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

STEN AHRLAND and NILS-OLOF BJÖRK

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

The enthalpy changes for the formation of cadmium(II) chloride, bromide, iodide, and thiocyanate complexes in dimethyl sulfoxide have been determined by means of a calorimetric titration method. 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 ionic strength 1.00 M.

For the halide systems ΔH_2 and ΔS_2 are particularly high, indicating that a change of coordination takes place at this very step. For the thiocyanate system the energy changes are rather small throughout.

It is also found that the total entropy gains on complex formation are much higher in DMSO than in water.

In order to elucidate the nature of the bonds involved in the formation of metal ion complexes in solution it is important to know all the thermodynamic functions for the pertinent reactions.[1,2] The free energy changes $\Delta G°_j$ for the stepwise formation of cadmium(II) chloride, bromide, iodide, and thiocyanate complexes in the protic solvent water and in the aprotic solvent dimethyl sulfoxide (DMSO) can be calculated from the stability constants reported previously.[2] The corresponding enthalpy changes ΔH_j are already known for water.[3-6] In the present investigation, the values of $\Delta H°_j$ for DMSO have been determined by direct calorimetric measurements. From the data thus available the corresponding entropy changes $\Delta S°_j$ can be calculated according to

$$\Delta G°_j = \Delta H°_j - T\Delta S°_j \qquad (1)$$

Enthalpy changes can be determined either by measuring the stability constants as a function of the temperature or calorimetrically, as here. The former method requires very precise measurements of K_j over a wide temperature range if the values of $\Delta H°_j$ are to be as reliable as those obtained by calorimetry.[7,8] Such a wide range is hardly accessible for DMSO of m.p. 18.5 °C. Further, within this range the change in heat capacity ΔC_p has to be negligible. The calorimetric method has also the advantage that fewer measurements are needed in order to achieve a certain precision.[9]

In most cases, the values of β_j have to be known already for the calculations of $\Delta H°_j$, as the calorimetric data as a rule do not allow a precise determination of both β_j and $\Delta H°_j$ from the experimental function Δh_v.[10,11] In certain well conditioned systems, however, it is possible to perform such a simultaneous determination.[10,12,13] This is in fact the case for the halide systems investigated here. If the values of β_j thus obtained agree with those found independently by potentiometric measurements, the result can of course be considered as very reliable.

The simultaneous determination of β_j and $\Delta H°_j$ for systems involving more than two complexes has until recently been a rather time-consuming task. The new program "Kalori" developed by Karlsson and Kullberg has very much eased this situation.[12,14] This program has been used for all calculations in the present paper.

Only a very exploratory calorimetric investigation of these systems has been performed previously.[15] In this study, which involved only the higher complexes, it was assumed that the dissolution of the solid halides results in a solution of the neutral complex ML_2. As this is certainly not true, the results reported are hardly correct.

NOTATION AND GENERAL EQUATIONS

Q_{exp} = heat change after addition of titrant (>0 if heat is evolved)

Q_{dil} = heat of dilution

$Q_{corr} = Q_{exp} - Q_{dil}$ = heat change corrected for heat of dilution.

V_0 = initial volume of the solution in the calorimeter vessel.

v = volume of titrant added.

V = total volume of the solution of the calorimeter vessel.

ε_v = heat equivalent (J/ohm) of the calorimeter at the volume V.

$\Delta h_v = -\sum_v \frac{Q_{corr}}{C_M V}$ = total molar heat change after addition of v ml titrant.

The quantity Δh_v is related to the stepwise enthalpy change as follows:

$$\Delta h_v = \sum_{j=1}^{N} \sum_{k=1}^{j} \beta_j [L]^j \Delta H°_k / X \qquad (2)$$

In the program "Kalori" applied here, a set of parameters is obtained which results in a minimum of the error square sum

$$U(\beta_j, \Delta H_j) = \sum_{i=1}^{N} w_i (Q_{i,calc} - Q_{i,corr})^2 \qquad (3)$$

where $w_i = 1$ is used.

