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Interactions of d^{10} Metal Ions and Organic Sulfur Ligands in Non-aqueous Solvents. A Thermodynamic Study on the Complex Formation Between Mercury(II) and Thiolates in Pyridine, and Between Silver(I) and Various Sulfides in Pyridine and Dimethylsulfoxide

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Abstract

The complex formation between mercury(II) and selected sodium thiolates and corresponding thiols in dilute pyridine solution, and between silver(I) and selected organic sulfides in dilute pyridine and DMSO solutions, was investigated by electrochemical and calorimetric measurements. The stability constants and heats for the stepwise complex formation were determined, and the complex formation entropies were calculated from these. The results are in close agreement with the tendencies which have been found for the coordination behaviour of organic chalcogen ligands towards mercury(II) and silver(I) in other solvent systems, and the solid state.

Introduction

Organic compounds containing sulfur atoms with lone electron pairs have for a long time been known to form very stable complexes with the soft type d^{10} closed shell electron acceptors mercury(II) copper(I), silver(I) and gold(I). Compounds such as $Hg(SR)_2$, $Hg(SR)X$, $HgX_2 \cdot zSR_2$ and $MX \cdot zSR_2$, M = Cu, Ag, Au, X = Cl, Br, I, O_2CR, ClO_4 or BF_4; $z = 1-4$, R = alkyl or aryl group, have been extensively studied by means of preparation [1–8], spectroscopy [7–17] and crystallography [5–19].

These studies have shown that the coordination to the metal ion normally is linear, trigonal or tetrahedral when large and soft donors, like sulfur, coordinate to the mercury(II) or silver(I) atom. Since the metal sulfur bonds are very strong in thiolate complexes of the monovalent acceptors copper(I), silver(I) and gold(I) and of mercury(II), the solid neutral compounds MSR (M = Cu, Ag, Au) and $Hg(SR)_2$ are often polymers linked via M–S(R)–M bridges and, consequently, many of them are virtually insoluble in aqueous media and often poorly soluble in weakly donating organic solvents, e.g. alcohols and ketones. Similarly, but to a lower extent, is the case of the stability of the bond to be formed and the solubility of addition compounds between organic sulfides RSR′ and the above mentioned metal acceptors.

The stepwise complex formation of silver(I) and organic sulfides have been eagerly studied in aqueous solutions and water/alcohol mixtures [23–30]. In most of these systems, the consecutive formation of 2–4 complexes has been reported, suggesting that the coordination geometries around the central metal ion is linear, trigonal-planar, or tetrahedral. On the other hand, only a few complex formation studies have been performed with mercury(II) and the same type of ligands and solvents [20–28]. This is mainly because organic sulfides and even their Ag(I) and mercury(II) complexes have very low solubility in aqueous solution. In most of the previous investigations, the solubility of the sulfides and of their heavy metal complexes was increased by introduction of one or several polar groups, such as –OH, $-SO_3^-$, $-CO_2H$, or $-NH_3^+$, to the carbon chains bonded to sulfur [23–29]. The silver thiolates AgSR exhibit poor solubility even in solvents that are relatively strong donors to mercury(II) and silver(I), e.g. amines and pyridines. On the other hand, the mercuric thiolates $Hg(SR)_2$ and the silver(I) and mercury(II) complexes with organic sulfides show sufficient solubility in these solvents to allow the investigation of complex formation without introduction of any potentially concurring polar groups on the ligands.

The purpose of this work was to examine the stepwise complex formation between some selected organic sulfides and silver(I) and mercury(II) in pyridine and DMSO solution, and the complex formation between two selected sodium thiolates and corresponding thiols and mercury(II) in pyridine, by electrochemical and calorimetrical measurements. Ligands such as di-n-butylsulfide, diphenylsulfide, tetrahydrothiophene, 1-butanethiol, thiophenol, and the sodium salts of the latter two, were chosen.

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Experimental

Chemicals

$Hg(ClO_4)_2 \cdot 4(CH_3)_2SO$ and $Hg(C_5H_5N)_2(ClO_4)_2$ were used as mercury(II) sources and were prepared and analyzed as described elsewhere [31–33]. Anhydrous silver(I) perchlorate was used as a source of silver(I). All sulfides and thiols were purified by distillation and stored under dry nitrogen in dark vessels. The distillations of diphenylsulfide and thiophenol were performed *in vacuo*, the other ligands were distilled in a stream of dry nitrogen at atmospheric pressure. Sodium thiophenolate was prepared from thiophenol and sodium hydroxide in ethanol. Sodium thio-n-butylate was prepared in absolute alcohol from 1-butanethiol and metallic sodium under nitrogen. The white solid products were obtained by boiling off the ethanol under nitrogen atmosphere. The sodium thiolates, and all pyridine solutions prepared from them, were analyzed according to previously described methods [34]. Whereby the analysis of solutions was repeated twice a day during storage (see below). DMSO was purified and stored as described previously [35]. Pyridine was purified by refluxing over potassium hydroxide for two hours, followed by distillation over potassium hydroxide.

