Thermodynamics and Structure of Isothiocyanate Complexes of Manganese(II), Cobalt(II) and Zinc(II) Ions in N,N-Dimethylacetamide

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Dedicated to Prof. Dr. Ohtaki on his occasion of 60th birthday

The complexation of manganese(II), cobalt(II) and zinc(II) with thiocyanate ions has been studied in N,N-dimethylacetamide (DMA) by calorimetry and spectrophotometry at 298 K. In these metal systems the formation of a series of four isothiocyanato complexes, $[M(NCS)_n]^{(2-n)+}$ $(n = 1 \div 4$; $M = $ Mn, Co, and Zn) was established, and their formation constants, enthalpies and entropies were determined. Interestingly, the complexation behavior in DMA is significantly different from that in N,N-dimethylformamide (DMF), despite of the similarity of the physicochemical properties of these solvents. The complexation is indeed enhanced significantly in DMA over DMF and is more exothermic in the former solvent. Furthermore, with cobalt(II) an octahedral to tetrahedral coordination geometry change was found to occur in DMA at an earlier step of complexation than in DMF. These results suggest that six-coordination of DMA molecules to a metal ion is severely sterically hindered.

Key words: Thiocyanato complexes, Transition metal(II) ions, N,N-dimethylacetamide, Calorimetry, Spectrophotometry.

Introduction

The complexation of metal ions in solutions depends strongly on the nature of the solvent. Particularly, the electron-pair donating and accepting properties of solvents play an essential role in the solvent effect on the metal-ion complexation. N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF) are typical aprotic oxygen-donor solvents, and their physicochemical properties such as dielectric constant and donor and acceptor properties, are so similar that the complexation behavior of metal ions is expected to be not significantly different.

Solvent	Formula	ε	DN	AN
DMF	$HCON(CH_3)_2$	36.71	26.6	16.0
DMA	$CH_3CON(CH_3)_2$	37.78	27.7	13.6

ε: Dielectric constant, DN: Donor number, AN: Acceptor number.

To elucidate the thermodynamics and structure of metal complexes in nonaqueous solution, we have so far studied systematically the halogeno complexation of divalent transition metal(II) ions, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in DMA and DMF. Interestingly, it was found that the complexation is enhanced remarkably in DMA over DMF [1–8]. Furthermore, the enthalpies of transfer of $[MCl_n]^{(2-n)+}$ $(M = $ Mn, Co, Ni, Zn; $n = 1-4)$ from DMF to DMA showed appreciable dependence on the metal ion and its complexes [9]. These results suggest that some specific interactions operate upon the solvation of metal ions in DMA. N,N-Dimethylacetamide involves a bulky acetylmethyl group, and thus it is supposed that the coordination of six DMA molecules to the metal ion is sterically hindered. On the other hand, with regard to DMF, no steric effect upon solvation is expected as it involves a sole formyl proton.

In the present study, to obtain further evidence of the steric effect upon the solvation of metal ions and complexes in DMA, we examined the formation of isothiocyanato complexes of manganese(II), cobalt(II) and zinc(II) ions in DMA and compared it with that in DMF [8, 10]. The thiocyanate ion, which involves

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hard N and soft S ends, binds to divalent transition metal ions through the N end.

Experimental

Chemicals

The DMA solvates of manganese(II), cobalt(II) and zinc(II) tetrafluoroborate, $M(BF_4)_2 \cdot n$DMA (M = Mn, Co, Zn) and tetra-*n*-butylammonium tetrafluoroborate were prepared as described previously [2, 3]. Tetra-*n*-butylammonium thiocyanate (Fluka) was used without further purification and dried in vacuum for one day. N,N-Dimethylacetamide was purified by distillation at 1200 Pa over BaO [11]. All chemicals were treated in a drybox over P_2O_5.

