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THE MECHANISM OF THE PRECIPITATION OF METALS BY HYDROGEN SULFIDE. A STUDY OF CERTAIN SULFUR COMPLEXES OF MERCURY

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Notwithstanding the steady evolution of the ionic theory of Arrhenius, with the complications involved, chemists have continued to make use of the theory in its original form to explain the *mechanism* of numerous reactions which are certainly too complicated for so simple an explanation. Inorganic compounds are often complex in structure, and frequently they are either difficult to obtain synthetically or the methods for their formation fail to furnish a satisfactory insight into their constitution. These remarks apply with especial emphasis to substances which are formed in the ordinary analytical procedures for the precipitation of heavy metals with hydrogen sulfide. In the effort to retain simplicity, and due to the existence of many well defined empirically simple sulfides of heavy metals, the possible formation of intermediate compounds, with their subsequent transformations, has been almost entirely neglected. In consequence, we have had but little insight into the manner of formation of the precipitates obtained.

Theoretical Part

The Role of Sulfide Ion Versus Hydrosulfide Ion in the Precipitation of Metallic Sulfides.—It has previously been shown[2] that sulfide ion can hardly be regarded as the active agent in the precipitation of metallic

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[1] From a thesis submitted by Waldo L. Semon to the Graduate School of the University of Washington, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

[2] Smith, This Journal, **44**, 1500 (1922).

sulfides, since calculations indicate that in a solution saturated with hydrogen sulfide, only a solitary sulfide ion is present in from several cubic centimeters to even liters, depending upon the acid concentration. From the simple ionic standpoint, hydrosulfide ion is more probably the active agent.[2] The precipitation of oxides from the corresponding salt solutions by means of sodium hydroxide is admittedly due to the formation of metallic hydroxides,[3] followed by decomposition. In spite of this, and of the recognized similarities between oxygen and sulfur compounds, very few have seemed willing to attribute the precipitation of sulfides to an analogous reaction. This is due in part, doubtless, to the solubility and instability of the intermediate products and to the apparently simple formulas of many of the sulfides obtained, *as final products prepared for weighing*. Nevertheless, certain hydrosulfides other than those of the alkali and alkaline earth metals are known, namely those of indium[4] and tin.[5] There are indications also of the partial formation of many others.[6] These are, however, very unstable and probably exist only in equilibrium with a solution of hydrogen sulfide.[7] These facts, with those presented in a previous paper,[2] render it probable that sulfide ion plays a minor role in the precipitation of metallic sulfides, as compared with hydrosulfide ion.

However, there are many considerations which indicate that the precipitation of sulfides cannot be adequately explained by such a simple action as the combination in solution of the metallic ions with the hydrosulfide ions, followed by the decomposition of the hydrosulfide. An im-

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[3] In the precipitation of copper oxide from a solution of the sulfate by sodium or potassium hydroxide solution, at the boiling temperature, it is not customary even to consider the oxide ion. The formulation is, of course, $Cu^{++} + 2OH^- \rightarrow Cu(OH)_2 \rightarrow CuO + H_2O$. Compare E. Müller and others, *Z. physik. Chem.*, **105**, 73 (1923).

[4] (a) Meyer, *Ann.*, **149**, 137 (1869). (b) Linder and Picton, *J. Chem. Soc.*, **61**, 135 (1892).

[5] *Jahrb. fort. Chem.*, **1883**, 401. Ditte, *Compt. rend.*, 97, 42 (1883).

[6] Antimony, arsenic, bismuth, cadmium, copper, gold, indium, mercury, molybdenum, silver, zinc. de Clermont and Fronnell, *Compt. rend.*, **87**, 330 (1878). Thomsen, *Ber.*, **11**, 2044 (1878). Baubigny, *Compt. rend.*, 97, 1417 (1883). v. Zotta, *Monatsh.*, **10**, 807 (1889). Ref. 4 a, p. 114. Picton, *J. Chem. Soc.*, **61**, 137 (1892). Mawrow and Nikolow, *Z. anorg. Chem.*, **95**, 188 (1916).

