

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WASHINGTON]

Addition Products of Metallic Salts with Certain Sulfur and Oxygen Compounds¹

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Several years ago, Smith and Semon² reported the probable formation of the soluble, unstable compound $[\text{Hg}(\text{HgS})](\text{ClO}_4)_2$ by the reaction between mercuric perchlorate and mercuric sulfide. Simultaneously, the insoluble decomposition product $[\text{Hg}(\text{HgS})_2](\text{ClO}_4)_2$ was reported, and the existence of possible oxygen analogs was suggested. The evidence for the composition of the former of these two complexes has been substantiated by the quantitative electrolysis of a solution of the former and by the preparation of analogous hydrated oxygen compounds.

Di-oxomercuro-mercuperchlorate $[\text{Hg}(\text{HgO})_2](\text{ClO}_4)_2$ has been prepared by Hayek³; the authors have prepared the oxomercuro-mercuperchlorates $[\text{Hg}(\text{HgO})](\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and $[\text{Hg}(\text{HgO})](\text{ClO}_4)_2 \cdot 3\text{H}_2\text{O}$ by the action of mercuric oxide on mercuric perchlorate solution. These hydrates further react with 1,4-dioxane to form the solvated $\text{Hg}(\text{ClO}_4)_2 \cdot 6\text{C}_4\text{H}_8\text{O}_2$, with liberation of mercuric oxide, and $[\text{Hg}(\text{HgS}_2)_2](\text{ClO}_4)_2$ reacts with water (in large excess) to yield mercuric perchlorate and insoluble mercuric sulfide.

The similarity between the oxygen and sulfur compounds is further emphasized by the reactions of dithiane, $\text{C}_4\text{H}_8\text{S}_2$, as contrasted with those of 1,4-dioxane, $\text{C}_4\text{H}_8\text{O}_2$. In the work of Rheinholdt, Luyden and Schittman,⁴ for example, $\text{HgCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$, $\text{Hg}(\text{CN})_2 \cdot 2\text{C}_4\text{H}_8\text{O}_2$, $\text{CuCl}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$, etc., were obtained, directly comparable to the dithiane addition compounds reported in this paper.

In its reaction with chloroplatinic acid in dioxane solution, dithiane produces $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2$ and $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$, while in alcohol, the same reagents produce $\text{PtCl}_4 \cdot 2\text{C}_4\text{H}_8\text{S}_2$. The divalent platinum compound, $\text{PtCl}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$, is formed by the action of potassium chloroplatinite and dithiane.

The copper halides readily form addition compounds with dithiane. Cupric chloride and dithiane yield $\text{CuCl}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$, with the dithiane held less firmly than is ammonia or pyridine, as evi-

denced by displacement with these reagents. Cupric bromide forms $\text{CuBr}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; cupric fluoride forms $\text{CuF}_2 \cdot 2\text{C}_4\text{H}_8\text{S}_2$. Dithiane is too weak a coördinating agent to stabilize cupric iodide. Nor was a reaction with dithiane obtained with cupric sulfate, tartrate, nitrate, acetate, perchlorate, or formate. Cuprous chloride and dithiane form $\text{Cu}_2\text{Cl}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$, and cuprous bromide forms $\text{Cu}_2\text{Br}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$. Cuprous iodide, however, forms $\text{Cu}_2\text{I}_2 \cdot 2\text{C}_4\text{H}_8\text{S}_2$ and cuprous cyanide forms the corresponding $\text{Cu}_2(\text{CN})_2 \cdot 2\text{C}_4\text{H}_8\text{S}_2$.

