

Metal Halide and Pseudohalide Complexes in Dimethyl Sulfoxide Solution. VI. Enthalpy Measurements on the Zinc(II) Chloride, Bromide, Iodide, and Thiocyanate Systems

STEN AHRLAND, NILS-OLOF BJÖRK and ROBERTO PORTANOVA

Inorganic Chemistry 1, Chemical Center, University of Lund, P.O.B. 740, S-220 07 Lund, Sweden

The enthalpy changes for the formation of zinc(II) chloride, bromide, iodide, and thiocyanate complexes in dimethyl sulfoxide have been determined calorimetrically. From the measured enthalpy changes, and the free energy changes computed from the stability constants, the entropy changes have been calculated. All data refer to 25.0 °C and an ammonium perchlorate medium of 1 M ionic strength.

For the chloride and bromide systems ΔH° , and ΔS° , are particularly high, while for the iodide and thiocyanate ΔH° , and ΔS° , are the highest. These high values are interpreted as due to a change of coordination. The total entropy gains found in DMSO are much higher than for the corresponding systems in water.

The thermodynamic functions governing the formation of cadmium(II) chloride, bromide, iodide, and thiocyanate systems in the aprotic solvent dimethyl sulfoxide (DMSO) have been reported in part IV of this series and the results compared with those previously obtained for the analogous reactions in aqueous solution.² As the complex formation depends much upon the acceptor characteristics of the metal ion, it is of great interest to extend the investigations to other metal ions which differ markedly from cadmium(II) in this respect. To facilitate the comparison, it is advisable to choose, in the first instance, ions analogous to cadmium(II), i.e. divalent d^{10} acceptors. Zinc(II) has therefore been the next acceptor to be investigated¹ and the stabilities of its chloride, bromide, iodide and thiocyanate complexes in DMSO have been reported in part V of this series.² For zinc(II), a much harder acceptor than the mildly soft cadmi-

um(II), an (α)-sequence $\text{Cl}^- > \text{Br}^- > \text{I}^-$ is found already in water and it becomes much more marked in DMSO.

This paper deals with the determination of the enthalpy changes, ΔH° , for the stepwise formation of complexes within the zinc(II) systems mentioned. The results have been obtained by direct calorimetric measurements (cf. part IV). From the values of ΔH° , and ΔG° , thus available, the entropy changes have been found.

As previously, the measurements refer to a 1 M ammonium perchlorate medium of 25 °C. Recently, a very exploratory calorimetric investigation of these systems has been performed.³ It was then assumed that the dissolution of the solid halides yields the neutral complex ML_2 in solution. From the present investigation it is obvious that this is not true. Consequently, the result is hardly correct, and in any case not comparable with the present ones.

EXPERIMENTAL

Chemicals. The hexasolvate $\text{Zn}(\text{DMSO})_6(\text{ClO}_4)_2$ and all ligand solutions were prepared and analyzed as described previously.^{1,2}

Apparatus. The calorimeter and the technique used have been described previously.² In each titration series a solution T was titrated into the reaction vessel initially containing V_0 ml of a solution S.

The heats of dilution were determined by analogous titration series where one of the reactant solutions was exchanged for 1 M ammonium perchlorate solution.

The notation is the same as before.² The calculations have been performed by the least

squares program "Kalori".^{4,5} The complete calorimetric data are available from the authors.

MEASUREMENTS AND RESULTS

The chloride and bromide systems. First, values of ΔH°_j were calculated with the potentiometrically determined β_j , including a value of β_4 equal to the upper limit (part V). In the next run, where all constants were treated as unknowns (with the sets of β_j and ΔH°_j already determined as initial values), no significant values of β_4 were obtained, Table 1, in spite of the fact that the calorimetric measurements were extended to $[L] \approx 375$ mM. Though this value is much higher than the highest ones that could be applied in the potentiometric measurements ($[Cl^-] \approx 30$ mM and $[Br^-] = 50$ mM) the data are nevertheless well fitted by the first three complexes. The extension of the range of $[L]$ also means a sizable increase in the highest value of \bar{n} reached. For chloride

this value is increased from 2.80 to 2.98, for bromide from 2.45 to 2.89, cf. Fig. 1 of part V.