EXPERIMENTAL

Chemicals. Hydrochloric acid, THAM (tris(hydroxymethyl)aminomethane) and sodium hydroxide used for testing the calorimeter were of analytical grade. All other chemicals were prepared and analyzed as described before.[1,2]

Apparatus. A titration calorimeter of the isothermal jacket type was used. Its main features have been described by Ots.[16] To make work with DMSO solutions possible, some modifications had to be introduced, however. Thus all parts in contact with DMSO have been made from either gold, glass, teflon, or trifluorochloropolyethen. The inner vessel, which holds 100 ml, is inserted in an outer can which is wholly immersed in a water thermostat bath. The water content of DMSO increased slightly during the titration, but never exceeded 0.12 vol % (analyzed according to Ref. 17). The LKB precision thermostat used maintained its temperature at 25.000 ± 0.001 °C. For shorter periods (1 – 2 h) the temperature was, as a rule, stable even within $\pm 2 \times 10^{-4}$ °C. The room temperature was kept at 25.0 ± 0.2 °C.

Procedure. Initially 80 ml of a solution S in the inner vessel is equilibrated in the thermostat over night. Before the titration is started, the solution S is cooled (by air) to a temperature a little below that of the surrounding bath. The stirring necessary to bring about good mixing causes the temperature to rise slowly. Solution T, passing a heat-exchanger placed in the bath, is added (at most 5 ml) by a piston burette. The addition is made at a special "addition temperature", defined as the temperature where 1 M NH_4ClO_4 in DMSO can be added to an identical solution without any temperature change. All additions are made at a standard rate of 1 ml/min.

When the reaction is completed, the addition temperature is restored by either cooling or heating, depending upon whether the reaction is exothermic or endothermic. A new cycle is then started.

The calibration constant ε_v was determined as reported by Ots.[16] It was found to depend upon V according to $\varepsilon_v = a + b(V-80)$ J ohm^{-1} where $a = 0.9780 \pm 0.0020$ J ohm^{-1} and $b = (1.236 \pm 0.020)10^{-2}$ J ohm^{-1} ml^{-1}.

Totally eight or nine titration series were performed for each system. In series 1 – 6, ligand solution T, of $C_L = 1.000$ M, was titrated into metal ion solutions S, with C_M varying from $\simeq 10$ to $\simeq 40$ mM. For series 7 – 9 solution T of $C_M \simeq 100$ mM was titrated into ligand solutions of $C_L \simeq 0.25$, 0.50 and 1.00 M. If only mononuclear complexes exist, the function $\Delta H_v(\bar{n})$ should be independent of C_M.

For all S solutions containing metal ions the heats of dilution on addition of ammonium perchlorate solution were negligible. For S solutions containing ligand as well as for all T solutions such dilutions gave quite large heat effects, at most 0.27 J per ml added T solution.

In eqn. (3), the input data are V_0, v, Q_{corr} and the initial concentrations of the metal ion and ligand solutions. The potentiometrically determined values of β_j were always taken as initial values in the calorimetric evaluation. The values of β_j determined calorimetrically have almost always larger errors than those found potentiometrically. This applies especially to the thiocyanate system, where the variation in Δh_v is fairly modest (*cf.* Fig. 1). In this case the potentiometrically determined values of β_j have been inserted in the program and not allowed to vary during the calculations.

