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Thermodynamics of Formation of Ternary (2,2′-Bipyridine)thiocyanatocadmium(II) Complexes in *N*,*N*-Dimethylformamide

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Synopsis. The formation of ternary (2,2′-bipyridine)thiocyanatocadmium(II) complexes has been studied by calorimetry in *N*,*N*-dimethylformamide containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ as a constant ionic medium at 25 °C. The formation of $[CdA(bpy)]^+$, $[CdA_2(bpy)]$, $[CdA_3(bpy)]^-$, $[CdA(bpy)_2]^+$, and $[CdA_2(bpy)_2]$ (A=SCN, bpy=2,2-bipyridine) is revealed, and their formation constants, enthalpies, and entropies were obtained. The result is compared with that in the corresponding halide systems in the same solvent.

Previously we reported the complexation in the ternary Cd^{II}-X^--bpy (X=Cl, Br, I, bpy=2,2′-bipyridine) systems in *N*,*N*-dimethylformamide (DMF) at 25 °C.[1)] In these systems the formation of the ternary complexes such as $[CdX(bpy)]^+$, $[CdX_2(bpy)]$, $[CdX_3(bpy)]^-$, $[CdX(bpy)_2]^+$, and $[CdX_2(bpy)_2]$ is demonstrated, in which 2,2′-bipyridine coordinates as a bidentate ligand. Among these the formation of $[CdX_3(bpy)]^-$ is of particular interest because this kind of complex is not found to form in the metal(II)-halide systems such as Mn^{II}, Ni^{II},[2)] Cu^{II},[3)] and Zn^{II} [4)] in DMF. It is revealed that the $[CdX_3(dmf)]^-$ complex is four-coordinated and the replacement of a monodentate dmf molecule with a bidentate bpy leads to the formation of five-coordinate $[CdX_3(bpy)]^-$. It is also revealed that the stability of the complex depends on the halide, indeed the ternary complex is formed for Cl and Br, though less marked than Cl, but not for I. Here, as an extension of the study on the ternary complexation, we studied the thermodynamics of formation of the ternary Cd^{II}-SCN^--bpy complexes in DMF at 25 °C by precise titration calorimetry, and the results are compared with those for the Cd^{II}-X^--bpy systems.

Experimental

Chemicals used were prepared or purified as described elsewhere.[1,5)] Calorimetric measurements were carried out using an on-line controlled calorimetry system.[6,7)] Cadmium(II) thiocyanate solutions (40 cm^3) of varying concentrations were titrated with a 0.1 mol dm^{-3} 2,2′-bipyridine solution. A constant ionic medium of 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ was used. The procedure of the measurements and the analysis of data are similar to those described elsewhere.[1)]

Results and Discussion

Calorimetric data obtained in the ternary system were analyzed on the basis of the thermodynamic parameters of formation of the binary cadmium(II) thiocyanato complexes determined previously in the same ionic medium,[5)] and of the binary cadmium(II) 2,2′-bipyridine complexes obtained in this work. The nonlinear least-squares analysis showed that five ternary complexes, $[CdA(bpy)]^+$, $[CdA_2(bpy)]$, $[CdA_3(bpy)]^-$, $[CdA(bpy)_2]^+$, and $[CdA_2(bpy)_2]$ (A=SCN) are yielded, as in the case for the Cd^{II}-X^--bpy (X=Cl, Br) systems.[1)] Simultaneously, their formation constants, reaction enthalpies, and entropies were obtained, which are listed in Table 1 along with those for the binary (2,2′-bipyridine)cadmium(II) complexes. The distribution of species, calculated by using the formation constants in Table 1, is shown in Fig. 1. Obviously, all the ternary complexes are favorably formed. This applies especially for the $[CdA_3(bpy)]^-$ complex in solution of $C_{bpy}/C_{Cd}>1$.

According to solution X-ray diffraction,[8)] the cadmium(II) ion is present as octahedral $[Cd(dmf)_6]^{2+}$ species in DMF, and on the complexation with bidentate 2,2′-bipyridine, a series of six-coordinate $[Cd(bpy)(dmf)_4]^{2+}$, $[Cd(bpy)_2(dmf)_2]^{2+}$, and $[Cd(bpy)_3]^{2+}$ are formed. If the cadmium(II) ion preserves six-coordination, and SCN^- ions stepwise replace coordi-

Table 1. Overall Formation Constants, $\log(\beta_{1mn}/\mathrm{mol}^{-(m+n)}\,\mathrm{dm}^{3(m+n)})$ and Enthalpies, $\Delta H^\circ_{\beta 1mn}/\mathrm{kJ\,mol^{-1}}$, of $[CdA_m(bpy)_n]^{(2-m)+}$ (A=SCN, bpy=2,2′-bipyridine) in *N*,*N*-Dimethylformamide Containing 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ at 25 °C[a)]