Reactions with Thiols and Thiolates

Stock pyridine solutions containing thiols and thiolates decompose, probably due to air oxidation. Disulfides or sulfonates are most probably formed at the oxidation. The decomposition reactions are, however, slow enough to allow electrochemical and calorimetric measurements as they were performed in this work.

Choice of Media

1.0 M ammonium perchlorate and 0.1 M tetraethylammonium perchlorate were used as supporting electrolyte in DMSO and pyridine, respectively.

Potentiometric Measurements

Metallic mercury reduces the solvated mercury(II) ion according to $Hg(l) + Hg^{2+} \rightleftharpoons Hg_2^{2+}$. The reproportionation constant $K_R = [Hg_2^{2+}][Hg^{2+}]^{-1}$ has previously been determined to 24.0(2.0) in DMSO with 1.0 M NH_4ClO_4 as ionic medium [36] and to 0.171(0.005) in pyridine with 0.1 M Et_4NClO_4 as supporting electrolyte [33]. The mercury/mercury(II) electrode can therefore only be used in the presence of ligands stabilizing mercury(II) over mercury(I). Fortunately this is the case for the studied thiolate ligands; no appreciable reproportionation was found in pyridine for the thiol and thiolate systems at $\bar{n} > 1.5$.

This implies that the stepwise stability constants K_j can be determined accurately by potentiometric measurements. To ensure that no solutions containing non-stabilized mercury(II) were introduced the mercury electrode compartment initially contained solutions of mercury(II) perchlorate and the studied ligand in a C_L/C_M ratio between 4 and 6 for thiol and thiolates, and in a C_L/C_M ratio of about 50 for the thioethers. To these solutions, aliquots of a mercury(II) perchlorate solution of the same concentration as in the electrode vessel, were added. The mercury(II) concentration was thus constant during the titrations. Titrations with C_M = 5, 10 and 20 mM were performed, with the ligand concentration ranging from 13 to 66 mM. A silver electrode, with a silver(I) concentration of 10 mM, was used as reference electrode.

In the silver systems, where there was no fear of reproportionation, silver perchlorate solutions with an initial concentration, C_M, ranging between 3–20 mM, were directly titrated with thioether solutions with an initial ligand concentration C_L between 50 and 600 mM. Pieces of thick silver foil were used as electrodes and the reference cell contained from the beginning a silver solution of the same concentration as in the reaction vessel.

To exclude moisture and to decrease the oxygen concentration, all titrations were performed in a glove box. In addition, dry nitrogen, which has passed through a couple of bottles containing solvent and supporting electrolyte, was bubbled through the electrode solutions throughout the titrations.

Calorimetric Measurements

The calorimeter and the procedure used have been described previously [37]. The initial solutions, of 40–80 ml volume, had mercury(II) concentrations ranging from 3.0 to 16.0 mM. To these solutions, aliquots of ligand solution were added, a total of 20 ml in each titration series. If the complex formation was not completed, 20 ml were then withdrawn from the calorimeter vessel and the titration was continued. This procedure was repeated until the complex formation was completed. Heats of dilution were determined for the mercury(II) ion and for the ligands. The heats of dilution of the ligands were especially important because of the feared air oxidation of thiols and thiolates in pyridine.

Following the same routine, calorimetric titrations on the complex formation reactions of the silver(I)–THT system in DMSO were performed.

Calculations

The emfs measured during the potentiometric titrations were used for calculation of the complex stability constants β_j by a computer program. Two different versions of this program were necessary. The version EMK [38] was applied for data of silver(I) systems where all the emfs needed to be corrected for dilution of the metal in solution according to Nernst's law. In the case of the mercury(I) systems no such dilution took place during the measurement.

Here the version EMKBAK [38], without this correction, was used. The obtained calorimetric data were corrected for heat of dilution and from these corrected values the enthalpy changes have been calculated by the computer program KALORI [39]. The stability constants β_j obtained from the potentiometric measurements were introduced as a fixed parameter in the calculations of the enthalpy changes.

