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# Solution Equilibria of Binary and Ternary Zinc(II) Halogeno Complexes in *N*,*N*-Dimethylacetamide

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Solution equilibria between zinc(II) and halide ions have been studied in *N*,*N*-dimethylacetamide (DMA) by calorimetry at 298 K. Formation constants, enthalpies, and entropies of mononuclear binary complexes, $[\mathrm{Zn^{II}Cl}_n]^{(2-n)+}$ ($n$=1—4), $[\mathrm{Zn^{II}Br}_n]^{(2-n)+}$ ($n$=1—3), and $[\mathrm{Zn^{II}I}_n]^{(2-n)+}$ ($n$=1,2), have been determined. In addition, mixed-ligand complexes have been detected in ternary Zn–Cl–Br and Zn–Br–I systems: [ZnClBr], $[\mathrm{ZnCl_2Br}]^-$, $[\mathrm{ZnClBr_2}]^-$, and [ZnBrI]. Complexation is more favorable and more exothermic in the order Cl>Br>I. Formation of the monohalogeno complexes is particularly endothermic and entropy-productive, suggesting that geometric transition from octahedral to tetrahedral is complete at this step, i.e., all the halogeno complexes are tetrahedral. Thus, the transition occurs earlier in DMA than in *N*,*N*-dimethylformamide (DMF). Compared with DMF, complexation in DMA is more favorable and more exothermic exclusively at the first and second steps, and little difference is found for the later steps. This is attributed to the steric hindrance of DMA molecules, which is crucial in octahedral coordination structures but not important in tetrahedral geometry. Among the first-row bivalent transition metal ions, $\mathrm{Zn^{II}}$ is exceptional in its $\Delta H^\circ_{\beta 4}$ and $\Delta S^\circ_{\beta 4}$ values of overall formation of the tetrachloro complex, consistent with the existence of a solvation equilibrium: $[\mathrm{Zn(dma)_6}]^{2+} \rightleftharpoons [\mathrm{Zn(dma)_4}]^{2+} + 2\mathrm{dma}$.

*N*,*N*-Dimethylacetamide (DMA) and *N*,*N*-dimethylformamide (DMF) are both commonly used O-donor solvents for electrochemical studies and synthetic purposes. Primarily, the two liquids are analogous in their molecular structures and physicochemical properties such as general scales for solvating power (e.g. dielectric constants, dipole moments, donor and acceptor numbers).[1—3] When DMA molecules coordinate octahedrally to a metal ion, however, the acetyl methyl group of DMA becomes an obstruction and causes a distortion in the coordination structure.[4] In solution equilibria of metal complexes, such steric hindrance of solvation may play an important role as well as that of entering ligands. DMA seems to be an ideal solvent to clarify this aspect, especially through quantitative comparision with DMF. Indeed, we have recently found that chloro complexes of manganese(II), cobalt(II), and nickel(II) are much more stable and the formation is less endothermic in DMA than in DMF.[5,6]

Interestingly, solvation structure of zinc(II) ion is exceptional among the first-row bivalent transition metal ions.[7] Our recent EXAFS study[8] has shown that the coordination number of the solvated $\mathrm{Zn^{2+}}$ ion is significantly smaller than six ($n$=4.6) in DMA solution, unlike the others ($n$=5.5—5.9 for $\mathrm{Mn^{2+}}$, $\mathrm{Co^{2+}}$, $\mathrm{Ni^{2+}}$, and $\mathrm{Cu^{2+}}$). In contrast, they are all six-coordinate in DMF ($n$=5.8—6.1). As solvation is essential in ionic activity in solution, one may also expect unusual thermodynamics for the zinc(II) ion in DMA. Therefore, this paper primarily aims at clarifying such thermodynamic aspects of $\mathrm{Zn^{II}}$ complexes in DMA and understanding their relation to solvation sturctures.

In addition to binary halogeno complexes (Zn–Cl, Zn–Br, and Zn–I), here we have also studied ternary Zn–Cl–Br and Zn–Br–I systems, because formation constants of chloro and bromo complexes are rather large and a competitive reaction approach is needed to obtain reliable log $K$ values.

## Experimental

**Reagents.** Zinc(II) tetrafluoroborate hydrate was synthesized from ZnO and tetrafluoroboric acid. Its DMA solvate, $\mathrm{Zn^{II}(BF_4)_2}\cdot x\mathrm{dma}$, was prepared by dissolving the hydrate in DMA and removing excess solvent in a rotary evaporator below 70 °C. It was recrystallized from DMA and dried in vacuo over $\mathrm{P_2O_5}$ at room temperature. (Caution: Contact with $\mathrm{HBF_4}$ or the salt should be avoided, because of possible decomposition of the anion.) The crystals were very hygroscopic and handled in a glove box over $\mathrm{P_2O_5}$. Analysis of $\mathrm{Zn^{2+}}$ by EDTA titrations[9] with Eriochrome Black T (BT) indicated slightly varied compositions of the solid ($x$=4.5—5.0). Hence, a stock solution of $\mathrm{Zn(BF_4)_2}$ in DMA was prepared, and the metal concentration was determined prior to calorimetric measurements. Tetra-*n*-butylammonium tetrafluoroborate (Tokyo Kasei) was tested with $\mathrm{AgNO_3}$ for the absence of halide ions, and dried in vacuum at 80 °C. Tetra-*n*-butylammonium bromide (Wako) was recrystallized from ethyl acetate and diethyl ether, and dried in vacuum at 60 °C.[10] Tetra-*n*-butylammonium iodide (Wako) was dried in vacuum at 50 °C and used without further purification. Other chemicals were purified as described elsewhere.[5]