[7] Additional experimental evidence that the sulfide precipitate contains both hydrosulfide and sulfide will be found in the experimental part. See also Young and Goddard, *J. phys. Chem.*, **21**, 1 (1917). Of course, the objection might be raised that hydrogen sulfide is here present in the adsorbed condition, and not combined as hydrosulfide. But, disregarding the uncertainty of whether adsorption itself may not be a case of surface combination, the existence of many crystalline addition compounds of sodium and potassium sulfides with the sulfides of antimony, bismuth, gold, mercury, etc., as well as the combinations which are known to occur between alkyl sulfides and the salts of many heavy metals, point strongly to the conclusion that the hydrogen sulfide contained in fresh sulfide precipitates is present in true chemical combination.

portant one of these is the existence of higher order intermediate compounds of other salts with metallic sulfides. In connection with the existence and nature of these, it is pertinent to review briefly the facility with which sulfur enters into the formation of higher order compounds.

The Tendency of Sulfur to Enter into the Formation of Higher Order Compounds.—In 1908, Tschugaeff[8] called attention to the fact that many organic monosulfides, R_2S, give fairly stable addition compounds with salts of platinum, palladium and mercury, while with cupric salts the compounds are only slightly stable, and with nickel salts such compounds could not be isolated. Further, in accordance with our knowledge of ring compounds,[9] with organic disulfides capable of yielding 5-membered rings he showed that complex formation is very pronounced, even in the cases of copper and nickel. With other disulfides, $R.S.(CH_2)_n\text{-}S.R$, requiring 3, 4, 6 and 8-membered rings, copper and nickel compounds could not be isolated.

This formulation has been further investigated by Morgan and Ledbury.[10] After a consideration of certain 5-membered ring complexes of copper and seven other metals, these investigators state: "The same selective affinity is at work between sulfur and the metallic radicals whether it is effective as principal valency in producing sulfides or whether it operates as residual affinity in the formation of coördination compounds."

In what we may regard as a continuation of the pioneering work of Blomstrand,[11] with the application of modern physicochemical methods, Tschugaeff and his students[12] made a detailed study of the addition compounds which are formed by the salts of bivalent platinum with many organic mono- and disulfides. They prepared and fully characterized numerous compounds, all of which were found to harmonize in properties with the requirements of the coördination theory.

The complex compounds of thio-urea with metallic salts were early investigated, the most common type being represented by the formula, $MCl_2.2SC(NH_2)_2$.[13] More recently, Kurnakow and others[14] have pre-

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[8] Tschugaeff, *Ber.*, **41**, 2222 (1908).

[9] Werner, *Ber.*, **40**, 61 (1907); **41**, 1062 (1908).

[10] Morgan and Ledbury, *J. Chem. Soc.*, **121**, 2882 (1922).

[11] (a) Blomstrand and others, *J. prakt. Chem.*, [2] **27**, 161 (1883); (b) **38**, 345 (1888). (c) Klason, *Ber.*, **28**, 1498 (1895). (d) Phillips, THIS JOURNAL, **23**, 250 (1901). (e) Herrmann, *Ber.*, **38**, 2813 (1905).

[12] Tschugaeff and others, (a) *Ber.*, **43**, 1200 (1910); (b) *Compt. rend.*, **154**, 33 (1912); (c) *Z. anorg. Chem.*, **82**, 401 (1913); (d) **82**, 420 (1913); (*e*) **83**, 8 (1913); (f) **86**, 241 (1914).

[13] (a) Reynolds, *Ann.* **150**, 232 (1869). (b) Claus, *Ann.*, **179**, 128 (1875); (c) *Ber.*, **9**, 226 (1876). (d) Maly, *Ber.*, **9**, 172 (1876). (e) Prätorius-Seidler, *J. prakt. Chem.*, [2] **21**, 142 (1880). (f) Rathke, *Ber.*, **14**, 1774 (1881).

[14] Kurnakow, *J. prakt. Chem.*, [2] **50**, 481 (1894); **51**, 234 (1895). Rathke, *Ber.*, **17**, 307 (1884). Blomstrand, *J. prakt. Chem.*, [2] **38**, 528 (1888). Bernthsen, *Ann.*, **184**, 290 (1877); **192**, 1 (1878).

pared and studied extensive series of complex salts of platinum, copper, palladium, silver, etc., with thio-urea and thio-acetamide. These compounds also agree with Werner's formulation.

