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

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The formation of chloride, bromide, iodide, and thiocyanate complexes of zinc(II) in dimethyl sulfoxide has been studied at 25 °C by central ion measurements. An approximately constant ionic medium of ionic strength = 1 M has been provided by means of ammonium perchlorate. All complexes formed are stronger in DMSO than in water and more so the harder the ligand, i.e. the more prone the ligand is to form hydrogen bonds. Consequently, the $(a)$-character of zinc(II) becomes even more marked in DMSO than in aqueous solutions.

In previous parts of this investigation, the changes of free energy, enthalpy and entropy accompanying the stepwise formation of chloride, bromide, iodide, and thiocyanate complexes of cadmium(II) have been measured and the results compared with those obtained earlier for the analogous reactions in aqueous solution.[1] The measurements have now been extended to the corresponding complexes of zinc(II). Though both zinc(II) and cadmium(II) are divalent $d^{10}$ acceptors and consequently often react in much the same way, their coordinating properties are nevertheless rather different. Contrary to cadmium(II), zinc(II) very much prefers the light donor atoms to the heavy ones in aqueous solution, i.e. zinc(II) is a hard acceptor, much harder than the mildly soft cadmium(II). A comparison between the behaviour of these two acceptors in DMSO and water is therefore of considerable interest.[2]

In the present study, the stabilities of the zinc(II) chloride, bromide, iodide, and thiocyanate complexes in DMSO have been deter-

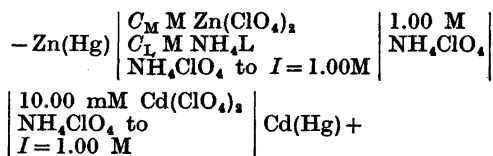mined potentiometrically by means of a zinc amalgam electrode at 25 °C.

As in the cadmium(II) measurements,[1] an ammonium perchlorate medium of ionic strength $I = 1$ M has been employed. The corresponding measurements in aqueous solution [3,4] have been performed in sodium perchlorate media but as sodium chloride is not very soluble in DMSO,[5] such media are not practical in the present measurements.

Seemingly, no investigations of the stability of the zinc(II) complexes in DMSO have been reported so far.

## CALCULATIONS

The notation is the same as before.[1] The stability constants have been calculated from the potentiometric measurements of the free central ion concentration, both graphically and numerically. The graphical method has earlier been discussed in detail. Only the final expressions will therefore be given here.

In the cells measured, the stable and reproducible cadmium amalgam electrode has been used as a reference:

$$-Zn(Hg) \left| \begin{array}{l} C_M \text{ M } Zn(ClO_4)_2 \\ C_L \text{ M } NH_4L \\ NH_4ClO_4 \text{ to } I = 1.00M \end{array} \right| \left| \begin{array}{l} 1.00 \text{ M} \\ NH_4ClO_4 \end{array} \right|$$

$$\left| \begin{array}{l} 10.00 \text{ mM } Cd(ClO_4)_2 \\ NH_4ClO_4 \text{ to} \\ I = 1.00 \text{ M} \end{array} \right| Cd(Hg) +$$

The difference $E_M$ between an emf $E$ measured at a certain value of $C_L$ and the emf $E'$ at $C_L = 0$, where $C_M = [M]$, is

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$$E_M = (RT/2F) \ln (C_M/[M]) \tag{1}$$

If only mononuclear complexes are formed

$$C_M/[M] = X = 1 + \sum_{j=1}^{N} \beta_j [L]^j \tag{2}$$

which with (1) yields

$$E_M = (RT/2F) \ln X \tag{3}$$

The ligand number is given by

$$\bar{n} = \sum_{j=1}^{N} j\beta_j [L]^j / X \tag{4}$$

or approximatively by

$$\bar{n} = \frac{2F}{RT \ln 10} \frac{\Delta E_M}{\Delta \log [L]} \tag{5}$$

The functions $C_L(C_M)_{E_M}$ will be straight lines with the intercepts $C_L = [L]$ for $C_M = 0$ and the slopes $= \bar{n}$. For the numerical calculations the least-squares program EMK [6] has been used. This program is a simplified and faster version of the program used earlier. The present version is restricted to calculations on systems of mononuclear complexes. The best set of $\beta_j$ is found by minimizing the following error square sum

$$U(\beta_j) = \sum_{i=1}^{N} w_i (E_{M,i,calc} - E_{M,i})^2 \tag{6}$$

where $w_i$ is a weighting term, here $= 1$.