Warning: Great caution must be exercised when handling DMSO solutions containing mercury salts because of the skin-penetrating properties of DMSO [40, 41]. Moreover, the ligands and ligand solutions must be kept under nitrogen in closed vessels not only because of their sensitivity to moisture and oxygen, but also because of their smell.

Results

In the silver(I) systems, no complex formation could be proved to have taken place with di-n-butylsulfide in either DMSO or pyridine, and with diphenylsulfide in pyridine. The formation of one weak mononuclear complex was found with diphenylsulfide in DMSO, and with THT in pyridine. Only one system, Ag^+–THT in DMSO, shows the formation of two weak mononuclear complexes, $Ag(THT)^+$ and $Ag(THT)_2{}^+$. The complex formation constants β_j and the free energy changes ΔG_j° are given in Table I. In the case of the system Ag^+–THT in DMSO, the determination of ΔH_j° from calorimetry allowed the calculation of the complex formation entropies ΔS_j° ($j = 1, 2$), which are included in this Table. The complex formation functions of the silver(I) complexes formed with THT and diphenylsulfide in DMSO are shown in Fig. 1. The complex formation function between silver(I) and THT in pyridine is very similar to that of silver(I) and diphenylsulfide in DMSO, and is therefore not shown here. The complex distribution function for the system Ag^+–THT in DMSO is given in Fig. 2.

TABLE I. Overall Stability (β_j (M^{-j})) and Stepwise Changes in Free Energy (ΔG_j (kJ mol^{-1})) of the Silver(I) Tetrahydrothiophene System in Pyridine and DMSO and the Silver(I) Diphenylsulfide System in DMSO, and Thermodynamic Functions [ΔH_j° (kJ mol^{-1}), ΔS_j° (J mol^{-1} K^{-1})] of Silver(I) Tetrahydrothiophene System in DMSO at 25 °C. Medium 0.1 M Et_4NClO_4 in Pyridine and 1.0 M NH_4ClO_4 in DMSO. The Limits of Error Refer to Three Standard Deviations

Ligand	Pyridine, 0.1 M Et_4NClO_4	DMSO, 0.1 M NH_4ClO_4	
	THT	THT	Ph_2S
β_1	0.89 ± 0.04	17.5 ± 2.6	3.0 ± 0.2
β_2		536 ± 30	
$-\Delta G_1^\circ$	−0.43	7.1	2.7
$-\Delta G_2^\circ$		8.5	
$-\Delta H_1^\circ$		44.4	
$-\Delta H_2^\circ$		−4.0	
ΔS_1°		−125	
ΔS_1°		−42	
$-\Delta G_{\beta 2}^\circ$		15.6	
$-\Delta H_{\beta 2}^\circ$		40.4	
$\Delta S_{\beta 2}^\circ$		−83	

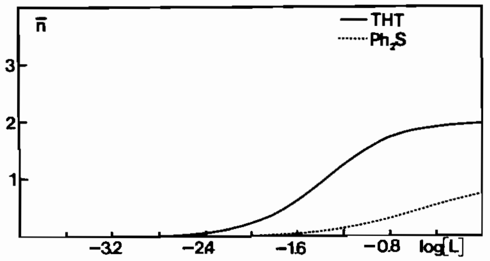

Fig. 1. Complex formation curves of the silver(I) tetrahydrothiophene (THT) and diphenylsulfide (Ph_2S) system.

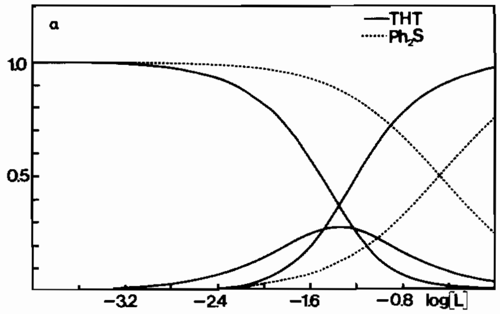

Fig. 2. Distribution of silver(I) tetrahydrothiophene and diphenylsulfide (Ph_2S) complexes in DMSO.

Furthermore, no complex formation between mercury(II) and thioethers has been proved in either DMSO or pyridine by potentiometric or calorimetric techniques. It is however possible that very weak complex formation occurs which cannot be discovered by the potentiometric technique which has to be used on these systems. Mercury(II) forms three strong complexes with thiolates in pyridine. In pyridine solution, the thiols will lose the proton, which is bonded to sulfur, to pyridine and a pyridinium ion is formed upon complex formation with mercury(II). The same complexes are thus formed independently of whether thiol or thiolate is used as the ligand.