Methods

The calorimetric measurements were performed using an automatic data acquisition system combined with a twin-type isoperibol calorimeter thermostated at (25.0 ± 0.1)°C. A metal tetrafluoroborate solution (30 cm^3; 3–40 mmol dm^{-3}) was titrated with a 0.1 mol dm^{-3} (Co and Zn) or 0.2 mol dm^{-3} (Mn) $(n\text{-}C_4H_9)_4NSCN$ solution. All solutions contained 0.1 or 0.2 mol dm^{-3} $(n\text{-}C_4H_9)_4NBF_4$ as a constant ionic medium.

The spectrophotometric measurement for the Co^{II} system was carried out using a 340 spectrophotometer (Hitachi). The metal solution of ca. 2 mmol dm^{-3} was titrated with a 14–40 mmol dm^{-3} $(n\text{-}C_4H_9)_4NSCN$ solution, and all the solutions contained 0.1 mol dm^{-3} $(n\text{-}C_4H_9)_4NBF_4$ as a constant ionic medium. The detailed procedure is described in [2, 3].

Data Analysis

Formation constants and enthalpies were simultaneously determined by analyzing calorimetric data using a nonlinear least-squares program MQCAL. Formation constants and electronic spectra of individual complexes were simultaneously determined by analyzing spectrophotometric data obtained at selected 50 wavelengths over the range 450–700 nm using a nonlinear least-squares program MQSPEC. The detailed procedure is described in [1, 10].

Results

Manganese(II) – Thiocyanate in DMA

Calorimetric titration curves for the Mn^{II}–NCS system are shown in Fig. 1, in which the $-q/[(\delta v) C_{NCS,titr}]$ values are plotted against the total concentration ratio C_{NCS}/C_{Mn} in solution, where q, δv, and $C_{NCS,titr}$ denote the measured heat of reaction, the volume of the added titrant at each titration point, and the concentration of the SCN$^-$ ion in the titrant, respectively. The reaction heat is small and endo-

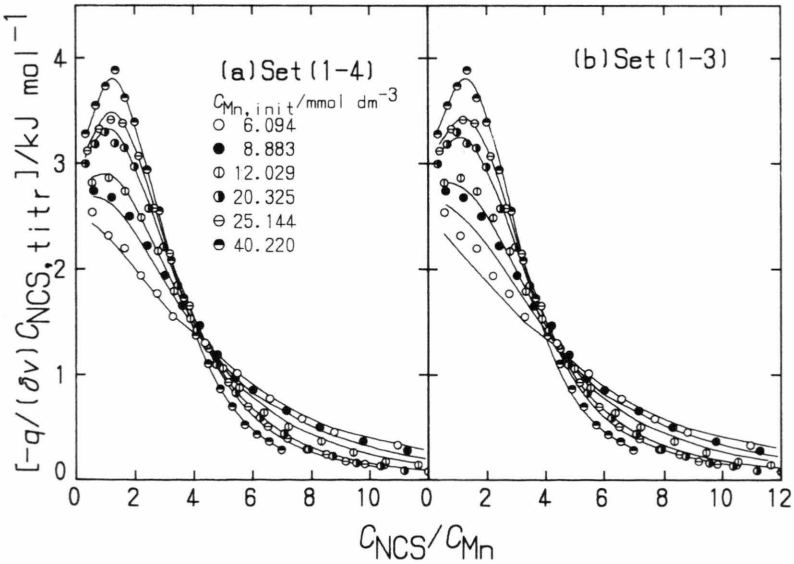

Fig. 1. Calorimetric titration curves of manganese(II)-thiocyanate-DMA solutions containing 0.2 mol dm^{-3} $(n\text{-}C_4H_9)_4NBF_4$ at 298 K for set (1–4) (a) and set (1–3) (b). Initial concentrations of metal ions ($C_{Mn,init}$/mmol dm^{-3}) are given in the figure. The solid lines were calculated by using the optimized parameters.