Cd^{II}-SCN^--bpy		Cd^{II}-bpy	
$\log\beta_{111}$	6.83(0.13)	$\log\beta_{101}$	2.91(0.11)
$\log\beta_{121}$	9.20(0.07)	$\log\beta_{102}$	5.29(0.14)
$\log\beta_{131}$	10.61(0.05)	$\log\beta_{103}$	6.30(0.28)
$\log\beta_{112}$	8.93(0.11)		
$\log\beta_{122}$	10.89(0.11)		
$\Delta H^\circ_{\beta 111}$	−17.7(0.4)	$\Delta H^\circ_{\beta 101}$	−13.3(0.3)
$\Delta H^\circ_{\beta 121}$	−25.3(0.9)	$\Delta H^\circ_{\beta 102}$	−30.1(1.0)
$\Delta H^\circ_{\beta 131}$	−26.8(0.7)	$\Delta H^\circ_{\beta 103}$	−43.3(2.5)
$\Delta H^\circ_{\beta 112}$	−35.8(0.7)		
$\Delta H^\circ_{\beta 122}$	−45.3(1.2)		
R[b)]	0.01029		0.01830
N[c)]	85		83

a) Values in parentheses refer to 3σ. The parameters for the binary Cd^{II}-bpy and Cd^{II}-SCN^- systems were fixed in the analysis of the ternary Cd^{II}-SCN^--bpy system. The overall formation constants and enthalpies of $[CdA_n]^{(2-n)+}$ (A=SCN) employed are $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$=3.57, 5.98, 7.59, and 8.81, and $\Delta H^\circ_n/\mathrm{kJ\,mol^{-1}}$=−4.9, −9.2, −7.32, and 2.6, for n=1, 2, 3, and 4, respectively. b) The Hamilton R factor. c) The number of data points.

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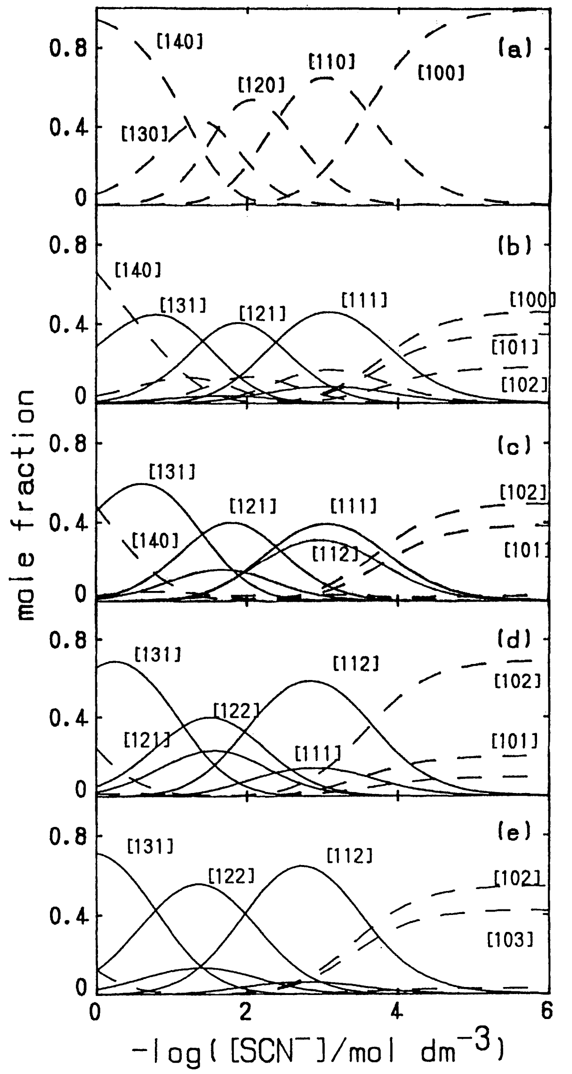

Fig. 1. Species distribution in the Cd^{II}-SCN^--bpy system in *N,N*-dimethylformamide at 25 °C at the total concentrations of $C_{Cd}/(mol\,dm^{-3})$ and $C_{bpy}/(mol\,dm^{-3})$: (a) 0.01, 0; (b) 0.01, 0.01; (c) 0.01, 0.02; (d) 0.01, 0.05; (e) 0.01, 0.10. The $[CdA_m(bpy)_n]^{(2-m)+}$ complex is represented by the symbol [1*mn*].

