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Accounts

Thermodynamic and Structural Aspects on Solvation Steric Effect in Nonaqueous Solution

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Formation thermodynamics and structure of halogeno and pseudo-halogeno complexes of transition metal(II) and lanthanide(III) ions have been studied in *N*,*N*-dimethylacetamide (DMA) and hexamethylphosphoric triamide (HMPA), and compared with those in *N*,*N*-dimethylformamide (DMF). Significant differences in the formation thermodynamics and structure among solvents has been explained in terms of a *solvation steric effect.* A structural survey by EXAFS demonstrates that solvent coordination number of a solvate metal ion is kept unchanged (*weak solvation steric effect*) or reduced (*strong solvation steric effect*) when the metal ion is transferred to DMA or HMPA, respectively, from DMF. DMA usually exhibits a weak solvation steric effect. It elucidates that a weak solvation steric effect of DMA is ascribable mainly to a distortion of the M–O–C–N dihedral angle. The solvent effect operates for a complex with a coordination number larger than four in DMF, but it does not for a complex of four-coordination. Lanthanide(III) ions exhibit a specific solvation steric effect, and an outer-sphere bromo complex in DMF changes to an inner-sphere complex in DMA. Besides, the solvent coordination number varies with solvent composition in DMF–DMA mixtures, and the variation manner strongly depends on the metal ion or the ionic radius. HMPA shows a strong solvation steric effect, and halogeno complexation is significantly enhanced in HMPA relative to that in DMF, although HMPA has a stronger electron-pair donating ability. The coordination number is four or five, and the M–O(HMPA) bondlength is significantly shortened.

Complexation of metal ions in solution plays an essential role in various field of chemistry. To reveal the solution chemistry of metal complexes, particularly from the molecular level, knowledge of their structure in solution, formation thermodynamics and mechanisms is indispensable. In solution, unlike the gas phase, complexation behavior cannot simply be described only in terms of an interaction between solutes, but solute–solvent and solvent–solvent interactions play an important role. Water, a typical and the most important solvent in our life, can dissolve various kinds of substances and provides an excellent reaction field to yield new substances. However, water is a specific solvent among others, i.e., a highly structured solvent with a relatively high dielectric constant, medium electron-pair donating and accepting abilities, and a significant acid-base property.[1] Our common sense on the nature and properties of "solution" has thus been created mainly on the basis of this unusual solution. Indeed, the structure and formation thermodynamics and mechanisms of metal complexes in nonaqueous solutions are markedly different from those in water. Such an aspect in nonaqueous solution may provide more general concepts on solute–solvent and solvent–solvent interactions in solution, and may highlight specific features of water as a solvent.

Solution properties, such as solubility, stability constant, redox potential and etc., vary dramatically depending on the nature of solvent. Particularly, it is widely accepted that electrolytes are more soluble in a solvent with a high dielectric constant, as electrostatic interaction is weakened in the solution. Indeed, water, with a relatively high dielectric constant, can dissolve electrolytes quite well. However, propylene carbonate is not as good a solvent as water for dissolving usual electrolytes, though its dielectric constant is as large as water. This implies that dielectric constant is not always an appropriate measure for solubility of electrolytes. In polar solvents, ion–solvent and solvent–solvent interactions play a rather more important role in solubility phenomena, as ion–ion interaction is weakened due to a strong solvation of ions and also due to the formation of a bulk solvent structure between solvent molecules.

Like the solubility, the stability of metal complexes depends strongly on ion–solvent and solvent–solvent interactions. A typical example is shown in Fig. 1 for the chloro–copper(II) complexation. In the figure, the average number of chloride ions bound per one copper(II) ion is plotted against $-\log([\mathrm{Cl}^-]/\mathrm{mol\,dm^{-3}})$ in solution.[2] The complexation is the most favorable in propylene carbonate (PC) and the most unfavorable in water, though their dielectric constants are high and almost similar. The complexation in

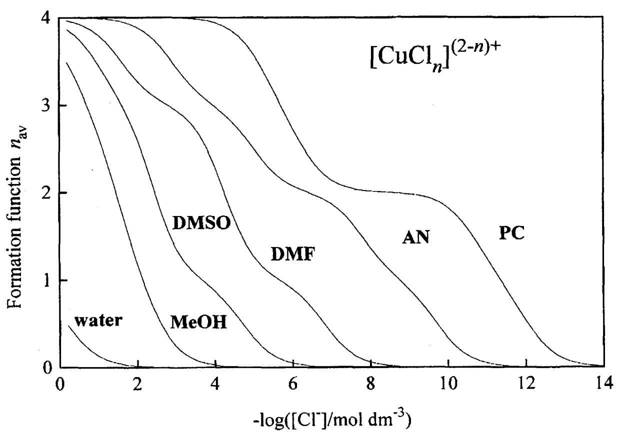

Fig. 1. Formation function, i.e., the average number of chloride ions bound per a copper(II) ion, plotted against $-\log([Cl^-]/mol\,dm^{-3})$ in propylene carbonate (PC), acetonitrile (AN), *N,N*-dimethylacetamide (DMA), *N,N*-dimethylformamide (DMF), dimethyl sulphoxide (DMSO), methanol (MeOH) and water at 298 K.

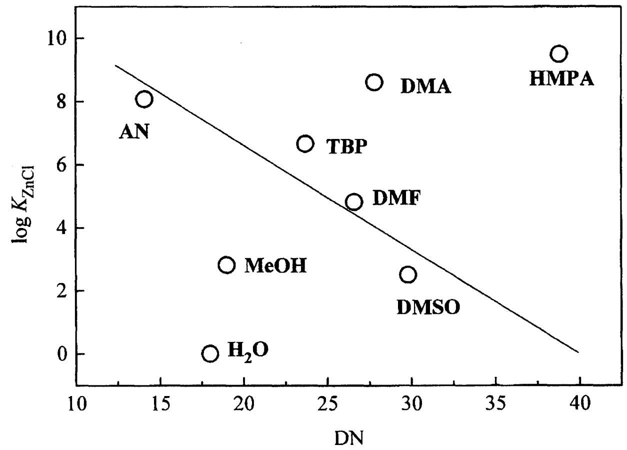

Fig. 2. Formation constants of $[ZnCl]^+$ plotted against the Gutmann's donor number: HMPA: hexamethylphosphoric triamide, TBP: tributylphosphate, AN: acetonitrile, DMA: *N,N*-dimethylacetamide, DMF: *N,N*-dimethylformamide, DMSO: dimethyl sulphoxide.

acetonitrile (AN) is more favorable compared with that in *N,N*-dimethylformamide (DMF), though their dielectric constants are medium and similar. Thus, the stability in these polar solvents is not a simple function of dielectric constant. The complexation is enhanced in the order, dimethyl sulphoxide (DMSO) < DMF < AN < PC, the order of decreasing electron-pair donating ability, indicating that the strength of metal-ion solvation seems to play a decisive role in the stability. However, note that the complexation is significantly weaker in water, although the electron-pair donating ability of water is weaker than that of DMSO or DMF. Furthermore, the complexation in DMSO is appreciably weaker relative to that in DMF, although their electron-pair donating abilities are not largely different. In water and DMSO, a specific solvent–solvent interaction plays a key role in the complexation.[3,4]

In Fig. 2, stability constants of $[ZnCl]^+$ are plotted against the Gutmann's donor number, a measure of electron-pair donating abilities for oxygen-donor solvents.[5] Here, the stability is not at all a simple function of the solvent donor strength. The values in DMA and HMPA are unusually large, while the value in water is small. To reveal the origin of such an unusual complexation, a comprehensive survey on the structure and formation thermodynamics of metal complexes in various nonaqueous solvents may be needed. We have thus far investigated nonaqueous solution chemistry of various divalent and trivalent metal ions and their halogeno and pseudo-halogeno complexes, and pointed out that solvent structure and solvation steric effect, as well as electron-pair donating and accepting abilities, play important roles in determining a specific feature on metal-ion complexation. In the present Account, we will highlight a *solvation steric effect* on the structure and formation thermodynamics of metal complexes in DMA and HMPA. Physicochemical properties of related aprotic donor solvents are listed in Table 1.

