The Reactions of Sodium Diethyldithiocarbamate and Tetraethylthiuram Disulfide with Mercury(II) Chloride[1)]

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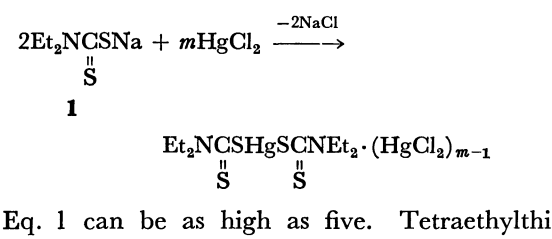
Sodium diethyldithiocarbamate (**1**) and tetraethylthiuram disulfide (**2**) have been found to react with excess mercury(II) chloride ($HgCl_2$) in water to give complexes with the general formula $Et_2NCS_2HgS_2CNEt_2\cdot(HgCl_2)_{m-1}$, where the m value can be as high as five. The complex with $m=2$ was isolated and characterized. The reaction pathway was discussed in some detail. Also studied were the reactions of **2** with $HgCl_2$ in organic solvents.

While the strong metal-binding properties of dithiocarbamates, notably sodium diethyldithiocarbamate (**1**), are well recognized,[2)] the previous investigations of the interaction of dithiocarbamates with mercury compounds have been made almost exclusively from the viewpoints of analytical chemistry. The simple question of what amount of mercury salt can react with dithiocarbamates has been left unanswered. During the course of an investigation on the sulfur-containing polymers, it became highly desirable to determine the complex-forming ability of dithiocarbamates and their derivatives with mercury. Accordingly, we have studied the reaction of **1** with mercury(II) chloride ($HgCl_2$). It was found that the reaction proceeds according to Eq. 1, and that the m value in Eq. 1 can be as high as five. Tetraethylthiuram disulfide (**2**), an oxidation product of **1**, has also been found to react with $HgCl_2$ in a smilar manner.



$$2\mathrm{Et_2N}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SNa} + m\mathrm{HgCl_2} \xrightarrow{-2\mathrm{NaCl}} \mathrm{Et_2N}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{SHgS}\underset{\underset{\mathrm{S}}{\|}}{\mathrm{C}}\mathrm{NEt_2}\cdot(\mathrm{HgCl_2})_{m-1} \qquad (1)$$

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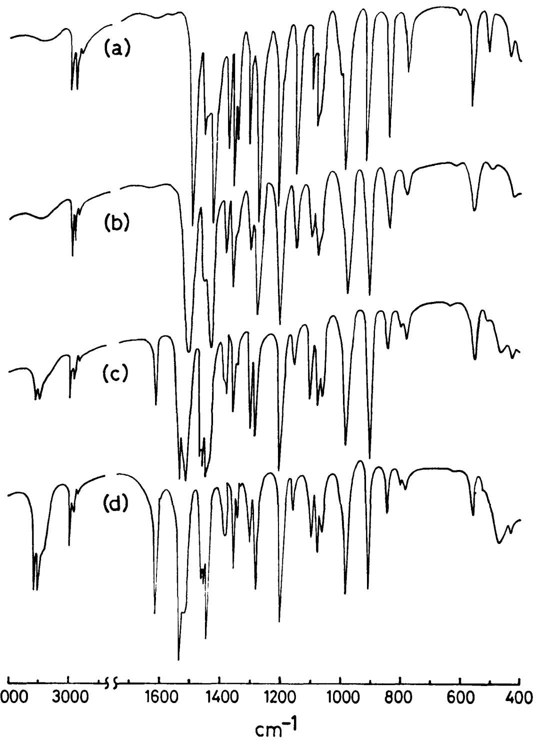


Fig. 1. The IR spectra of the mercury complexes formed in the reaction of **1** with $HgCl_2$ in water (KBr disks). **1**/$HgCl_2$; (a) 1: 0.5, (b) 1 : 1, (c) 1 : 2, and (d) 1 : 3.