In the final calculation of ΔH°_1 to ΔH°_3 for the chloride system, weighted mean values of β_1 to β_3 were used, Table 1. For the bromide system, on the other hand, where the calorimetric data did not provide any significant value of β_1 it was considered most appropriate to use the potentiometrically determined values of β_1 to β_3 for the final calculation. The thermodynamic functions found are given in Table 2. The function $\Delta h_p(\bar{n})$ is independent of C_M , again² indicating the absence of polynuclear complexes.

The iodide system. When both β_j and ΔH°_j were treated as unknowns, the values of β_j had quite large errors, Table 1. This applies particularly to β_1 . The potentiometrically determined constants were therefore used for the final calculations of the thermodynamic functions, Table 2. The function $\Delta h_p(\bar{n})$ is given in Fig. 1.

Table 1. The stability constants of zinc(II) chloride, bromide, iodide, and thiocyanate complexes in DMSO at 25 °C, determined by potentiometric and calorimetric methods. The errors given correspond to three standard deviations. Ionic medium 1 M ammonium perchlorate.

<i>j</i>	Pot.	Cal.	Mean
Chloride (β_j, M^{-j})			
1	86 ± 25	89 ± 45	87 ± 26
2	$(6.8 \pm 0.2)10^5$	$(7.2 \pm 0.8)10^5$	$(6.9 \pm 0.4)10^5$
3	$(1.18 \pm 0.04)10^8$	$(1.7 \pm 0.3)10^8$	$(1.24 \pm 0.15)10^8$
4	$< 10^8$	$(1 \pm 4)10^7$	
Bromide (β_j, M^{-j})			
1	7 ± 2	1 ± 3	
2	$(5.4 \pm 0.4)10^3$	$(5.0 \pm 0.3)10^3$	
3	$(1.2 \pm 0.1)10^5$	$(1.3 \pm 0.2)10^5$	
4	$< 2 \times 10^5$	0	
Iodide (β_j, M^{-j})			
1	0.20 ± 0.04	0.05 ± 0.21	
2	5.1 ± 0.3	5.0 ± 1.8	
3	7.2 ± 0.5	6.5 ± 3.0	
4			
Thiocyanate (β_j, M^{-j})			
1	24 ± 2	24^a	
2	$(6 \pm 4)10^2$	$(6 \pm 9)10^2$	
3	$(1.6 \pm 0.3)10^5$	$(1.7 \pm 0.5)10^5$	
4	$(7.2 \pm 0.6)10^6$	$(9.6 \pm 2.4)10^6$	

^a No variation.

Table 2. Thermodynamics of the stepwise coordination of chloride, bromide, iodide, and thiocyanate to zinc(II) in DMSO at 25 °C, in 1 M ammonium perchlorate. Errors correspond to three standard deviations.

Step, <i>j</i>	ΔG_j° (kJ mol ⁻¹)	ΔH_j° (kJ mol ⁻¹)	ΔS_j° (J K ⁻¹ mol ⁻¹)
Chloride			
1	-11.1 ± 0.8	22.3 ± 3.8	112 ± 13
2	-22.2 ± 0.9	0.8 ± 4.3	77 ± 15
3	-12.9 ± 0.2	-10.2 ± 0.2	9.1 ± 0.9
1 + 2	-33.3 ± 0.2	23.1 ± 0.4	189 ± 2
Bromide			
1	-4.8 ± 0.8	27.8 ± 5.2	110 ± 17
2	-16.5 ± 2.0	9.1 ± 5.4	85 ± 19
3	-7.7 ± 0.3	-4.2 ± 0.4	12 ± 2
1 + 2	-21.3 ± 0.2	36.9 ± 0.5	195 ± 3
Iodide			
1	4.0 ± 0.6	19.0 ± 7.5	50 ± 25
2	-8.0 ± 0.7	29.4 ± 7.8	127 ± 26
3	-0.9 ± 0.3	12.7 ± 2.3	45 ± 8
Thiocyanate			
1	-7.9 ± 0.2	5.5 ± 0.7	45 ± 3
2	-8.1 ± 2.1	23.5 ± 3.7	105 ± 15
3	-13.7 ± 2.2	-17.8 ± 3.7	-13 ± 15
4	-9.4 ± 0.5	-10.7 ± 0.6	-4 ± 3