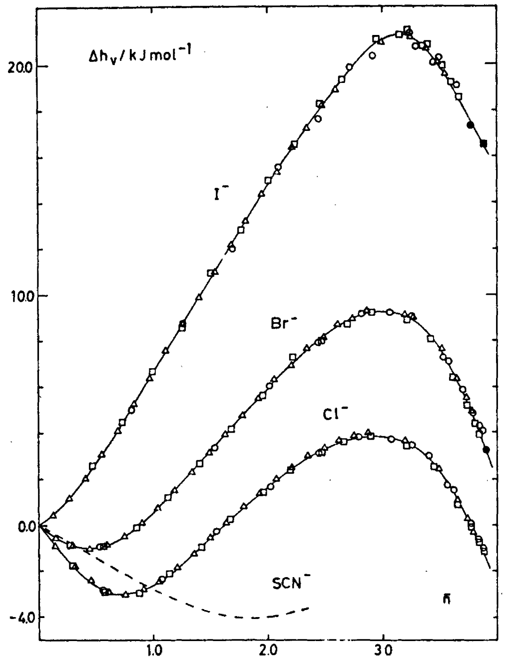

Fig. 1. The total molar enthalpy change Δh_v as a function of $\bar{n}$ for the halide systems. The fulldrawn curves are calculated from the mean values of β_j given in Table 1 and $\Delta H°_j$ from Table 2. The thiocyanate curve is dashed for comparison.

When values of β_j are determined both calorimetrically and potentiometrically, a weighted mean of these was used for the final calculations of $\Delta H°_j$ and $\Delta S°_j$. The complete calorimetric data are available from the authors.

Testing the calorimeter. To check the accuracy of the calorimeter, the heat of protonation of THAM and the heat of neutralisation of sodium hydroxide have been determined. In the first test THAM ($C_T = 20.0$ mM and $C_{TH^+} = 10.0$ mM) was protonated by 100.25 mM hydrochloric acid. The value found, $\Delta H_{corr} = 46.92 \pm 0.07$ J mol^{-1}, is significantly lower than those found by Öjelund and Wadsö,[18] -47.48 ± 0.03 kJ mol^{-1} or by Grenthe *et al.*,[19] -47.44 ± 0.05 kJ mol^{-1}.

Since the use of protonation of THAM as standard reaction has been somewhat in doubt,[20] no further attempts to obtain better values have been made.

In the second test 9.87 mM hydroxide solution was neutralized by the same hydrochloric acid as above. The value found, $\Delta H_{W\infty} = -55.84 \pm 0.04$ kJ mol^{-1} agrees very well with other determinations (Grenthe *et al.*,[19] -55.84 ± 0.05 kJ mol^{-1}; Vanderzee and Swanson,[21] -55.84 kJ mol^{-1}; Ots[16] -55.83 ± 0.02 kJ mol^{-1}). Corrections for the dilutions have been made according to SVCTP.[22,23]

RESULTS

The chloride system. Even when only the first four mononuclear constants, as determined potentiometrically, were applied in the "Kalori" program, no significant discrepancy was found between the series of different C_M. Only for the highest C_L (series 9) a very slight difference, at most 0.2 J, corresponding to $\simeq 3\sigma_Q$, was observed. When the values of β_j were allowed to vary an even better fit resulted though a slight difference at the higest C_L still persisted. The complexes ML_6 and M_2L_9 indicated by the potentiometric measurements should exist in perceptible amounts already in the calorimetric series 1 – 7 where, however, an excellent fit was obtained without them. The slight discrepancy in series 9 might well

Table 1. The stability constants of cadmium(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 perchloride.

j	Pot.	Cal.	Mean
Chloride (β_j, M^{-j})			
1	1600 ± 100	1800 ± 160	1680 ± 90
2	$(1.2 \pm 0.7)10^5$	$(1.8 \pm 0.5)10^5$	$(1.6 \pm 0.4)10^5$
3	$(5.2 \pm 0.8)10^7$	$(6.9 \pm 1.3)10^7$	$(5.9 \pm 0.8)10^7$
4	$(2.7 \pm 0.5)10^9$	$(4.3 \pm 0.8)10^9$	$(3.3 \pm 0.5)10^9$
Bromide (β_j, M^{-j})			
1	850 ± 80	820 ± 60	830 ± 50
2	$(5 \pm 3)10^4$	$(8 \pm 2)10^4$	$(6.8 \pm 1.8)10^4$
3	$(3.6 \pm 0.5)10^7$	$(4.0 \pm 0.5)10^7$	$(3.8 \pm 0.4)10^7$
4	$(1.6 \pm 0.2)10^9$	$(2.0 \pm 0.3)10^9$	$(1.8 \pm 0.2)10^9$
Iodide (β_j, M^{-j})			
1	156 ± 10	142 ± 26	152 ± 14
2	$(4 \pm 2)10^3$	$(3.4 \pm 3)10^3$	$(3.8 \pm 1.8)10^3$
3	$(3.2 \pm 0.2)10^6$	$(3.1 \pm 0.4)10^6$	$(3.2 \pm 0.2)10^6$
4	$(4.9 \pm 0.2)10^7$	$(4.0 \pm 0.9)10^7$	$(4.7 \pm 0.5)10^7$
Thiocyanate (β_j, M^{-j})			
1	64 ± 1	(79 ± 18)	
2	520 ± 30	(490 ± 240)	
3	850 ± 90	(2500 ± 2500)	

