected, considering four-coordination of [CdX$_3$(DMF)] as discussed in a previous section. However, [CdI$_3$(bpy)]$^-$ is not found, so we suppose that five-coordination might be sterically hindered for [CdI$_3$(bpy)]$^-$ involving relatively large iodide ions.

In Table III, for [Cd(bpy)]$^{2+}$ the $\Delta H°_2$ values are not so large as compared with the corresponding $\Delta H°_1$ and $\Delta H°_3$ values. The $\Delta H°_2$ value, for a given X$^-$ ion, is less by ca. 10 kJ mol^{-1} for [Cd(bpy)]$^{2+}$ than for Cd^{2+}, although the $\Delta H°_1$ and $\Delta H°_3$ values are not remarkably different. Furthermore, the $\Delta S°_2$ value is considerably smaller for [Cd(bpy)]$^{2+}$ than for Cd^{2+}. These imply that the cadmium(II) ion in [CdX$_2$(bpy)], unlike that in [CdX$_2$], still preserves the high coordination number. We thus suppose the O_h–T_d equilibrium analogous to eq 7

$$[CdX_2(bpy)(DMF)_2] = [CdX_2(bpy)] + 2DMF \quad (8)$$
$$O_h \qquad\qquad\qquad T_d$$
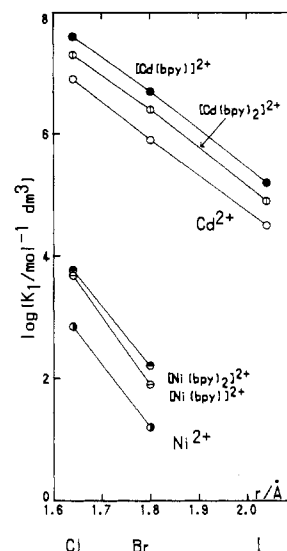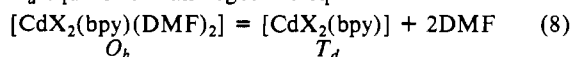
Figure 7. Plots of log ($K_1/$(mol^{-1} dm^3)) values of halogeno complexes of M^{2+}, [ML]$^{2+}$, and [ML$_2$]$^{2+}$ (M = Ni^{II}, Cd^{II}; L = 2,2′-bipyridine) in N,N-dimethylformamide against the ionic radii ($r/$Å) of X$^-$ ions.

which is rather shifted toward the O_h side. This deduction is further supported by the $\Delta S°_3$ values. On the formation of [CdX$_3$(bpy)]$^-$, which is five-coordinated as discussed in a previous section, the $\Delta S°_3$ value may be negative if the unsolvated [CdX$_2$(bpy)] species is predominant, because the coordination number of the cadmium(II) ion increases upon its complexation. However, the $\Delta S°_3$ values observed are in fact large and positive, suggesting the extensive liberation of solvent molecules upon complexation, i.e., the solvated [CdX$_2$(bpy)(DMF)$_2$] is present and the complexation proceeds mainly through [CdX$_2$(bpy)-(DMF)$_2$] + X$^-$ → [CdX$_3$(bpy)]$^-$ + 2DMF.

Effect of 2,2′-Bipyridine on Cd^{II}–X Interactions. The log K_1 values for the formation of [MX]$^+$ (M^{2+} = Cd^{2+}, [Cd(bpy)]$^{2+}$, [Cd(bpy)$_2$]$^{2+}$ are plotted against the ionic radii of the halide ions in Figure 7, along with those for the Ni^{II}–X–bpy systems.[19,28] The log K_1 value decreases in the sequence Cl > Br > I in DMF as in DMSO.[2] As seen in Figure 7, the slope for Cd^{2+} is practically the same as those for [Cd(bpy)]$^{2+}$ and [Cd(bpy)$_2$]$^{2+}$. A similar trend is observed also for the Ni^{II} systems. Note that the slope is evidently steeper for Ni^{II} than for Cd^{II} and that the log K_1 value is generally larger for Cd^{II} than for Ni^{II}, both reflecting a softer character of the cadmium(II) ion.

Interesting features are seen in the enthalpy and entropy values (Table III). The $\Delta H°_1$ values are practically the same for all the Cd^{2+}, [Cd(bpy)]$^{2+}$, and [Cd(bpy)$_2$]$^{2+}$ in the chloride system, as in the Ni^{II}–X–bpy (X = Cl, Br) systems. The $\Delta H°_1$ value decreases along the series Cd^{2+} > [Cd(bpy)]$^{2+}$ > [Cd(bpy)$_2$]$^{2+}$ for bromide, and even more markedly so for iodide. This suggests that the soft (covalent) character of the cadmium(II) ion is enhanced when the ion is bound to 2,2′-bipyridine molecules. On the other hand, the $\Delta S°_1$ value increases by about 10 J K^{-1} mol^{-1} for both [Cd(bpy)]$^{2+}$ and [Cd(bpy)$_2$]$^{2+}$ compared with that for Cd^{2+}, and interestingly the increment is the same as that for the ternary Ni^{II}–X–bpy (X = Cl, Br) systems. The $\Delta S°_1$ values vary along the series [Cd(bpy)]$^{2+}$ > Cd^{2+} ≈ [Cd(bpy)$_2$]$^{2+}$ for bromide. With iodide, the value for Cd^{2+} is almost the same as that for [Cd(bpy)]$^{2+}$ and is even reduced by about 10 J K^{-1} mol^{-1} for [Cd(bpy)$_2$]$^{2+}$.

(28) Ishiguro, S.; Ozutsumi, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2392.