Results and Discussion

*Reaction of **1** with $HgCl_2$* The reaction of **1** with $HgCl_2$ was carried out in water for 22 h at room temperature. The solid product was filtered, washed with water, and then dried. The results are summarized in Table 1. As can be seen, the yields and the mercury contents of the products increased with an increase in the amount of $HgCl_2$ used. The IR spectra of the products varied depending on the mercury content, especially in the C–N partial double bond region (around 1500 cm^{-1}) (Fig. 1). In the case of the products with high mercury content, new bands appeared at 460, 1610, 3500, and 3560 cm^{-1} (Fig. 1c and 1d). The first band is characteristic of $HgCl_2$, thus indicating the presence of weakly bonded $HgCl_2$. No reasonable explanation could be given for the second band. The last two bands seem to be similar in nature to those observed for some tertiary amide–$HgCl_2$ complexes.[3)] The FIR spectra of these products showed two strong band at 300 and 345 cm^{-1}.

The product of the 1 : 0.5 reaction was a light yellow crystalline solid; its IR spectrum (Fig. 1a) was very close to that of bis(diethyldithiocarbamato)mercury (**3**). Recrystallization of the product from acetonitrile gave **3** in 85% yield.

The product of the 1 : 1 reaction was a faintly yellow solid and gave dichlorobis(diethyldithiocarbamato)dimercury(II) (**4**) in 85% yield as colorless rod-like crystals on recrystallization from acetonitrile–acetone (4 : 1) below 60 °C. The confirmation of the structural formula of **4** was obtained by elemental analysis, IR, FIR, and NMR spectra, and independent synthesis; **4** was synthesized in high yields by the reaction of **3** with a stoichiometric quantity of $HgCl_2$ in acetone. It should be noted that **4** is a new type of stable mercury complex. The IR spectrum resembles that of dichlorotetrakis(diethyldithiocarbamato)trimercury(II), $Hg_3Cl_2(S_2CNEt_2)_4$.[4)] However, there are distinct differences in elemental composition and thermal properties between these two complexes.[5)]

All the other reaction products were white solids. Attempts to purify them were unsuccessful, because they were relatively unstable toward organic solvents;[6)]

TABLE 1. REACTION OF **1** WITH $HgCl_2$ IN WATER[a)]

$HgCl_2$ (g)	**1**/$HgCl_2$	Yield (g)	Mp (°C)	Analysis (%)		
				C	H	Hg
1.36	1 : 0.5	1.91	110—114			
2.71	1 : 1	3.82	101—103			
4.07	1 : 1.5	5.07	100—104	11.85	1.85	57.20
5.42	1 : 2	6.27	—[b)]	9.34	1.68	58.99
6.78	1 : 2.5	7.17	—[b)]	9.08	1.44	61.80[c)]
8.13	1 : 3	7.99	—[b)]	7.57	1.11	63.11[d)]

a) Reaction conditions: **1** (as trihydrate) 2.55 g, H_2O 80 ml, stirring for 22 h at room temperature. b) A distinct mp was not observed. c) Calcd for $C_{10}H_{20}N_2S_4Hg_4Cl_6$: C, 9.16; H, 1.54; Hg, 61.17%. d) Calcd for $C_{10}H_{20}N_2S_4Hg_5Cl_8$: C, 7.59; H, 1.27; Hg, 63.35%.

TABLE 2. REACTION OF **3** WITH $HgCl_2$ IN WATER[a)]

$HgCl_2$ (g)	**3**/$HgCl_2$	Yield (g)	Mp (°C)	Hg/DEDC[b)]	$\nu_{C=N}$ (cm^{-1})	Hg (%)
0.54	1 : 1	1.48	107—109	0.95	1510	51.16
2.17	1 : 4	2.42	—[c)]	1.82	1515, 1530	61.32

a) Reaction conditions: **3** 0.99 g, H_2O 40 ml, stirring for 90 h at room temperature. b) Based on yield. c) A distinct mp was not observed.