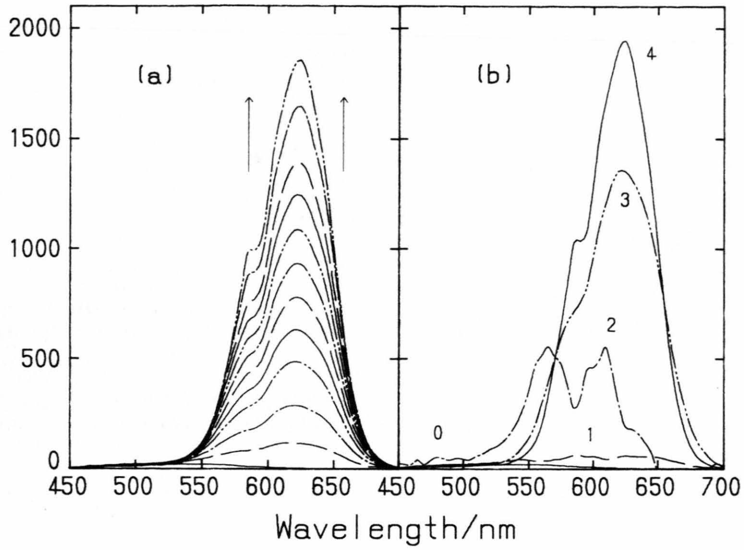

Fig. 2. (a) Measured electronic spectra of cobalt(II) thiocyanate-DMA solutions at 298 K. The C_{NCS}/C_{Co} ratio increased from 0 to 5.95 as indicated by arrows. (b) Extracted electronic spectra of cobalt(II) isothiocyanato complexes in DMA at 298 K. The numbers represents n $[Co(NCS)_n]^{(2-n)+}$.

Table 1. Overall formation constants, $\log(\beta_n/\mathrm{mol}^{-n}\,\mathrm{dm}^{3n})$, and enthalpies, $\Delta H^0_{\beta n}/\mathrm{kJ\,mol}^{-1}$, for the reactions $M^{2+} + n\mathrm{NCS}^- = [\mathrm{M(NCS)}_n]^{(2-n)+}$ (M = Mn, Co and Zn; $n = 1-4$) obtained by calorimetry and spectrophotometry in N,N-dimethylacetamide containing 0.2 mol dm^{-3} (Mn$^{\mathrm{II}}$) or 0.1 mol dm^{-3} (Co$^{\mathrm{II}}$ and Zn$^{\mathrm{II}}$) $(n\text{-}C_4H_9)_4NBF_4$ as a constant ionic medium at 298 K.

	Mn$^{\mathrm{II}}$	Co$^{\mathrm{II}}$			Zn$^{\mathrm{II}}$
	cal	spec	cal		cal
$\log\beta_1$	2.7 (0.1)	4.06 (0.05)	3.7 (0.4)	4.06^a	5.3 (0.4)
$\log\beta_2$	4.5 (0.1)	7.4 (0.2)	7.2 (0.4)	7.4^a	10.3 (0.7)
$\log\beta_3$	6.1 (0.2)	12.0 (0.1)	11.5 0(.6)	12.0^a	14.8 (0.9)
$\log\beta_4$	7.4 (0.2)	15.4 (0.1)	15.1 (0.6)	15.4^a	18.0 (0.9)
$\Delta H^0_{\beta1}$	3.28 (0.07)	–	5 (3)	6.7 (0.3)	–0.3 (0.4)
$\Delta H^0_{\beta2}$	10 (1)	–	45 (29)	36 (3)	–7 (1)
$\Delta H^0_{\beta3}$	14 (2)	–	3 (2)	3.5 (0.4)	–24.3 (0.2)
$\Delta H^0_{\beta4}$	14.5 (0.8)	–	–17.9 (0.2)	–18.1 (0.2)	–45.5 (0.2)
N^b	103	4350	157	157	87
R^c	0.018	0.0051	0.021	0.032	0.012

Values in parentheses refer to three standard deviations.
[a] Fixed. [b] Total number of data points. [c] The Hamilton R factor.