**Calorimetric Measurements.** We performed calorimetric titrations in a twin-type isoperibol calorimeter (Tokyo Riko) regulated at a constant temperature (298 or 318 K) with baseline fluctuations of ±0.0001 K. An autoburet was placed in a thermostatic room at 298 K and connected to the outlet through a 15m-long Teflon® tube, which was coiled round an aluminium block inside the calorimeter. Blank titration and gravimetric calibration assured that

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temperature difference between the titrant and titrate was negligible at a slow titration speed.

An ionic medium of 0.1 mol dm$^{-3}$ $(n\text{-}C_4H_9)_4NBF_4$ was used throughout. A $Zn(BF_4)_2$ DMA solution (2—30 mmol dm$^{-3}$) of 20 cm$^3$ was titrated with a 0.1 mol dm$^{-3}$ $(n\text{-}C_4H_9)_4NX$ (X = Cl, Br, or I) solution under an argon atmosphere. For ternary systems, we prepared titrates containing both metal ion and a second ligand; a solution of $Zn(BF_4)_2$ (9—15 mmol dm$^{-3}$) and $(n\text{-}C_4H_9)_4NBr$ (8—30 mmol dm$^{-3}$) was titrated with an $(n\text{-}C_4H_9)_4NX$ (X=Cl or I) solution, and a solution of $Zn(BF_4)_2$ (10—15 mmol dm$^{-3}$) and $(n\text{-}C_4H_9)_4NI$ (10—20 mmol dm$^{-3}$) was titrated with an $(n\text{-}C_4H_9)_4NBr$ solution. Heats of titration at each point ranged from −2.0 to +2.5 J with a typical uncertainty less than 0.02 J. Heats of dilution measured by titrating a metal-free solution with the titrant were small ($\leq$0.1 J) and used for correction of the reaction heats. All solutions were prepared in a glove box over $P_2O_5$ at 298 K. The volumes and concentrations at 318 K were calculated from density changes determined in advance.

**Data Analysis.** We analyzed the observed reaction heats on the basis of the following complexation equilibria:

$$Zn^{2+} + nX^- \rightleftharpoons [ZnX_n]^{(2-n)+} \quad (X = Cl, Br, or I). \tag{1}$$

Total concentrations of metal ($C_M$) and ligand ($C_X$) ions at the $i$th titration point are expressed as

$$C_{M,i} = [M]_i + \sum_n \beta_n [M]_i [X]_i^n, \tag{2}$$

$$C_{X,i} = [X]_i + \sum_n n\beta_n [M]_i [X]_i^n, \tag{3}$$

where $[M]_i$ and $[X]_i$ denote the concentrations of free metal and ligand ions, respectively, and $\beta_n$ the overall formation constant for the reaction (1). A heat of complexation at the point is then calculated as

$$q_{i,\text{calcd}} = -\sum_n \Delta H^\circ_{\beta n} \beta_n \left( [M]_i [X]_i^n V_i - [M]_{i-1} [X]_{i-1}^n V_{i-1} \right), \tag{4}$$

where $\Delta H^\circ_{\beta n}$ is the enthalpy of reaction (1) and $V_i$ the volume of the solution. Formation constants and enthalpies of the complexes were determined by minimizing the error-square sum, $U = \sum_i (q_{i,\text{calcd}} - q_{i,\text{obsd}})^2$.

For the ternary (Zn–Cl–Br and Zn–Br–I) systems, the following equilibria were considered together with (1):

$$Zn^{2+} + pX^- + qY^- \rightleftharpoons [ZnX_pY_q]^{(2-p-q)+}$$
$$(\{X, Y\} = \{Cl, Br\} \text{ or } \{Br, I\}). \tag{5}$$

Extension of Eqs. 2, 3, and 4 to a ternary system is straightforward and described previously.[11]

## Results

**Binary Zinc(II) Halogeno Complexes.** Figure 1 shows calorimetric titration curves obtained for the binary zinc(II) halide systems at 298 K. Plots are made for the heat of titration $\Delta H^\circ_{\text{titr}} = -q(C_{X,\text{titr}}\delta v)^{-1}$ against the metal-to-halide concentration ratio $C_X/C_M$, where $C_{X,\text{titr}}$ denotes the halide concentration in the titrant, and $\delta v$ the volume of the titrant added at each point. In the Zn–Cl system, complexation is everywhere exothermic ($\Delta H^\circ_{\text{titr}} < 0$), with the maximum heat evolved at $C_X/C_M = 2$. In the bromide system, reaction is first endothermic at $C_X/C_M \leq 1$ and then turns exothermic. Endothermic reaction is observed throughout in the iodide system.

