

CONTRIBUTION FROM THE ISTITUTO DI CHIMICA FISICA E SPETTROSCOPIA,  
UNIVERSITÀ DI BOLOGNA, 40136 BOLOGNA, ITALY

## Dissociation and Structure of Addition Compounds between Thioethers and Mercury(II) Chloride

BY P. BISCARINI,\* L. FUSINA, AND G. D. NIVELLINI

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The reactivity of compounds between aliphatic thioethers and mercury(II) chloride,  $R^1R^2S \cdot nHgCl_2$  ( $n = 1, 1.5, 2$ ), was investigated, molecular weight and conductivity measurements were carried out, and ultraviolet spectra were recorded. A strong dissociation in solution was evidenced. It is suggested that the mercury(II) chloride derivatives of aliphatic thioethers should be classified as addition compounds,  $R^1R^2S \cdot nHgCl_2$ , and not as sulfonium salts,  $[R^1R^2SHgCl]^+Cl^-$ . A mechanism of adduct formation consistent with low stability in solution and other experimental results is proposed.

In a previous investigation<sup>1</sup> infrared spectra of adducts between aliphatic thioethers and mercury(II) chloride were analyzed and the results rationalized in terms of a correlation with the crystal structure. No evidence was found to corroborate the existence of ionic species postulated by Bränden<sup>2</sup> in the crystalline state. His hypothesis is based on the presence of a Hg-Cl bond 2.7 Å long in  $(C_2H_5)_2S \cdot 2HgCl_2$  and 2.62 Å in  $C_4H_9S \cdot HgCl_2$ , and the author, pointing out that the linear Cl-Hg-Cl unit does not exist in these adducts, states that sulfur forms a covalent bond with mercury. Consequently Hg-S is a strong bond, and, in contrast with other authors,<sup>3,4</sup> these compounds are considered "substitution" rather than "addition" compounds and represented as sulfonium salts, *i.e.*,  $[ClHgS(C_2H_5)_2]^+Cl^-$  and  $[ClHgSC_4H_9]^+Cl^-$ . In this case these compounds should have very interesting chemical and physical properties different from those of compounds that mercury(II) chloride forms with other ligands as pyridine, dioxane, and triphenylarsenic oxide and that are considered addition compounds.<sup>2,5,6</sup> Recently the structural parameters of  $[(C_6H_5)_3PSe \cdot HgCl_2]_2$  were reported.<sup>7</sup> They are very similar to those obtained by Bränden<sup>2</sup> for  $[C_4H_9S \cdot HgCl_2]_2$ , but the conclusions reached are different. The triphenylphosphine selenide complex is in fact defined as an addition compound and considered to consist of discrete dimeric chlorine-bridged molecules with the mercury atom in a distorted tetrahedral configuration.

The situation for mercury(II) chloride-thioether complexes is thus far from being established. The aim of this work is to study their behavior in solution in order to obtain information on the strength of the sulfur-metal bond, to clarify if they should be considered either addition or substitution compounds, and to explain the reasons of their behavior.

### Experimental Section

**Preparation.**—Thioethers and addition compounds with mercury(II) chloride were prepared as described previously,<sup>1</sup> with the exception of the di-*tert*-butyl thioether derivative. By adding di-*tert*-butyl thioether to a cold ethanol solution of mercury(II) chloride a white crystalline precipitate separates im-

mediately. Analyses correspond to those expected for the di-*tert*-butyl thioether-mercury(II) chloride 1:1 complex,  $[(tert-C_4H_9)_2S \cdot HgCl_2]_2$ . *Anal.* Calcd for  $C_8H_{18}Cl_2HgS$ : C, 23.0; H, 4.55; S, 7.65; Hg, 48.0. Found: C, 22.1; H, 5.1; S, 7.4; Hg, 47.85. This mole ratio is confirmed by the infrared spectrum that shows a strong band at 288  $cm^{-1}$  due to the  $\nu(S-HgCl_2)$  vibration, consistent with the spectroscopic behavior of 1:1 adducts of thioethers with mercury(II) chloride.<sup>1</sup> The melting point could not be determined because the compound decomposes. Also, its crystallization is impossible because it decomposes on warming the ethanol solution, where it is slightly soluble, to mercury sulfide chloride,  $2HgS \cdot HgCl_2$ .<sup>8</sup> *Anal.* Calcd for  $Hg_3S_2Cl_2$ : Hg, 81.65; S, 8.7. Found: Hg, 79.0; S, 8.55. By warming  $[(tert-C_4H_9)_2S \cdot HgCl_2]_2$  suspended in  $CCl_4$ , mercury sulfide chloride separates, while *tert*-butyl chloride and di-*tert*-butyl thioether were identified in the solution by nmr ( $CCl_4$ ,  $(CH_3)_4Si$ ): two singlets are observed at  $\delta$  1.59 and 1.39 ppm, respectively.

