

## Thermodynamics of Complex Formation between Cadmium(II), Thiosemicarbazide and 4-Methylthiosemicarbazide

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

The enthalpy changes for the complex formation between  $\text{Cd}^{2+}$ , thiosemicarbazide and 4-methylthiosemicarbazide, respectively, in aqueous solution have been determined calorimetrically at 25.00 °C. From the changes of free energy calculated from the previously determined stability constants and from the enthalpy changes determined in this investigation, the changes of entropy have been calculated.

The variations in these thermodynamic functions during the consecutive complex formation are interpreted by a model, in which the coordination geometry around the central cadmium(II) ion is changed twice, so that the coordination number is six in the cadmium aqua ion, only four in the  $\text{CdL}_2^{2+}$  and  $\text{CdL}_2^{2+}$  species and six again in  $\text{CdL}_3^+$ .

The complex formation between  $\text{Cd}^{2+}$  and thiosemicarbazide in aqueous solution has been studied by several authors. From a polarographic investigation Toropova and Naimushina<sup>1</sup> found that the cadmium ion takes up a maximum of two ligands, while Christensen and Rasmussen<sup>2</sup> were able to detect a third complex from potentiometric measurements using a cadmium amalgam electrode. The third consecutive stability constant  $K_3$  was, however, an order of magnitude smaller than the preceding constants (370 and 135 for  $K_1$  and  $K_2$  respectively compared to *ca.* 15 for  $K_3$ ).

The present author has extended the work of Christensen and Rasmussen to include a series of

alkyl substituted thiosemicarbazides.<sup>3</sup> This investigation shows that the values of the consecutive stability constants are closely related to the electronegativity of the introduced substituent as far as  $K_1$  and  $K_2$  are concerned. Within the experimental uncertainty however,  $K_3$  is independent of the type and position of substituents. This unusual behaviour indeed calls for a further investigation. On the basis of the abnormally high value of  $K_2/K_3$ , Christensen and Rasmussen suggested<sup>2</sup> that a change in configuration around the central metal ion takes place from tetrahedral in the bis complex to octahedral in the tris complex. Since the hydrated cadmium ion in aqueous solution is known from X-ray scattering experiments to be six coordinated with octahedral configuration,<sup>4,5</sup> this suggestion implies that two such changes in coordination number and geometry take place during the complex formation. It has been the purpose of the present work to test this hypothesis with further experiments.

Although it is difficult to get definite information about the structure of labile complexes in solution, the results obtained from calorimetric measurements have often been of great value in such discussions.<sup>6,7</sup> From this type of experiment both the stepwise enthalpies of formation ( $\Delta H_n$ ) and the stability constants ( $K_n$ ) may be obtained simultaneously, the so called entropy titration method,<sup>8</sup> or  $\Delta H_n$  alone can be determined, provided that the stability constants are known from other sources. Once the stepwise formation constants and the enthalpies of formation have been determined, the

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free energy change  $\Delta G_n$  and the entropy of formation  $\Delta S_n$  are calculated from the relations (1) and (2):

$$\Delta G_n = -RT \log K_n \quad (1)$$

$$\Delta G_n = \Delta H_n - T\Delta S_n \quad (2)$$

## EXPERIMENTAL

**Chemicals.** Thiosemicarbazide (abbreviated Htsc) of analytical grade from BDH was recrystallized twice from water using charcoal to remove dark coloured impurities and once from 1:1 ethanol/water. 4-Methylthiosemicarbazide was prepared as described by Jensen *et al.*<sup>9</sup> from methylisocyanate and hydrazine and purified in the same way as the unsubstituted thiosemicarbazide. All other chemicals were commercial analytical grade reagents and were used without further purification. Stock solutions of cadmium nitrate were standardized by EDTA titrations.

**Apparatus.** The calorimeter used in this investigation was a titration calorimeter of the isothermal jacket type, described by Grenthe *et al.*<sup>10</sup>

**Procedure.** The experiments were performed as a series of titrations: 79.73 ml of the ligand solutions (4 different concentrations between 12 and 147 mM were used for Htsc and 11–67 mM for the methyl substituted ligand) were placed in the reaction vessel and titrated with CdNO<sub>3</sub> solution (50 and 220 mM). All solutions were adjusted to  $I=1.0$  with sodium nitrate and to pH=4.0 with HNO<sub>3</sub>. In every experiment between 1 and 3 ml of titrant was added. 8 different series of titrations were performed for each of the systems. Each titration consisted of between 6 and 11 additions of titrant. The detailed experimental results are available from the author upon request.