Metal-Ion Solvation Structure

Solvation structure of a metal ion in solution has been studied by large angle X-ray diffraction (*LAXD*), neutron diffraction (*ND*), extended X-ray absorption fine structure (*EXAFS*), etc., and structural parameters such as bondlength and coordination number for hydrated metal ions have been reviewed.[6] Though no enough, the solvation structure has also been established in nonaqueous solvents. In Table 2,

Table 1. Physicochemical Properties of Solvents[a]

	DMF	DMA	TMU	HMPA
Molecular weight	73.09	87.12	116.16	179.20
Density/g cm^{-3}	0.944	0.936	0.962	1.020
Boiling point/°C	153.0	166.1	175.2	233
Freezing point/°C	−64.43	−20	−1.2	7.20
Heat of vaporization/J mol^{-1}	47.514	49.15	51.12	61.1
Dipole moment/10^{-30}C m	10.80[b]	14.23[c]	11.67[b]	18.47[b]
Dielectric constant	36.71	37.78	23.60	29.30[d]
Donor number (DN)	26.6	27.8		38.8
Accept number (AN)	16.0	13.6		10.6

a) Values refer to 25 °C and 1.0132×10^{-5} Pa. b) In benzene. c) In 1,4-dioxane. d) 20 °C.

Table 2. Structural Parameters of Transition Metal Ions in Solution

		Water H_2O	DMF $OHCN(CH_3)_2$	DMA $O(CH_3)CN(CH_3)_2$	TMU $\{(CH_3)_2N\}_2CO$	HMPA $\{(CH_3)_2N\}_3PO$
Mn(II)	r/pm	217	216	216	209	207
	n	6	5.8	5.8	4.9	4.9
Fe(II)	r/pm	211	210		205	198
	n	6	5.8		4.9	4.0
Co(II)	r/pm	208	208	207	200	195
	n	6	5.9	5.5	4.1	3.9
Ni(II)	r/pm	205	204	205	200	197
	n	6	5.9	5.9	4.8	4.2
Cu(II)	r_{ex}/pm	197	196	196	192	192
	n_{ex}	4	4.1	4.1	3.9	3.7
Cu(II)	r_{ax}/pm	229	229	227		
	n_{ax}	2	2	1.8		
Zn(II)	r/pm	207	208	199	195	193
	n	6	5.8	4.6	3.8	4.1
Cd(II)	r/pm	227			228	223
	n	6			5.9	4.8

DMF: *N*,*N*-dimethylformamide, DMA: *N*,*N*-dimethylacetamide, TMU: tetramethylurea, HMPA: hexamethylphosphoric triamide.

M–O(solvent) bondlength and solvent coordination number of some transition metal(II) ions in oxygen-donor solvents, water, DMF, DMA, tetramethylurea (TMU) and hexamethylphosphoric triamide (HMPA), are listed.[7—9] These metal(II) ions are octahedrally six-coordinated in water and DMF, although the copper(II) solvate ion is distorted due to the Jahn–Teller effect. The M–O bondlength is practically the same in these solvents. The metal ions are also octahedrally six-coordinated in DMA, except for the zinc(II) ion, which exhibits significantly smaller coordination number and shorter M–O bondlength. DMA coordinates through its carbonyl oxygen atom of a bulky acetylmethyl group. It is thus supposed that simultaneous coordination of six DMA molecules around the zinc(II) ion is sterically hindered. The six-coordination about a metal ion is also sterically hindered in HMPA, i.e., the solvent coordination number is close to five for Mn(II) and Cd(II) ions, and four for Co(II), Ni(II), and Zn(II) ions, and the M–O bondlength is thus significantly shortened. In particular cases, the coordination number of a solvate metal ion changes depending on the environment. Indeed, with the cadmium(II) ion, the coordination number of HMPA is four in the crystalline state, and the average coordination number increases with increasing concentration of HMPA in nitromethane (NM)–HMPA mixtures. With TMU, the average coordination number is close to six for Cd(II), five for Mn(II), Fe(II) and Ni(II), and four for Co(II) and Zn(II) ions, suggesting that a six-coordination of TMU is also sterically hindered.

Solvation steric effect of solvents generally increases in the order; DMF < DMA < TMU < HMPA, the order of increasing bulkiness. However, the solvent coordination number of the zinc(II) ion, six in water and DMF, less than five in DMA and four in TMU and HMPA, is different from that of the nickel(II) ion, six in water, DMF and DMA, five in TMU and four in HMPA, implying that the electronic configuration of metal ions also plays a key role. The crystal structure of metal solvates gives also useful information on the solvation steric effect, which will be discussed in a latter section.

Thermodynamic Aspects of Metal-Ion Solvation

Divalent transition metal ions: Mn(II), Co(II), Ni(II), Zn(II), and Cd(II), form a tetrahedral four-coordinate $[MCl_4]^{2-}$ complex in both DMA and DMF. Solute-solvent interaction of $[MCl_4]^{2-}$, as well as Cl^-, may be weak and similar in these aprotic solvents. In fact, an extracted intrinsic electronic spectrum of $[NiCl_4]^{2-}$ in DMA is practically the same as that in DMF.[10,11] Therefore, overall thermodynamic parameters for the reactions; $M^{2+} + 4Cl^- = [MCl_4]^{2-}$ may mainly reflect the difference in metal-ion solvation. As shown in Table 3, the overall formation constant $\log \beta_4$ in DMA is larger than the value in DMF for all the metal systems.[10—14] This is ascribable to the reaction enthalpy that is significantly

Table 3. Overall Thermodynamic Parameters of Formation of $[MCl_4]^{2-}$ in *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) at 25 °C

	Mn(II)		Co(II)		Ni(II)		Zn(II)		Cd(II)	
	DMA	DMF	DMA	DMF	DMA	DMF	DMA	DMF	DMA	DMF
$\log \beta_4$	14.4	12.6	18.9	14.1	14.8	7.4	24	19.3	24.1	21.7
$\Delta H_{\beta 4}°$kJ mol^{-1}	8.5	21.3	0.8	27.6	40.7	77.2	−49.2	−9.4	−44.8	−28.4
$\Delta S_{\beta 4}°$J K^{-1}mol^{-1}	304	313	365	363	419	400	295	338	311	320

Quoted from Refs. 10, 11, 12, 13, and 14.

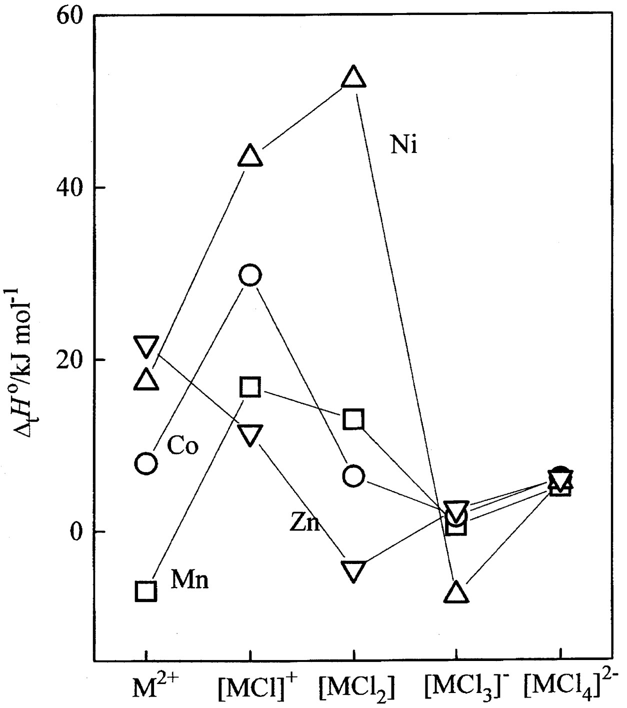

Fig. 3. Enthalpies of transfer of $[MCl_n]^{(2-n)+}$ (n=1—4) (M= Mn, Co, Ni, and Zn) from *N*,*N*-dimethylformamide to *N*,*N*-dimethylacetamide.

less positive or more negative in DMA. This implies that the M–O(DMA) bond is weakened due to the steric interaction between DMA molecules. On the other hand, the corresponding entropy values are large and positive, due to ion desolvation, and not significantly different in these solvents. Note that the metal ions, except for the zinc(II) ion, are six-coordinated in both DMA and DMF. In the Zn(II)–Cl^- system, the entropy in DMA is appreciably smaller than the value in DMF. This is expected because the zinc(II) ion has a smaller solvent coordination number in DMA.