It may reasonably be assumed that the liquid junction potentials are negligible in the cells measured. From the values of $E'$, it is then possible to calculate the difference $\Delta E°$(DMSO) between the formal standard potentials of the cadmium and zinc amalgam electrodes, on the concentration scale and in a medium of $I = 1$ M ($NH_4ClO_4$):

$$\Delta E°(DMSO) = E°\{Cd(Hg)\} - E°\{Zn(Hg)\}$$
$$= E' + \frac{RT}{2F} \ln \frac{C_M}{0.01} \tag{7}$$

For water, the corresponding difference $\Delta E°$(aq) has not been measured in the medium stated. The very similar activity functions [7] found for such salts of cadmium(II) and zinc(II) which are extensively dissociated in aqueous solution (nitrates, sulfates) indicate, however, that the activity coefficients of $Cd^{2+}$ and $Zn^{2+}$

varies in much the same way with the medium, as might also be expected. The difference $\Delta E°$(aq) should therefore be approximately the same for $I = 1$ M ($NH_4ClO_4$) and for $I = 0$ where it is very accurately known.[8] Hence $\Delta E° = \Delta E°$(aq) $- \Delta E°$(DMSO) referring to $I = 1$ M ($NH_4ClO_4$) can be calculated with fair accuracy. This quantity is the change between water and DMSO for the difference between the formal standard potentials of cadmium and zinc amalgam. An identical change occurs, of course, between the standard potentials of cadmium and zinc metal as these differ from the amalgam electrodes only with respect to the activity of the metal in the electrode phase. The quantity $\Delta E°$ is in fact the emf of a cell with the cell reaction

$$Cd^{2+}(aq) + Zn^{2+}(DMSO) \rightarrow Cd^{2+}(DMSO)$$
$$+ Zn^{2+}(aq) \tag{8}$$
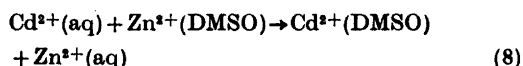
which is evidently independent of the electrode material. The free energy change of this exchange reaction is

$$\Delta G°_{ex} = - 2F\Delta E° \tag{9}$$

## EXPERIMENTAL

*Chemicals.* The hexasolvate $Zn(DMSO)_6$-$(ClO_4)_2$ and all *ligand solutions* were prepared and analyzed as described previously.[1,2]

*Zinc amalgam* was prepared and stored as described by Persson.[9] The amalgam contained $\simeq 2.5$ % zinc. The exact concentration is not critical since a two-phase amalgam is formed [10] between 2.18 and 45 % at 25 °C.

The *apparatus* and the *procedure* have been the same as before.[1] The reproducibility of the emf's measured was generally better than $\pm 0.04$ mV for low values of $C_L$. At values of $C_L \simeq 50$ mM, it was still better than $\pm 0.2$ mV for all the systems. For higher values of $C_L$, the emf's were increasingly less reproducible. The reason for this is that the higher complexes predominating in this concentration range do not contribute to the exchange current, as has been shown by measurements of the electrode kinetics.[11] At $C_L \simeq 500$ mM, the reproducibility had decreased to about $\pm 2$mV for the chloride and thiocyanate systems and to $\pm 1$ mV for the bromide. For the weak iodide system the reproducibility was better than $\pm 0.1$ mV even at the highest values of $C_L$ used ($\simeq 500$ mM).