thermic throughout the titration. As seen in Fig. 1 (a), all the experimental points were well explained in terms of the formation of four mononuclear complexes $[Mn(NCS)_n]^{(2-n)+}$ ($n = 1-4$) with an R factor of 0.018. Also set (1–3), assuming the formation of mono-, di- and triisothiocyanato complexes, only gave a relatively small R factor of 0.027. The parameter values thus obtained for set (1–3) are $\log\beta_1 = 2.6$ ($3\sigma = 0.2$), $\log\beta_2 = 4.3$ (0.2), $\log\beta_3 = 5.9$ (0.2) and $\Delta H^0_{\beta1} = 3.4$ (0.1) kJ mol^{-1}, $\Delta H^0_{\beta2} = 10$ (1) and $\Delta H^0_{\beta3} = 15.3$ (0.5), which are not appreciably different from the corresponding values for set (1–4), as seen in Table 1. However, the formation of $[Mn(NCS)_4]^{2-}$ cannot be neglected, because the calculated curves deviate systematically from the experimental points, as shown in Figure 1 (b).

Cobalt (II) Thiocyanate in DMA

Electronic spectra of cobalt(II) thiocyanate solutions with varying metal to ligand ratio are shown in Figure 2 (a). The initial solution of cobalt(II) tetrafluoroborate (light purple) exhibited a weak absorption band at 541 nm, a typical spectrum of an octahedral six-coordinate cobalt(II) chromophore. With the addition of the $(C_2H_5)_4NSCN$ titrant, the color changed to dark blue and a new intense band grew at around 625 nm. Spectrophotometric data were analyzed by assuming the formation of a series of four $[Co(NCS)_n]^{(2-n)+}$ ($n = 1-4$) complexes with an R factor of 0.0051 (set 1–4). However, set (1, 3, 4) assuming the formation of the mono-, tri- and tetraisothiocyanato complexes only, also gave a small R factor of 0.0059, suggesting that the formation of $[Co(NCS)_2]$ is strongly suppressed. Indeed, the formation constants thus obtained for set (1, 3, 4) are $\log\beta_1 = 4.35$ ($3\sigma = 0.03$), $\log\beta_3 = 12.47$ (0.08) and $\log\beta_4 = 16.01$ (0.08), which are not significantly different from those for set (1–4) (Table 1). Set (2–4) and set (3, 4) result in

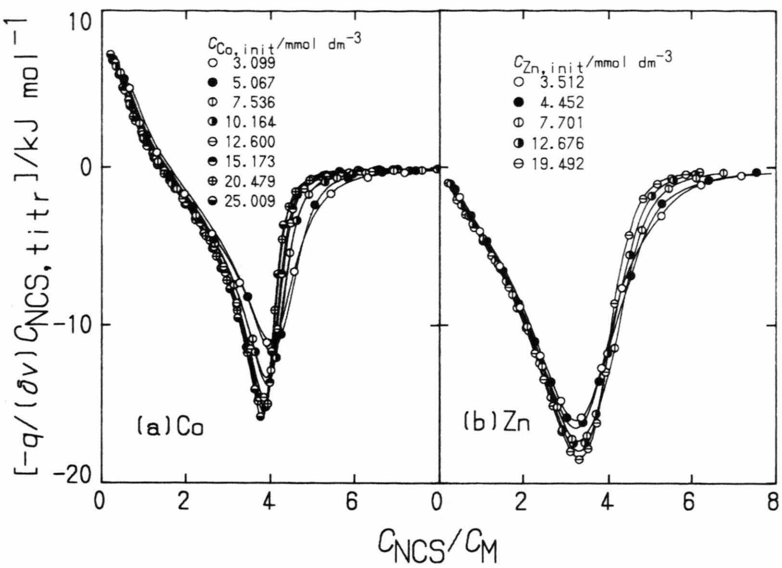

Fig. 3. Calorimetric titration curves of (a) cobalt(II)- and (b) zinc(II)-thiocyanate-DMA solutions containing 0.1 mol dm^{-3} $(n\text{-}C_4H_9)_4NBF_4$ at 298 K. Initial concentrations of metal ions ($C_{M,init}$/mmol dm^{-3}) are given in the figure. The solid lines were calculated by using the optimized parameters in Table 1.

larger R factors of 0.014 and 0.051, respectively, indicating that the formation of $[Co(NCS)]^+$ cannot be neglected. The extracted electronic spectra of individual $[Co(NCS)_n]^{(2-n)+}$ ($n = 1-4$) complexes are shown in Figure 2(b). Note that the spectrum of $[Co(NCS)_2]$ involves large uncertainties, as its formation is strongly suppressed.