The thiocyanate system. When all parameters were treated as unknowns the values of β_1 and ΔH_1° , and also those of β_2 and ΔH_2° , were so strongly interdependent that no significant results ensued. If the well determined $\beta_{1,\text{pot}}$ was introduced, however, reasonable values were obtained for β_2 to β_4 , though the error in β_2 is still extremely large, Table 1. Like for the chloride and bromide systems, much higher values of [L] can be applied in the calorimetric measurements than in the potentiometric ones. In the former, a value of [SCN] \approx 470 mM was reached, corresponding to $\bar{n} \approx 3.95$, while in the latter the range is limited to [SCN] \lesssim 50 mM, and hence to $\bar{n} \lesssim 3.5$, (cf. Fig. 1 of part V).

In the final calculations of the thermodynamic functions the potentiometrically determined values of β_j have been used, Table 2. The function $\Delta h_v(\bar{n})$ is given in Fig. 1.

DISCUSSION

In the halide systems of zinc(II) the first complex has a narrow range of existence in DMSO solution (cf. part V). Also for the systems of weak chloride and bromide complexes formed in aqueous solution, a similar phenomenon occurs, though in these cases the second step is disfavoured.^{6,7} Quantitatively, this is expressed by low values of the ratios K_1/K_2 and K_2/K_3 , respectively. In Table 3, summarizing the thermodynamic functions, these conditions are reflected in the very positive values of $(\Delta G_1^\circ - \Delta G_2^\circ)$ for DMSO and of $(\Delta G_2^\circ - \Delta G_3^\circ)$ for water. A narrow range of existence of a certain complex thus depends upon an interaction between the changes of enthalpy and entropy which in the case of a suppressed first complex, i.e. when $\Delta G_1^\circ \gg \Delta G_2^\circ$, can be expressed as follows (cf. part IV).

$$\Delta H_1^\circ + T\Delta S_2^\circ \gg \Delta H_2^\circ + T\Delta S_1^\circ$$

From the present measurements it is obvious that the first complex is disfavoured for different reasons in the chloride and bromide systems on the one hand and in the iodide system on the other. In the two former systems ΔH_1° is so much more positive than ΔH_2° , that the decrease of the entropy gain from ΔS_1° to ΔS_2° is completely outweighed. In the iodide system, on the other hand, ΔS_2° is so much larger than ΔS_1° that the increase of the enthalpy change from ΔH_1° to ΔH_2° is completely outweighed. For the chloride and bromide systems in water⁷ the narrow range of existence of the second complex is due to the very high values of ΔH_2° , Table 3.

Due to the narrow range of existence of the first complex, only the sums of the thermodynamic functions for the first two steps can be precisely determined but not the individual functions, Table 2 (cf. also part IV).

The zinc(II) hydrate is a regular octahedron in aqueous solution.⁸ No structural studies of the weak halide complexes formed in water have been performed, however. In DMSO, no direct information exists at all about the structures. The solvate is presumably hexacoordinated, however, both in the solid state and also in the solution. This inference is strengthened by the fact that in the closely related solid solvate $\text{Zn}(m \text{ DTSO})_6(\text{ClO}_4)_2$, where *m* DTSO stands