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

j	ΔG°_j (kJ mol^{-1})	ΔH°_j (kJ mol^{-1})	ΔS°_j (J K^{-1} mol^{-1})
Chloride			
1	-18.4 ± 0.2	-6.3 ± 0.1	40.6 ± 0.7
2	-11.2 ± 0.7	15 ± 2	88 ± 7
3	-14.7 ± 0.7	1 ± 2	53 ± 7
4	-10.0 ± 0.5	-12.2 ± 0.3	-7 ± 2
2+3	-25.9 ± 0.3	15.5 ± 0.4	139 ± 3
Bromide			
1	-16.7 ± 0.2	-3.9 ± 0.2	43.0 ± 0.9
2	-10.9 ± 0.7	17 ± 2	94 ± 7
3	-15.7 ± 0.7	2 ± 3	59 ± 10
4	-9.5 ± 0.4	-13.0 ± 0.2	-12 ± 2
2+3	-26.6 ± 0.3	18.9 ± 0.5	153 ± 3
Iodide			
1	-12.5 ± 0.2	2.4 ± 0.1	50.0 ± 0.8
2	-7.8 ± 1.4	27 ± 2	117 ± 8
3	-16.8 ± 1.4	-5 ± 2	40 ± 8
4	-6.7 ± 0.3	-9.54 ± 0.08	-10 ± 1
2+3	-24.6 ± 0.2	22.6 ± 0.2	158 ± 2
Thiocyanate			
1	-10.31 ± 0.04	-2.97 ± 0.02	24.6 ± 0.2
2	-5.2 ± 0.2	-2.8 ± 0.2	8 ± 1
3	-1.2 ± 0.5	4.2 ± 0.6	18 ± 3

be caused by the great change in ionic medium. In the final calculation series 9 was excluded, as well as series 8, where also a small systematic deviation was observed. The resulting set of β_j is given in Table 1. The final stepwise enthalpy changes were determined by use of an error weighted mean value from the two sets $\beta_{j,\text{pot.}}$ and $\beta_{j,\text{cal.}}$ (Table 1). The result is given in Table 2. In accordance with this result, the function $\Delta h_v(\bar{n})$ is independent of C_M, Fig. 1.

The bromide system. Also in this system, the potentiometric measurements indicated the existence of the complexes ML_6 and M_2L_9, though to a much less degree than for the chloride system. Just as for chloride, however, no trace of any complexes beyond the first four mononuclear ones were found calorimetrically, see Tables 1 and 2 and Fig. 1.

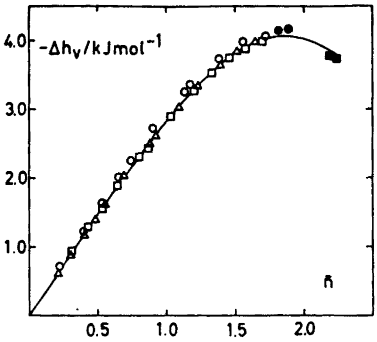

Fig. 2. The total molar enthalpy change Δh_v as a function of $\bar{n}$ for the thiocyanate system. Approximately the half of the experimental points, chosen at random, have been plotted. The fulldrawn curve is calculated from the sets of β_j and ΔH°_j given in Tables 1 and 2.