nating solvent molecules upon complexation, one expects the formation of ternary complexes such as $[CdA(bpy)]^+$, (A=SCN) $[CdA_2(bpy)]$, $[CdA_3(bpy)]^-$, $[CdA_4(bpy)]^{2-}$, $[CdA(bpy)_2]^+$, and $[CdA_2(bpy)_2]$. In fact, all of the complexes except for $[CdA_4(bpy)]^{2-}$ are found. Note that it occurs the formation of $[CdA_3(bpy)]^-$, which is in parallel with that of $[CdX_3(bpy)]^-$ in the Cd^{II}-X^--bpy systems.[1)] In the Cd^{II}-X^--bpy systems, the $[CdX_3(bpy)]^-$ complex is indeed formed for X as Cl and Br, but not for I which is relatively large and soft. The SCN^- ion binds to the metal ion with either the relatively hard N or the soft S atom, and the favorable formation of $[CdA_3(bpy)]^-$ suggests that the SCN^- ion is coordinated with the N end in the complex. This is expected because the SCN^- ion binds favorably with the N end to the cadmium(II) ion in DMF, as evidenced by the formation of the N-coordinating $[Cd(NCS)]^+$ and $[Cd(NCS)_2]$ in DMF.[5)]

Table 2. Stepwise Formation Constants, log (K_l/mol⁻¹ dm³), Enthalpies, $\Delta H°$/kJ mol⁻¹, and Entropies, $\Delta S°$/J K⁻¹ mol⁻¹ of Binary and Ternary Cadmium(II) Complexes with 2,2′-Bipyridine(bpy) and Thiocyanate ion (A^-) in *N,N*-Dimethylformamide at 25 °C

	log*K*	$\Delta H°$	$\Delta S°$
$Cd^{2+}+A^- \rightarrow [CdA]^+$	3.57	−4.9	52
$[Cd(bpy)]^{2+}+A^- \rightarrow [CdA(bpy)]^+$	3.92	−4.4	60
$[Cd(bpy)_2]^{2+}+A^- \rightarrow [CdA(bpy)_2]^+$	3.64	−5.5	50
$[CdA]^{+}+A^- \rightarrow [CdA_2]$	2.41	−4.3	32
$[CdA(bpy)]^{+}+A^- \rightarrow [CdA_2(bpy)]$	2.37	−7.6	20
$[CdA(bpy)_2]^{+}+A^- \rightarrow [CdA_2(bpy)_2]$	1.96	−9.4	6
$[CdA_2]+A^- \rightarrow [CdA_3]^-$	1.61	1.9	37
$[CdA_2(bpy)]+A^- \rightarrow [CdA_3(bpy)]^-$	1.40	−1.5	22

In Table 2, the log*K*, $\Delta H°$ and $\Delta S°$ are compared with respect to reaction (1).

$$M^{2+}+A^- \rightarrow [MA]^+ \quad (M=Cd, [Cd(bpy)], [Cd(bpy)_2]) \qquad (1)$$

The difference in the log*K* values by varying M is small, and the $\Delta H°$ and $\Delta S°$ values remain virtually unchanged, suggesting that no change in the coordination geometry and in the linkage mode of the SCN^- ion occurs on the complexation of the ternary complexes. With respect to the reaction, $[MA]^+ + A^- \rightarrow [MA_2]$, the log*K* value decreases slightly in the order of M as Cd>[Cd(bpy)]>$[Cd(bpy)_2]$. The $\Delta H°$ and $\Delta S°$ values decrease in the same order, but it is stressed that the decrement is significantly smaller than that for the corresponding halide systems. For example, in the Cl system, a remarkable decrease in the $\Delta H°$ and $\Delta S°$ values, by ca. 12 kJ mol⁻¹ and 40 J K⁻¹ mol⁻¹, is indeed observed in going from M as Cd to [Cd(bpy)], which is ascribed to the fact that, with both $[CdX_2]$ and $[CdX_2(bpy)]$, an equilibrium is established between octahedral and tetrahedral isomers,

$$[CdX_2(dmf)_4]\ (O_h) = [CdX_2(dmf)_2]\ (T_d) + 2dmf \qquad (2)$$

$$[CdX_2(bpy)(dmf)_2]\ (O_h) = [CdX_2(bpy)]\ (T_d) + 2dmf \qquad (3)$$

and the equilibrium is more shifted to the T_d side for reaction (2).[1)] On the other hand, in the Cd^{II}-SCN^--bpy system, there is no structural isomer for $[CdA_2]$.[5)] The relatively small differences in the $\Delta H°$ values, as well as $\Delta S°$, for M=Cd and [Cd(bpy)] imply that there is no isomer for $[CdA_2(bpy)]$ as well. As the formation of six-coordinate $[Cd(NCS)(dmf)_5]^+$ and $[Cd(NCS)_2(dmf)_4]$, in which the SCN^- ion binds with the N end, is established in DMF,[5)] dmf molecules in these complexes may be replaced with bidentate bpy molecules to form six-coordinate $[Cd(NCS)(bpy)]^+$, $[Cd(NCS)_2(bpy)]$, $[Cd(NCS)(bpy)_2]^+$, and $[[Cd(NCS)_2(bpy)_2]$ complexes.

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