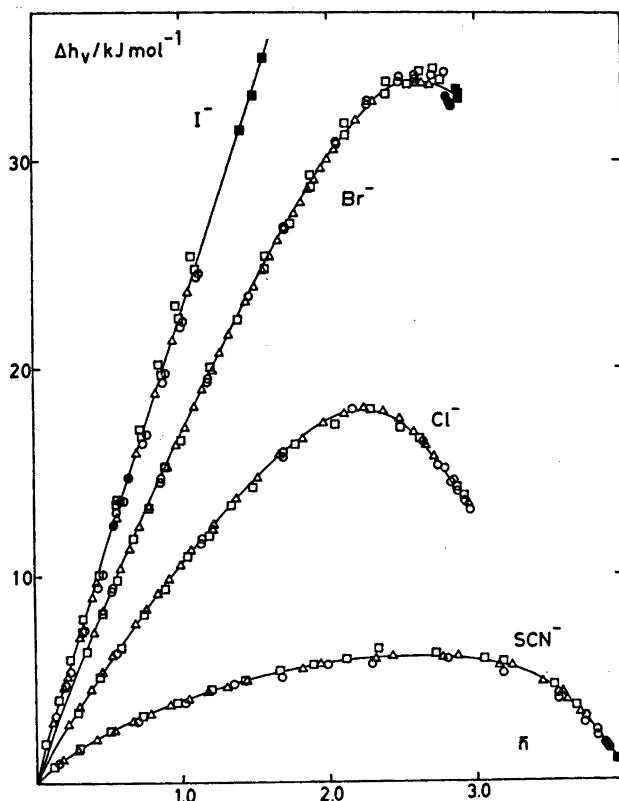


Fig. 1. The total molar enthalpy change Δh_v as a function of \bar{n} for the halide systems. The full-drawn curves are calculated from the mean values of β_i in the case of the chloride system. For the other systems the potentiometrically determined sets are used, cf. Table 1. The corresponding ΔH° are given in Table 2. Some of the experimental points are excluded at random.

for 1,3-dithian-monosulfoxide, the zinc ion is octahedrally surrounded by the sulfoxide molecules (coordinated, *via* oxygen, as expected).⁹ On the other hand, all solid trihalido and tetrahalido complexes of zinc so far investigated contain discrete tetrahedral units, with water in the fourth position in the case of the trihalides.^{10,11} A change of coordination thus certainly occurs in the course of the complex formation just as it does for the cadmium(II) halide system.²

The thermodynamic irregularities connected with certain steps of the complex formation should thus no doubt be interpreted along the same lines as for these, especially as the effect observed is so obviously of the same nature in both cases.

As indicated by the abnormally high entropy gains, the change of coordination for the zinc

chloride and bromide systems mainly takes place already at the first step in DMSO but at the second step in water. This is different from the corresponding cadmium systems where the coordination change mainly takes place at the second step in DMSO and at the third step in water. For the zinc iodide system, on the other hand, the change evidently takes place mainly at the second step in DMSO, just as for the cadmium iodide system, cf. part IV, Table 3. In water, the zinc iodide system is too weak for a safe determination of the pertinent functions.⁷

For steric reasons it is not unexpected that the structural change occurs at an earlier step for zinc(II) than for cadmium(II) and also that a solvate of bulky DMSO molecules breaks up at an earlier step than a hydrate. The chloride and bromide systems throughout

Table 3. Thermodynamics of zinc halide and thiocyanate complexes in DMSO and water, at 25 °C, in the media stated. ΔG°_j and ΔH°_j in kJ mol⁻¹, ΔS°_j in JK⁻¹ mol⁻¹.

	DMSO				Water		
	1 M Cl ⁻	NH ₄ ClO ₄ Br ⁻	I ⁻	SCN ⁻	3 M NaClO ₄ Cl ⁻	Br ⁻	1 M NaClO ₄ SCN ⁻
ΔG°_1	-11.1	-4.8	4.0	-7.9	1.1	3.3	-4.0
ΔG°_2	-22.2	-16.5	-8.0	-8.1	2.4	4.7	-1.9
ΔG°_3	-12.9	-7.7	-0.9	-13.7	-4.3	-3	-0.8
ΔG°_4	-	-	-	-9.4	-	-	-1.9
ΔH°_1	22.3	27.8	19.0	5.5	5.5	1.5	-5.8
ΔH°_2	0.8	9.1	29.4	23.5	38	42	-2
ΔH°_3	-10.2	-4.2	12.7	-17.8	0	-8	-1
ΔH°_4	-	-	-	-10.7	-	-	-8
ΔS°_1	112	110	50	45	15	-5.9	-6
ΔS°_2	77	85	127	105	120	125	0
ΔS°_3	9.1	12	45	-13	8	-17	0
ΔS°_4	-	-	-	-4	-	-	-20
$\Delta H^\circ_{\beta_3}$	13	33	61	11	44	36	-9
$\Delta S^\circ_{\beta_3}$	198	207	222	137	143	102	-6