The iodide system. In this case, only the first four mononuclear complexes were indicated by the potentiometric investigation. Even at the highest ligand concentrations such a set of complexes also fit the calorimetric data excellently. Within the larger errors that are unavoidably connected with values of β_j determined calorimetrically, the constants moreover agree very well with these found potentiometrically, Table 1. This applies even to the second complex, the concentration of which never exceeds 6 %. The value of β_2 found calorimetrically is, at least formally, hardly significant but it still agrees with that found potentiometrically. The results for the iodide system are collected in Tables 1 and 2 and Fig. 1.

The thiocyanate system. An excellent fit was obtained with the values of β_j determined potentiometrically for the first three mononuclear complexes. For this system, however, the function Δh_v did not allow any simultaneous determination of β_j and ΔH°_j. The precision of the constants obtained in this way was very poor (Table 1) and it was therefore decided to use only the potentiometrically determined set of β_j for the final calculation of ΔH°_j. The results are reported in Tables 1 and 2 and Figs. 1 and 2.

DISCUSSION

The emf measurements on the chloride [2,24] and bromide [2] systems indicate that the complex formation might extend beyond the fourth mononuclear complex, and that polynuclear complexes might be formed, especially in the chloride system. The calorimetric measurements do not bear this out. The most likely cause of this discrepancy is that, at high concentrations of chloride and bromide, activity changes take place and/or liquid junctions potentials change, influencing the emf's measured in a way that can formally be interpreted as a formation of higher complexes. Such phenomena have been observed in several instances, and also in the case of other chloride and bromide systems.[25,26] Calorimetric measurements need not be at all affected by a corresponding change of medium.

In the following, it seems therefore most reasonable to consider only the first four mononuclear complexes for all the halide systems. The existence and strength of these complexes have, on the other hand, been amply confirmed by the calorimetric measurements.

A most remarkable feature of all the halide systems is that the second complex has a very narrow range of existence in DMSO, as reflected by the small values of $-\Delta G^\circ_2$ relative to $-\Delta G^\circ_3$. The same effect, though less marked is also observed in water, Table 3. This has already been discussed in the preceding paper of this series where it was also pointed out that such a peculiarity generally indicates a change of structure, taking place mainly at a certain step of the complex formation.[2] For the cadmium halides, the change most probably involves a switch from an octahedral coordination in the solvated ion to a tetrahedral coordination in the tetrahalide complexes. The step of the main change is indicated by the peculiar trends of ΔS°_j and ΔH°_j of the consecutive complexes. As long as the complex formation only implies the substitution of a solvent molecule in the inner coordination sphere by a halide ion, a monotonous decrease of ΔS°_j is expected to take place between each step.[27] If, on the other hand, a switch from octahedral to tetrahedral coordination takes place, more solvent molecules are set free, resulting in a large increment of ΔS°_j. Simultaneously, the energy needed for desolvation increases which results in a more positive, or less negative, value of ΔH°_j. The interaction of these two changes results in the peculiarities in ΔG°_j, *i.e.* K_j, originally observed.[2]

In water, the values of ΔS°_3 are abnormally high for all the halide systems, indicating that the change of structure takes place mainly at the third step. At least for chloride and bro-

Table 3. Thermodynamics of cadmium 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 J mol^{-1} K^{-1}.