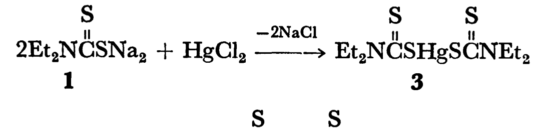
TABLE 3. REACTION OF **2** WITH $HgCl_2$ IN WATER[a)]

$HgCl_2$ (g)	**2**/$HgCl_2$	Yield (g)	Mp (°C)	Hg/DEDC[b)]	$\nu_{C=N}$ (cm^{-1})	Hg (%)
0.54	1 : 1	0.94	109—113	0.44	1495	43.21
1.08	1 : 2	1.46	97—101	0.94	1515	53.19
1.63	1 : 3	2.01	100—104	1.44	1515, 1530	56.68
2.17	1 : 4	2.32	—[c)]	1.73	1515, 1530	58.77
2.71	1 : 5	2.52	—[c)]	1.92	1515, 1530	60.76
3.25	1 : 6	2.78	—[c)]	2.00	1515(sh), 1530	61.92

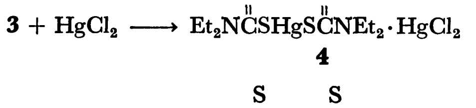
a) Reaction conditions: **2** 0.59 g, H_2O 40 ml, stirring for 90 h at room temperature. b) Based on yield. c) A distinct mp was not observed.

recrystallization from acetone lowered the mercury content, and repeated recrystallization resulted in the formation of **4**. The products of the 1 : 2.5 and 1 : 3 reaction had essentially the elemental analyses for $Et_2NCS_2HgS_2CNEt_2\cdot(HgCl_2)_3$ and $Et_2NCS_2HgS_2CNEt_2\cdot(HgCl_2)_4$, respectively.

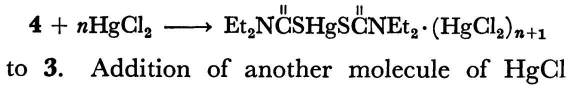
From these findings, the following pathway for the reaction of **1** with $HgCl_2$ may be assumed. The initial step involves the condensation reaction giving rise



$$\underset{\mathbf{1}}{2Et_2N\overset{S}{\overset{\|}{C}}SNa_2} + HgCl_2 \xrightarrow{-2NaCl} \underset{\mathbf{3}}{Et_2N\overset{S}{\overset{\|}{C}}SHgS\overset{S}{\overset{\|}{C}}NEt_2} \qquad (2)$$



$$\mathbf{3} + HgCl_2 \longrightarrow \underset{\mathbf{4}}{Et_2N\overset{S}{\overset{\|}{C}}SHgS\overset{S}{\overset{\|}{C}}NEt_2\cdot HgCl_2} \qquad (3)$$



$$\mathbf{4} + nHgCl_2 \longrightarrow Et_2N\overset{S}{\overset{\|}{C}}SHgS\overset{S}{\overset{\|}{C}}NEt_2\cdot(HgCl_2)_{n+1} \qquad (4)$$

to **3**. Addition of another molecule of $HgCl_2$ to **3** gives a stable complex **4**. Further addition of $HgCl_2$ to **4** yields relatively unstable complexes with higher mercury contents. The net reaction is represented by Eq. 1. On the basis of the above assumptions the number of mercury atoms per diethyldithiocarbamate residue (DEDC), Hg/DEDC, in the product complex was calculated from the yield. The Hg/DEDC values were also calculated from the analytical values of carbon and mercury. In Fig. 2, Hg/DEDC in the product is plotted against the reactant ratio, $HgCl_2$/**1**. The Hg/DEDC values obtained from the yield are in

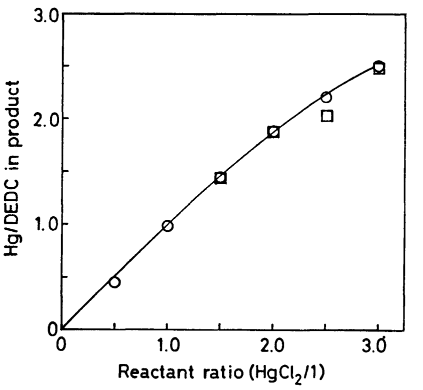


Fig. 2. Influence of reactant ratio on Hg/DEDC in product: ○ based on yield, □ based on analysis.