behave according to this expectation. Also for cadmium iodide in DMSO and water, the rule holds. A very striking exception is found, however, *viz.* that the iodide systems of zinc and cadmium both change their coordination at the second step. This is the more remarkable as one would rather expect the rule to be more strictly valid for the large iodide ion than for its lighter congeners. Some other influence must evidently also be at work. Most likely, the unexpected trend depends upon that the effective charge on the central zinc ion increases in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$, the neutralization being more extensive the higher the charge density on the halide ion. With increasing effective charge, the central ion will more easily keep an extensive solvation, hence the retarded desolvation in the iodide system. For the cadmium systems, on the other hand, where the metal to ligand bonds are increasingly covalent in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$, the neutralization of the cationic charge is presumably more extensive, the more polarizable the halide ion. In this case, the charge on the central cadmium ion should therefore *decrease* from Cl^- to I^- . Consequently, no retarded desolvation is to be expected for the cadmium iodide system.

The inferences put forward above as to the variation with the halide of the effective

charge on the central ion have in fact been verified by direct measurements¹⁵ of the solvation enthalpies of the neutral complexes ML_4 .

For the zinc thiocyanate system in DMSO, the change of coordination mainly takes place at the second step, as for iodide. This is different to the cadmium thiocyanate system where no very striking increases in entropy occur in the course of formation of the first three complexes, part IV, Table 3. The same also applies to both zinc and cadmium thiocyanate in aqueous solution.¹³⁻¹⁴

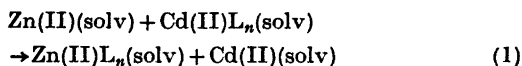
A most remarkable feature of the chloride and bromide systems of zinc(II) is that no fourth complex exists even at the highest ligand concentrations reached here. If such complexes can be formed at all they are in any case extremely weak relative to their predecessors as is evident from the complex formation curves which show quite marked shelves for $\bar{n} = 3$ (cf. V, Fig. 1). The fourth tetrahedral position is clearly not at all attractive which is in marked contrast not only to the cadmium halides (cf. III, Fig. 6) but also to the zinc thiocyanate (V, Fig. 1). For all these systems, $\bar{n} = 4$ is approached without any previous stops. The zinc iodide and the cadmium thiocyanate systems are too weak to allow any conclusions about their behaviour in this respect.

For all the zinc systems, the total gain of entropy is much higher in DMSO than in water, as is found by comparing $\Delta S^\circ_{\beta_3} = \sum_{j=1}^3 \Delta S^\circ_j$ for the two solvents, Table 3. The corresponding cadmium systems behave in the same way, part IV, Table 3. As suggested in part IV, this difference is most probably due to the higher degree of order prevailing in water, on account of the strong hydrogen bonding between the water molecules which has no counterpart in DMSO. A desolvation thus implies a larger loss of order, and hence a larger gain of entropy, in DMSO than in water. The stronger solvation¹⁵ of Zn^{2+} and Cd^{2+} in DMSO also contributes to the higher total gain of entropy, however.

As for the cadmium halides, the values of $\Delta S^\circ_{\beta_3}$ in DMSO increase for the zinc halides in the sequence $\text{Cl}^- < \text{Br}^- < \text{I}^-$ which means a reversal of the sequence observed in aqueous solution. The difference of solvation between the halides in DMSO¹⁵ and in water certainly acts in the direction observed, but is hardly large enough to account for the whole effect produced, as discussed in part IV.

For the thiocyanate system, the value of $\Delta S^\circ_{\beta_3}$ is much lower than for any of the halides, a phenomenon that in an even higher degree was observed for the corresponding cadmium systems, part IV. As suggested there, the relatively low thiocyanate values are certainly due to losses of vibrational and rotational freedom sustained by the triatomic thiocyanate ion on coordination. These losses have of course no counterpart in the reactions of the halide ions.