In addition to the more or less thoroughly studied addition compounds already discussed, there exists a host of other addition products of metallic salts with sulfides, both organic and inorganic which, as a rule, are less stable or less well understood. Most of them have been prepared in connection with special lines of research and frequently in non-aqueous solvents. A few, however, are met with in the course of ordinary analytical work, the most familiar of these being the white and orange-red transition products, $HgCl_2.2HgS$[15] and $PbCl_2.xPbS$, formed in the precipitation of the respective metals from chloride solutions by means of hydrogen sulfide, and the white compound, $Hg(NO_3)_2.2HgS$, sometimes observed in seeking to separate mercuric sulfide from the sulfides of copper, bismuth, etc., especially when the nitric acid employed is too concentrated. Also, cadmium salt solutions give with hydrogen sulfide precipitates of all colors from bright yellow, through orange almost to brown, depending upon the nature and concentration of the acid present. These precipitates are never pure cadmium sulfide, but contain varying amounts of $CdCl_2.xCdS$, etc., according to the conditions of precipitation.[16] Further, there are alkaline sulfo salts containing arsenic, antimony, tin, etc., which in solution are familiar to all analytical chemists. In addition to these, Ditte[17] has prepared various crystalline addition compounds of alkali sulfide with the sulfides of antimony, bismuth, copper, gold, mercury, silver and tin. Addition compounds of simple organic sulfides with salts of metals not belonging to the platinum family, may also be cited.[18] And finally, by the action of dry hydrogen sulfide, *in excess*, upon anhydrous solutions of metallic salts in organic solvents, various sulfide addition products have been prepared.[19]

The Mechanism of the Interaction of Hydrogen Sulfide and Metallic Salts in Aqueous Solution.—In the light of the foregoing evidence, and in view of the fact that compounds are often present in solution either too

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[15] This compound was first obtained by H. Rose, by the slow addition of hydrogen sulfide to mercuric chloride in aqueous solution, *and also by the action of aqueous mercuric chloride upon freshly precipitated mercuric sulfide.* Compare *Pogg. Ann.*, **13,** 60 (1822).

[16] Compare Treadwell-Hall, "Analytical Chemistry," Wiley and Sons, New York, **1,** 223 (1921).

[17] Ditte, *Ann. chim. phys.*, [8] **12,** 229 (1907). For example, -$HgS.K_2S.H_2O$; $HgS.K_2S.7H_2O$; and $5HgS.K_2S.H_2O$. See also Knox, *Trans. Faraday Soc.*, **4,** 36 (1908), according to whom Na_2HgS_2 is the predominating complex formed by HgS in Na_2S solution, and who obtained crystalline $2 Na_2S.5HgS.2H_2O$ from this solution.

[18] Beilstein, "Handbuch," 3rd ed., vol. 1, pp. 354–365. Foerster, Cooper and Yarrow, *J. Chem. Soc.*, **111,** 809 (1917).

[19] Naumann and others, (a) *Ber.*, **32,** 999 (1899); (b) **37,** 3600, 4328 (1904); (c) **42,** 3789 (1909); (d) **43,** 313 (1910); (e) **47,** 247; (f) 1369 (1914).