The overall stability constants, β_j, calculated from the potentiometric data in pyridine are summarized in Table II. The complex formation and complex distribution functions of the mercury(II) complexes formed with the sodium thiolates are given in Figs. 3 and 4, respectively. The analogous functions from complex formation between mercury(II) and the free thiols are, in fact, so similar to those for the sodium thiolates that they need not be shown in an additional figure.

TABLE II. Overall Stability Constants (β_j (M^{-j})) of Mercury(II) Thiol and Thiolate Complexes in Pyridine at 25 °C. Medium 0.1 M Et_4NClO_4. The Limits of Error Refer to Three Standard Deviations. NP Denotes the Number of Observations for Each System

Ligand	PhS^-	PhSH	BuS^-	BuSH
β_1	$(5.28 \pm 0.46) \times 10^{10}$	$(2.63 \pm 0.28) \times 10^{10}$	$(5.98 \pm 0.65) \times 10^{9}$	$(4.89 \pm 0.34) \times 10^{9}$
β_2	$(4.79 \pm 0.99) \times 10^{19}$	$(1.93 \pm 0.40) \times 10^{18}$	$(5.18 \pm 1.51) \times 10^{16}$	$(2.94 \pm 0.78) \times 10^{16}$
β_3	$(3.43 \pm 0.55) \times 10^{28}$	$(7.66 \pm 1.62) \times 10^{25}$	$(2.04 \pm 0.57) \times 10^{23}$	$(1.75 \pm 0.31) \times 10^{23}$
NP	185	94	96	88

TABLE III. Overall Enthalpy Changes ($\Delta H^\circ_{\beta j}$ (kJ mol^{-1})) for the Formation of Mercury(II) Thiol and Thiolate Complexes in Pyridine at 25 °C. Medium 0.1 M Et_4NClO_4. The limits of Error Refer to Three Standard Deviations; NP Denotes the Number of Aliquots Added for Each System

Ligand	PhS^-	PhSH	BuS^-	BuSH
$-\Delta H^\circ_{\beta 1}$	60.8 ± 1.1	65.4 ± 0.9	73.1 ± 4.5	65.2 ± 2.4
$-\Delta H^\circ_{\beta 2}$	115.1 ± 2.4	124.7 ± 1.8	112.3 ± 11.9	97.5 ± 5.6
$-\Delta H^\circ_{\beta 3}$	163.6 ± 1.9	178.2 ± 1.6	177.9 ± 8.5	149.8 ± 4.2
NP	22	54	51	76

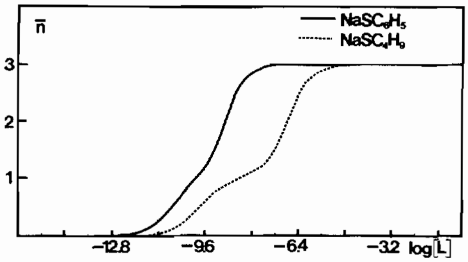

Fig. 3. Complex formation curves of the mercury(II) 1-butanethiolate and thiophenolate systems in pyridine.

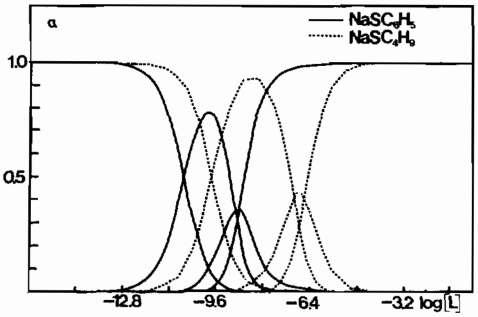

Fig. 4. Distribution of mercury(II) 1-butanethiolate and thiophenolate complexes in pyridine.

The overall enthalpy changes, $\Delta H^\circ_{\beta j}$, calculated from calorimetric data in pyridine are summarized in Table III. From the obtained β_j values, the stepwise stability constants K_j and the standard free energy changes ΔG_j° are calculated for each consecutive step. The stepwise enthalpy changes ΔH_j° are calculated from the overall enthalpy changes $\Delta H^\circ_{\beta j}$. The stepwise entropy changes ΔS_j° are obtained by combining the ΔG_j° and ΔH_j° values. The thermodynamic functions for the stepwise formation of mercury(II) thiol and thiolate complexes in pyridine are summarized in Table IV.