For a closer comparison of the entropies involved in the formation of zinc and cadmium complexes in DMSO, the differences between the total entropy changes, $\Delta S^\circ_{\beta_n} = \sum_{j=1}^n \Delta S^\circ_j$, have been calculated. These differences $\Delta S^\circ_{\beta_n}(\text{Zn}-\text{Cd})$ give the entropy changes of the reactions



As the abnormally high entropy increases occur at earlier steps for all the zinc systems, except the iodide, (*cf.* p. 273) the reaction (1) must involve a rather large gain of entropy for $n=1$

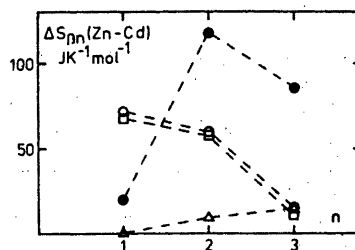


Fig. 2. The entropy change $\Delta S^\circ_{\beta_n}(\text{Zn}-\text{Cd})$ plotted against the number of participating ligands [*cf.* reaction (1)]. The signs refer to: Cl^- , O; Br^- , □; I^- , Δ and SCN^- , ●.

and 2 in the case of chloride, bromide and thiocyanate. For iodide on the other hand, no large gain is to be expected. At the end of the complex formation, where the coordination change is certainly complete for both zinc and cadmium, $\Delta S^\circ_{\beta_n}(\text{Zn}-\text{Cd})$ should be very similar for all the ligands. The values of ΔS°_j even suggest that the coordination change is virtually completed with the third step. If so, already $\Delta S^\circ_{\beta_3}(\text{Zn}-\text{Cd})$ should not differ very much between the various systems. Since zinc(II) is more strongly solvated than cadmium(II) in DMSO¹⁵ $\Delta S^\circ_{\beta_3}$ is moreover expected to be positive.

The values of $\Delta S^\circ_{\beta_n}(\text{Zn}-\text{Cd})$ have been plotted in Fig. 2. For $n=1$ and 2, the values found for chloride and bromide are, as expected, very different from those found for iodide. In contrast to this, the values for $n=3$ are practically the same, $\approx 14 \text{ J K}^{-1}$, as would also be expected provided that the coordination change is really completed for all the halides as the third ligand enters the inner sphere. It is further striking that for chloride and bromide the values of $\Delta S^\circ_{\beta_n}(\text{Zn}-\text{Cd})$ are much the same for each step. For thiocyanate, the values are for all steps remarkably different from those found for the halides. It is especially noticeable that the value for $n=3$ is so much higher, 86 J K^{-1} . This most probably implies that the change to a tetrahedral coordination has not been completed for the cadmium thiocyanate system with the third step.

REFERENCES

1. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A* 28 (1974) 823.
2. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A* 30 (1976) 249, 257, 265.
3. Gorenbein, E. I., Vainstein, M. N. and Skorobogatko, E. P. *Ukr. Chem. Zh.* 9 (1974) 923.
4. Karlsson, R. and Kullberg, L. *Chem. Scr.* 9 (1976) 54.
5. Kullberg, L. *Acta Chem. Scand. A* 28 (1974) 829.
6. Sillén, L. G. and Liljeqvist, B. *Svensk Kem. Tidskr.* 56 (1944) 85.
7. Gerding, P. *Acta Chem. Scand.* 23 (1969) 1695.
8. Bol, W., Gerrits, G. J. A. and van Panthaleon van Eck, G. L. *J. Appl. Crystallogr.* 3 (1970) 486.
9. Driessen-Fleur, T. *Cyclic Sulfoxides as Ligands*, Diss., Univ. of Leiden 1975.
10. Follner, H. and Brehler, B. *Acta Crystallogr. B* 24 (1968) 1339.
11. Wells, A. F. *Structural Inorganic Chemistry*, 4th Ed., Clarendon Press, Oxford 1975, pp. 390 and 394.
12. Ahrland, S. and Kullberg, L. *Acta Chem. Scand.* 25 (1971) 3692.
13. Gerding, P. and Johansson, B. *Acta Chem. Scand.* 22 (1968) 2255.
14. Gerding, P. *Acta Chem. Scand.* 20 (1966) 2771.
15. Ahrland, S. Kullberg, L. and Portanova, R. *To be published.*

Received October 1, 1975.