The experiments were corrected for heats of dilution; these were determined in separate experiments with only one of the reactants present.

Calibrations were done electrically and showed the heat equivalent as a linear function of the volume of titrant added.

Each titration series was done at least twice and the reproducibility was generally better than 0.06 J.

**Calculations** were performed by a computer program similar to the one described previously for determination of stability constants from potentiometric data.<sup>3</sup> The calculations were done on an IBM 370/165 computer at the computing center NEUCC at the Technical University of Denmark.

**Table 1.** Thermodynamic constants for the systems Cd<sup>2+</sup> thiosemicarbazide and 4-methylthiosemicarbazide at 25 °C in aqueous sodium nitrate solution with ionic strength 1.00. The free energies of formation are calculated from Ref. 3 and the enthalpies of formation from the present investigation. The entropy terms are calculated from expression (2). Calculated standard deviations in units of the least significant digit of the parameters are given in parentheses.

<i>n</i>	$\Delta G_n$ (kJ M <sup>-1</sup> )	$\Delta H_n$ (kJ M <sup>-1</sup> )	$\Delta S_n$ (J M <sup>-1</sup> K <sup>-1</sup> )
<b>Cd<sup>2+</sup>-thiosemicarbazide</b>			
1	-14.84(7)	-19.74(6)	-16.4(3)
2	-11.87(13)	-19.23(15)	-24.7(7)
3	-6.70(15)	-15.25(26)	-28.7(10)
<b>Cd<sup>2+</sup>-4-methylthiosemicarbazide</b>			
1	-15.67(9)	-19.85(7)	-14.0(4)
2	-13.36(13)	-20.79(16)	-24.9(7)
3	-6.94(34)	-15.55(37)	-28.9(17)

## RESULTS AND DISCUSSION

Table 1 collects the calculated values of free energy, enthalpy and entropy changes for the stepwise complex formation in the two investigated systems. It is noted that the enthalpy of formation is the driving force in the complex formation, while the entropy term is counteracting.

**Enthalpy contributions.** There are three main sources for the enthalpy change in the complex formation between a central ion and a ligand: Disruption of coordinated solvent from the central ion and from the ligand which will increase the enthalpy, and formation of bonds between the donor and the acceptor that leads to a decrease in enthalpy. The liberation of water molecules coordinated to the ligand and to the second coordination sphere of the cadmium complexes can be considered of minor importance since neither are strongly solvated. The breaking of bonds between cadmium and the water molecules in the inner coordination sphere as well as the formation of bonds between cadmium and the thiosemicarbazide ligands both gives important contributions to the enthalpy of the reaction. Since the Cd<sup>2+</sup> ion is a fairly soft acceptor and thiosemicarbazide a distinctly more soft donor than water, the net effect of the ligand exchange reaction is expected to be a considerable loss of enthalpy,<sup>11</sup> thus giving an exothermic reaction. It is seen from Table 1 that this is indeed the case for all steps in the reaction.

For interaction between soft acceptors and donors the enthalpy changes in consecutive steps in the complex formation are likely to be of about the same size as long as there is no significant change in the type of bond established between the ligands and the central atom.<sup>6</sup> If a change in the coordination number around the central atom does occur during the complex formation, a change in the type of bond between central atom and ligands is most likely to occur, thus giving rise to a variation of  $\Delta H$  for the various steps. When the change in coordination geometry takes place on uptake of one single ligand and not spread over several steps, the associated enthalpy is also likely to change abruptly at this step. From Table 1 it is noted that  $\Delta H_1$  and  $\Delta H_2$  are almost identical while  $\Delta H_3$  is smaller. This indicates that the first two ligands are bound in the same way to the metal ion and that a change in coordination geometry takes place on uptake of the third ligand.