We analyzed these data by considering several sets of plausible complexes (Table 1). For the chloride system, consideration of four mononuclear complexes $[ZnCl_n]^{(2-n)+}$ ($n = 1$—4) successfully reproduced the whole observed heats, with an $R$ factor of 2.2% (set [1-4]). We also examined other sets in which one or more complexes were eliminated, but none of them explained the data with an acceptable $R$ factor. For example, set [1,3,4] in the table resulted in a much larger $R$ factor (9.3%), which considered mono, tri-, and tetrachloro complexes only. Therefore, the four complexes are necessary to account for the observed heat data.

For the bromide system, the data were well reproduced by considering three complexes $[ZnBr_n]^{(2-n)+}$ ($n$=1—3) with $R$=3.6% (set [1-3] in Table 1). These three complexes are indispensable, because set [1,2] failed to reproduce the data ($R$=35%). On the other hand, inclusion of the fourth complex $[ZnBr_4]^{2-}$ did not improve the fit and gave a very small value of $\beta_4$, indicating negligible formation of the tetrabromo complex in the concentration range examined.

In the case of the Zn–I system, observed monotonic heats were sufficiently reproduced by considering mono- and diiodo complexes only (set [1,2] in the table, $R$= 1.8%). Inclusion of triiodo complex (set [1-3]) made the fit little improved, $R$=1.7%, and $\log\beta_3$ and $\Delta H^\circ_{\beta 3}$ values were uncertain. Since $\log\beta_n$ and $\Delta H^\circ_{\beta n}$ values for the mono- and diiodo complexes are unchanged in both sets, we propose that contribution from the formation of triiodo complex is insignificant, if any. The heat data obtained for the Zn–I system at 318 K were similarly analyzed, the results of which are included in the table.

As the formation constants of the chloro and bromo complexes are comparatively large, we improved the accuracy of the parameters by including reaction heats of an appropriate ternary system in the analysis. This approach made $q_{i,\text{calcd}}$ values more sensitive to $\beta_n$ through competing reactions of the different halide complexes, and allowed more reliable determination of large $\log\beta_n$ values, as will be shown below.

**Ternary Zn–Cl–Br and Zn–Br–I Complexes.** Titration curves obtained by titrating solutions containing both $Zn^{2+}$ and $Br^-$ ions with $(n\text{-}C_4H_9)_4NCl$ solution are shown in Fig. 2. Theoretical curves calculated by considering only binary chloro and bromo complexes (depicted with dotted lines) systematically deviate from the observed heats, especially at $C_{Cl}/C_M > 2$, indicating significant contributions from the formation of mixed-ligand complexes. Accordingly, we analyzed the data by considering plausible Zn–Cl–Br ternary complexes to-

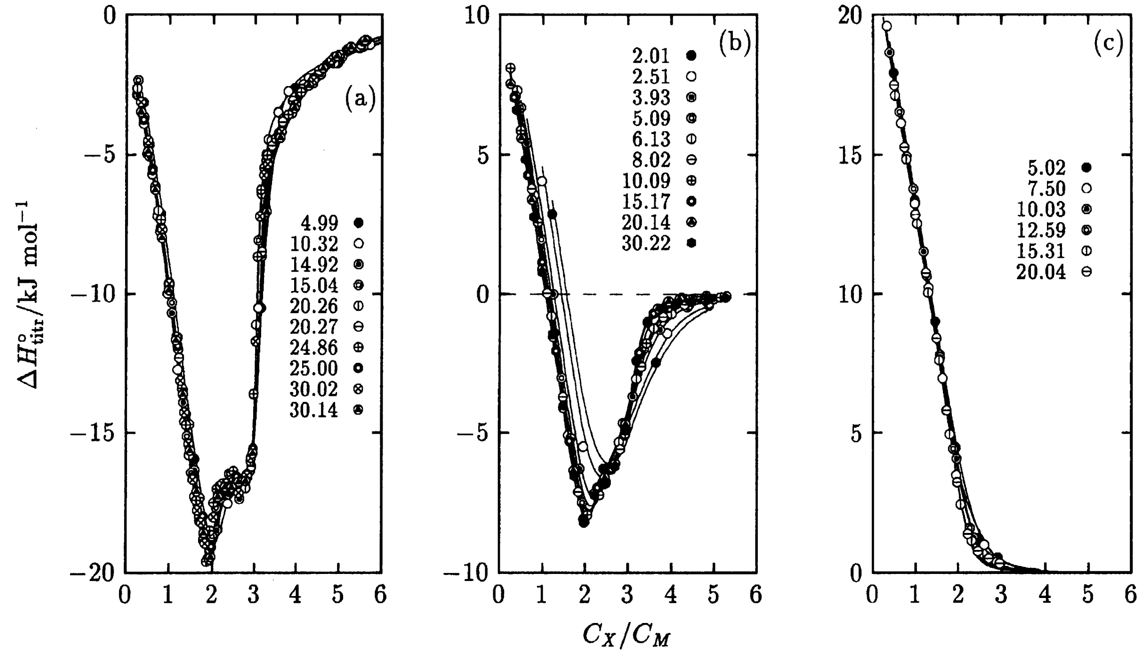

Fig. 1. Calorimetric titration curves of binary zinc(II) halide solutions in DMA containing 0.1 mol dm$^{-3}$ $(n\text{-}C_4H_9)_4NBF_4$ at 298 K: (a) Zn–Cl system; (b) Zn–Br system; (c) Zn–I system. Initial concentrations of metal ion ($C_{\mathrm{M,init}}$/mmol dm$^{-3}$) are given in the figure. The solid lines were calculated by using the constants in Table 1.