Enthalpies of transfer $\Delta_t H°$ from DMF to DMA show another aspect of the metal-ion solvation, as seen in Fig. 3. The $\Delta_t H°$ values of single metal and halide ions are obtained by analyzing enthalpies of solution of various electrolytes in DMF and DMA on the basis of an extrathermodynamic tetraphenylarsonium tetraphenylborate (TATB) assumption.[15] The enthalpies of transfer of free metal ions from DMF to DMA, $\Delta_t H°(M^{2+})$, increase in the order : Mn^{2+} (−6.9 kJ mol^{-1}) < Co^{2+} (7.9) < Ni^{2+} (17.4) < Zn^{2+} (21.8). The negative enthalpy value of Mn^{2+} may be expected if we take into account that DMA has an electron-pair donating ability slightly stronger than DMF. The positive $\Delta_t H°$ values of Co^{2+}, Ni^{2+}, and Zn^{2+} may indicate that the M–O(DMA) bond is weakened due to a solvation steric effect. However, note that the Mn^{2+}, Co^{2+}, and Ni^{2+} ions are octahedrally six-coordinated, and the M–O bondlengths are virtually the same

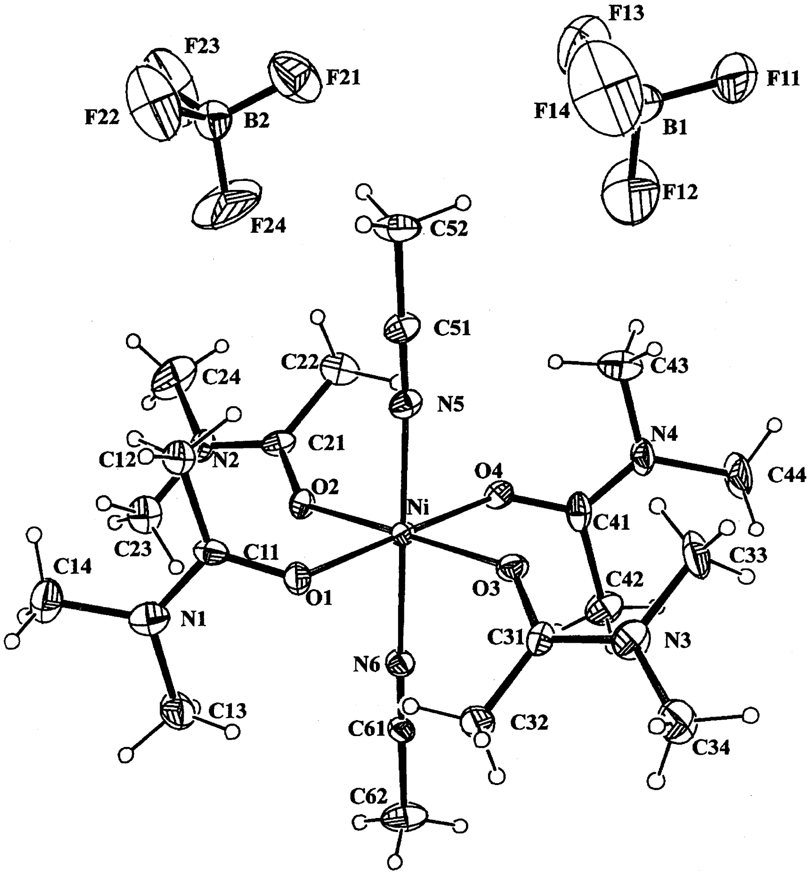

Fig. 4. Crystal structure of $[Ni(DMA)_4(AN)_2](BF_4)_2$.

Table 4. Thermodynamic Parameters of the Stepwise Halogeno Complexation in *N*,*N*-Dimethylacetamide (DMA) and *N*,*N*-Dimethylformamide (DMF) at 25°C

	N,*N*-Dimethylacetamide[a]										*N*,*N*-Dimethylformamide[b]									
	Mn		Co		Ni		Zn		Cd		Mn		Co		Ni		Zn		Cd	
	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br	Cl	Br
$\log K_1$	4.1	2.29	5.42	3.49	4.31	1.94	8.6	6.2	6.89	5.40	3.69	1.91	3.43	1.55	2.85	1.20	4.81	1.86	6.9	5.9
$\log K_2$	3.9	2.1	6.42	4.41	4.22	1.98	7.8	5.5	6.8	5.65	2.40		3.42		0.91		6.99	3.31	5.2	4.5
$\log K_3$	4.3	2.59	4.45	2.76	4.51	2.68	5.0	3.39	6.5	5.51	3.93		4.99		1.77		5.26	1.98	5.8	5.3
$\log K_2K_3$												2.24		4.05						
$\log K_4$	2.12		1.97		1.73		1.94		3.84	2.95	2.61		2.29	0.7	1.87		2.22		3.8	3.0
$\Delta H_1°$	18.6	29	26	33.3	28.4	34	−1.7	9.0	1.9	9.9	1.1	14.1	6.3	19.4	8.6	17.5	14.7	22.3	−12.0	−6.1
$\Delta H_2°$	16	27	−4	12.6	22	41	−20.6	−9.9	−3	4	25.6		52.2		19.1		1.4	19.3	7.7	13.1
$\Delta H_3°$	−13	−1	−13.6	−1.2	−3.3	7	−16.9	−6.9	−20	−19	5.1		−24.8		62.9		−17.6	−5.9	−3.3	−2.1
$\Delta H_2°+\Delta H_3°$												58.8		53.3						
$\Delta H_4°$	−12.3		−7.5		−6.4		−10.4		−23.2	−19.1	−10.5		−6.1	−19.5	−13.4		−7.9		−20.9	−16.1
$\Delta S_1°$	141	140	190	178	178	150	159	148	138	137	74		87	95	84	82	142	110	91	93
$\Delta S_2°$	126	132	111	127	154	176	80	71	121	121	132		241		82		139	130	124	130
$\Delta S_3°$	38	47	40	49	75	73	39	43	57	41	92		12		245		42	18	101	95
$\Delta S_2°+\Delta S_3°$												244		256						
$\Delta S_4°$	−1		12		12		2		−4	−7.5	15		23	−52	−9		16		3	4

a) 0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$. b) 0.4 (Cl) and 0.16 (Br) mol dm^{-3} $(C_2H_5)_4NClO_4$. $\Delta H°$/kJ mol^{-1}, $\Delta S°$/J K^{-1} mol^{-1}. Quoted from Refs. 10, 11, 12, 13, 14, 21, 22, 23, 24, 25, and 26.

in both DMA and DMF. As shown in Fig. 4, the crystal structure of $[Ni(dma)_4(an)_2](BF_4)_2$ indicates that the coordination of DMA molecules is distorted, i.e., the M–O–C–N dihedral angle of the DMA solvate is significantly different from that of the DMF one.[16] Indeed, the molecular O–C–N plane of DMA is largely declined from the metal equatorial plane,[17] unlike the DMF analogue.[18] This implies that an acetylmethyl group causes a steric hindrance upon simultaneous coordination of DMA molecules to a metal ion. The extent of steric distortion may be larger the smaller the metal ion, i.e., in the order of decreasing ionic radii, Mn^{2+} (83 pm) > Co^{2+} (74.5 pm) > Ni^{2+} (69 pm).[19] Furthermore, in the case for Co^{II} and Ni^{II}, the distortion may lead simultaneously to a reduction of the ligand field stabilization energy (*LFSE*).[20] In order to compare the M–O–C–N dihedral angle, the determination of crystal structures of various metal solvates may be needed. However, the crystal structure of a full DMA solvate has never been reported so far for any metal ion (recently, we succeeded in determining the $[Ni(dma)_6]^{2+}$ structure). We suppose that the steric hindrance within $[Mn(dma)_6]^{2+}$ is not so severe, according to the negative $\Delta_t H°$ (Mn^{2+}) value. On the other hand, the $\Delta_t H°$ value of Zn^{2+} is even larger than that of Ni^{2+}, although the zinc(II) ion has a larger ionic radius (74 pm) than the nickel(II) ion (69 pm) of six-coordination. This is ascribed to a decreased coordination number of Zn^{2+}, from 6 to 4.6, upon transfer from DMF to DMA.