Table 4. Reaction of **2** with $HgCl_2$ in benzene–ethanol[a)]

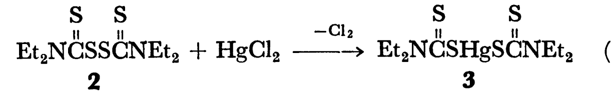
$HgCl_2$ (g)	**2**/$HgCl_2$	Benzene (ml)	Ethanol (ml)	Yield (g)	Mp (°C)
2.71	1 : 1	50	70	2.64	133—138
5.42	1 : 2	50	70	7.94	134—137
8.13	1 : 3	50	70	8.26	132—135
10.80	1 : 4	70	100	8.30	134—137
13.55	1 : 5	70	100	8.28	131—133

a) Reaction conditions: **2** 2.96 g, stirring for 30 min at room temperature.

fair agreement with those obtained from the results of elemental analysis. Figure 2 also shows that the reaction proceeds almost quantitatively in the region $HgCl_2/\mathbf{1}<1.5$, and that **1** can react with more than 2.5-mol of $HgCl_2$, that is, the m value in Eq. 1 can be as high as five.

Further support for these assumptions is the fact that the reaction of $HgCl_2$ with **3**, in place of **1**, proceeds in a similar manner to give the same mercury complexes as above (Table 2).

*Reaction of **2** with $HgCl_2$* Since tetraethylthiuram disulfide (**2**) is practically insoluble in water, the reaction of **2** with $HgCl_2$ in water requires more than 50 h for completion.[7)] Thus the reaction was conducted by stirring a mixture of $HgCl_2$ and **2** in water for 90 h at room temperature. The results are summarized in Table 3. The yields and the mercury contents of the products increased with an increase in the amount of $HgCl_2$ used. It is clear that **2** can react with more than 4 mol of $HgCl_2$.[8)] The $\nu_{C=N}$ band shifted to a higher wavelength with mercury content. In addition, the products with higher mercury contents gave new bands at 1610, 3500, and 3560 cm^{-1}. This tendency is the same as that observed in the reaction of **1** with $HgCl_2$. It therefore seems reasonable to conclude that the reaction of $HgCl_2$ with **2** proceeds like the reaction with **1**, except that the first step is the insertion reaction of mercury into the S–S bond of **2**, as evidenced by the isolation of **3** from the 1 : 1 reaction product.



$$\underset{\mathbf{2}}{\mathrm{Et_2N\overset{\overset{S}{\|}}{C}S S\overset{\overset{S}{\|}}{C}NEt_2}} + \mathrm{HgCl_2} \xrightarrow{-\mathrm{Cl_2}} \underset{\mathbf{3}}{\mathrm{Et_2N\overset{\overset{S}{\|}}{C}SHgS\overset{\overset{S}{\|}}{C}NEt_2}} \quad (5)$$

This type of reaction has been reported for several heavy metals, including mercury.[9—13)]

The literature contains some reports on the mercury complexes of thiuram disulfides, which were prepared in organic media and have elemental compositions that can not be explained by the reaction pathway described above.[14,15)] So the reaction of $HgCl_2$ with **2** was studied in several organic solvents.

A solution of **2** in benzene was added to a stirred solution of $HgCl_2$ in ethanol,[16)] and the mixture was stirred for 30 min. The precipitate was filtered, washed with ethanol, and dried. Table 4 lists the results of the reaction. Interestingly, all the products were essentially identical in physical appearance, thermal properties, and IR spectra. The IR spectra were characterized by a prominent band of $\nu_{C=N}$ at 1530 cm^{-1}. The results of the elemental analysis indicated the incorporation of about 2 atoms of mercury per molecule of **2**.

Table 5 summarizes the results of the reaction in acetone and ethanol. The 1 : 1 reaction in acetone gave the same product as that obtained in benzene–ethanol. On the other hand, an undertemined oily material was formed in ethanol. In both solvents, the use of excess $HgCl_2$ afforded products which resembled those obtained in water judging from IR spectra.