**Decomposition.**—Addition compounds were decomposed by adding to their ethanol solution (a) diluted hydrochloric acid or solutions of alkali halides, (b) sodium hydroxide solution, (c) diluted ammonia. By distillation in the vapor stream the thioether was separated from the solution of the complex. By adding (b) or (c) a precipitate of mercury(II) oxide or ammonobasic mercury(II) chloride was obtained, respectively.

**Oxidation.**—To an ethanol solution of the addition compound was added a solution of hydrogen peroxide and the reaction followed by iodometric titration. The solvent was evaporated and the residue identified through its infrared absorption as the corresponding sulfoxide complexed with mercury(II) chloride. These new complexes were isolated and identified.<sup>9</sup>

**Spectra.**—Ultraviolet spectra were recorded in ethanol distilled from magnesium and iodine, with a Cary spectrophotometer between 3000 and 2000 Å, with 1-cm cells. Infrared spectra were recorded as described previously.<sup>1</sup>

**Molecular Weights.**—These were determined cryoscopically in *tert*-butyl alcohol and osmotically in absolute and 95% ethanol. The cryoscopic procedure gave 147 as the molecular weight of camphor (theoretical 152). The average of several measurements on solvent and solution was always taken. Osmotic measurements were made with a Mechrolab 302b vapor pressure osmometer by using an injector with glass needles and avoiding any contact between metal and solutions thermostated 15 or 20 min at 37°. Benzil was used as the standard. The method applied to bromocamphor and cinchonidine yielded molecular weights of 233–231 (theoretical 231.0) and 291–305 (theoretical 294.4), respectively. The molecular weight of mercury(II) chloride was obtained by averaging the results of several sets of measurements (concentration in the range 0.01–0.20 *M*). The values were extrapolated to infinite dilution.

**Conductivity Measurements.**—These were performed at  $25 \pm 0.1^\circ$  (constant of cell 0.05  $cm^{-1}$ ) in absolute ethanol distilled from  $CaO$ .

### Results and Discussion

The reactions of mercury(II) chloride adducts with halogen ions, sodium hydroxide, or ammonia and the

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TABLE I  
MOLAR CONDUCTIVITIES IN ABSOLUTE ETHANOL AT 25 ± 0.1° AND MOLECULAR WEIGHTS OF THIOETHER-MERCURY(II) CHLORIDE ADDUCTS DETERMINED OSMOTICALLY IN ABSOLUTE ETHANOL AT 37°