TABLE IV. Equilibrium Constants (K_j (M^{-1})) and Thermodynamic Functions ΔG_j°, ΔH_j° (kJ mol^{-1}); ΔS_j° (J mol^{-1} K^{-1}) for the stepwise Formation of Mercury(II) Thiolate and Thiol Complexes in Pyridine at 25 °C. Medium 0.1 M Et_4-$NClO_4$.

Ligand	PhS^-	PhSH	BuS^-	BuSH
$\log K_1$	10.72	10.42	9.77	9.69
$\log K_2$	8.96	7.87	6.94	6.78
$\log K_3$	8.86	7.60	6.60	6.77
K_1/K_2	58.1	357	691	813
K_2/K_3	1.3	1.9	2.2	1.0
$-\Delta G_1^\circ$	61.2	59.5	55.8	55.3
$-\Delta G_2^\circ$	51.1	44.9	39.6	38.7
$-\Delta G_3^\circ$	50.5	43.4	37.7	38.7
$-\Delta H_1^\circ$	60.8	65.4	73.1	65.2
$-\Delta H_2^\circ$	54.4	59.3	39.2	32.3
$-\Delta H_3^\circ$	48.5	53.5	65.6	52.3
ΔS_1°	+2	−20	−58	−33
ΔS_2°	−11	−48	+1	+21
ΔS_3°	+7	−37	−94	−46
$-\Delta G^\circ_{\beta 3}$	162.9	147.7	133.0	132.7
$-\Delta H^\circ_{\beta 3}$	163.6	178.2	177.9	149.8
$\Delta S^\circ_{\beta 3}$	−2	−102	−151	−57

Discussion

No complex formation between mercury(II) and thioethers, tetrahydrothiophene, diphenylsuflide and di-n-butylsulfide has been established in neither DMSO nor pyridine. On the other hand, the formation of two or more fairly strong mercury(II) thioether complexes have been shown to take place in aqueous and alcoholic solutions [21–28].

Studies of the donor properties of a large number of solvents to mercury(II) halides have shown that the thioethers are only slightly stronger donors than

DMSO and pyridine, while water is a markedly weaker donor than the thioethers [42, 43]. It is therefore reasonable that the larger activity of the solvent compensates for the somewhat stronger donor properties of the thioethers in the case of DMSO and pyridine, and no or only weak complex formation takes place. In aqueous solution the water activity cannot compensate for the large difference in donor property, and consequently mercury(II) thioether complexes are formed.

A similar tendency is obvious from the measurements on the silver(I) systems. The stronger donor pyridine manages to suppress complex formation between Ag^+ and two of the sulfides, while the weaker donor DMSO can bring about the same effect for just one of them. All three ligands, however, are known to form insoluble addition compounds when they are added to concentrated silver(I) solutions in water or water–alcohol mixtures [44].

Three very strong mercury(II) thiolate complexes are formed in pyridine. There are no indications of a fourth complex in any of the studied systems. The complex distribution follows an unusual pattern for mercury(II) complexes, where the second complex normally is strongly predominating. In these systems the first complex is very strongly predominating, while the second complex is suppressed. In pyridine, the second complexes never exceed 45% predominance, see Fig. 2 and the K_2/K_3 ratios in Table IV. The extraordinary stability of the mercury(II) thiolate complexes is shown by the formation of the final third complex, which is completed already at free ligand concentrations lower than 10 μM. No mercury(II) thiol complexes are formed in pyridine due to the fairly strong basicity of pyridine. This means that the following equilibrium is established far to the right

$$R(H)S{-}Hg^{2+} + py \rightleftharpoons R{-}S{-}Hg^{+} + py{-}H^{+}$$

It is surprising that the mercury(II) thiophenolate complexes are stronger than the corresponding thiobutylate complexes. One possible explanation might be that the thiobutylate ion is a bulkier ligand than the thiophenolate ion. If the coordinated ligands can come in contact with each other, the complex will be thermodynamically destabilized.

The very strong complex formation between mercury(II) and thiolates is followed by very negative enthalpy changes, see Table III. The enthalpy changes are indeed so negative for all steps that the stepwise entropy changes are slightly negative with a few exceptions. The very negative enthalpy changes indicate that very strong Hg–S bonds, with a high degree of covalency, are established at the formation of all mercury(II) thiolate complexes.

Structure determinations of the $Hg(SBu)_3^-$ and $Hg(SPh)_3^-$ in pyridine solution have shown that mercury(II) is trigonally coordinating the three thiolate ligands [45]. The mercury(II) pyridine solvate is six-coordinated in solution [46]. This means that one or several coordination switches take place during the consecutive complex formation.

Acknowledgements

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