Compounds similar to these are also produced by salts of mercury (2), silver, and cadmium: mercuric perchlorate and dithiane form $\text{Hg}(\text{ClO}_4)_2 \cdot 2\text{C}_4\text{H}_8\text{S}_2$; mercuric nitrate and dithiane form $\text{Hg}(\text{NO}_3)_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; mercuric chloride forms $\text{HgCl}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; mercuric bromide forms $\text{HgBr}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; mercuric iodide forms $\text{HgI}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; silver perchlorate and dithiane form $\text{AgClO}_4 \cdot \text{C}_4\text{H}_8\text{S}_2$; silver nitrate and dithiane form $2\text{AgNO}_3 \cdot \text{C}_4\text{H}_8\text{S}_2$ or $\text{AgNO}_3 \cdot 2\text{C}_4\text{H}_8\text{S}_2$, depending on conditions; cadmium chloride and dithiane form $\text{CdCl}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; cadmium bromide forms $\text{CdBr}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$; and cadmium iodide forms $\text{CdI}_2 \cdot \text{C}_4\text{H}_8\text{S}_2$. Representing the mercuric perchlorate-dithiane complex as $[\text{Hg}(\text{C}_4\text{H}_8\text{S}_2)_2](\text{ClO}_4)_2$, the relationship between it and $[\text{Hg}(\text{HgS})_2](\text{ClO}_4)_2$ is immediately apparent.

To further support Smith and Semon's¹ formulation of the mechanism of hydrogen sulfide precipitation, attempts were made to combine directly sulfides of several strongly coördinating metals with their respective metal perchlorates. In no case was a reaction observed. The ethyl mercaptides of the metals, with two exceptions, failed to react under similar conditions. Lead ethyl mercaptide with lead perchlorate gave the addition compound $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{Pb}(\text{SC}_2\text{H}_5)_2$. In the reaction between aurous ethyl mercaptide and chloroauric acid, a hitherto unreported type of compound, $\text{AuCl}_2(\text{SC}_2\text{H}_5)$, identical with that produced by the action of dilute aqua regia on the mercaptide, was isolated. This compound was characterized by its extreme stability, even toward boiling aqua regia.

The exact mechanism of some of these reactions is still indefinite; and the possibility that some of

(1) Abstract of a thesis presented by Joseph W. Bouknight to the University of Washington in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Smith and Semon, *THIS JOURNAL*, **46**, 1325 (1924).

(3) Hayek, *Z. anorg. allgem. Chem.*, **223**, 382 (1935).

(4) Rheinholdt, Luyden and Schittman, *J. prakt. Chem.*, **149**, 30 (1937).