Compound	Range of molar concn (×10 <sup>3</sup> )	Mol wt		Theoretical mol wt for a complete molecular dissociation	Min dissociation degree, α, %	Molar conductivity, mhos cm <sup>2</sup> (concn 3-7.5 × 10 <sup>-4</sup> M)
		Calcd	Found			
2(CH <sub>3</sub> ) <sub>2</sub> S·3HgCl <sub>2</sub>	4.9-8.8	938.8	338	187.7	44.4	...
2CH <sub>3</sub> (C <sub>2</sub> H <sub>5</sub> )S·3HgCl <sub>2</sub>	4.5-7.0	966.8	327	193.3	48.9	...
2(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S·3HgCl <sub>2</sub>	4.0-8.7	994.9	342	198.9	47.5	...
(C <sub>2</sub> H <sub>5</sub> ) <sub>2</sub> S·2HgCl <sub>2</sub>	7.7-13.1	633.2	321	216.6	48.6	1.1
CH <sub>3</sub> ( <i>n</i> -C <sub>3</sub> H <sub>7</sub> )S·2HgCl <sub>2</sub>	6.9-14.1	683.2	309	216.6	52.4	1.0
[( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> S·HgCl <sub>2</sub> ] <sub>2</sub>	5.2-10.8	779.4	385	194.8	34.1	...
( <i>n</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> S·2HgCl <sub>2</sub>	6.3-11.7	661.3	318	220.4	53.9	1.3
[( <i>i</i> -C <sub>3</sub> H <sub>7</sub> ) <sub>2</sub> S·HgCl <sub>2</sub> ] <sub>2</sub>	1.1-2.9	779.4	399	194.8	31.7	2.5
CH <sub>3</sub> ( <i>n</i> -C <sub>4</sub> H <sub>9</sub> )S·2HgCl <sub>2</sub>	6.5-14.1	647.2	322	215.7	50.5	1.0
( <i>n</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S·2HgCl <sub>2</sub>	6.5-12.8	688.4	300	229.4	64.7	1.5
[CH <sub>3</sub> ( <i>tert</i> -C <sub>4</sub> H <sub>9</sub> )S·HgCl <sub>2</sub> ] <sub>2</sub>	1.4-8.5	751.4	363	187.8	35.6	2.5
[( <i>tert</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S·HgCl <sub>2</sub> ] <sub>2</sub>	4.0-11.0	825.6	338	208.9	48.1	...
[( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S·HgCl <sub>2</sub> ] <sub>2</sub>	0.6-10.8	825.6	353	208.9	41.0	2.3
( <i>i</i> -C <sub>4</sub> H <sub>9</sub> ) <sub>2</sub> S·2HgCl <sub>2</sub>	6.2-12.7	688.4	303	229.4	63.6	...
( <i>n</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> S·2HgCl <sub>2</sub>	5.7-12.9	717.4	271	239.1	82.9	1.5
( <i>i</i> -C <sub>6</sub> H <sub>11</sub> ) <sub>2</sub> S·2HgCl <sub>2</sub>	6.0-11.3	717.4	279	239.1	78.5	1.0
HgCl <sub>2</sub>	10.0-200	271.5	283	...	...	0.9
LiCl	...	...	...	...	...	22.4 <sup>a</sup>

<sup>a</sup> Concentration 98.0 × 10<sup>-4</sup> M.

oxidation by hydrogen peroxide<sup>9,10</sup> suggest the existence in solution of the free components thioether and mercury(II) chloride, originating from partial or complete dissociation of the compounds by the solvent.

Molar conductivities (concentration ≈ 10<sup>-3</sup> M) in the range 1.0-2.5 mhos cm<sup>2</sup> mol<sup>-1</sup> were measured for thioether adducts. The values are rather low and of the same order of magnitude as those observed for mercury(II) chloride and for nonelectrolytes. Molecular adducts between mercury(II) chloride and triphenylarsine oxide in nitrobenzene exhibit in fact molar conductivities around 1 mho cm<sup>2</sup> mol<sup>-1</sup>, while uni-univalent electrolytes show conductivities in the range 20-30 mhos cm<sup>2</sup> mol<sup>-1</sup>.<sup>11,12</sup> We can then exclude the existence of ionic species in solution.

Ultraviolet spectra of adducts in ethanol show a strong absorption with a maximum located probably below 200 mμ. Figure 1 shows as an example the spectrum of [(*i*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S·HgCl<sub>2</sub>]<sub>2</sub>, A, which, in the range investigated, is approximately the sum, B, of those of the corresponding thioether, D, and mercury(II) chloride, C. From these results we infer that the compounds are dissociated at the concentration (≈ 10<sup>-4</sup> M) used to obtain the spectra, even if the amount of dissociation cannot be determined quantitatively.

Molecular weights of 1:2 and 2:3 complexes (see Table I) are much lower than theoretical values, a fact that does not allow for an assessment as to whether the complexes are in dimeric or monomeric form. Considering the crystalline structure of 1:1 complexes,<sup>1,2</sup> the spectroscopic results showing a remarkable dissociation and the molecular weights close to or higher than the values expected for the monomers leads one to presume that 1:1 complexes exist in dimeric form.

The results are indicative of a strong molecular dissociation in ethanol solution. Thus, compounds between thioethers and mercury(II) chloride should be classified as addition compounds.