Solvation Steric Effect on Metal-Ion Complexation

Stepwise thermodynamic parameters of formation of a series of halogeno and thiocyanato-N complexes in DMA, together with those in DMF for comparison, are summarized in Tables 4 and 5, respectively, which were determined by precise titration calorimetry and spectrophotometry systems developed in our laboratory. Species distribution of chloro and thiocyanato-N complexes are depicted in Figs. 5 and 6. The complexation of divalent transition metal ions is significantly enhanced in DMA relative to DMF, and the extent of enhancement is particularly large at the first step. As described in a previous section, no appreciable difference is found for solvent coordination number and M–O(solvent) bondlength of the metal solvate ions, Mn(II), Fe(II), Co(II), Ni(II), Cu(II), and Cd(II), in DMA and DMF, while the coordination number of the zinc(II) ion is reduced in DMA. Therefore, the solvent coordination number relative to that in DMF is reduced, *strong solvation steric effect*, or kept unchanged, *weak solvation steric effect*, depending on the metal ion and the solvent.

Coordination Geometry Change

Bound solvent molecules are replaced with ligands upon complexation. With divalent transition metal ions, a series of four chloro complexes are formed in DMA. Coordination geometry generally changes from an octahedral six-coordination to a tetrahedral four-coordination upon chloro complexation. The stage of coordination geometry change depends on the metal ion and the solvent. The coordination geometries of chloro complexes, which are deduced from

Table 5. Thermodynamic Parameters of the Stepwise Thiocyanato-N Complexation in *N*,*N*-Dimethylacetamide (DMA) and *N*,*N*-Dimethylformamide (DMF) at 25 °C

	Mn		Co		Ni		Zn		Cd		Be[a)]	
	DMA	DMF[b)]	DMA	DMF[b)]	DMA	DMF[b)]	DMA	DMF[b)]	DMA	DMF[b)]	DMA	DMF
$\log K_1$	2.7	2.3	4.06	2.7	3.88	2.7	5.3	3.3	3.7	3.57	3.0	2.6
$\log K_2$	1.8	1.6	3.3	1.4	2.80	1.9	5.1		2.7	2.41	2.1	1.8
$\log K_3$	1.6	0.8	4.6	3.2	2.02	0.8	3.5		2.1	1.61	1.9	1.4
$\log K_2K_3$								6.9				
$\log K_4$	1.3	1.0	3.48	3.0	1.50	0.8	3.16	3.2	1.9	1.23		
$\Delta H_1{}^\circ$	3.28	−1.0	6.7	−1.0	1.34	−0.7	−0.3	4.9	0.54	−4.9	5.9	5.5
$\Delta H_2{}^\circ$	7	−1.6	29	−22	−0.7	−1.8	−6		2.3	−4.3	4	6
$\Delta H_3{}^\circ$	4	9.3	−32	35	5.9	−3.0	−18		6	1.9	−2	2
$\Delta H_2{}^\circ + \Delta H_3{}^\circ$								4.6				
$\Delta H_4{}^\circ$	0	8.6	−21.7	−7.0	0.0	1.4	−21.2	−17.4	−4	9.9		
$\Delta S_1{}^\circ$	63	40	100	49	79	50	100	80	72	52	77	69
$\Delta S_2{}^\circ$	58	24	161	−45	51	31	75		59	32	54	54
$\Delta S_3{}^\circ$	44	46	−20	180	58	6	27		59	37	31	35
$\Delta S_2{}^\circ + \Delta S_3{}^\circ$								147				
$\Delta S_4{}^\circ$	26	49	−6	34	29	21	−11	3	22	56		

0.1 mol dm^{-3} $(C_2H_5)_4NBF_4$. a) 0.1 mol dm^{-3} $(C_2H_5)_4NClO_4$. b) 0.4 mol dm^{-3} $(C_2H_5)_4NClO_4$ ΔH°/kJ mol^{-1}, ΔS°/J K^{-1} mol^{-1}. Quoted from Refs. 23, 26, 27, 28, 29, and 30.

Table 6. The Coordination Geometry of Chloro and Thiocyanato Complexes of Metal(II) Ions in *N*,*N*-Dimethylformamide (DMF) and *N*,*N*-Dimethylacetamide (DMA) at 25 °C

	Mn		Co		Ni		Zn		Cd	
	DMA	DMF	DMA	DMF	DMA	DMF	DMA	DMF	DMA	DMF
M^{2+}	**6**	**6**	**6**	**6**	**6**	**6**	**6,4**	**6**	**6**	**6**
$[MCl^+]$	**6,4**	**6**	**6,4**	**6**	**6,5**	**6**	**4**	**6,4**	**6,4**	**6**
$[MCl_2]$	**4**	**4**	**4**	**4**	**5,4**	**6**	**4**	**4**	**4**	**6,4**
$[MCl_3]^-$	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**4**
$[MCl_4]^{2-}$	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**4**	**4**
$[M(NCS)_1]^+$	**?**	**6**	**6**	**6**	**6,5**	**6**	**4**	**6**		
$[M(NCS)_2]$	**?**	**6**	**4**	—	**6,5**	**6**	**4**	—		
$[M(NCS)_3]^-$	**4**	**6,4**	**4**	**4**	**6,5**	**6**	**4**	**4**		
$[M(NCS)_4]^{2-}$	**4**	**4**	**4**	**4**	**5,4**	**6**	**4**	**4**		

6: Octahedral. **5**: Possibly trigonal bipyramidal. **4**: Tetrahedral.

electronic spectra and formation thermodynamic parameters of complexes, are summarized in Table 6, together with those of the corresponding thiocyanato complexes. It is evident that geometry change usually occurs at an earlier stage in DMA, indicating that the change is enhanced by a solvation steric effect.

With nickel(II), an unusual coordination number is established in DMA due to a solvation steric effect.[11)] This is evident from electronic spectra in Fig. 7. The nickel(II) ion is octahedrally six-coordinated in DMA, as well as DMF, although a detailed spectrophotometric study indicates that the DMA solvate ion is partly five-coordinated.[31)] The monochloro complex is six-coordinated in DMF, while in DMA the complex is mainly five-coordinated, as suggested from an intrinsic electronic spectrum with an intense band typical of five-coordination. Furthermore, it is expected that a geometry equilibrium will be established between five- and six-coordination, as the band is intensified with increasing temperature. The dichloro complex is five- or four-coordinated, i.e., a geometry equilibrium is established in DMA. Indeed, electronic spectra in DMA show an isosbestic point, and the shoulder band ascribed to a five-coordinate complex is weakened and the band ascribed to a four-coordinate one is intensified with increasing temperature. The heat capacity change of complexation obtained from temperature dependence of a reaction enthalpy leads to the same conclusion for the geometry equilibria.

The nickel(II)-thiocyanate system also shows a specific feature of solvation steric effect on complexation.[30)] All the mono- to tetra(thiocyanato-N) complexes are octahedrally six-coordinated in DMF, while the mono- to tri(thiocyanato-N) complexes are in geometry equilibrium between six- and five-coordination, and the tetra(thiocyanato-N) complex between five- and four-coordination in DMA. The high-spin nickel(II) ion reduces to a large extent the ligand field stabilization energy (*LFSE*) upon geometry change from octahedral to tetrahedral. Therefore, the nickel(II) ion may prefer a five-coordination to a tetrahedral four-coordination,