TABLE I
 ADDITION COMPOUNDS OF DITHIANE

Inorg. comp.	Solvent ^a	Solubility	Color	Formula	Metal analyses, %		
					Calcd.	Found	Found
H ₂ PtCl ₆	Alcohol	Insol. org. solv., sl. sol. liq. phenol	Yellow	PtCl ₄ ·2C ₄ H ₈ S ₂	Pt, 33.83	33.33	33.54
K ₂ PtCl ₄	Aq. alcohol	Insol. org. solv., v. sl. sol. CS ₂	White-pink	PtCl ₂ ·C ₄ H ₈ S ₂	Pt, 50.56	50.40	50.83
CuCl ₂	Alcohol	Insol. org. solv., dec. concd. HNO ₃ , H ₂ O, NH ₃ , pyridine	Black	CuCl ₂ ·C ₄ H ₈ S ₂	Cu, 24.97	24.83	25.12
CuBr ₂	Alcohol	Dec. slowly in H ₂ O	Black	CuBr ₂ ·C ₄ H ₈ S ₂	Cu, 18.48	18.31	18.47
CuF ₂	Aq. alcohol	Insol. org. solv., dec. sl. H ₂ O, rapid. concd. HNO ₃	Black	CuF ₂ ·2C ₄ H ₈ S ₂	Cu, 18.65	19.37	19.07
Cu ₂ Cl ₂	Satd. HCl	Insol. org. solv., dec. concd. Na ₂ S ₂ O ₃ or HNO ₃	White	Cu ₂ Cl ₂ ·C ₄ H ₈ S ₂	Cu, 39.97	39.96	39.52
Cu ₂ Br ₂	Concd. KBr or HCl	Similar to Cu ₂ Cl ₂ ·C ₄ H ₈ S ₂	White	Cu ₂ Br ₂ ·C ₄ H ₈ S ₂	Cu, 31.24	31.54	31.64
Cu ₂ I ₂	Concd. KI soln.	Dec. slightly in concd. HCl	White	Cu ₂ I ₂ ·2C ₄ H ₈ S ₂	Cu, 20.47	20.52	20.78
Cu ₂ (CN) ₂	Concd. HCl	Insol. org. solv., sol. concd. NaCN soln.	White	Cu ₂ (CN) ₂ ·2C ₄ H ₈ S ₂	Cu, 29.85	30.33	
Hg(ClO ₄) ₂	Water	Sl. sol. water at 20° ^b	White	Hg(ClO ₄) ₂ ·2C ₄ H ₈ S ₂	Hg, 31.37	31.13	31.63
Hg(NO ₃) ₂	Dil. HNO ₃	Sl. sol. hot water, insol. cold water	White	Hg(NO ₃) ₂ ·C ₄ H ₈ S ₂	Hg, 44.30	44.07	44.00
HgCl ₂	Satd. alc. soln.	Insol. common org. solv.	White	HgCl ₂ ·C ₄ H ₈ S ₂	Hg, 51.23	51.95	
HgBr ₂	Satd. alc. soln.	Insol. common org. solv.	White	HgBr ₂ ·C ₄ H ₈ S ₂	Hg, 41.75	41.59	
HgI ₂	Satd. alc. soln.	Insol. common org. solv.	White	HgI ₂ ·C ₄ H ₈ S ₂	Hg, 34.92	34.94	35.18
AgClO ₄	Alcohol	Sol. NH ₄ OH, dil. HNO ₃ , dec. by H ₂ S	White	AgClO ₄ ·C ₄ H ₈ S ₂	Ag, 32.95	32.48	32.41
AgNO ₃	Alcohol ^c	Dec. concd. HNO ₃	White	2AgNO ₃ ·C ₄ H ₈ S ₂	Ag, 46.93	46.81	46.22
AgNO ₃	Alcohol ^d	Dec. concd. HNO ₃	White	AgNO ₃ ·2C ₄ H ₈ S ₂	Ag, 26.32	26.04	26.33
CdCl ₂	Satd. alc. soln.	Dec. hot water	White	CdCl ₂ ·C ₄ H ₈ S ₂	Cd, 37.05	36.77	
CdBr ₂	Satd. alc. soln.	Dec. hot water	White	CdBr ₂ ·C ₄ H ₈ S ₂	Cd, 28.94	28.75	
CdI ₂	Satd. alc. soln.	Stable in hot water	White	CdI ₂ ·C ₄ H ₈ S ₂	Cd, 23.12	23.17	

^a Excess dithiane in alcohol was mixed with the inorganic reagent in the solvent specified. ^b Explodes gently at red heat. ^c 0.14 g. of dithiane in 5 ml. of alcohol was added to 0.5 g. of silver nitrate in 10 ml. of alcohol. ^d 0.199 g. of silver nitrate in 10 ml. of alcohol was added to 0.3 g. of dithiane in 5 ml. of alcohol.

these complexes exist in dimeric form also requires further investigation.

Experimental

Electrolysis of Thiomercurio-mercuroperchlorate.—Five and four-tenths grams of mercuric perchlorate hexahydrate was dissolved in water to a total volume of 47 ml. Mercuric sulfide was precipitated from 25 ml. of this solution with hydrogen sulfide, and the washed solid added to the remaining 22 ml. of perchlorate solution. The slight excess of sulfide was removed by rapid filtration, the solution made up to 250 ml., and electrolyzed in a transference apparatus, using 63 m. a. The sulfide was dissolved in bromine water, the mercury in nitric acid, and the mercury and sulfur determined.

