

## Thermodynamics of the Formation of some Mercury(II) Amine Complexes in Dimethyl Sulfoxide

INGMAR PERSSON\* and BERNHARD SCHNEIDER\*\*

*Inorganic Chemistry 1, Chemical Center, University of Lund, P.O. Box 124, S-221 00 Lund, Sweden*

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### Abstract

The stabilities and the heats of formation of mercury(II) *n*-hexylamine, di-*n*-butylamine and piperidine complexes have been studied in dimethyl sulfoxide (DMSO) by means of potentiometric and calorimetric measurements. Three mononuclear complexes are formed with the secondary amines, and there the second complex is the strongest one; about ten times stronger than the first complex. This means that the first complex only reaches about 15% predominance. The two first complexes are formed in strongly exothermic reactions, while the entropy changes are negative. The third complexes are also formed in exothermic reactions, but the entropy terms are small and positive. In the mercury(II)–*n*-hexyl-amine system only the second complex has been established probably due to a very small  $K_1/K_2$  ratio. The different trends in the stabilities of amine complexes of silver(I) and mercury(II) in water and DMSO are discussed and explained on basis of different structures of the complexes in aqueous and DMSO solutions.

### Introduction

The thermodynamics of the formation of some mercury(II) amine complexes in the aprotic solvent dimethyl sulfoxide, DMSO, are reported in this paper. These and some other mercury(II) amine systems have previously been studied in aqueous solution [1–3]. Studies of mercury(II) and silver(I) phosphine complexes in DMSO [4–6] and pyridine [7, 8] have shown that the stabilities of these complexes are a function of some physical and chemical parameters such as dipole moment, basicity in aqueous solution and donor strength of the phosphine ligand [8]. This

is, however, not the case for the amines, there the basicity in water is almost identical for all simple amines [1–3]. Furthermore, there is no correlation between the basicity in water and donor properties towards mercury(II) for the amines [9].

The solvation of the mercury(II) and silver(I) ions is markedly stronger in DMSO than in water; the heats of solvation of the mercury(II) ion are  $-1845$  and  $-1921$  kJ mol<sup>-1</sup> in water and DMSO [10, 11], respectively, and the corresponding values for the silver(I) ion are  $-488$  and  $-539$  kJ mol<sup>-1</sup> [11, 12]. For a certain mercury(II) or silver(I) phosphine complex the stability decreases in the order water < DMSO < pyridine due to increasing solvation of the metal ions. This pattern is, however, not seen for the silver(I) amine complexes where these have almost identical stabilities in water and DMSO in spite of stronger solvation of the metal ion in DMSO. One can however assume that the amines are stronger solvated in water due to the ability to form hydrogen bonds. However, the difference in solvation of the metal ions in water and DMSO is certainly much larger than the difference in solvation of the amines [13].

### Experimental

#### Chemicals

DMSO was purified by refluxing over calcium hydride for several hours followed by distillation under reduced pressure (10 mm Hg) over calcium hydride (Fluka). The amines were refluxed over potassium hydroxide and then distilled at atmospheric pressure. Hg(ClO<sub>4</sub>)<sub>2</sub>·4DMSO was prepared as described previously [14]. The mercury(II) content was determined by EDTA titration [15].

#### Potentiometric Measurements

The potentiometric measurements were performed in a glove box with nitrogen atmosphere, and dried with phosphorus pentoxide. The set up and the procedure used are described elsewhere [16, 17]. The free mercury(II) concentration was determined by a mercury pool electrode. Mercury(II) must be

\*Present address: Department of Chemistry, Swedish University of Agricultural Sciences, P.O. Box 7015, S-75007 Uppsala, Sweden.

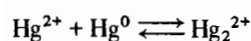
\*\*Present address: Department of Inorganic Chemistry, Technical University of Vienna, Getreidemarkt 9, A-1060 Vienna, Austria.