Table 1. Overall Formation Constants, log ($\beta_n$/mol$^{-n}$ dm$^{3n}$), and Enthalpies, $\Delta H^\circ_{\beta n}$/kJ mol$^{-1}$, of $[ZnX_n]^{(2-n)+}$ (X=Cl, Br, I; $n$=1—4) in $N,N$-Dimethylacetamide at 298 K

| | Cl | | | Br | | | I | | |
|---|---|---|---|---|---|---|---|---|---|
| | [1-4] | [1,3,4] | [1-4][a)] | [1-3] | [1,2] | [1-3][b)] | [1,2] | [1-3] | [1,2][c)] |
| log $\beta_1$ | 8.7(5) | 8(11) | 8.6(4) | 7.1(8) | 3.1(3) | 6.2(2) | 3.8(1) | 4.0(4) | 4.1(2) |
| log $\beta_2$ | 17(1) | — | 16.4(8) | 14(2) | 5.5(4) | 11.6(3) | 7.1(3) | 7.3(8) | 7.5(4) |
| log $\beta_3$ | 22(1) | 22(32) | 21.4(8) | 17(2) | — | 15.0(3) | — | 8(3) | — |
| log $\beta_4$ | 24(1) | 24(32) | 23.4(8) | — | — | — | — | — | — |
| $\Delta H^\circ_{\beta 1}$ | −1.7(2) | −3.3(6) | −1.8(3) | 8.7(2) | 12(3) | 9.0(3) | 21.3(5) | 21.3(5) | 21.2(4) |
| $\Delta H^\circ_{\beta 2}$ | −22.1(1) | — | −22.5(2) | −1.0(1) | −10(3) | −1.0(2) | 23.7(2) | 23.6(3) | 22.6(2) |
| $\Delta H^\circ_{\beta 3}$ | −38.9(2) | −38.6(7) | −39.4(2) | −8.0(2) | — | −7.8(2) | — | 25(5) | — |
| $\Delta H^\circ_{\beta 4}$ | −49.2(4) | −49(3) | −50.0(5) | — | — | — | — | — | — |
| $N$[d)] | 275 | 275 | 435 | 148 | 148 | 236 | 65 | 65 | 52 |
| $\sigma_{\mathrm{obsd}}$[e)] | 0.018 | 0.075 | 0.023 | 0.015 | 0.15 | 0.019 | 0.013 | 0.013 | 0.012 |
| $R$[f)] | 0.022 | 0.093 | 0.027 | 0.036 | 0.35 | 0.043 | 0.018 | 0.017 | 0.014 |

Values in parentheses are 3$\sigma$ in the last significant digits. a) Improved by using heat data of both binary (Zn–Cl) and ternary (Zn–Cl–Br) systems. b) Improved by using heat data of both binary (Zn–Br) and ternary (Zn–Br–I) systems. c) 318 K. d) Number of data points. e) Standard deviation of the observed heats (J). f) Hamilton $R$ factor.

gether with the binary complexes. Among the examined sets of complexes, consideration of the following three mixed-ligand complexes gave the most reasonable fit to the whole heat data ($R$=2.7%): [ZnClBr], $[ZnCl_2Br]^-$, and $[ZnClBr_2]^-$. Major contributions to the net heats come from the first two complexes. We also assumed other complexes such as $[ZnCl_2Br_2]^{2-}$ and $[ZnCl_3Br]^{2-}$, but the resulting formation constants were so small that we finally eliminated them.

According to the competitive approach, we determined final log $\beta_n$ and $\Delta H^\circ_n$ values of the binary chloro complexes by optimizing them simultaneously with the parameters of the mixed-ligand complexes. It resulted in smaller 3$\sigma$ values for log $\beta_n$ than those from the binary heat data alone, with comparable $\sigma_{\mathrm{obsd}}$ and $R$ values (Table 1). The solid lines in Figs. 1 and 2 calculated with the final parameters successfully reproduced the whole heat data.

The observed heats in the Zn–Br–I system were similarly analyzed by considering several ternary complexes. We concluded that formation of one ternary complex, [ZnBrI], is enough to explain the whole data. Final