Anal. Calcd. for [Hg(HgS)](ClO₄)₂: Hg:S, 2:1. Found: Hg:S, 2.14:1, 1.88:1.

Oxomercurio-mercuroperchlorates.—Mercuric oxide was added to a hot, concentrated solution of mercuric perchlorate until no further solution occurred. White crystals separated on cooling and were dried over calcium chloride.

Anal. Calcd. for [Hg(HgO)](ClO₄)₂·6H₂O: Hg, 55.41; ClO₄, 27.46. Found: Hg, 55.84, 55.39; ClO₄, 27.13.

The hexahydrate effloresced to a white powder on long standing in the desiccator.

Anal. Calcd. for [Hg(HgO)](ClO₄)₂·3H₂O: Hg, 59.87; ClO₄, 29.68. Found: Hg, 60.36, 59.89; ClO₄, 29.64, 29.84.

1,4-Dioxane, at its boiling point, decomposed the perchlorates. The liberated mercuric oxide was filtered off:

and on cooling, large, clear crystals deposited. They were dried over sulfuric acid.

Anal. Calcd. for Hg(ClO₄)₂·6C₄H₈O₂: 1:6. Found, 1:6.01.

Preparation of Dithiane.—The methods of Husemann⁵ and Fasbender⁶ proved unsatisfactory for the preparation of large quantities. The following method was developed.

Twenty grams of pulverized sodium hydroxide in 50 ml. of absolute alcohol was treated with hydrogen sulfide until the sodium sulfide initially formed redissolved. A mixture of 20 g. of pulverized sodium hydroxide and 84.6 g. of ethylene bromide in 150 ml. of absolute alcohol was added in small portions with shaking. The mixture was cooled and reconnected to the hydrogen sulfide generator for about three hours. A small amount of solid sodium hydroxide was added and the dithiane distilled with steam: best yield obtained, 45% of the theoretical⁷; m. p. 110–111°.

Dithiane Addition Compounds.—With a few exceptions, the behavior of dithiane toward the inorganic reagents tested was similar and the compounds formed analogous to those previously reported for both dithiane and 1,4-dioxane. Thus the results when dithiane and the inorganic compound are allowed to react are presented in tabular form. The inorganic compound was dissolved in the solvent specified and treated with dithiane in alcohol. The formulas and analyses of each complex are listed and color and solubility data given as far as available.

(5) Husemann, *Ann.*, **126**, 269 (1863).

(6) Fasbender, *Ber.*, **20**, 460 (1887).

(7) J. R. Meadow and E. E. Reid, *This Journal*, **56**, 2177 (1934), have noted the formation of by-products of high molecular weight in this reaction.

Chloroplatinic Acid and Dithiane.—The mixing of dioxane solutions containing, respectively, four mols. of dithiane and one of chloroplatinic acid gave the yellow compound $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2$, reported by Husemann.⁵ This was removed by filtration after thirty minutes. In the filtrate, a finely divided lemon-yellow crystalline precipitate continuously formed for eighteen days. Analysis showed this precipitate to be $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$. It is insoluble in water and common organic solvents and soluble in liquid phenol.

Anal. Calcd. for $\text{PtCl}_4 \cdot \text{C}_4\text{H}_8\text{S}_2 \cdot \text{C}_4\text{H}_8\text{O}_2$: Pt, 35.82. Found: Pt, 36.24, 36.31, 36.38.

Lead Perchlorate and Lead Ethyl Mercaptide.—Lead mercaptide⁸ was added to a very concentrated solution of lead perchlorate and the mixture heated on the water bath. After two days, the light yellow product was filtered, washed with cold water, and dried in air.

Anal. Calcd. for $\text{Pb}(\text{ClO}_4)_2 \cdot 3\text{Pb}(\text{SC}_2\text{H}_5)_2$: 1:3. Found: 1:3.02, 1:2.96, 1:2.98.