Conclusion. The reaction of **1** with $HgCl_2$ in water proceeds according to Eq. 1. The first step of the reaction is the formation of **3**, which can react with other molecules of $HgCl_2$ to give **4** and complexes with higher mercury content. The **4** complex is stable and it can be purified by recrystallization. The reaction of **2** with $HgCl_2$ proceeds in a similar manner. It is, however, to be emphasized that this is true only in water; the reaction is greatly affected by the solvent or solvent system used. These findings may be helpful in the design of heavy-metal adsorbing resins.

Experimental

Instrumentation. The following instruments were used in this study: a Hitachi EPI-G3 grating infrared spectrophotometer, a Hitachi FIS-3 far-infrared spectrophotometer, a Varian T-60 NMR spectrometer, a Perkin-Elmer DSC-2 differential scanning calorimeter, and a Yanaco micro melting point apparatus.

Materials. Sodium diethyldithiocarbamate (**1**) was prepared as trihydrate by the reaction of diethylamine with carbon disulfide in the presence of sodium hydroxide. Commercial tetraethylthiuram disulfide (**2**) was recrystallized from ethanol. $HgCl_2$ (Kanto Kagaku guaranteed reagent) was used as received.

*Reaction of **1** with $HgCl_2$.* The reaction of **1** with $HgCl_2$ was carried out in water. The results are summarized in Table 1. The following is an example of the general procedure. A mixture of 2.25 g of **1** (as trihydrate), a prescribed amount of $HgCl_2$, and 80 ml of water was stirred

Table 5. Reaction of **2** with $HgCl_2$ in acetone and ethanol

2 (g)	$HgCl_2$ (g)	**2**/$HgCl_2$	Solvent (ml)	Time (h)	Yield (g)[a)]	$\nu_{C=N}$ (cm^{-1})
2.96	2.71	1 : 1	Acetone (50)	3	1.28[b)]	1530
1.48	6.78	1 : 5	Acetone (200)	20	1.11[c)]	1510, 1530
2.96	2.71	1 : 1	Ethanol (120)	3	—[d)]	
2.96	8.13	1 : 3	Ethanol (200)	20	6.71[c)]	1515(sh), 1530

a) For solid product precipitated during the reaction. b) Mp 128—132 °C. c) A distinct mp was not observed. d) An oily yellow material was formed.

magnetically for 22 h at room temperature. The solid was filtered off, washed thoroughly with water, and then dried at room temperature under a vacuum.

The 1 : 0.5 reaction product was recrystallized from acetonitrile to give **3** as a yellow crystal in 85% yield; mp 139—141 °C (lit,[13] mp 138—139 °C).

IR (KBr disk): 1500 cm^{-1} ($\nu_{C=N}$).

NMR ($CDCl_3$): δ 1.33 (t, J=7 Hz, 12H), 3.84 (q, J=7 Hz, 8H).

Found: C, 24.32; H, 4.19; Hg, 39.98%. Calcd for $C_{10}H_{20}N_2S_4Hg$: C, 24.16; H, 4.06; Hg, 40.35%.

The 1 : 1 reaction product was recrystallized from acetonitrile-acetone (4 : 1) below 60 °C to give **4** as a colorless rod in 85% yield: mp 105—107 °C.

IR (KBr disk): 1510 cm^{-1} ($\nu_{C=N}$).

FIR (Nujol mull): 334 cm^{-1} (ν_{Hg-Cl}).

NMR (d_6-acetone): δ 1.34 (t, J=7 Hz, 12H), 3.85 (q, J=7 Hz, 8H).

Found: C, 15.66; H, 2.68; S, 16.70; Hg, 52.27%. Calcd for $C_{10}H_{20}N_2S_4Hg_2Cl_2$: C, 15.63; H, 2.62; S, 16.69; Hg, 52.19%.

Recrystallization of 2.00 g of the 1 : 3 reaction product from 150 ml of acetone gave 0.99 g of white crystals. The IR spectrum showed a single band due to $\nu_{C=N}$ at 1510 cm^{-1}, but the bands at 460, 1530, 1610, 3500, and 3560 cm^{-1} characteristic of the original product (Fig. 1d) were completely absent.

Found: C, 12.59; H, 1.51; Hg, 56.34%.