Calorimetric titration curves for the $Co^{II}-SCN$ system are shown in Figure 3(a). The reaction heat is endothermic at the initial stage of complexation and then turns to exothermic at about $C_X/C_M = 1$. All data were well explained in terms of the formation of a series of four mononuclear complexes, set (1–4), with an R factor of 0.021. Set (2–4) and set (1, 3, 4) gave larger R factors of 0.043 and 0.077, respectively, indicating that the formation of $[Co(NCS)_2]$ cannot be neglected. Thus, set (1–4) was adopted as the final choice. Finally, the calorimetric data were analyzed on the basis of the formation constants of set (1–4) obtained by spectrophotometry.

Zinc(II) Thiocyanate in DMA

Calorimetric titration curves for the $Zn^{II}-SCN$ system are shown in Figure 3(b). The reaction heats were strongly exothermic throughout the titration. This is exceptional among the metal thiocyanate systems so far examined, because the reaction heats are generally small throughout titrations. The data were well analyzed in terms of set (1–4) with an R factor of 0.012. Set (2–4) gave rather large values of the R factor (0.031) and standard deviations (3σ), suggesting that the formation of $[Zn(NCS)]^+$ cannot be neglected. Similarly, set (1, 3, 4) gave a large R factor of 0.166, indicating that the dichloro complex cannot be eliminated in DMA, unlike DMF. Therefore, set (1–4) is the most plausible. Thermodynamic parameters thus obtained are summarized in Table 1.

4. Discussion

The complexation of metal ions with thiocyanate ions is very weak in water, but is markedly enhanced in aprotic donor solvents such as DMSO, DMF, and DMA. However, as metal ions are much more strongly solvated in these aprotic solvents than in water, the reaction enthalpies are usually small and negative, or even positive. Therefore, the enhanced complexation is utterly due to the entropy term, which is positive and significantly larger in an aprotic solvent than in water. This suggests that solvent–solvent interactions in the bulk play an important role. As aprotic donor solvents form no hydrogen bonds with each other in the bulk, solvent molecules may have relatively large freedom of motion, while those coordinated to a metal ion do not. Therefore, solvent molecules liberated from the primary coordination sphere of metal ions upon complexation will increase significantly their freedom of motion in an aprotic

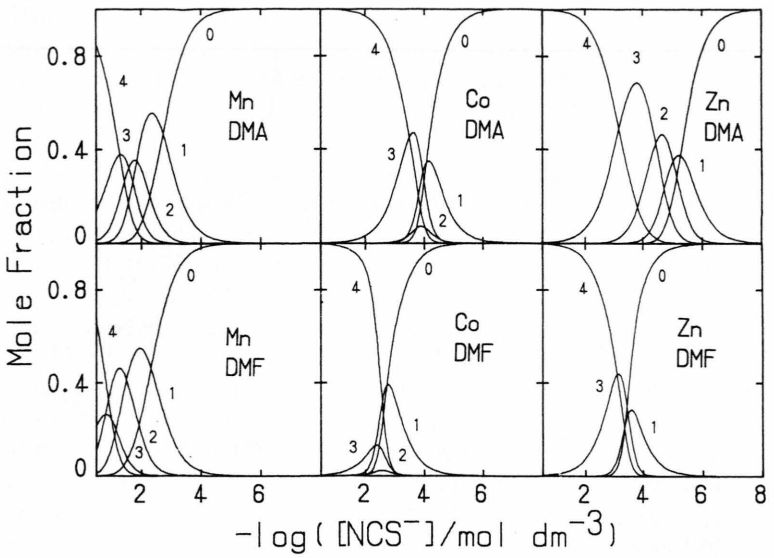

Fig. 4. Species distribution for $[M(NCS)_n]^{(2-n)+}$ complexes (M = Mn, Co and Zn; $n = 1-4$) in DMA and DMF at 298 K. The number represents n $[M(NCS)_n]^{(2-n)+}$.

solvent. On the other hand, in water, liberated water molecules from the coordination sphere of metal ions upon complexation are again structured into the extended hydrogen-bonded net work of the bulk and thus loose their freedom of motion.