	DMSO				Water				
	1 M NH_4 ClO_4				3 M $NaClO_4$				1 M $NaClO_4$
	Cl^-	Br^-	I^-	SCN^-	Cl^-	Br^-	I^-	SCN^-	I^-
ΔG°_1	−18.4	−16.7	−12.5	−10.3	−9.0	−10.0	−11.9	−8.0	−10.7
ΔG°_2	−11.2	−10.9	−7.8	−5.2	−3.7	−3.3	−4.0	−4.8	−4.6
ΔG°_3	−14.7	−15.7	−16.8	−1.2	−1.0	−5.6	−12.2	−1.3	−9.6
ΔG°_4	−10.0	−9.5	−6.7			−2.1	−9.2	0.0	−7.6
ΔH°_1	−6.3	−3.9	2.4	−3.0	−0.4	−4.1	−9.5	−8.1	−10.2
ΔH°_2	15	17	27	−2.8	0.1	−2.4	−0.8	−7.2	−2.1
ΔH°_3	1	2	−5	4.2	7.7	7.2	−3.1	−6.6	−5.9
ΔH°_4	−12.2	−13	−9.5			1.3	−15.9	−4	−16.8
ΔS°_1	41	43	50	25	29	20	8	0	2
ΔS°_2	88	94	117	8	13	3	10	−8	8
ΔS°_3	53	59	40	18	29	43	31	−18	12
ΔS°_4	−7	−12	−10			11	−23	−15	−33
$\Delta H\beta_3$	10	15	24	−2	7	1	−13	−22	−18
$\Delta S\beta_3$	182	196	207	51	77	66	49	−26	22

mide, this is also corraborated by very positive values of ΔH°_3, Table 3. In DMSO, on the other hand, the values of ΔS°_2 and ΔH°_2 stand out as exceedingly high. In this solvent, therefore, the change of structure mainly takes place already at the second step.

As the solvent molecules must be considerably more crowded in the DMSO hexasolvate then in the hexahydrate, it is not surprising that a disrupture occurs at an earlier stage in DMSO than in water. The hydrate is likely to accomodate more halide ions, even in awkward positions, before the situation becomes impossible.

By means of X-ray diffraction, the hydrated cadmium(II) ion has recently been shown to be a regular octahedron in aqueous solution,[28,29] while CdI_4^{2-} is a regular tetrahedron.[29] In water, a change of coordination therefore certainly takes place, and the thermodynamics of the formation reactions indicate that this change preferably takes place at a certain step, *viz.* at the third one. In DMSO, like in water, a solid hexasolvate is formed.[1] The structure of this compound is still unknown, as well as that of the solvated ion in solution, but in all probability they are both octahedral. Also, the structures of the highest complexes formed, all of the formula CdL_4^{2-}, are probably tetrahedral. The peculiarities in ΔH°_j and ΔS°_j should therefore naturally be interpreted along the same lines as for aqueous solution.

Strikingly enough, the narrow range of existence of the second complex is caused by a change of coordination at the third step in water but at the second step in DMSO. The range of existence of a complex is conveniently expressed by the maximum molar ratio $(\alpha_j)_{max}$ that it reaches in equilibrium with its neighbours. For most systems where besides ML_j only ML_{j-1} and ML_{j+1} exist in appreciable amounts at $(\alpha_j)_{max}$, this quantity is well approximated by (cf. eqn. 18 of Ref. 30)

$$(\alpha_j)_{max} = 1/[1 + 2(K_{j+1}/K_j)^{\frac{1}{2}}] \qquad (4)$$

Thus, the range of existence of the jth complex is determined by the ratio between two consecutive equilibrium constants, *viz.* K_j for the formation of the complex from the preceding one, and K_{j+1} for its conversion into the succeeding one. Moreover, the range becomes narrower, *i.e.* $(\alpha_j)_{max}$ smaller, the smaller the ratio K_j/K_{j+1}.

The ratio K_j/K_{j+1} depends upon the corresponding changes of enthalpy and entropy according to

$$K_j/K_{j+1} = \exp\ (RT)^{-1}[\Delta H^\circ_{j+1} - \Delta H^\circ_j - T(\Delta S^\circ_{j+1} - \Delta S^\circ_j)] \qquad (5)$$

For the systems discussed K_2/K_3 is abnormally small. This may occur either because $\Delta H^\circ_2 \gg \Delta H^\circ_3$ or because $\Delta S^\circ_3 \gg \Delta S^\circ_2$, or because these conditions are both fulfilled at the same time. The condition for a ratio $K_2/K_3 < 1$ is evidently that $\Delta H^\circ_2 + T\Delta S^\circ_3 > \Delta H^\circ_3 + T\Delta S^\circ_2$.