unstable or relatively too soluble for isolation, the occurrence may be deduced of *addition reactions*, analogous to the combination of salts with alkyl sulfides, *in which hydrogen sulfide itself takes the role of the organic sulfide.* For example, in the case of bivalent platinum, we might expect a reaction similar to that represented by the equation:[12f] $2H_2PtCl_4 + 4R_2S \rightleftharpoons [Pt(SR_2)_4]PtCl_4 + 4HCl$; namely, $2H_2PtCl_4 + 4H_2S \rightleftharpoons [Pt(SH_2)_4]PtCl_4 + 4HCl$. In that case, however, we should expect the product to be of an unstable nature, because of the presence of mobile hydrogen, and to decompose more or less promptly:[20] $[Pt(SH_2)_4]PtCl_4 \rightleftharpoons [(H_2S)_2Pt(SH)_2] + H_2PtCl_4$, and $[(H_2S)_2Pt(SH)_2] \rightleftharpoons Pt(SH)_2 + 2H_2S$. Now, to consider more in detail the case of mercury, in the transition from a mercuric salt to mercuric mercaptide, the following types of compounds are possible: I. HgX_2; II. $Hg(SR)_2.3HgX_2$; III. $Hg(SR)_2.2HgX_2$; IV. $Hg(SR)_2.HgX_2$; and V. $Hg(SR)_2$, or $M_2(HgS_2)$; in which R represents hydrogen or a univalent organic radical, X a univalent negative radical, and M a univalent positive radical. Of addition compounds of mercuric salts with organic sulfides, the following types exist: VI. $R_2S.HgX_2$; VII. $2R_2S.HgX_2$; and VIII. $C_2H_4(SR)_2.HgX_2$. Many representatives of these types have been prepared and studied,[21] and within a given type the members often differ widely in stability. In general however, those compounds having hydrogen for a radical, while very unstable, can nevertheless be studied by means of their decomposition products. Among these latter, we may list the following types: IX. $HgS.HgX_2$; X. $2HgS.HgX_2$; and, in general, XI. $n HgS.HgX_2$, of which $3HgS.HgX_2$ is a known member, and to which $[n HgS.Hg]S$, or $(HgS)_n$, may be ascribed.[22]

In the interaction of hydrogen sulfide and mercuric chloride, neglecting a possible hydration of the compounds, we might, in view of what has been

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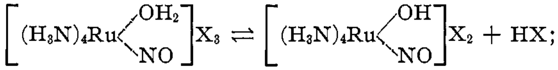
[20] The first of these decompositions is analogous to hydrolysis as interpreted by Werner, but with hydrogen sulfide in the compound, instead of water. Compare, for example, the hydrolytic decomposition,



$$\left[(H_3N)_4Ru\begin{matrix}OH_2\\NO\end{matrix}\right]X_3 \rightleftharpoons \left[(H_3N)_4Ru\begin{matrix}OH\\NO\end{matrix}\right]X_2 + HX;$$

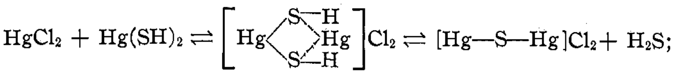
Werner, *Ber.*, **40**, 2617 (1907).

The $Pt(SH)_2$ formed in the last reaction might decompose directly into PtS and H_2S; but more probably it would react with other substances present. See under mercury.

[21] *Type II:* (a) Sachs, *Ber.*, **54**, 1849 (1921). *Type III:* (b) Bertram, *Ber.*, **25**, 64 (1892); Sachs, *loc. cit.* *Type IV:* (c) Debus, *Ann.*, **72**, 1 (1849); (d) Hofmann and Rabe, *Z. anorg. Chem.*, **17**, 26 (1898); (e) Ray, *J. Chem. Soc.*, **109**, 131 (1916); (f) **115**, 871 (1919); Sachs, *loc. cit.* *Type V:* (g) Claeson, *J. prakt. Chem.*, [2] **15**, 193 (1877); (h) *Ber.*, **20**, 3407 (1887). *Type VI:* (i) Smiles, *J. Chem. Soc.*, **77**, 160 (1900); Ref. 11d. *Type VII:* (j) Ref. 13c. *Type VIII:* (k) Beilstein, "Handbuch," 3rd ed., **1893**, vol. 1, p. 364.