The final values of $E$ were reached within 30 min and were extremely stable. Within the

next 5 h, the variation generally did not exceed $\pm 0.02$ mV. If left for 24 h, the values changed by $\simeq 0.3$ mV. Also at high values of $C_L$ ( $> 50$ mM), a similar change was observed when the cell was left standing.

The validity of Nernst's law has been checked[1] in the range 5 mM $\leq C_M \leq 40$ mM. The value of $E°$(DMSO) was constant within $\pm 0.3$ mV.


## MEASUREMENTS AND RESULTS

*The difference between the standard potentials of cadmium and zinc in DMSO and water.* A value of $\Delta E°$(DMSO) $= 363.9$ mV is found. In water, at $I = 0$, $E°\{Cd(Hg)\} = -352.0$ mV, *i.e.* 50.5 mV more positive than $E°$(Cd) $= -402.5$ mV,[8] while no perceptible difference exists between the potentials of zinc and zinc amalgam[12], $E°\{Zn(Hg)\} = E°$(Zn) $= -762.8$ mV.[8] A value of $\Delta E°$(aq) $= 410.8$ mV results, judged to be approximately valid also at $I = 1$. Hence $\Delta E° = 46.9$ mV, and $\Delta G°_{ex} = -9.05$ kJ (eqn. 9), implying that Cd$^{2+}$ is favoured relative to Zn$^{2+}$ by a transfer from water to DMSO, *cf.* eqn. 8. Evidently, the solvation in DMSO relative to water is markedly more favourable for Cd$^{2+}$ than for Zn$^{2+}$.

*Zinc chloride and zinc bromide.* If data referring to the highest values of $C_L$ employed ($\gtrsim 60$ mM) are included in the calculations, the error square sum of eqn. 6 becomes much higher than if they are omitted. If the high values are included, the first three mononuclear complexes are unambiguously identified. The fourth one cannot be positively proved, especially as the random errors are so large in that upper range of concentration where it might possibly exist. The upper limit of the stability constant is given in Table 1.

Since other evidence [1,13,14] also indicates that central ion measurements at high ligand concentrations may be subject to serious systematic errors, no data for $C_L \gtrsim 60$ mM are included in the final calculations.

In the range of $C_L$ thus chosen, both the numerical and the graphical evaluation indicates only the first three complexes. The constants calculated by the two methods agree very well. The complex formation function calculated from $\beta_1$ to $\beta_3$, eqn. 4, coincides well both with the values of $\bar{n}$ calculated from eqn. 5 and with those found from the slopes of the $C_L(C_M)$-lines, Fig. 1.
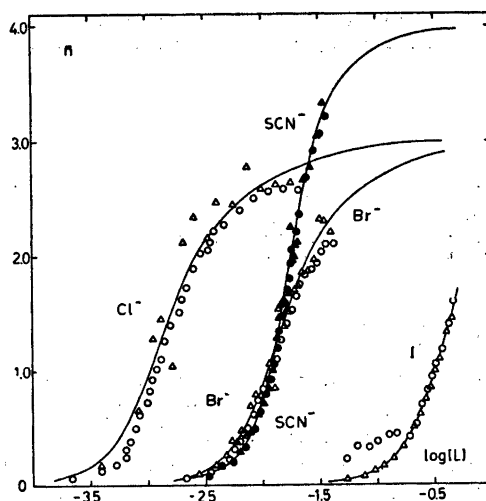
*Fig. 1.* The complex formation functions of the zinc(II) systems. The curves are calculated from eqn. (4). The slopes of the $C_L(C_M)_{E_M}$-lines are denoted by circles, values from eqn. (5) by triangles. The symbols are filled for the thiocyanate system. The potentiometric measurements reach as far as $\bar{n} = 2.80$ for Cl$^-$, 2.45 for Br$^-$ and 3.5 for SCN$^-$. The parts of the curves extending beyond these values of $\bar{n}$ are based on the calorimetric measurements described in the next paper.