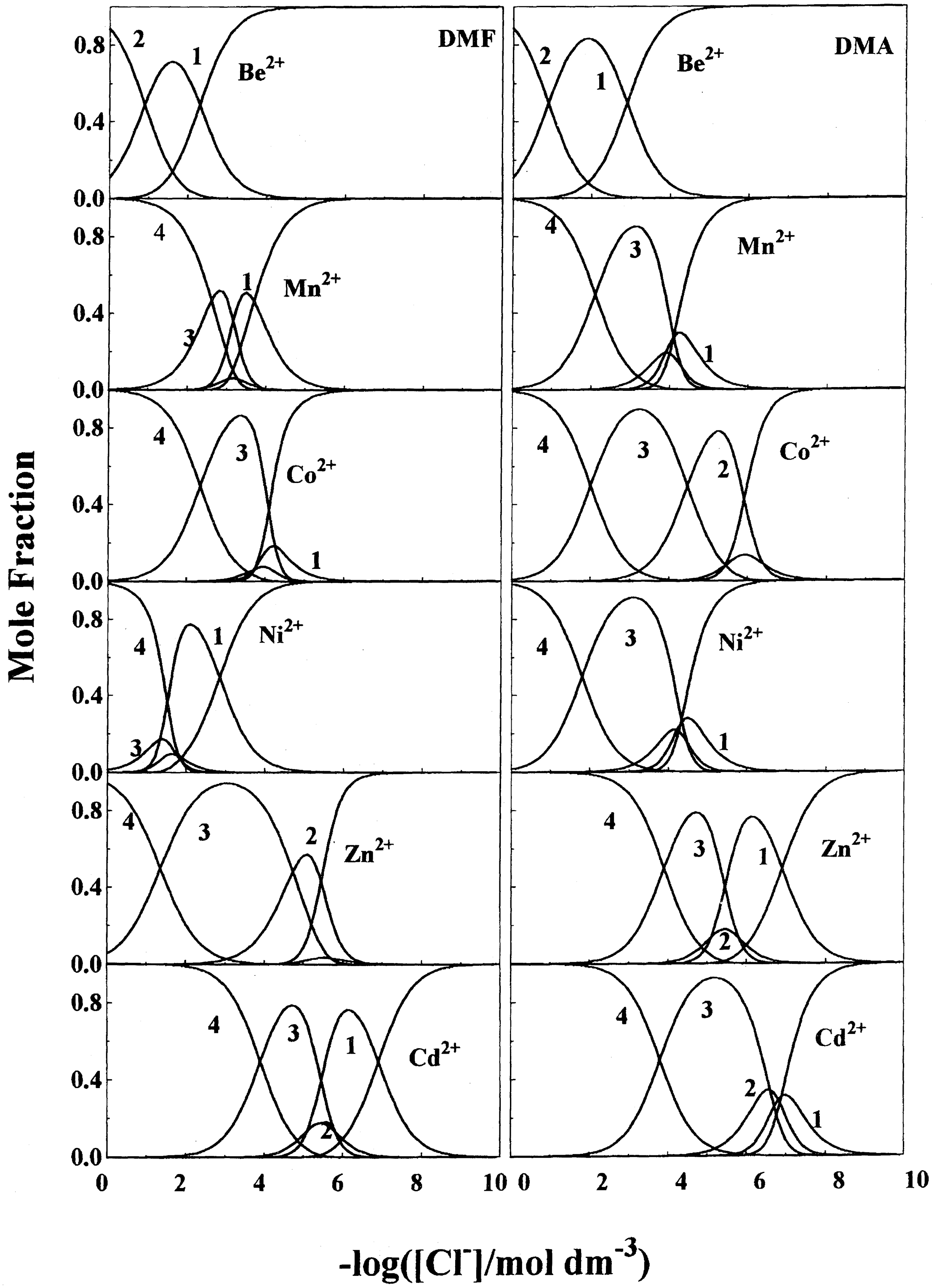

Fig. 5. Species distribution of chloro complexes in *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) at 298 K.

when steric repulsion between ligands prevents the metal ion from forming an octahedral geometry. The five-coordination is also observed for the nickel(II) complexes in TMU and *N*,*N*-dimethylpropionamide (DMPA).[32]

Solvation Steric Effect and Coordination Number

The solvation steric effect may be reduced if the coordination number about a metal ion is decreased, as it originates from an interaction between solvent molecules simultaneously coordinating to a central metal ion. The dichloro

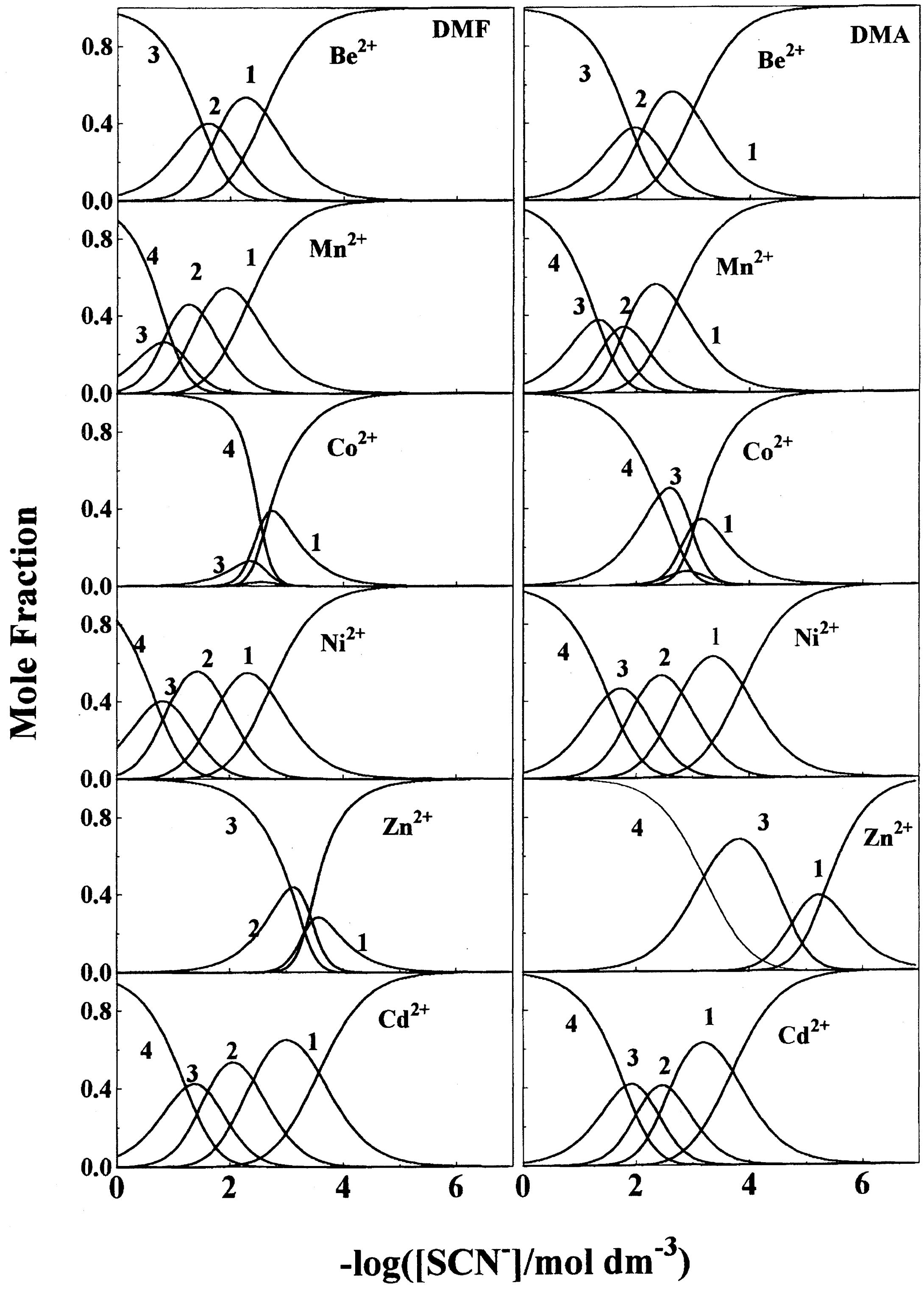

Fig. 6. Species distribution of thiocyanato-N complexes in *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) at 298 K.

zinc(II) complex is expected to have a tetrahedral coordination geometry with two bound solvent molecules in both DMA and DMF, like those in the crystalline state (Fig. 8). If no solvation steric effect operates in the dichloro complex, the complexation thermodynamics at the third and fourth consecutive steps may be similar due to similar electron-pair donating and accepting abilities of DMA and DMF. Indeed, calorimetric titration curves obtained in DMA and DMF show a similar variation at $C_X/C_M > 3$,[10,24)] while the variation manner at $C_X/C_M < 3$ is quite different due to a solvation steric effect in DMA. Stepwise thermodynamic parameters for the third step thus determined are as follows:

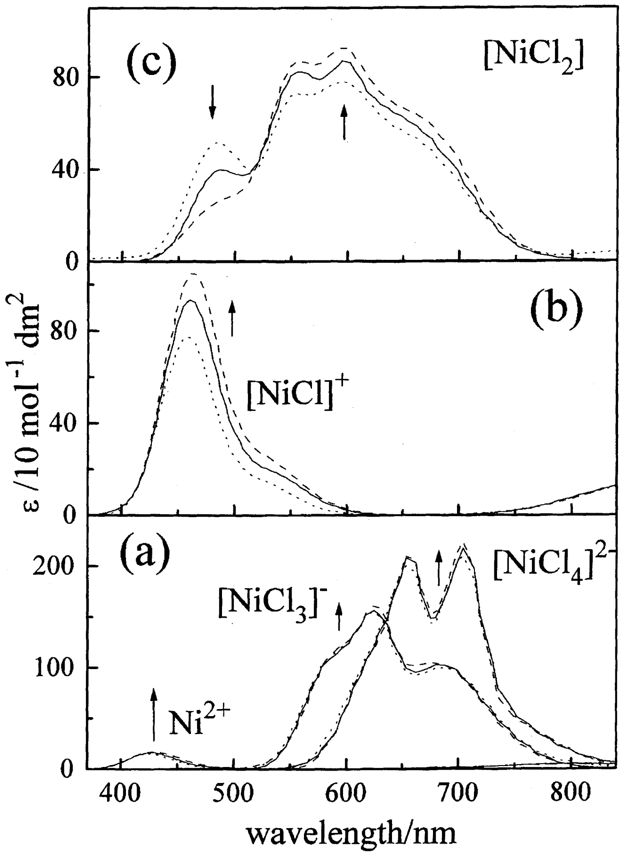

Fig. 7. Intrinsic electronic spectra of Ni^{2+}, $[NiCl_3]^-$ and $[NiCl_4]^{2-}$ (a), and $[NiCl]^+$ (b) and $[NiCl_2]$ (c) extracted in *N,N*-dimethylacetamide at 278 (····), 298 (——), and 318 (- - -) K.

$$[ZnCl_2(sol)_2] + Cl^- \rightarrow [ZnCl_3(sol)]^- + sol \qquad (1)$$

$$\Delta H_3{}^\circ = -16.9 \text{ (DMA) and } -17.6 \text{ (DMF) kJ mol}^{-1}$$

$$\Delta S_3{}^\circ = 42 \text{ (DMA) and } 39 \text{ (DMF) J K}^{-1}\text{ mol}^{-1}$$

The enthalpy and entropy values are not significantly different, indicating that practically no solvation steric effect operates for the tetrahedral complex in DMA.

Some further evidence is obtained for the complexation of the beryllium(II) ion.[26] The beryllium(II) ion, with a small ionic radius, is tetrahedrally four-coordinated in DMA and DMF, as well as water. In both DMA and DMF, the beryllium(II) ion forms mono- and dichloro complexes, and mono-, di-, and tri(thiocyanato-N) complexes, and their thermodynamic parameters of formation have been obtained:

$$[Be(sol)_4]^{2+} + Cl^- \rightarrow [BeCl(sol)_3]^+ + sol \qquad (2)$$

$$\Delta H_1{}^\circ = 4.0 \text{ (DMA) and } 5.8 \text{ (DMF) kJ mol}^{-1}$$

$$\Delta S_1{}^\circ = 70 \text{ (DMA) and } 64 \text{ (DMF) J K}^{-1}\text{ mol}^{-1}$$

$$[Be(sol)_4]^{2+} + SCN^- \rightarrow [Be(NCS)(sol)_3]^+ + sol \qquad (3)$$

$$\Delta H_1{}^\circ = 5.9 \text{ (DMA) and } 5.5 \text{ (DMF) kJ mol}^{-1}$$

$$\Delta S_1{}^\circ = 77 \text{ (DMA) and } 69 \text{ (DMF) J K}^{-1}\text{ mol}^{-1}$$

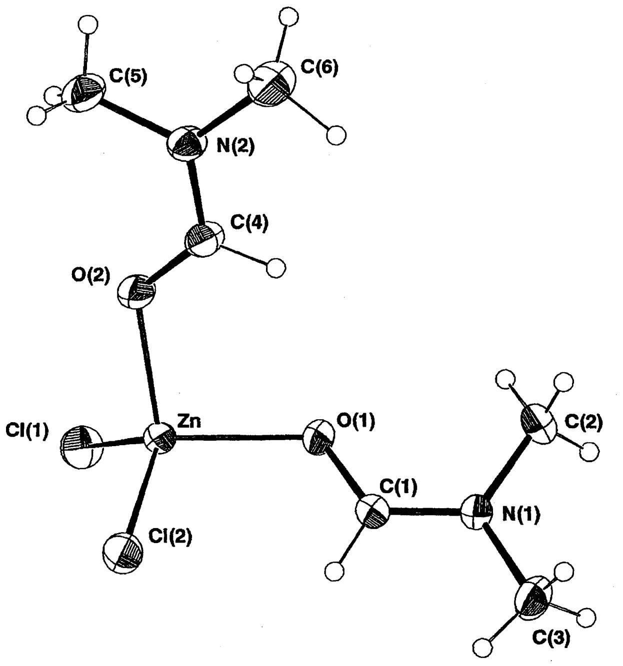

Fig. 8. Crystal structure of $[ZnCl_2(dma)_2]$.

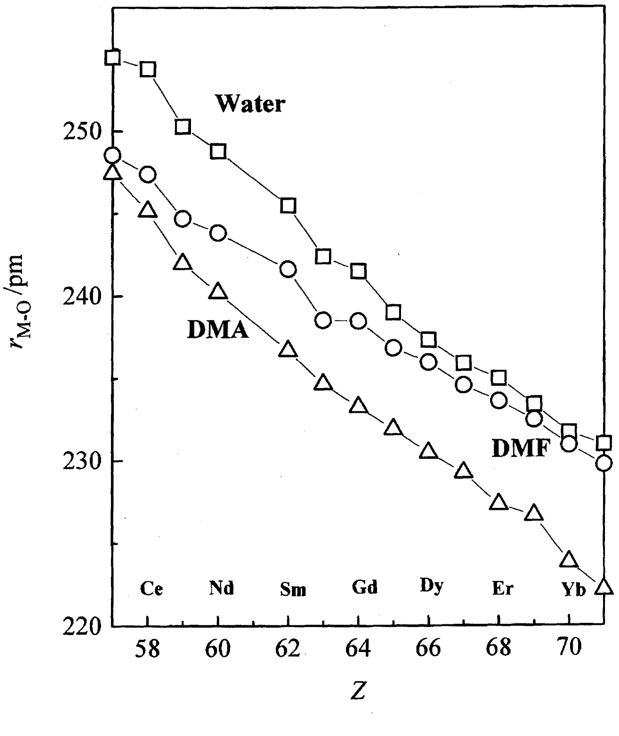

Fig. 9. Ln–O(solvent) bondlength of lanthanide(III) ions in water, *N,N*-dimethylformamide (DMF) and *N,N*-dimethylacetamide (DMA) determined by EXAFS.

$$[Be(NCS)(sol)_3]^+ + SCN^- \rightarrow [Be(NCS)_2(sol)_2] + sol \qquad (4)$$

$$\Delta H_2{}^\circ = 4 \text{ (DMA) and } 6 \text{ (DMF) kJ mol}^{-1}$$

$$\Delta S_2{}^\circ = 54 \text{ (DMA) and } 54 \text{ (DMF) J K}^{-1}\text{ mol}^{-1}$$

The corresponding enthalpies and entropies in DMA and DMF are not largely different, indicating that practically no

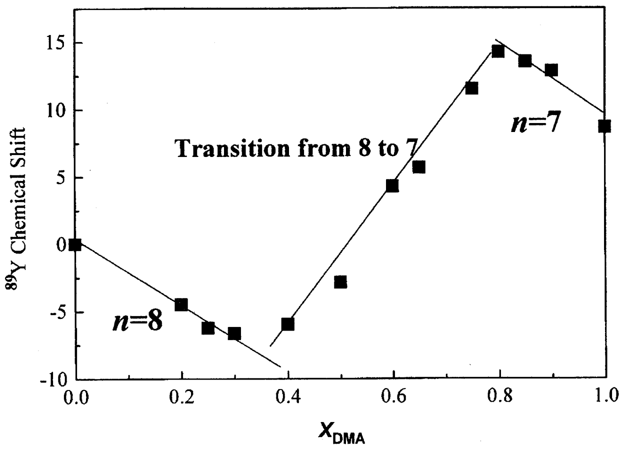

Fig. 10. ^{89}Y NMR chemical shifts of $Y(ClO_4)_3$ in DMF–DMA mixtures.