From molecular weights and by supposing for each

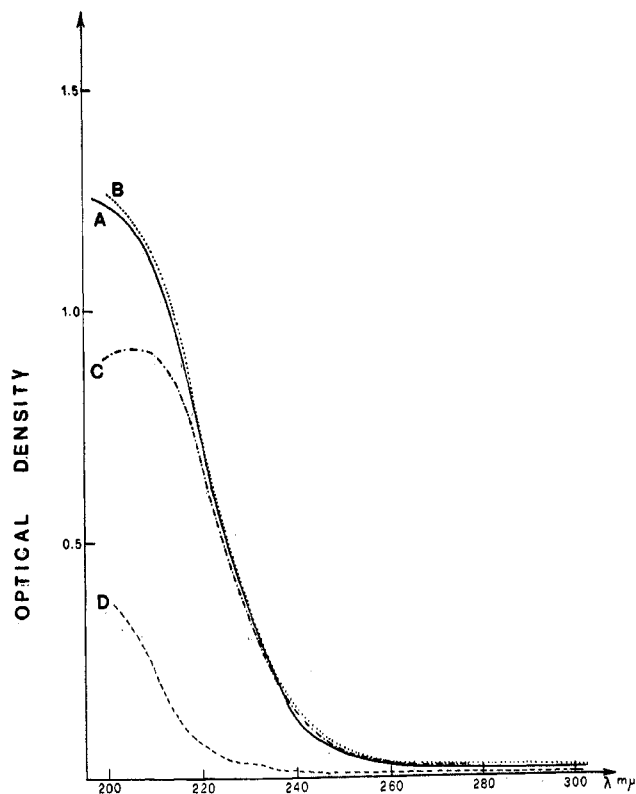
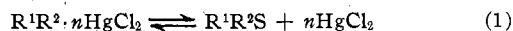


Figure 1.—Uv spectra in ethanol: A (—), [(*i*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S·HgCl<sub>2</sub>]<sub>2</sub>, 0.99 × 10<sup>-4</sup> M; B (·····), sum of C and D; C (---), HgCl<sub>2</sub>, 1.99 × 10<sup>-4</sup> M; D (-·-·-), (*i*-C<sub>4</sub>H<sub>9</sub>)<sub>2</sub>S, 1.99 × 10<sup>-4</sup> M.

complex a dissociation leading to thioether and mercury(II) chloride (eq 1), degrees of dissociation were



calculated (see Table 1), which represent lower limits at the experimental conditions. In fact other dissociation processes would lead to higher values of α,<sup>13</sup> since the number of species originating from the dissociation of one molecule of complex is lower.

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Keeping in mind the molecular nature of adducts, their crystalline structures, and their instability in solution we can hypothesize a scheme of formation (see Figure 2) consistent with the experimental results.

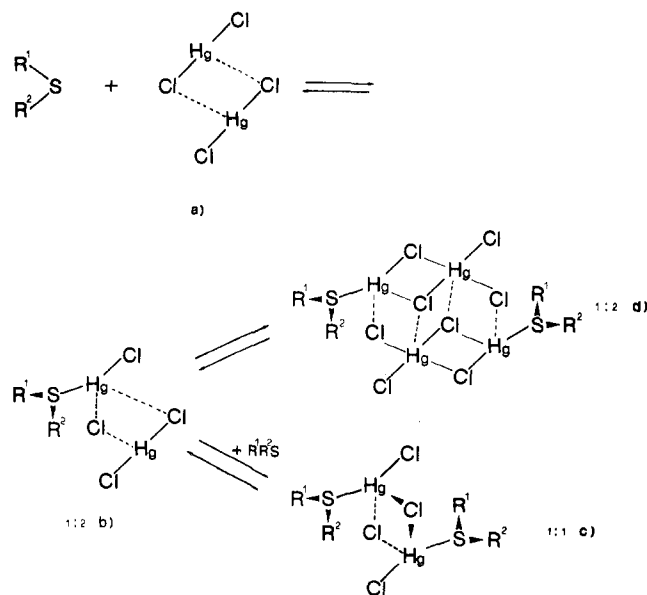
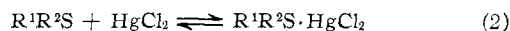


Figure 2.—Possible reaction scheme for adduct formation between mercury(II) chloride and thioethers.