*Zinc iodide.* Graphical and numerical evaluation of the measurements indicate three mononuclear complexes. The sets of $\beta_j$ found by the two methods of calculation agree very well. The complex formation function calculated from the set given in Table 1 coincides well with the values of $\bar{n}$ found from eqn. 5 but not so well with those found from the slopes of the $C_L(C_M)$-lines. For such a weak complex system as the present one this is not very surprising, however, as the $E_M(C_L)$-functions vary only little with $C_M$.

*Zinc thiocyanate.* As for the chloride and bromide systems, no data for $C_L \gtrsim 60$ mM are included in the final calculations of the thiocyanate system. In this system, however, both the graphical and the numerical evaluation indicate four mononuclear complexes, with good agreement between the two sets of $\beta_j$. The complex formation function calculated from the numerical set (Table 1) is fulldrawn in Fig. 1. Both the values of $\bar{n}$ from eqn. 5 and those found from the slopes of the $C_L(C_M)$-lines fit very well to this function.

*Table 1.* The overall stability constants $\beta_J$ for the halide and thiocyanate systems of zinc(II) investigated. The limits of error given correspond to three standard deviations. Medium: 1 M $NH_4ClO_4$.

|  | Cl⁻ | Br⁻ | I⁻ | SCN⁻ |
|---|---|---|---|---|
| $\beta_1/M^{-1}$ | $86 \pm 25$ | $7 \pm 2$ | $0.20 \pm 0.04$ | $24 \pm 2$ |
| $\beta_2/M^{-2}$ | $(6.8 \pm 0.2)10^5$ | $(5.4 \pm 0.4)10^3$ | $5.1 \pm 0.3$ | $630 \pm 430$ |
| $\beta_3/M^{-3}$ | $(1.18 \pm 0.04)10^8$ | $(1.2 \pm 0.1)10^5$ | $7.2 \pm 0.5$ | $(1.6 \pm 0.3)10^5$ |
| $\beta_4/M^{-4}$ | $(<10^9)$ | $(<2 \times 10^5)$ | – | $(7.2 \pm 0.6)10^6$ |

## DISCUSSION

As pointed out in the introductory paper of this series,[2] complexes formed by ligands able to participate in hydrogen bonding should be relatively more stable in the aprotic solvent DMSO than in water. All the systems inves-tigated here are in fact stronger in DMSO than in water, Table 2. Particularly the chloride, but also the bromide complexes are much stronger. For the iodide and thiocyanate complexes the increase is relatively modest. The stabilities thus increase as expected, *viz.* more the harder the ligand. The result is, of course, that zinc(II) acquires an even more marked (a)-character in DMSO than in water.

For all the zinc halide systems, the first complex has a very narrow range of existence

*Table 2.* Stability of zinc halide and thiocyanate complexes in DMSO and water, at 25 °C.

|  | Cl⁻ | Br⁻ | I⁻ | SCN⁻ |
|---|---|---|---|---|
|  | DMSO, 1 M $NH_4ClO_4$ | | | |
| $K_1$ | 86 | 7 | 0.20 | 24 |
| $K_2$ | 7900 | 770 | 26 | 26 |
| $K_3$ | 170 | 22 | 1.4 | 250 |
| $K_4$ | < 10 | < 2 | | 45 |
| $K_1/K_2$ | 0.011 | 0.009 | 0.008 | 0.92 |
| $K_2/K_3$ | 46 | 35 | 19 | 0.10 |
| $K_3/K_4$ | > 17 | > 11 | | 5.6 |
|  | Water, 3 M $NaClO_4$ | | 1 M $NaClO_4$ | |
| $K_1$ | 0.65 | 0.27 | 0.03 | 5.10 |
| $K_2$ | 0.38 | 0.15 | | 2.2 |
| $K_3$ | 5.6 | 3.3 | | 1.4 |
| $K_4$ | | | | 2.1 |
| $K_1/K_2$ | 2 | 2 | | 2.3 |
| $K_2/K_3$ | 0.07 | 0.05 | | 1.6 |
| $K_3/K_4$ | | | | 0.67 |
| Ref. | 3 | 18 | 18 | 4 |

in DMSO, as shown by the very low value of the ratio $K_1/K_2$, Table 2. Also in the cadmium halide systems,[1] one of the complexes has a very narrow range of existence in DMSO, but in these systems the second complex is the disfavoured one.