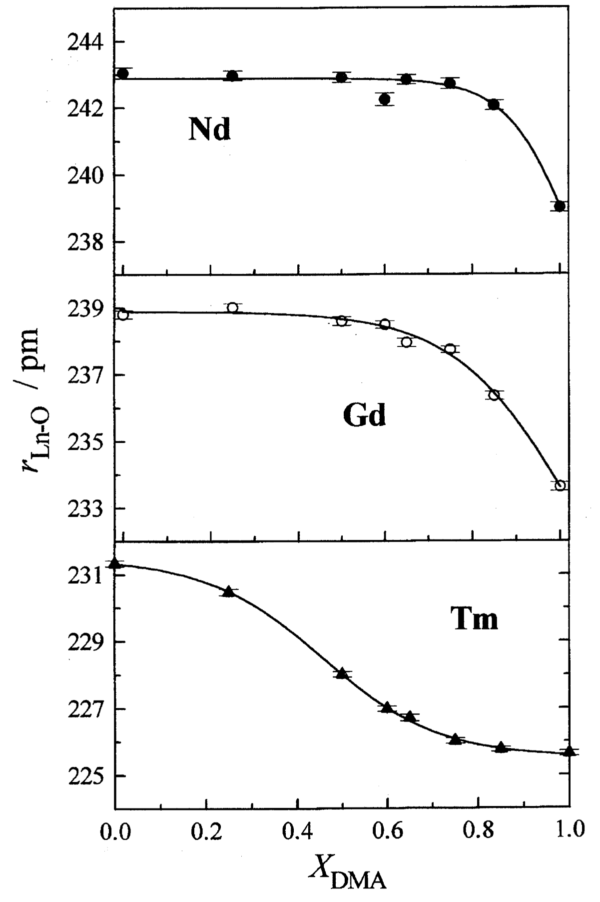

Fig. 11. Variation of Ln–O bondlength as a function of the DMA content in DMA–DMF mixtures.

steric effect operates around the four-coordinated beryllium(II) ion.

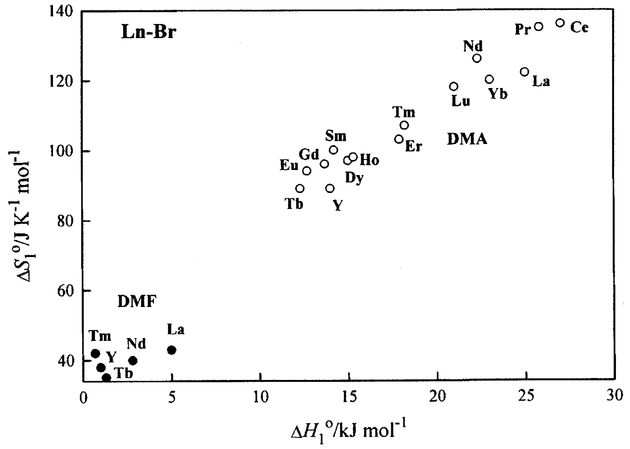

Fig. 12. The enthalpy–entropy relationship of formation of $[LnBr]^{2+}$ in *N*,*N*-dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF).

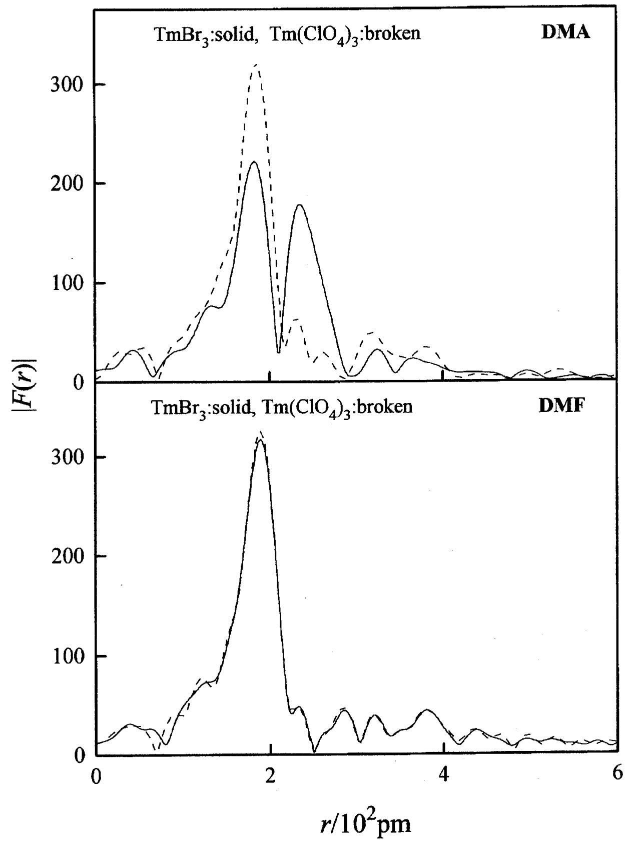

Fig. 13. Structure functions of $Tm(ClO_4)_3$ and $TmBr_3$ obtained by EXAFS in *N*,*N*-dimethylacetamide and *N*,*N*-dimethylformamide.

Solvation Steric Effect on Lanthanide(III) Ions

Lanthanide(III) ions exhibit a strong solvation steric effect in DMA, unlike that of transition metal(II) ions. As shown in Fig. 9, the M–O(solvent) bondlength for lanthanide ions in solution decreases with atomic number.[33] A shorter bondlength usually reflects a smaller coordination number. For a given metal ion, the M–O bondlength decreases in the order: water > DMF > DMA, implying that solvent coordination number reduces in the same order of solvents. With heavy lanthanides, the M–O(DMA) bondlength is significantly shorter than the M–O(DMF) bond. It is thus supposed that the metal ion is seven-coordinated in DMA. This is supported by ^{89}Y NMR measurements in DMF–DMA mixtures as shown in Fig. 10.[34] The yttrium(III) ion behaves chemi-

Table 7. Stepwise Thermodynamic Parameters of Formation of Halogeno Complexes in Hexamethylphosphoric Triamide at 25 °C[a)]

	Mn		Co			Zn			Cd	
	Cl	Br	Cl	Br	I	Cl	Br	I	Br	I
$\log K_1$	5.80	4.1	6.7	5.55	2.69	9.5	6.7	4.1	9.3	7.2
$\log K_2$	4.4	2.4	4.2	3.19	0.89	6.5	3.9	1.54	7.0	5.4
$\log K_3$	2.6		2.7	0.79		3.6			4.5	2.26
$\log K_4$			(0.8)			2.3			1.9	
ΔH_1°	−1.7	12.2	−15.2	−2.7	13.0	−20.0	−7.7	7.3	0.6	14.7
ΔH_2°	0.3	13.6	−12.6	0.3	6.9	−15.2	−3.4	9.8	−5.4	−4.9
ΔH_3°	−11.0		−12.8	2.1		−11.6			−18.4	−12.2
ΔH_4°			(−8)			−3.4			−6.4	
ΔS_1°	105	120	78	97	95	115	101	102	179	187
ΔS_2°	85	92	38	62	40	74	63	62	116	86
ΔS_3°	12		9	22		31			25	10
ΔS_4°			(−10)			32			15	

a) 0.1 mol dm^{-3} $(n\text{-C}_4\text{H}_9)_4\text{NClO}_4$. ΔH°/kJ mol^{-1}, ΔS°/J K^{-1} mol^{-1}.

cally as the holmium(III) or erbium(III) ion of a similar ionic radius. With increasing mole fraction of DMA in the mixture, the ^{89}Y ($s=1/2$) NMR signal shifts to a higher magnetic field in the range of the DMA content $0<X<0.4$, to a lower field at $0.4<X<0.8$, and again to a higher at $0.8<X<1$. As the electron-pair donating ability of DMA is slightly stronger than that of DMF, the shift to a higher magnetic field with increasing DMA content is expected, if DMF molecules bound to the metal ion are stepwise replaced with DMA molecules without change in the total number of coordinating solvent molecules. This applies to the shift in the mixture of DMA content $0<X<0.4$ and $0.8<X<1$. On the other hand, the shift to a lower magnetic field at $0.4<X<0.8$ is explained in terms of decreasing coordination number from 8 to 7. As shown in Fig. 11, the M–O(solvent) bondlength of Tm(III), with a similar ionic radius to Y(III), in a DMF–DMA mixture decreases, i.e., the corresponding coordination number is reduced, at almost the same solvent composition.[34)] With light lanthanide ions, La(III)–Nd(III), more evidence is obtained for a geometry equilibrium between nine- and eight-coordinations in DMF, and between eight- and seven-coordinations in DMA.[35,36)] Therefore, lanthanide ions are nine- and/or eight-coordinated in DMF, as well as water, while eight- and/or seven-coordinated in DMA, indicating that a solvation steric effect operates also for lanthanide(III) ions with a relatively large ionic radius or coordination number.