TABLE 1. Overall Stability Constants,  $\beta_j$  ( $M^{-1}$ ) for some Mercury(II) Amine Complexes in DMSO at 25 °C<sup>a</sup>

Ligand	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	C <sub>6</sub> H <sub>11</sub> NH	C <sub>6</sub> H <sub>13</sub> NH <sub>2</sub>
$\beta_1$	$(2.9 \pm 0.8) \times 10^4$	$(3.0 \pm 0.9) \times 10^5$	
$\beta_2$	$(1.2 \pm 0.2) \times 10^{10}$	$(8.4 \pm 1.2) \times 10^{11}$	$(2.7 \pm 0.3) \times 10^{13}$
$\beta_3$	$(4 \pm 2) \times 10^{11}$	$(3 \pm 1) \times 10^{13}$	
NP	102	88	44

<sup>a</sup>Ionic medium 0.1 M Et<sub>4</sub>NClO<sub>4</sub>. The limits of error refer to three standard deviations. NP denotes the number of e.m.f.s measured.

stabilized to such a degree that the reproporation reaction



does not occur [17]. This requirement is fulfilled for n-hexylamine, di-n-butylamine and piperidine, but not for triethylamine. Titrations with 20 mM constant mercury(II) concentration were performed and the ligand concentration varied in the range  $35 < C_L < 65$  mM. The numerical calculations of the stability constants have been performed by means of a modified version of the least-squares program EMK [16].

#### Calorimetric Measurements

The titration calorimeter used is described elsewhere [18]. The calorimeter vessel initially contained 40 ml mercury(II) solution with an initial concentration of 5, 10 or 20 mM. To this solution a 100 mM amine solution, totalling 20 ml, was added. If the complex formation was not completed, 20 ml was withdrawn, and the titration was continued. The heats of dilution of the Hg<sup>2+</sup> ion and of the amines were determined separately. The overall enthalpy changes,  $\Delta H_{\beta_j}^\circ$ , of the complex formation were calculated by the computer program KALORI [19], which minimizes the least-squares sum  $U = \Sigma(Q_{\text{calc}} - Q_{\text{exp}})^2$ . The stability constants obtained in the potentiometric measurements were used as fixed parameters in these calculations.

#### Results

Mercury(II) forms three mononuclear complexes with the secondary amines di-n-butylamine and piperidine in DMSO. For the primary amine n-hexylamine only the second mononuclear mercury(II) complex has been established in DMSO. The overall stability constants are given in Table 1. In the systems with secondary amines the second complex is markedly stronger than the other complexes,  $K_1/K_2 \approx 0.1$  and  $K_2/K_3 > 10^4$ . This means that the first complex does not reach more than 15% of the total mercury(II) concentration at  $\bar{n} = 1$ , see Fig. 1. The first complex in the mercury(II)–n-hexylamine

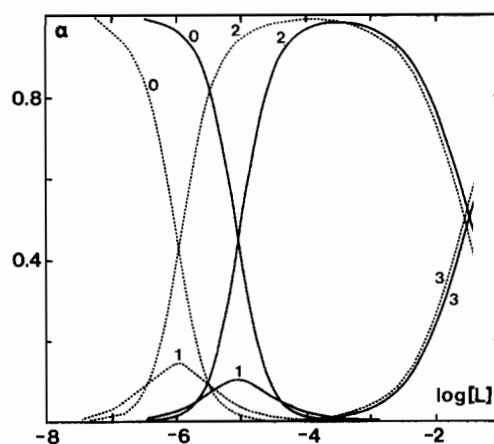


Fig. 1. Distribution of the species present in the mercury(II) piperidine (dashed lines) and di-n-butylamine (solid lines) systems in DMSO, as a function of free ligand concentration. Ionic medium 0.1 M Et<sub>4</sub>NClO<sub>4</sub>.

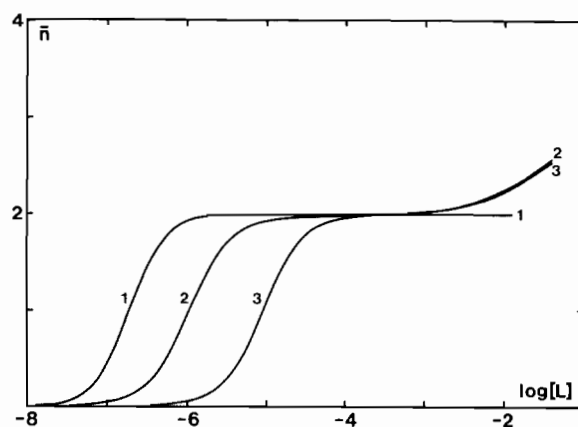


Fig. 2. The complex formation functions of the mercury(II) amine systems in DMSO, hexylamine (1), piperidine (2) and di-n-butylamine (3). Ionic medium 0.1 M Et<sub>4</sub>NClO<sub>4</sub>.

system has not been established in this study, most probably due to a very small  $K_1/K_2$  ratio. The complex formation functions are given in Fig. 2.