The stepwise formation constants, enthalpies and entropies for the Mn^{II}, Co^{II} and Zn^{II}–SCN systems are summarized in Table 2, along with those in DMF for comparison [8, 10]. Evidently, in all the metal systems, the complexation is significantly enhanced in DMA over DMF. However, note that the solvent–solvent interactions in the bulk DMA and DMF are weak and are not appreciably different. Also, the dielectric constant ε and the donor number DN of DMA and DMF are similar [11, 12], although the acceptor number of DMA is slightly smaller than that of DMF, i.e., the thiocyanate ion is more active in DMA [9], this contributes only partly to an enhanced stability of thiocyanato complexes in DMA. Figure 4 shows species distributions of the isothiocyanato complexes of manganese(II), cobalt(II) and zinc(II) ions in DMA, together with those in DMF. Indeed, the species distributions differ considerably between the solvents, which can not be expected solely from the difference in

Table 2. Stepwise formation constants, $\log(K_n/\text{dm}^3\,\text{mol}^{-1})$, enthalpies, $\Delta H_n^0/\text{kJ mol}^{-1}$, and entropies, $\Delta S_n^0/\text{kJ mol}^{-1}$, for reactions $[M(NCS)_{n-1}]^{(3-n)+} + NCS^- = [M(NCS)_n]^{(2-n)+}$ in N,N-dimethylacetamide (DMA) and N,N-dimethylformamide (DMF) at 298 K.

	Mn^{II}		Co^{II}		Zn^{II}	
	DMA	DMF[a]	DMA	DMF[a]	DMA	DMF[b]
$\log K_1$	2.7 (0.1)	2.3	4.06 (0.05)	2.7	5.3 (0.4)	3.3
$\log K_2$	1.8 (0.2)	1.6	3.3 (0.2)	1.4	5.1 (0.3)	—
$\log K_3$	1.6 (0.2)	0.8	4.6 (0.2)	3.2	4.5 (0.2)	$\log K_2 K_3 = 6.9$
$\log K_4$	1.3 (0.2)	1.0	3.48 (0.02)	3.0	3.16 (0.02)	3.1
ΔH_1^0	3.28 (0.07)	−1.0	6.7 (0.3)	−1.0	−0.3 (0.4)	4.9
ΔH_2^0	7 (1)	−1.6	29 (3)	−22	−6 (1)	—
ΔH_3^0	4 (3)	9.3	−32 (3)	35	−18 (1)	$\Delta H_2^0 + \Delta H_3^0 = 4.6$
ΔH_4^0	0 (2)	8.6	−21.7 (0.4)	−7.0	−21.2 (0.2)	−17.4
ΔS_1^0	63 (3)	40	100 (1)	49	100 (7)	80
ΔS_2^0	58 (1)	24	161 (10)	−45	75 (4)	—
ΔS_3^0	44 (5)	46	−20 (10)	180	27 (8)	$\Delta S_2^0 + \Delta S_3^0 = 147$
ΔS_4^0	26 (6)	49	−6 (1)	34	−11 (1)	3

Values in parentheses refer to three standard deviations. [a] [10], [b] [8].

the electron-pair accepting properties of the solvents. Therefore, there may be other key factors that determine the reactivity of metal ions in DMA.