*Reaction of **3** with $HgCl_2$ in Acetone.* A mixture of 4.96 g of **3** and 120 ml of acetone was heated at about 60 °C until it became homogeneous. To this solution was added 2.71 g of $HgCl_2$, and the mixture was stirred for 1 h under reflux. After cooling, the white crystals of **4** were collected and dried. From the filtrate a small amount of **4** was obtained by concentration, followed by crystallization. The total yield of **4** was 7.35 g (95%). Recrystallization of the raw product from acetonitrile-acetone gave 6.02 g (78%) of **4** in a pure form.

*Reaction of **3** with $HgCl_2$ in Water.* A mixture of 0.99 g of **3**, a prescribed amount of $HgCl_2$, and 40 ml of water was stirred for 90 h at room temperature. The work-up procedure was the same as that followed with **1**. The results are summarized in Table 2. The IR spectra were very close to those of the corresponding products obtained in the reaction of **1** with $HgCl_2$.

*Reaction of **2** with $HgCl_2$ in Water.* The results of the reaction are summarized in Table 3. The following is a typical example. A mixture of 0.59 g of **2**, 2.17 g of $HgCl_2$, and 40 ml of water was stirred for 90 h at room temperature. The solid product was filtered, washed thoroughly with water, and then dried at room temperature under a vacuum. The yield was 2.32 g. The IR spectrum revealed characteristic bands at 460, 1515, 1530, 1610, 3500, and 3560 cm^{-1}.

Found: C, 9.33; H, 1.22; Hg, 58.77%.

*Reaction of **2** with $HgCl_2$ in Benzene-Ethanol.* The results of the reaction are summarized in Table 4. The following is a typical example. To a stirred solution of 8.13 g of $HgCl_2$ in 70 ml of ethanol was added dropwise a solution of 2.96 g of **2** in 50 ml of benzene. A white crystalline precipitate started to separate almost immediately. The mixture was stirred for 30 min at room temperature and filtered. The filtered solid was washed with ethanol and then dried at room temperature under a vacuum. The yield was 8.26 g; mp 132—135 °C (dec.).

IR (KBr disk): 1530 cm^{-1} ($\nu_{C=N}$).

Found: C, 15.64; H, 2.67; S, 16.30; Cl, 11.14; Hg, 48.08%.

Repeated recrystallization of the product from acetonitrile gave a small amount of **4**: mp 105—107 °C.

Found: C, 15.35; H, 2.36; S, 16.63%. Calcd for $C_{10}H_{20}N_2S_4Hg_2Cl_2$: C, 15.63;, H, 2.62; S, 16.69%.

*Reaction of **2** with $HgCl_2$ (1 : 5) in Acetone.* To a stirred solution of 6.78 g of $HgCl_2$ in 150 ml of acetone was added a solution of 1.48 g of **2** in 50 ml of acetone. The mixture was stirred for 20 h at room temperature. The white precipitate was filtered and dried. The yield was 1.11 g. The IR spectrum showed characteristic bands at 460, 1510, 1530, 1610, 3500, and 3560 cm^{-1}. Essentially the same product was obtained from the filtrate by concentration, followed by treatment of the residue with acetone-ether. The yield was 2.44 g.

Found: C, 7.69; H, 1.23; S, 8.23%.

*Reaction of **2** with $HgCl_2$ (1 : 3) in Ethanol.* A solution of 8.13 g of $HgCl_2$ in 80 ml of ethanol was added to a stirred solution of 2.96 g of **2** in 120 ml of ethanol. In time, the system became cloudy, and then a viscous yellow material began to separate. The stirring was continued for 20 h. During this period the yellow material turned to a white crystalline solid. The solid was filtered, washed with ethanol, and dried. The yield was 6.71 g. The IR spectrum showed characteristic bands at 460, 1515 (sh), 1530, 1610, 3500, and 3560 cm^{-1}.

Found: C, 13.11; H, 2.16; S, 13.35; Hg, 50.50%.

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6) They were reasonably stable toward water. A sample of the 1 : 3 reaction product was stirred in water for 90 h. The mercury content of the sample before and after this treatment were 63.11 and 63.01%, respectively.

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