The overall enthalpy changes for the mercury(II)–di-n-butylamine and –piperidine systems are given in Table 2. All complexes are formed in exothermic

TABLE 2. Overall Enthalpy Changes,  $\Delta H_{\beta_j}^{\circ}$  ( $\text{kJ mol}^{-1}$ ) for the Formation of Mercury(II) Amine Complexes in DMSO at 25 °C<sup>a</sup>

Ligand	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	C <sub>6</sub> H <sub>11</sub> NH
$-\Delta H_{\beta_1}^{\circ}$	50.7 ± 5.2	65.1 ± 4.4
$-\Delta H_{\beta_2}^{\circ}$	98.1 ± 1.6	106.8 ± 1.7
$-\Delta H_{\beta_3}^{\circ}$	104.8 ± 4.5	109.4 ± 4.5
NP	85	98

<sup>a</sup>The limits of error refer to three standard deviations. NP denotes the number of aliquots added.

TABLE 3. Equilibrium Constants,  $K_j$  ( $\text{M}^{-1}$ ) and Thermodynamic Functions  $\Delta G_j^{\circ}$ ,  $\Delta H_j^{\circ}$  ( $\text{kJ mol}^{-1}$ ),  $\Delta S_j^{\circ}$  ( $\text{J mol}^{-1} \text{K}^{-1}$ ) for the Stepwise Complex Formation Between Mercury(II) and Amines in DMSO and Aqueous Solution at 25 °C<sup>a</sup>

Ligand	DMSO		Water
	(C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> NH	C <sub>6</sub> H <sub>11</sub> NH	C <sub>6</sub> H <sub>11</sub> NH <sup>b</sup>
$K_1$	$2.9 \times 10^4$	$3.0 \times 10^5$	$5.5 \times 10^8$
$K_2$	$4.3 \times 10^5$	$2.8 \times 10^6$	$5.0 \times 10^8$
$K_3$	33	37	
$K_1/K_2$	0.066	0.11	1.1
$K_2/K_3$	$1.3 \times 10^4$	$7.6 \times 10^4$	
$-\Delta G_1^{\circ}$	25.4	31.3	49.9
$-\Delta G_2^{\circ}$	32.2	36.8	49.7
$-\Delta G_3^{\circ}$	8.7	8.9	
$-\Delta H_1^{\circ}$	50.7	65.1	
$-\Delta H_2^{\circ}$	47.4	41.7	
$-\Delta H_3^{\circ}$	6.7	2.6	
$\Delta S_1^{\circ}$	-85	-113	
$\Delta S_2^{\circ}$	-51	-16	
$\Delta S_3^{\circ}$	+7	+21	
$-\Delta G_{\beta_3}^{\circ}$	66.2	77.0	
$-\Delta H_{\beta_3}^{\circ}$	104.8	109.4	
$\Delta S_{\beta_3}^{\circ}$	-129	-109	

<sup>a</sup>0.1 M Et<sub>4</sub>NClO<sub>4</sub> and 0.5 M C<sub>6</sub>H<sub>11</sub>H<sub>2</sub>NO<sub>3</sub> have been used as supporting electrolytes in DMSO and water, respectively. <sup>b</sup>Ref. 20.

reactions. The thermodynamic functions for the stepwise complex formation are given in Table 3, as well as corresponding values in water.