With cobalt(II), the extracted electronic spectra clearly show the coordination geometry change around the metal ion upon complexation. The monoisothiocyanato complex shows a weak band like octahedrally six-coordinated $[Co(DMA)_6]^{2+}$, suggesting the structure of an octahedral $[Co(NCS)(DMA)_5]^+$. On the other hand, both tri- and tetraisothiocyanato complexes show intense bands at around 625 nm with molar extinction coefficients of ca. 1350 and 1940, respectively, a typical band for a tetrahedrally four-coordinated cobalt(II) chromophore, and thus these complexes may have the four-coordination as $[Co(NCS)_3(DMA)]^-$ and $[Co(NCS)_4]^{2-}$, respectively. Practically the same spectra of $[Co(NCS)_4]^{2-}$ have been observed in DMF and DMSO [10, 13]. Although the obtained molar absorption coefficients of $[Co(NCS)_2]$ involve rather large uncertainties because of it suppressed formation, the electronic spectrum suggests that the complex is tetrahedrally four-coordinated. Therefore, we propose that the coordination geometry around the cobalt(II) ion in DMA changes upon complexation as follows: $[Co(DMA)_6]^{2+}$ (*Oh*) → $[Co(NCS)(DMA)_5]^+$ (*Oh*) → $[Co(NCS)_2(DMA)_2]$ (*Td*) → $[Co(NCS)_3(DMA)]^-$ (*Td*) → $[Co(NCS)_4]^{2-}$ (*Td*). This conclusion is supported by the thermodynamic data as discussed below.

With cobalt(II), the ΔS_2^0 value is particularly large and positive, while the ΔS_3^0 value is even negative. The large and positive entropy suggests that liberation of solvent molecules occurs extensively upon complexation, and thus it is supposed that an *Oh* to *Td* geometry change occurs upon the formation of $[Co(NCS)_2]$. The ΔH_2^0 value is relatively large and positive, also suggesting that more than two metal–solvent bonds are simultaneously ruptured upon complexation. This conclusion is consistent with that drawn from electronic spectra.

A similar geometry change is associated with the complexation in DMF. However, it has been established that an *Oh* to *Td* geometry change occurs upon the formation of $[Co(NCS)_3]^-$ in DMF. Thus, the geometry change occurs at an earlier stage of complexation in DMA than that in DMF. The same conclusion has been obtained for the halogeno complexation of the cobalt(II) ion, where the stage of geometry change is shifted from the second step in DMF to the first step in DMA [2].

According to our EXAFS study [14], the cobalt(II) ion is coordinated with six solvent molecules in both DMF and DMA, and the $Co^{II}-O$ bond lengths are practically the same. However, N,N-dimethylacetamide, $CH_3CON(CH_3)_2$, involves a bulky acetylmethyl group, and therefore the coordination of six DMA molecules to the cobalt(II) ion may be accompanied by severe steric hindrance. The steric interaction upon solvation may reduce significantly the solvation Gibbs energy to lead to higher stabilities of metal complexes. On the other hand, N,N-dimethylformamide, $HCON(CH_3)_2$, involves a sole formyl proton, and there may be practically no steric effect upon solvation.

The manganese(II) ion is octahedrally six-coordinated in both DMA and DMF [14]. With Mn^{II}, the variation of stepwise ΔH_n^0 and ΔS_n^0 values with n in DMA show no anomaly, and therefore it seems to be rather difficult to discuss the geometry change upon complexation. However, it may be stressed that the extent of stability enhancement is smallest for Mn^{II}. This may be expected because the manganese(II) ions has the largest ionic radius among the transition metal(II) ions.

With Zn^{II}, the stepwise ΔH_n^0 and ΔS_n^0 values decrease monotonically with n in DMA. According to our EXAFS study, the coordination number of the zinc(II) ion is 4.6 and 6 in DMA and DMF, respectively [14]. The smaller coordination number than 6 in DMA implies that only a part of zinc(II) ions are octahedrally solvated in the solvent. Although we have no direct structural evidence, we suppose that a solvation equilibrium is established between $[Zn(DMA)_4]^{2+}$ and $[Zn(DMA)_6]^{2+}$, and the equilibrium is shifted more to the four-coordination. If we take into account a solvation equilibrium in DMA, the relatively large and positive ΔH_1^0 and ΔS_1^0 values indicate that solvent molecules are extensively liberated from $[Zn(DMF)_6]^{2+}$ upon complexation to yield the four-coordinated monoisothiocyanato complex, $[Zn(NCS)(DMA)_3]^+$.

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