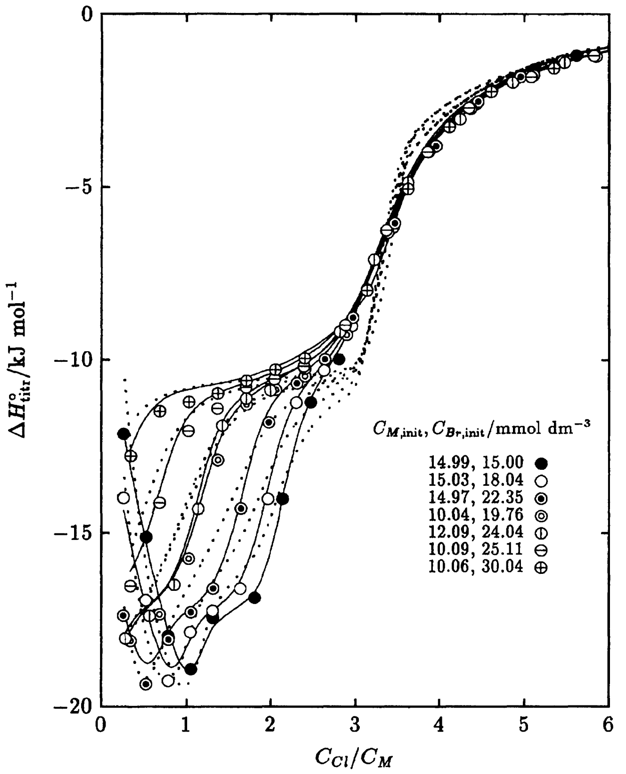

Fig. 2. Calorimetric titration curves of ternary Zn–Cl–Br solutions in DMA containing 0.1 mol dm$^{-3}$ ($n$-$C_4H_9$)$_4$NBF$_4$ at 298 K. Initial concentrations of zinc and bromide ions ($C_{M,init}$, $C_{Br,init}$/mmol dm$^{-3}$) are given in the figure. The solid lines were calculated by using the constants in Tables 1 and 3.

parameters for the binary bromo complexes thus determined are listed in Table 1.

Stepwise formation constants, enthalpies, and entropies of the binary systems are summarized in Table 2, and those of the ternary complexes in Table 3. The $\log K_1$ value for [ZnBr]$^+$ (6.2) is larger than the value (4.7) previously estimated.[12] To our knowledge, this is the only literature value available for comparison with our result. Distribution of the binary complexes calculated from the formation constants is shown in Fig. 3.

## Discussion

**Thermodynamics and Structures of Binary Complexes.** Stepwise enthalpies and entropies of formation of the chloro complexes in Table 2 indicate that formation of the monochloro complex is much less exothermic and more entropy-productive than that of the others:

$$\Delta H^\circ_1 \gg \Delta H^\circ_2 < \Delta H^\circ_3 < \Delta H^\circ_4, \qquad (6)$$

$$\Delta S^\circ_1 \gg \Delta S^\circ_2 > \Delta S^\circ_3 > \Delta S^\circ_4. \qquad (7)$$

The relation also holds for the bromo and iodo complexes. For all systems, the difference between the first and second steps is outstanding and amounts to $\Delta H^\circ_1 - \Delta H^\circ_2 = 19$ kJ mol$^{-1}$ and $\Delta S^\circ_1 - \Delta S^\circ_2 = 75$—79 J K$^{-1}$ mol$^{-1}$.

Table 2. Thermodynamic Quantities, $\log(K_n/\text{mol}^{-1}\,\text{dm}^3)$, $\Delta G^\circ_n$/kJ mol$^{-1}$, $\Delta H^\circ_n$/kJ mol$^{-1}$, and $\Delta S^\circ_n$/J K$^{-}$ mol$^{-1}$, for the Stepwise Formation of [ZnX$_n$]$^{(2-n)+}$ (X=Cl, Br, I; $n$=1—4) in $N,N$-Dimethylacetamide at 298 K

| | Cl | Br | I | |
|---|---|---|---|---|
| | | | 298 K | 318 K |
| $\log K_1$ | 8.6(4) | 6.2(2) | 3.8(2) | 4.1(2) |
| $\log K_2$ | 7.8(4) | 5.5(2) | 3.3(1) | 3.4(2) |
| $\log K_3$ | 5.0(2) | 3.39(8) | — | — |
| $\log K_4$ | 1.94(5) | — | — | — |
| $\Delta G^\circ_1$ | −49(2) | −35.1(9) | −21.8(8) | −25(1) |
| $\Delta G^\circ_2$ | −45(2) | −31.2(8) | −18.6(7) | −21(1) |
| $\Delta G^\circ_3$ | −29(1) | −19.4(5) | — | — |
| $\Delta G^\circ_4$ | −11.1(3) | — | — | — |
| $\Delta H^\circ_1$ | −1.8(3) | 9.0(3) | 21.3(5) | 21.2(4) |
| $\Delta H^\circ_2$ | −20.7(3) | −9.9(3) | 2.4(5) | 1.4(4) |
| $\Delta H^\circ_3$ | −17.0(2) | −6.9(2) | — | — |
| $\Delta H^\circ_4$ | −10.5(4) | — | — | — |
| $\Delta S^\circ_1$ | 159(8) | 148(3) | 145(2) | 145(3) |
| $\Delta S^\circ_2$ | 80(8) | 71(3) | 70(3) | 69(4) |
| $\Delta S^\circ_3$ | 39(4) | 42(2) | — | — |
| $\Delta S^\circ_4$ | 2(2) | — | — | — |

Values in parentheses are $3\sigma$ in the last significant digits.

Such anomalous endothermicity and entropy production are diagnostic of a structural transition or a decrease in the coordination number upon complexation.[13,14] Our EXAFS study suggests that the Zn$^{2+}$ ion is in a solvation equilibrium between octahedral and tetrahedral species in DMA:

$$[\text{Zn(dma)}_6]^{2+} \rightleftharpoons [\text{Zn(dma)}_4]^{2+} + 2\text{dma}, \qquad (8)$$

with ca. 70% of zinc ion being four-coordinate.[8] Accordingly, we may propose that the transition to tetrahedral geometry is complete at the first step. Then, the formation of [ZnCl]$^+$ consists of two reactions:

$$[\text{Zn(dma)}_6]^{2+} + \text{Cl}^- \rightarrow [\text{ZnCl(dma)}_3]^+ + 3\text{dma}, \qquad (9)$$

$$[\text{Zn(dma)}_4]^{2+} + \text{Cl}^- \rightarrow [\text{ZnCl(dma)}_3]^+ + \text{dma}, \qquad (10)$$

where the former reaction (9) may have an exceedingly positive contribution to the net $\Delta H^\circ_1$ and $\Delta S^\circ_1$ values, owing to the bond breakage and the emergent degrees of freedom in liberation of DMA molecules.