In a first step a nucleophilic attack of a thioether molecule on the mercury atom of a dimeric group ( $\text{HgCl}_2$ )<sub>2</sub> (a) leads to the formation of the 1:2 adduct (b). The attack of the organic ligand induces a strong distortion on the bonds of mercury in (b) and thus the instability of the 1:2 adduct which tends to develop a conformation of higher symmetry and higher stability. This implies that (i) the reaction is reversible, (ii) in presence of an excess of thioether a second nucleophilic attack can take place on the other mercury atom with formation of the symmetric 1:1 adduct (c), and (iii) the 1:2 adduct (b) can be stabilized by subsequent dimerization and precipitation in the crystalline form (d). We can thus understand the possibility of obtaining adducts of the same thioether with various mole ratios 1:1, 1:2, or 2:3 by changing the solvent or crystallization conditions. The equilibria will be completely shifted in the direction of the less soluble adduct. The possibility exists also for a competitive reaction consisting of the attack of the thioether on a monomeric molecule of mercury(II) chloride

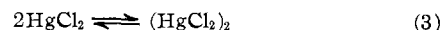


However these 1:1 monomeric species appear not to be stable enough to be isolated in the crystalline state.

The hypothesis that considers the first step of adduct formation as a 1:2 adduct formation can explain why with mercury(II) chloride it is possible to obtain only adducts with molar ratios 1:1 and 1:2. The mercury atom of (b), with distorted tetrahedral coordination, cannot bind a second molecule of organic ligand to give a 2:1 adduct. Analogous conclusions were reached for sulfoxide-mercury(II) chloride adducts.<sup>9</sup>

The existence of dimeric mercury(II) chloride (a) in solutions of water, ethanol, or other organic solvents

has been hypothesized by many authors to explain cryoscopic, ebullioscopic, solubility, kinetic, and dipole moment data.<sup>14-18</sup> The stability constant of the equilibrium



at various temperatures in water is known ( $\log K_{25^\circ} = -0.55$ ).<sup>19</sup> We have measured the molecular weight of mercury(II) chloride in *tert*-butyl alcohol and in absolute and 95% ethanol.

The cryoscopic method does not allow an extension to a concentration range above 0.17 *M*. The molecular weight increases with concentration and above 0.12 *M* becomes greater than the theoretical value, but the concentration range is too small to assess whether the plot is characteristic of a dimerization.<sup>20</sup>

Osmotic measurements give for mercury(II) chloride the same molecular weight in absolute and 95% ethanol ( $283 \pm 5$  and  $283 \pm 17$ , theoretical 271.5). Thus it seems reasonable to postulate the existence of some dimers ( $\text{HgCl}_2$ )<sub>2</sub> in alcoholic solution, even if their concentration appears to be very low ( $\sim 7\%$  at 37°, concentration of total  $\text{HgCl}_2$  0.1–0.15 *M*).

The presence of dimers ( $\text{HgCl}_2$ )<sub>2</sub> would explain why the halogen atom, simultaneously bonded to two mercury atoms, cannot be completely substituted by a thioether molecule to obtain the characteristic linear bis coordination of the  $\text{Hg}^{2+}$  ( $d^{10}$ ) ion.<sup>21</sup> The charge density on the mercury, increased by the thioether attack, is not lowered by  $\text{Cl}^-$  removal and the S–Hg–Cl linear structure is less likely to be formed. In fact the S–Hg–Cl angle is 158 and 143° for 1:2 and 1:1 adducts, respectively.<sup>2</sup>

Steric repulsion between aliphatic chains of thioether and the bridging chlorine atom can also contribute to the lability of the S–Hg bond. To verify this hypothesis we have prepared  $[(\text{tert-C}_4\text{H}_9)_2\text{S}\cdot\text{HgCl}_2]_2$ . It is interesting to notice that a highly sterically hindered thioether like di-*tert*-butyl thioether forms the adduct with mercury(II) chloride only at room temperature and that, by warming, the adduct is decomposed and mercury sulfide chloride and *tert*-butyl chloride are formed. Decomposition seems to follow an intramolecular mechanism where there is a direct interaction between alkyl groups and the halogen-bridging atom.<sup>8</sup>

The results of the present work demonstrate that thioethers and mercury(II) chloride form addition compounds and not sulfonium salts; the expected substitution does not go to completion for the particular structure of mercury(II) chloride. Moreover a weak interaction exists between sulfur and mercury atoms and the dissociation of adducts in solution should be represented in molecular form.

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