A series of lanthanide(III) ions form mono-, di-, and tribromo complexes in DMA and mono- and dibromo complexes in DMF. The formation constant $\log\beta_1$ is slightly larger in DMA for all the metal systems examined, while the corresponding enthalpy ΔH_1° and entropy ΔS_1° values for the formation of $[\text{LnBr}]^{2+}$ depend strongly on the solvent.[36,37)] The $\Delta H_1^\circ-\Delta S_1^\circ$ relationship is shown in Fig. 12. Evidently, these plots fall on different regions depending on the solvent. The ΔH_1° and ΔS_1° values in the Ln(III)–Br$^-$ system in DMA vary systematically with the atomic number, as in the Ln(III)–Cl$^-$ system in DMF,[35)] while the values in DMF are relatively small without a significant metal-ion dependence. Note that in DMF the ΔH_1° value is generally more positive in the chloride system than in the bromide one. This is unusual, if we take into account the HSAB principle, as lanthanide(III) ions are classified as hard acids. Furthermore, the corresponding ΔS_1° value in the bromide system is significantly smaller than that in the chloride one, indicating that the desolvation of a metal ion occurs only very weakly in the former system. This is explained well in terms of the formation of an outersphere complex in DMF, but the formation of an inner-sphere complex occurs in DMA. The chloride ion forms an inner-sphere complex in both solvents.

More direct evidence on inner- and outer-sphere bromo complexation is obtained from ^{89}Y NMR and EXAFS studies.[37)] The ^{89}Y NMR signal of a YBr_3 DMF solution, in which ca. 80% of yttrium ions exist as the monobromo complex, exhibits practically the same chemical shift as that of a $\text{Y(ClO}_4)_3$ solution. This indicates that the yttrium(III) ion is fully solvated in DMF and the bromide ion locates in the second coordination sphere to from a $[\text{Y(dmf)}_8]^{3+}\text{Br}^-$ ion-pair. In contrast, a significant shift to a lower magnetic field was observed for the bromide relative to the perchlorate solution in DMA. This implies that the bromide ion can penetrate into the first coordination sphere to form an inner-sphere $[\text{YBr(dma)}_n]^{2+}$ complex in DMA. The ^{89}Y NMR signals of a chloride solution exhibit a significant chemical shift in both DMF and DMA, indicating the formation of inner-sphere species in both solvents.

Direct evidence is also obtained by EXAFS.[36)] As seen in Fig. 13, with thulium(III) perchlorate, the $F(r)$ function shows a single peak at 232.5 and 226.7 pm in DMF and DMA, respectively, which is ascribed to the Tm–O interaction. With a thulium(III) bromide solution that involves the monobromo complex as a predominant species, the $F(r)$ function in DMF shows a single peak at r=232.3 pm, practically the same distance as that in a perchlorate DMF solution. This suggests that the bromo complex is an ion-pair or outer-sphere complex with direct coordination of sole DMF molecules. The $F(r)$ function can be well reproduced without considering the presence of a direct Tm–Br bond. On the other hand, the $F(r)$ function of a thulium(III) bromide DMA solution also involving the mono bromo complex as a predominant species, exhibits two peaks at r=225.3 and 278.9 pm ascribable to Tm–O and Tm–Br interactions, respectively. The data were satisfactorily optimized by assuming the number of bound bromide ions n_{Br}=1.1. The $r_{\mathrm{M-O}}$ value of 225.3 pm thus obtained is slightly shorter than the value of 226.7 pm in a thulium(III) perchlorate DMA solution. The $r_{\mathrm{M-Br}}$ value of 278.9 pm is expected as the sum of ionic radii of thulium(III) and bromide ions. Observation of a direct Tm–Br interaction gave clear evidence for the formation of an inner-sphere bromo complex in DMA.

Remarkable solvent effects on the structure of lanthanide solvates and complexes, as well as thermodynamics of complexation, are explained well in terms of the solvation steric effect of DMA.

Strong Solvation Steric Effect of HMPA

HMPA is a strong donor solvent relative to DMF, as indicated by the Gutmann's donor numbers: 38.8 (HMPA) and 26.6 (DMF). Halogeno complexation in HMPA has been established for Mn(II), Co(II), Zn(II), and Cd(II) ions, and the results are summarized in Table 7.[38—41] Interestingly, halogeno complexation in HMPA is more favorable than that in DMF. Besides, the chloro complexation in HMPA is exothermic in all the metal systems examined, even though that the corresponding reaction in DMF is endothermic. This cannot simply be explained in terms of the electron-pair donating ability of HMPA.

Solvation steric effects of HMPA play an important role in the complexation. A six-coordination of bulky HMPA is sterically hindered. Indeed, the solution color of a cobalt(II) perchlorate is deep blue in HMPA, which is typical of four-coordination. Structural parameters of four-coordinated metal ions: Mn(II), Fe(II), Co(II), Ni(II), and Zn(II), in HMPA are summarized in Table 1. Bound HMPA molecules are one by one replaced with halide ions to form $[\mathrm{MX_4}]^{2-}$ at the final step of complexation, and no coordination geometry change thus occurs throughout the complexation. Unusual thermodynamics of complexation in HMPA implies that the chemistry of four-coordination is essentially different from that of six-coordination.

With regard to the cobalt(II) solvate ion, the M–O(HMPA) bondlength is shorter than the M–O(DMF) one, suggesting that the former bond is stronger than the latter.[42] It needs, therefore, more energy to break the metal–solvent bond in HMPA. Then, what is the reason why the reaction is exothermic? The possible answer is that the Co–Cl bond of a four-coordination is significantly stronger than that of a six-coordination.[42] The binding energy generally increases with decreasing bondlength, and the increases may be more marked for the M–Cl bond than the M–O(HMPA) bond . Indeed, the Co–Cl bondlength (224 pm) in $[\mathrm{CoCl(hmpa)_3}]^+$ is appreciably shorter than that (235 pm) in $[\mathrm{CoCl(H_2O)_5}]^+$.[43,44] On the other hand, the Co–O bondlength is 208 and 214 pm in $[\mathrm{Co(H_2O)_6}]^{2+}$ and $[\mathrm{CoCl(H_2O)_5}]^+$, respectively, indicating that the Co–O bond is elongated when the chloride ion binds to the six-coordinate metal ion. The same may apply to the DMF solvates, although the structural parameters of $[\mathrm{CoCl(dmf)_5}]^+$ cannot be determined, as the extent of formation is extremely weak. In contrast, under a four-coordinate environment, no elongation of Co–O bond occurs, i.e., the bondlength is 195 pm in both $[\mathrm{Co(hmpa)_4}]^{2+}$ and $[\mathrm{CoCl(hmpa)_3}]^+$. These suggest that structure and formation thermodynamics of metal complexes of four-coordination are remarkably different from that of six-coordination.

Conclusion

Bulky organic solvents show a specific solvent effect, i.e., *solvation steric effect*, and its thermodynamic and structural aspects of metal-ion complexation have been investigated in *N,N*-dimethylacetamide and hexamethylphosphoric triamide relative to *N,N*-dimethylformamide. It turned out that *N,N*-dimethylacetamide shows a *weak solvation steric effect* for transition metal(II) ions, except for zinc(II), while hexamethylphosphoric triamide exhibits a *strong solvation steric effect*. A metal ion with coordination number larger than four exhibits a significant solvation steric effect on thermodynamics of complexation in *N,N*-dimethylacetamide, while the steric effect practically disappears in a metal complex of four-coordination. Lanthanide(III) ions show a specific feature of solvation steric effect on both structure and thermodynamics in *N,N*-dimethylacetamide. Also, hexamethylphosphoric triamide shows a specific feature typical of four-coordination. Formation thermodynamics and structure of metal complexes in *N,N*-dimethylacetamide and hexamethylphosphoric triamide well demonstrate that the solvation steric effect plays an essential role in the coordination chemistry in bulky organic solvents.

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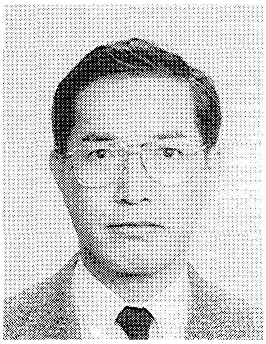

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