For the cadmium systems the thermody-namics of the formation of the consecutive steps indicate that the narrow range of the second complex most probably depends upon a change of coordination.[1] This change mainly takes place at this very step.

It has been proved by X-ray analysis[15] that the zinc ion in aqueous solution exists as a hexahydrate, of regular octahedral struc-ture. For the DMSO solvate in solution no such structure determination has been performed. A solid solvate $Zn(DMSO)_6(ClO_4)_2$ is easily prepared,[2] however. The hexacoordination most probably persists in solution, with the solvent molecules in a regularly octahedral arrange-ment. On the other hand, solid halide complexes containing discrete tetrahedral groups $ZnL_4^{2-}$ and $XnL_2(H_2O)^-$ are known,[16,17] indicating a preference for tetrahedral coordination in zinc halide complexes. It is therefore likely that the narrow range of existence of the first complex in the zinc halide systems is due to a change from octahedral to tetrahedral coordination. A closer scrutiny of this must await the determination of the enthalpy and entropy changes of the complex formation, however, which will be the theme of the next paper in this series.

The thiocyanate systems of cadmium(II) and zinc(II) behaves quite differently. In the former,[1] none of the three complexes is dis-favoured, while in the latter the second complex has a fairly narrow range of existence, Table 2. In water,[4] the third zinc complex is the weakest. Also for the thiocyanate system, a full dis-

cussion can be undertaken only when the changes of enthalpy and entropy for the various steps have been measured.

## REFERENCES

1. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A 30* (1976) 249, 257.
2. Ahrland, S. and Björk, N. O. *Acta Chem. Scand. A 28* (1974) 823.
3. Sillén, L. G., Liljeqvist, B. *Sv. Kem. Tidskr. 56* (1944) 85.
4. Ahrland, S. and Kullberg, L. *Acta Chem. Scand. 25* (1971) 3692.
5. Kenttämaa, J. *Suom. Kemistil. B 33* (1960) 179.
6. Karlsson, R. and Kullberg, L. *Chem. Scr. 9* (1976) 54.
7. Robinson, R. A. and Stokes, R. H. *Electrolyte Solutions*, Butterworth, London 1955.
8. Sillén, L. G. and Martell, A. E., Eds., *Stability Constants of Metal-Ion Complexes*, Chemical Society, Special Publications Nos. 17 and 25, London 1964, 1971.
9. Persson, H. *Acta Chem. Scand. 24* (1970) 3739.
10. Hansen, M. *Constitution of Binary Alloys*, 2nd Ed., 1958, p. 846, as quoted in *Gmelin*, 8th Ed. Nr *34* [*A*] Quecksilber, 1962, p. 1062.
11. Fronæus, S. and Johansson, C. L. *J. Electroanal. Chem. In press.*
12. Clayton, W. J. and Vosburgh, W. C. *J. Amer. Chem. Soc. 58* (1936) 2093.
13. Sandell, A. *Acta Chem. Scand. 24* (1970) 3391; *25* (1971) 1795.
14. Ahrland, S. and Johansson, L. *Acta Chem. Scand. 18* (1964) 2125.
15. Bol, W., Gerrits, G. I. A. and van Panthaleon van Eck, C. L. *J. Appl. Crystallogr. 3* (1970) 486.
16. Follner, H. and Brehler, B. *Acta Crystallogr. B 24* (1968) 1339.
17. Wells, A. F. *Structural Inorganic Chemistry* 4th Ed., Clarendon Press, Oxford 1975, pp. 390 and 394.
18. Gerding, P. *Acta Chem. Scand. 23* (1969) 1695.