In water, the low values of K_2/K_3 observed for the bromide and iodide systems are due to the high values of ΔS°_3 which are not compensated by commensurate increases in ΔH°_3. In DMSO, on the other hand, the low values of K_2/K_3 observed for all the halide systems are due to the very high values of ΔH°_2 relative to ΔH°_3, which are not compensated by the *per se* high value of ΔS°_2 relative to ΔS°_3.

At the coordination change, the gain of entropy thus dominates over the desolvation energy in aqueous solution which makes the complex mainly connected with the change, *i.e.* the third one, especially stable relative to its predecessor, *i.e.* K_2/K_3 becomes small. In DMSO, on the other hand, the desolvation energy dominates over the entropy gain which makes the complex mainly connected with the change, in this case the second one, especially unstable relative to its successor. Again K_2/K_3 becomes small, but for a different reason than in water.

An experimental consequence of the narrow range of existence of the second complex is that only the sums of the thermodynamic functions of the second and third steps can be very precisely determined, but not the individual functions, Table 2.

Another remarkable difference between the thermodynamics in aqueous and DMSO solution is that the entropy gains on complex formation are generally much higher in DMSO. This stands out very clearly from a comparison of the sums $\Delta S_{\beta_3} = \sum_{j=1}^{3} \Delta S^\circ_j$ which for both solvents include most of the gains due to desolvation, Table 3. The difference is not unexpected, however, in view of the higher degree of order that ought to prevail in water relative to DMSO, on account of the strong hydrogen bonds between the water molecules which have no counterpart in DMSO. On dehydration, the water molecules therefore move from a well-ordered hydrate shell to a fairly well-ordered bulk solvent, resulting in a relatively modest increase of entropy. On desolvation in DMSO, on the other hand, the solvent molecules move from a well-ordered solvate shell to a much less well-ordered bulk solvent, resulting in a much larger increase of entropy. The solvation of Cd^{2+} is moreover certainly stronger in DMSO than in water [31] which also contributes to the increased entropy gains in DMSO. The relative importance of the two factors considered is at present difficult to assess.

In water, $\Delta S^\circ_{\beta_3}$ decreases in the sequence $Cl^- > Br^- > I^-$, Table 3, as expected from the decrease of hydration [32] of the halide ions in the same sequence. In DMSO, on the other hand, ΔS_{β_3} increases in the sequence mentioned. The solvation of Cl^- is presumably weaker in DMSO than in water, and that of I^- stronger, which evidently acts in the direction observed.[31,33] Still, even if the differences between the solvation energies are much smaller in DMSO than in water, the sequence remains $Cl^- < Br^- < I^-$. It seems therefore not possible to account for the actual *reversal* of ΔS_{β_3} only by this factor.

Analogously, the total enthalpy change $\Delta H_{\beta_3} = \sum_{j=1}^{3} \Delta H_j$ decreases in water in the sequence $Cl^- > Br^- > I^-$, as expected from the decrease of the dehydration energies of the ligands in the same sequence.[32] In DMSO, on the other hand, ΔH_{β_3} increases in the order mentioned, as does ΔS_{β_3}. The reason must evidently be the same, though still obscure.

In both solvents, thiocyanate behaves very differently from the halides, Table 3. The entropy changes are all small, slightly positive in DMSO and slightly negative (or zero) in water. The decrease of entropy relative to the halides is certainly accounted for by the losses of vibrational and rotational entropy on coordination of the triatomic SCN^-. The lack of extraordinarily high values of ΔS°_j and ΔH°_j at any particular step might indicate that the coordination change presumably taking place also in this system is spread out fairly evenly over several steps.[27] Another possibility would be that the rather weakly coordinating thiocyanate ion does not bring about any coordination change. In DMSO, a change might conceivably still occur at the fourth step which has not been reached in the present measurements.

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