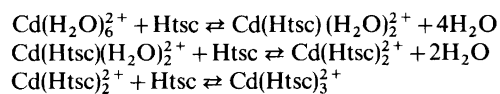
*Entropy contributions.* The changes in  $\Delta S$  that may be attributed to ligand exchange on a metal ion are the following: (1) Liberation of solvating molecules prior to coordination (giving a positive contribution to  $\Delta S$ ). (2) Removal of the ligand from the solution thereby allowing the solvent to arrange in a more ordered way (this will give a negative contribution to the entropy) and (3) (in case of polyatomic ligands): Loss of rotational and vibrational degrees of freedom due to complex formation; (this again gives a negative  $\Delta S$  contribution). The first of these terms is of only small importance for thiosemicarbazide since this molecule is not strongly solvated. Both of the two other terms are significant, however. Since thiosemicarbazide is a bulky ligand, it is considered very structure-breaking and the coordination of this polyatomic ligand is certainly followed by a significant decrease in degrees of freedom. The contribution to the entropy of formation coming from the ligand is thus expected to be strongly negative and moreover constant for all the consecutive steps.

In order to coordinate a ligand, the central ion must liberate solvent molecules from the coordination sphere, giving a positive contribution to the entropy term; the amount depends on the exact number of solvent molecules liberated.

From Table 1, it is noted that  $\Delta S$  is negative for all three steps in the complex formation, indication that the structure-breaking ability of the ligand and/or the loss of degrees of freedom by coordination are dominating the entropy term.

The variation of  $\Delta S_n$  between the various steps is attributed primarily to the contribution to the entropy term from the liberation of solvent molecules from the central metal ion. The cadmium aqua ion is only fairly weakly solvated and in consequence the main contribution to  $\Delta S$  from liberation of solvent is likely to be due to solvent molecules from the inner coordination sphere. Since the variation of entropy is  $|\Delta S_1| < |\Delta S_2| < |\Delta S_3|$ , less and less solvating molecules are liberated during the complex formation.

*Conclusions.* The variations in the enthalpy and entropy contributions to the free energy of complex formation are consistent with the following equilibria:



with an entropy contribution from the ligand of about  $-29 \text{ J M}^{-1} \text{ K}^{-1}$  and a contribution from liberation of solvated water of about  $+2 \text{ J M}^{-1} \text{ K}^{-1}$  per water molecule liberated. In this model the six coordinated octahedral cadmium hexaqua ion changes its coordination number of four with uptake of the first ligand while four solvent molecules are set free. The second ligand is bound in the same way as the first, thus  $\Delta H_1$  and  $\Delta H_2$  are close to the same value, two solvent molecules are liberated, giving half as great a contribution to  $\Delta S$  as the first step. With uptake of the third ligand the coordination number is once again increased to six, and this change in coordination geometry is reflected in a drop in  $\Delta H$  from  $\Delta H_2 \simeq 20$  to  $\Delta H_3 \simeq 15$ .

One single change in coordination number and geometry during the consecutive complex formation is observed in many systems,<sup>6</sup> the group 2B metal ions being an excellent example of acceptors showing this behaviour. Examples of more than one change in coordination number are numerous in the case of Hg(II) complexes but rare with Cd(II) as the central ion. Recently, however, this has been assumed in a polarographic investigation of the cadmium-imidazole system.<sup>12</sup>

The structure of a  $\text{Cd}(\text{Htsc})_2^{2+}$  ion in the crystalline state is known from the X-ray structure determination of bis(thiosemicarbazide)cadmium(II) sulfate.<sup>13</sup> In this complex, cadmium is six coordinated, with the two bidentate thiosemicarbazide ligands (nearly) in plane and two oxygen atoms from sulfate ions — bridging two complexes — as axial ligands.

This structure in the solid state is, however, not in contradiction with the result of the present investigation, which assumes a coordination number of only four for the  $\text{Cd}(\text{Htsc})_2^{2+}$  ion in solution. The coordination geometries of cadmium compounds in the solid state are known to be very much influenced by the packing forces in the crystal as well as the ability of the counterion to form bridges between two cadmium ions.<sup>1,3</sup> Both four and six coordinated cadmium(II) is found in the crystalline state and six coordination is often observed as a result of bridge formation in crystals.

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