[22] *Type IX:* Borelli, *Gazz. chim. ital.*, **39**, 458 (1909). *Type X:* Barfoed, *Jahrb. Chem.*, **1864**, 281; Spring, *Ann.*, **199**, 116 (1879); Ref. 19. *Type XI:* Borelli, *loc. cit.*, p. 455.

said concerning bivalent platinum, expect an analogous conversion of a portion of the salt, that is, through a compound such as $[(H_2S)_nHg]HgCl_4$, into mercuric hydrosulfide, and this in turn to react with mercuric chloride, as shown in the equations.[23]



$$HgCl_2 + Hg(SH)_2 \rightleftharpoons \left[Hg\begin{matrix}S—H\\ \\S—H\end{matrix}Hg\right]Cl_2 \rightleftharpoons [Hg—S—Hg]Cl_2 + H_2S;$$

$$2[HgSHg]Cl_2 \rightleftharpoons [(HgS)_2Hg]Cl_2 + HgCl_2;$$

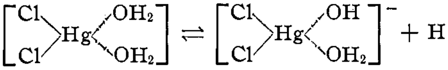
$$[(HgS)_2Hg]Cl_2 + 2SH^- \rightleftharpoons [(HgS)_2Hg](SH)_2 + 2Cl^-;$$

and, more slowly,

$$[(HgS)_2Hg](SH)_2 \rightleftharpoons [(HgS)_2Hg]S + H_2S$$

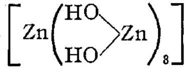
These reactions, through $Hg(SH)_2.HgCl_2$, of Type IV, coupled with the possibility of others through Types II and III, would seem to account in a satisfactory manner for the various well-known color changes which occur during the slow passage of hydrogen sulfide into mercuric chloride solutions acidified with hydrochloric acid; moreover, their reversible nature readily accounts for the conversion of black mercuric sulfide into the white compound, $HgCl_2.2HgS$, by aqueous mercuric chloride.[15] Furthermore, the behavior of the colloidal sulfides of the heavy metals, including instances of their complete reversibility with respect to hydrogen sulfide,[7] is in full harmony with this interpretation,[24] as are also many phenomena which have been noted in the precipitation of metallic sulfides.[25]

[23] The writers consider that, in aqueous solution, the unpolymerized portion of mercuric chloride exists, partly at least, in the equilibrium forms:



$$\left[\begin{matrix}Cl\\Cl\end{matrix}Hg\begin{matrix}OH_2\\OH_2\end{matrix}\right] \rightleftharpoons \left[\begin{matrix}Cl\\Cl\end{matrix}Hg\begin{matrix}OH\\OH_2\end{matrix}\right]^- + H^+.$$

This assumption, while based upon analogy, accounts satisfactorily for several well-known properties of this solution, including its distinctly acid reaction.

Regarding the existence of oxygen compounds of the type shown in these equations, such as  $\left[Zn\left(\begin{matrix}HO\\HO\end{matrix}Zn\right)_3\right](NO_3)_2$, see A. Werner, *Ber.*, **40**, 4441 (1907), and for clear confirmation of the structural formula, *Ber.*, **47**, 3087 (1914). See also V. Borelli, *C. A.* **5**, 1716 (1911), regarding the nature of higher order compounds of mercuric sulfide with mercuric acetate (sulfur migrates to the cathode, showing its presence in a complex cation).

Sulfur compounds of mercury analogous to that formed in the first equation are representatives of Type IV. Similar decomposition reactions are amply furnished by the sulfide complexes of mercury. For instance, $Hg(SC_7H_7)_2 \rightarrow HgS + (C_7H_7)_2S$ [R. Otto, *Ber.*, **13**, 1290 (1880)].

[24] In the decomposition of the complex hydrosulfide, according to the equation, $x[Hg(SH)_2Hg](SH)_2 - yH_2S \rightleftharpoons Hg_{2x}S_{4x-y}H_{4x-2y}$, the product may be regarded as consisting of colloidal particles, flocculated or not, according to the proportion of combined H_2S still retained, etc., and of a size depending upon the value of x. Nor is the electrically charged nature of the particles difficult of comprehension on this basis.

[25] For example: (a) The precipitation of zinc by H_2S, in a solution 0.01 *N* with respect to hydrogen ion, under quantitative analytical conditions, does not begin to occur for about 10 minutes [Fales and Ware, THIS JOURNAL, **41**, 493 (1919)]; (b) The

Facts especially difficult to explain in simple ionic terms are the failure of the precipitates of nickel and cobalt with hydrogen sulfide to dissolve in acid strong enough to prevent their formation,[26] and the precipitation of lead sulfide from solution before the attainment of the experimentally determined solubility product.[27] Jellinek and Czerwinski[28] have recently investigated the behavior of lead sulfide, and conclude that different modifications of the compound are precipitated from solutions containing sodium sulfide and sodium hydrosulfide, and others have held similar views concerning the sulfides of nickel and cobalt. Nevertheless, a more likely explanation is the probable existence of intermediate complexes, the properties of which would in such cases account for the observed facts.