In contrast, $\Delta H^\circ_n$ and $\Delta S^\circ_n$ values ($n \geq 2$) are quite regular, getting less exothermic by 3.0—6.5 kJ mol$^{-1}$ and less entropy-productive by 30—40 J K$^{-1}$ mol$^{-1}$ at each step, for both chloro and bromo complexes. Such regularity has also been noticed for zinc(II) halogeno complexes in hexamethylphosphoric triamide (HMPA), where the solvated metal ion and the complexes are

Table 3. Thermodynamic Quantities, $\log(K/\text{mol}^{-1}\,\text{dm}^3)$, $\Delta G^\circ/\text{kJ mol}^{-1}$, $\Delta H^\circ/\text{kJ mol}^{-1}$, and $\Delta S^\circ/\text{J K}^{-1}\,\text{mol}^{-1}$, for the Formation of Ternary $\text{Zn}^{\text{II}}$ Halide Complexes in *N*,*N*-Dimethylacetamide at 298 K

| | $\log K$ | $\Delta G^\circ$ | $\Delta H^\circ$ | $\Delta S^\circ$ |
|---|---|---|---|---|
| Group 1: $[\text{ZnX}]^+ + \text{Cl}^- \rightleftharpoons [\text{ZnXCl}]$ | | | | |
| $[\text{ZnCl}]^+ + \text{Cl}^- \rightleftharpoons [\text{ZnCl}_2]$ [a] | 7.8(4) | −45(2) | −20.7(3) | 80(8) |
| $[\text{ZnBr}]^+ + \text{Cl}^- \rightleftharpoons [\text{ZnClBr}]$ | 8.1(4) | −46(3) | −20.6(5) | 86(8) |
| Group 2: $[\text{ZnXY}] + \text{Cl}^- \rightleftharpoons [\text{ZnXYCl}]^-$ | | | | |
| $[\text{ZnCl}_2] + \text{Cl}^- \rightleftharpoons [\text{ZnCl}_3]^-$ [a] | 5.0(2) | −29(1) | −17.0(2) | 39(4) |
| $[\text{ZnClBr}] + \text{Cl}^- \rightleftharpoons [\text{ZnCl}_2\text{Br}]^-$ | 5.5(5) | −31(3) | −17.9(8) | 44(12) |
| $[\text{ZnBr}_2] + \text{Cl}^- \rightleftharpoons [\text{ZnClBr}_2]^-$ | 6.3(7) | −36(4) | −17.2(5) | 63(14) |
| Group 3: $[\text{ZnX}]^+ + \text{Br}^- \rightleftharpoons [\text{ZnXBr}]$ | | | | |
| $[\text{ZnCl}]^+ + \text{Br}^- \rightleftharpoons [\text{ZnClBr}]$ | 5.6(2) | −32(1) | −9.8(6) | 75(4) |
| $[\text{ZnBr}]^+ + \text{Br}^- \rightleftharpoons [\text{ZnBr}_2]$ [a] | 5.5(2) | −31.2(8) | −9.9(3) | 71(3) |
| $[\text{ZnI}]^+ + \text{Br}^- \rightleftharpoons [\text{ZnBrI}]$ | 5.8(2) | −33(1) | −9.4(3) | 80(4) |
| Group 4: $[\text{ZnXY}] + \text{Br}^- \rightleftharpoons [\text{ZnXYBr}]^-$ | | | | |
| $[\text{ZnCl}_2] + \text{Br}^- \rightleftharpoons [\text{ZnCl}_2\text{Br}]^-$ | 3.3(2) | −19(1) | −7.1(9) | 39(7) |
| $[\text{ZnClBr}] + \text{Br}^- \rightleftharpoons [\text{ZnClBr}_2]^-$ | 3.7(4) | −21(2) | −6.6(8) | 49(10) |
| $[\text{ZnBr}_2] + \text{Br}^- \rightleftharpoons [\text{ZnBr}_3]^-$ [a] | 3.39(8) | −19.4(5) | −6.9(2) | 42(2) |
| Group 5: $[\text{ZnX}]^+ + \text{I}^- \rightleftharpoons [\text{ZnXI}]$ | | | | |
| $[\text{ZnBr}]^+ + \text{I}^- \rightleftharpoons [\text{ZnBrI}]$ | 3.50(8) | −20.0(5) | 3.0(4) | 77(2) |
| $[\text{ZnI}]^+ + \text{I}^- \rightleftharpoons [\text{ZnI}_2]$ [a] | 3.3(1) | −18.6(7) | 2.4(5) | 70(3) |

Values in parentheses are $3\sigma$ in the last significant digits. a) Table 2.