Chloroauric Acid and Aurous Ethyl Mercaptide.—To 1.09 g. of dry aurous ethyl mercaptide were added 1.72 g. of freshly prepared chloroauric acid and 50 ml. of chloro-

(8) Lead mercaptide was difficult to obtain in stable form, but was finally prepared with success by dissolving litharge in 6 *N* sodium hydroxide solution and adding an equivalent quantity of ethyl mercaptan, also dissolved in 6 *N* sodium hydroxide, the mixture being cooled by cracked ice. The bright yellow precipitate was washed with water and then dried over calcium chloride in a desiccator.

form, containing 0.75% alcohol. The suspension was stirred and, after three minutes, filtered. On standing the filtrate turned from red to yellow and bright yellow needles slowly deposited. The solid was washed with chloroform.

Anal. Calcd. for $\text{AuCl}_2(\text{SC}_2\text{H}_5)$: Au, 59.91; Cl, 20.93. Found: Au, 60.08, 60.05; Cl, 20.63, 20.26.

This compound is also obtained by heating aurous mercaptide with aqua regia, made from the 6 *N* acids.

Summary

1. The probable presence of soluble $[\text{Hg}(\text{HgS})](\text{ClO}_4)_2$ as an intermediate product in the precipitation of mercuric sulfide by the action of hydrogen sulfide upon mercuric perchlorate has been confirmed by the electrolysis of its solution.

2. The analogous oxygen compound has been prepared.

3. Addition compounds of dithiane and metallic salts corresponding to dioxane addition compounds have been prepared.

4. The metal salt addition complexes of ethyl mercaptides have been studied.

5. Lead mercaptide has been prepared in pure stable condition.

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A Phase Rule Study¹ of the Mixed Soap System Sodium Palmitate–Sodium Laurate–Sodium Chloride–Water at 90°

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Proceeding from the known phase behavior of systems made from pure single soaps, the present work undertakes to ascertain the results of using the simplest mixture, that containing two single soaps. The correlation of these results with the properties of the two pure soaps is of interest.

Studies of commercial soap systems² have shown that where only liquid or liquid crystalline phases are involved, the behavior of a mixture of soaps with salt and water is qualitatively the same as that of a single soap. Quantitatively, the salt concentrations at the various phase boundaries are closer to the values for the soap of lower molecular weight than to the average of the values for the two separate soaps. In the system potassium oleate–potassium laurate–water, the same

phases are found as with either soap alone and here again, where the soap is an equimolar mixture of potassium oleate and potassium laurate, the phase boundaries occur at soap concentrations twice as close to those for $\text{KL}-\text{H}_2\text{O}$ as for $\text{KOI}-\text{H}_2\text{O}$.³

Sodium palmitate and sodium laurate were selected for the present study since their phase rule diagrams with salt and water are well known,⁴ and since the two soaps differ only in the length of the hydrocarbon chain. The isotropic solution boundary and the position of the neat-nigre-lye triangle are here determined in the $\text{NaP}-\text{NaL}-\text{NaCl}-\text{H}_2\text{O}$ system at 90° for the cases (a) that the soap is 50 wt. % sodium palmitate, 50 wt. % sodium laurate and (b) that the soap is 75 wt. % so-

(1) See THIS JOURNAL, 60, 1866 (1938), for preceding papers in this series.

(2) J. W. McBain in Alexander's "Colloid Chemistry," Vol. 1, 1926, p. 160; R. H. Ferguson and A. S. Richardson, *Ind. Eng. Chem.*, 24, 1329 (1932).

(3) J. W. McBain, L. H. Lazarus and A. V. Pitter, *Z. physik. Chem.*, A147, 87 (1930).

(4) Cf. reference 3; R. D. Vold and R. H. Ferguson, THIS JOURNAL, 60, 2066 (1938); J. W. McBain, G. C. Brock, R. D. Vold and M. J. Vold, *ibid.*, 60, 1870 (1938).