Finally, the solvent action of aqueous acids upon certain sulfides suggests the occurrence of reactions such as are indicated by the equations,[29] $MS + 2H^+ = [M...SH_2]^{++}$; $[M...SH_2]^{++} + 5H_2O = [(H_2O)_5M...SH_2]^{++}$; and $[(H_2O)_5M.SH_2]^{++} + H_2O = [M(OH_2)_6]^{++} + H_2S$.

Experimental Part

I. The Presence of Hydrosulfide in Equilibrium with Metallic Sulfide.—Into each of six numbered test-tubes, almost filled with freshly saturated hydrogen sulfide water, about 1 cc. of ethyl iodide or bromide was introduced. Nothing further was added to mixture No. 1; to Nos. 2, 3 and 4, respectively, freshly precipitated ferrous sulfide, cadmium sulfide and mercuric sulfide were added; to No. 5 was added a slightly acidified solution of ferrous chloride; and to No. 6, dried and heated mercuric sulfide, either black or red. The tubes were then tightly stoppered and allowed to stand. In Nos. 2, 3 and 4, the odor of mercaptan was detected within two or three hours, and in No. 4, in case ethyl iodide was used, crystals of mercuric iodide appeared within a week. In No. 6, the odor of mercaptan was noted in about a week; but in Mixtures 1 and 5 the odor of mercaptan could not be detected at any time during a month.

In the case of the mercuric sulfide mixture, in order to demonstrate with certainty the formation of mercaptan, the following experiment was performed. A slow current of hydrogen sulfide was passed for several days through three wash bottles, in series, the first containing mercuric

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very pronounced tendency of the zinc sulfide to carry down *cobalt sulfide* when cobalt is also present in the solution described above [Fales and Ware, *loc. cit.*, p. 497]. In connection with the contamination of precipitates in such cases, see G. McP. Smith [*ibid.*, **39**, 1152 (1917)]; and (c) the precipitation of lead sulfide from a solution of lead chloride by means of freshly precipitated zinc sulfide.

[26] Thiel and others, *Z. anorg. Chem.*, **61**, 396 (1909); **86**, 1 (1914).

[27] Stieglitz, "Elements of Qualitative Analysis," The Century Co., New York, **1**, 212 (1913).

[28] Jellinek and Czerwinski, *Z. physik. Chem.*, **102**, 474 (1922).

[29] Compare, for example, with the solution of cobaltous oxide in dil. HNO_3, with the formation of hydrated cobalt nitrate, $Co(NO_3)_2.6H_2O$, or $[Co(OH_2)_6]$ $(NO_3)_2$.

sulfide, water and ethyl iodide, the second mercuric sulfide and water, and the third mercuric oxide and dilute alcohol. Finally, to mention only the third bottle, the solid material in this was filtered off, extracted with hot alcohol, and the extract filtered. Upon cooling, this liquid deposited in small quantity a crystalline substance, which was readily identified as mercuric mercaptide.

The formation of mercaptan as noted in these experiments cannot be ascribed to a direct reaction between hydrogen sulfide and ethyl halide, because, in the absence of metallic sulfide, these substances yield no mercaptan. Nor can the formation of the mercaptan be ascribed to a catalytic action of the metallic ion because, in the absence of metallic sulfide, no mercaptan is formed in the mixture containing ferrous chloride. We are forced to the conclusion that in the tubes containing the sulfide precipitates, in which alone mercaptan formation takes place, *both hydrosulfide and sulfide are present, in equilibrium,*[7] *and that the formation of mercaptan is due to an exchange of halogen for hydrosulfide radical.* The formation of the mercaptan may therefore be represented by the following equations: $MS + H_2S \rightleftharpoons M(SH)_2$; and $M(SH)_2 + 2C_2H_5I \rightleftharpoons MI_2 + 2C_2H_5SH$.