all tetrahedral.[15] Therefore, all the halogeno complexes may have tetrahedral coordination structures in DMA: $[\text{ZnX}(\text{dma})_3]^+$, $[\text{ZnX}_2(\text{dma})_2]$, $[\text{ZnX}_3(\text{dma})]^-$, and $[\text{ZnX}_4]^{2-}$. In fact, $[\text{ZnCl}_2(\text{dma})_2]$ can be isolated from solution,[16,17] and a tetrahedral geometry has been reported for its crystal structure.[18]

For the iodo complexes, we also performed calorimetric titrations at 318 K to examine the thermodynamic consistency and temperature dependence of $\Delta H^\circ_n$ and $\Delta S^\circ_n$. As is expected from the van't Hoff relationship, $\log K_1$ slightly increases with temperature increase. The $\Delta H^\circ_1$ and $\Delta S^\circ_1$ values are practically unchanged, implying that the shift of the solvation equilibrium (8) may not be significant in this temperature range.

Complexation is more favorable and more exothermic in the order Cl>Br>I, whereas the entropies are similar, so that the stability difference is of enthalpic origin. This is a general observation on zinc(II) halides in aprotic solvents[15,19—21] and consistent with the behavior of 'hard' (or class a) metal ions; the order is opposite in the case of mercury(II) halides.[21,22]

**Interligand Interactions in Ternary Complexes.** The first two entries (Group 1) in Table 3 show that the reaction,

$$[\text{ZnX}]^+ + \text{Cl}^- \rightarrow [\text{ZnXCl}], \tag{11}$$

has very similar thermodynamic parameters, whether X is Cl or Br. The observation also holds for the sets of reactions with different entering ligands (Groups 2—5 in the table).

It suggests that interactions between the entering anion and the coordinated ones within these complexes are insensitive to the diverse ionic radius and softness of the latter anions.[15] As all these complexes are considered to have analogous tetrahedral structures, steric consideration is less important, and we may ascribe this insensitiveness to the relatively hard nature of $\text{Zn}^{\text{II}}$. In contrast, in the case of ternary cadmium(II) halogeno complexes, the relevant $\Delta H^\circ$ values are definitely dependent on the coordinated anion type, as is expected from the relatively soft Cd–halide interactions.[23]

**Solvent Effects.** The most striking difference between the thermodynamic parameters in DMA and DMF is seen exclusively at the early stages of complexation. For example, the monochloro complex is far more stable in DMA than in DMF[24] ($K_1(\text{DMA})/K_1(\text{DMF}) = 6\times10^3$), whereas the stepwise formation constants of the other chloro complexes are similar in both solvents ($K(\text{DMA}/K(\text{DMF}) = 0.5$—$6$). In consequence, all the successive complexes emerge in a significant amount in DMA (Fig. 3), whereas zinc(II) monohalogeno complexes are very minor in DMF.[20,24] As for enthalpies, formation of the mono and dichloro complexes is more exothermic in DMA than in DMF by 17—22 kJ mol$^{-1}$, but the $\Delta H^\circ_3$ and $\Delta H^\circ_4$ values are similar in both solvents. The tendency is also seen in entropies, $\Delta S^\circ_2$ being smaller in DMA than in DMF by 60 J K$^{-1}$ mol$^{-1}$. The argument also holds for the bromo and iodo[20] complexes.

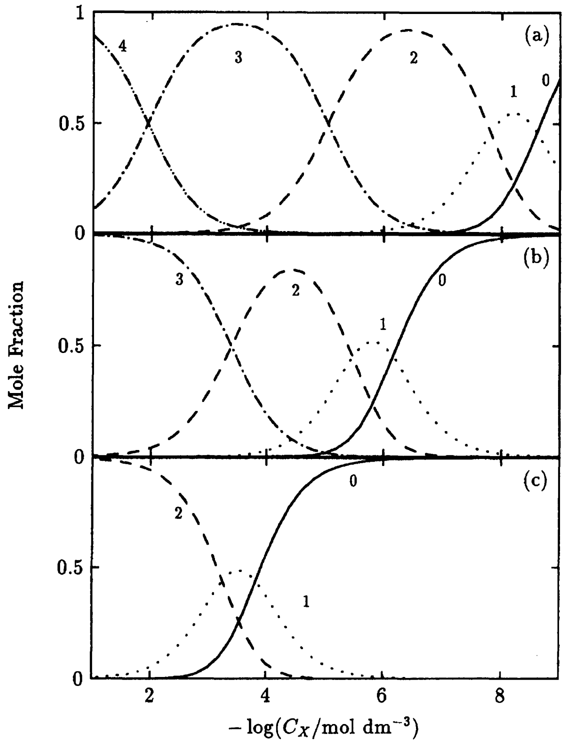

Fig. 3. Distribution of the binary zinc(II) halogeno complexes in DMA at 298 K: (a) X=Cl; (b) X=Br; (c) X=I. The numbers represent $n$ within $[\mathrm{ZnX}_n]^{(2-n)+}$.

The anomalous stabilization of the monohalogeno complex in DMA is a clear sign of the steric hindrance of the solvent. As the solvation equilibrium (8) is seen only in DMA and not in DMF, more than half of the desolvation energy required for geometric transition is dispensable in DMA. In other words, contribution from reaction (10) is predominant in DMA, making the complexation more exothermic and more favorable.