## Discussion

The effect of DMSO on the basicity of primary, secondary and tertiary amines with *p*-nitrophenol as reference acid in DMSO:benzene mixtures has been reported [21]. The basicity of the amines in this mixture follows the donor scales and the stabilities of the silver(I) and mercury(II) amines in DMSO

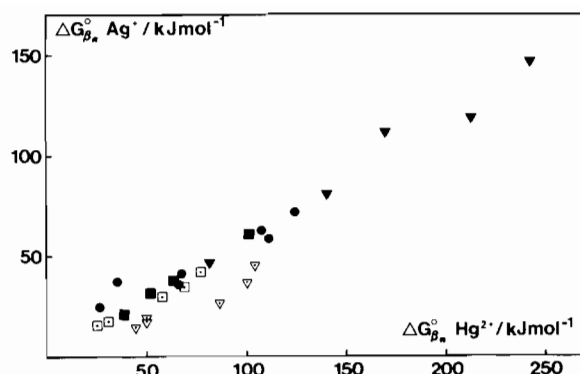


Fig. 3. The free energy relationship of the complex formation of silver(I) and mercury(II) amines (open symbols), and phosphines (filled symbols), in water (triangles) [1–4, 20, 25], DMSO (squares) [5, 6, 26] and pyridine (circles) [7, 8].

nically. The proton is stronger solvated in DMSO than in water [22]. DMSO has the ability to form stronger covalent interactions than water, which probably is the main reason for the stronger solvation of the proton in DMSO than in water [9, 23, 24].

The stabilities of the mercury(II) amine complexes are proportional to corresponding silver(I) complexes in DMSO. This proportionality is furthermore identical to corresponding phosphine complexes in water, DMSO and pyridine, Fig. 3; the slope of an assumed line in Fig. 3 is 1.7. This shows that the stabilities of the silver(I) and mercury(II) amine and phosphine complexes are a function of the electron donating ability of the ligand and of the solvation of the metal ion. The value of the second overall stability constant,  $\beta_2$ , of the silver(I)–triethylamine system in DMSO is about  $500 \text{ M}^{-1}$  [27] which shows that tertiary amines are weaker electron donors than the primary and secondary amines. From the relationship shown in Fig. 3 the  $\beta_2$  of the mercury(II)–triethylamine system in DMSO is estimated to be  $10^5$ – $10^6 \text{ M}^{-2}$ . This is in accordance with the experimental observations.

It is somewhat surprising that the stabilities of the silver(I) amine complexes are almost the same in water and DMSO, since silver(I) is markedly more strongly solvated in DMSO [11]. It might be explained by the fact that amines are more strongly solvated in water than in DMSO due to the ability of the amines to form hydrogen bonds. This seems, however, not to be the main reason, as the mercury(II)–amine systems in water do not fit into that pattern. Instead a plausible explanation is that the silver(I) amine complexes in aqueous and DMSO solutions have different structures. Only very few structures of silver(I) amine complexes or related complexes in solution have been reported. The structure of the silver(I) ammonia complex in concentrated aqueous ammonia solution,  $\text{Ag}(\text{NH}_3)_2^+$ , is

found to be linear [28], while the silver(I) hydrate is tetrahedral [29]. The  $\text{Ag}(\text{P}(\text{C}_6\text{H}_5)_3)_2^+$  and  $\text{Ag}(\text{Sb}(\text{C}_4\text{H}_9)_3)_2^+$  complexes in pyridine solution are tetrahedral with pyridines in the remaining positions [30, 31]; the pyridine solvate of silver(I) is also tetrahedral [31, 32]. It is therefore reasonable to assume that silver(I) amine complexes are linear in aqueous solution, while the tetrahedral structure remains in the more strongly solvating solvents DMSO and pyridine. Mercury(II) has a strong tendency to form linear or pseudolinear complexes in most solvents [20]. Any structural measurements of mercury(II) amine or phosphine complexes in solution have not been reported so far, but they are most probably linear or pseudolinear in the solvents discussed here. Thus for the  $\text{Hg}^{2+}$  complexes no differences in the desolvation mechanism in the solvents discussed have to be taken into account. The changes in stability constants can therefore be explained conclusively by changes in solvation of the  $\text{Hg}^{2+}$  ion and the ligands, the former contribution dominating. For the silver(I) complexes a change in the desolvation mechanism on going from water to stronger donor solvents has to be considered. When the second complex is formed, most probably no water molecules are coordinated to silver giving a linear complex. In DMSO there are probably two DMSO molecules coordinated to silver forming a tetrahedral complex. Thus the expected increase in stability due to weaker solvation of the  $\text{Ag}^+$  ion in water compared to DMSO is not seen due to the more rigorous desolvation.

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