The geometry of the complexes may change from octahedral to tetrahedral at the first step in DMA according to reaction (9), whereas the transition may occur at both the first and second steps in DMF.[20,24] The geometric transition thus occurs at earlier steps of complexation in DMA than in DMF. Therefore, the more exothermicity and less entropy production of the formation of the dihalogeno complex may be interpreted in this context; because the geometric transition is complete in DMA but not in DMF at the first step, the energy loss and entropy gain at the second step are both less in DMA.

It is noteworthy that, once the complex turns tetrahedral, little difference is seen between their thermodynamic quantities in the two solvents. This is consistent with the previous structural observation that steric hindrance of coordinated DMA molecules is seen only in octahedral structures and not in less-crowded tetrahedral geometry.[6,18,25]

Comparison of the solvent effect among different metal systems is of particular interest, in view of the exceptional solvation structure of $\mathrm{Zn^{2+}}$ in DMA. Reported values for the tetrachloro complexes are summarized in Table 4. The overall formation,

Table 4. Thermodynamic Quantities, $\Delta G^\circ_{\beta 4}/\mathrm{kJ\,mol^{-1}}$, $\Delta H^\circ_{\beta 4}/\mathrm{kJ\,mol^{-1}}$, and $\Delta S^\circ_{\beta 4}/\mathrm{J\,K^{-1}\,mol^{-1}}$, for the Reaction $\mathrm{M^{2+}+4Cl^- \rightleftharpoons [MCl_4]^{2-}}$ (M=Mn, Co, Ni, Cu, Zn) in DMF and in DMA at 298 K

| | Mn | Co | Ni | Cu | Zn |
|---|---|---|---|---|---|
| $\Delta G^\circ_{\beta 4}$(DMF) | −72.1[a] | −80.7[a] | −42.2[b] | −96.2[c] | −110.0[b] |
| $\Delta G^\circ_{\beta 4}$(DMA) | −82[d] | −104.2[d] | −84.3[e] | — | −133 |
| Difference | 10 | 23.5 | 42.1 | — | 23 |
| $\Delta H^\circ_{\beta 4}$(DMF) | 21.3[a] | 27.6[a] | 77.2[b] | 19.2[c] | −9.4[b] |
| $\Delta H^\circ_{\beta 4}$(DMA) | 8.5[d] | 1.0[d] | 40.7[e] | — | −50.0 |
| Difference | 12.8 | 26.6 | 36.5 | — | 40.6 |
| $\Delta S^\circ_{\beta 4}$(DMF) | 313[a] | 363[a] | 401[b] | 387[c] | 338[b] |
| $\Delta S^\circ_{\beta 4}$(DMA) | 305[d] | 353[d] | 419[e] | — | 280 |
| Difference | 8 | 10 | −18 | — | 58 |

a) Ref. 27. b) Ref. 24. c) Ref. 28. d) Ref. 6. e) Ref. 5.

$$\mathrm{M^{2+} + 4Cl^- \rightarrow [MCl_4]^{2-}}, \tag{12}$$

is more favorable and less endothermic in DMA than in DMF for all the metal ions, indicating the weaker solvation of these ions in DMA due to the steric hindrance.[26]

As the ionic radius varies in the order Mn>Co>Ni<Zn and the ligand-field stabilization energy for octahedral geometry is in the order Mn<Co<Ni>Zn, we might expect that extent of the steric hindrance would have a maximum at Ni.[6] Curiously, however, the difference $\Delta H^\circ_{\beta 4}(\mathrm{DMF})-\Delta H^\circ_{\beta 4}(\mathrm{DMA})$ is largest for zinc ion, in the order Mn<Co<Ni<Zn. Also, the corresponding entropy difference $\Delta S^\circ_{\beta 4}(\mathrm{DMF})-\Delta S^\circ_{\beta 4}(\mathrm{DMA})$ is exceptionally large for Zn (58 $\mathrm{J\,K^{-1}\,mol^{-1}}$), more than twice as large as those for the other metals. The solvation equilibrium (8) again proves consistent here, which is specific to $\mathrm{Zn^{II}}$ in DMA; it may lead to extraordinarily small solvation energy on the average, and thus make the formation of $\mathrm{[ZnCl_4]^{2-}}$ more exothermic and less entropy-productive in DMA.

## Conclusion

Steric hindrance of DMA solvation toward a metal ion manifests itself in both structures and stabilities of the zinc(II) halogeno complexes. Comparison with DMF reveals different coordination structures of the solvated complexes in the two solvents:

| | $\mathrm{Zn^{2+}}$ | $\mathrm{ZnCl^+}$ | $\mathrm{ZnCl_2}$ | $\mathrm{ZnCl_3^-}$ | $\mathrm{ZnCl_4^{2-}}$ |
|---|---|---|---|---|---|
| In DMA: | $O_h \rightleftharpoons T_d$ | $T_d$ | $T_d$ | $T_d$ | $T_d$ |
| In DMF: | $O_h$ | $O_h \rightleftharpoons T_d$ | $T_d$ | $T_d$ | $T_d$ |

The reduced number of solvation in DMA results in marked stabilization and exothermicity of formation of the mono- and dihalogeno complexes. The solvation equilibrium in DMA is also reflected in the overall enthalpy and entropy values of $[ZnCl_4]^{2-}$, which are exceptional among the bivalent metal series $Mn^{II}$–$Zn^{II}$.

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