II. Analytical Methods.

Mercury.—Volumetric and distillation methods for determining mercury, in the sulfur complexes, were found to be less satisfactory than the familiar sulfide method. In general the following procedure was adopted, although in a few cases it was necessary first to remove the organic matter. In such cases, the material was oxidized with fuming nitric acid, after which the solution containing the mercury was diluted, filtered, and then treated with the sodium sulfide.

The sample was moistened with water and dissolved in freshly prepared 6 *N* sodium sulfide solution. The mixture was diluted to 100 cc., heated to boiling, and saturated ammonium nitrate solution added, in quantity sufficient for the precipitation and flocculation of the mercuric sulfide. The ammonia was mostly expelled by boiling, after which the precipitate was filtered into a weighed Gooch crucible, in which it was dried at 105°. It was then extracted with carbon disulfide, washed with alcohol and ether, and again dried at 105°. The gain in weight was taken as mercuric sulfide.

Sulfur in Inorganic Complexes.—The sample, mixed with 50 cc. of water, was treated with 1 cc. of bromine, and the reaction allowed to go to completion. Sodium peroxide was then added, and after a short time the excess was decomposed by boiling. The liquid was finally neutralized with hydrochloric acid, ammonium carbonate was added to precipitate the mercury, and sulfate was determined in the filtrate by the usual procedure.

Acid Radicals in Mercury Complexes.—A weighed sample of 0.5–1.0 g. was boiled with water until thoroughly disintegrated; then fresh hydrogen sulfide water was added in sufficient quantity to coagulate the mercuric sulfide formed. The filtrate was freed from volatile sulfides by boiling, after which the liberated acid was titrated with standard alkali, with the use of a suitable indicator. For example, $[Hg(SC_2H_5)_2Hg](ClO_4)_2 + 2H_2S \longrightarrow 2HgS + 2C_2H_5SH + 2HClO_4$; a blank was run at the same time, and the necessary correction applied for any (atmospheric) oxidation of sulfides.

Nitrogen.—In nitrates and nitrites, nitrogen was determined as nitric oxide, by means of the nitrometer.

Chlorine.—Chlorides were analyzed in certain cases by double decomposition with silver nitrate; that is, by adding a standard solution of the latter in excess, filtering from the precipitated mixture of complex nitrate and silver chloride, and titrating the excess according to Volhard. When this proved inadequate, the method of decomposing the substance with a solution of sodium in liquid ammonia was used. This elegant method of Chablay[30] was found to be generally applicable.

III. Preparation of Materials.

Mercuric Perchlorate.—Chikashige[31] prepared this salt, and recorded its existence as a hexahydrate; the formula, according to his data, fell halfway between 6.0 and 6.5 molecules of water.

The salt for our use was made by warming red mercuric oxide with a slight excess of 10% perchloric acid, filtering through asbestos, evaporating the filtrate to a sirupy consistence, and cooling rapidly with stirring. After three recrystallizations from water the salt which separated at 40–50° was allowed to come to equilibrium in a vacuum desiccator over some of the same partially dehydrated material. Upon analysis, the crystals were found to correspond to a tetrahydrate.

Analyses. Calc. for $Hg(ClO_4)_2.4H_2O$ (mol. wt., 471.6): Hg, 42.54; ClO_4, 42.18. Found: Hg, 42.28; ClO_4, 42.06.

Crystals separating at 10–15° and kept in a desiccator over the tetrahydrate were found to correspond in composition to a pentahydrate.

Analyses. Calc. for $Hg(ClO_4)_2.5H_2O$ (mol. wt., 489.6): Hg, 40.97; ClO_4, 40.63. Found: Hg, 40.67; ClO_4, 41.09.

Upon the slow evaporation of a 25% aqueous solution of the salt, at 0° over sulfuric acid in a vacuum desiccator, long needle-like crystals were obtained. These were freed from mother liquid by drainage for several days at 0° in a closed vessel. The crystals, apparently dry, were found upon analysis to contain 6.5 molecules of water; but very likely they correspond to a hexahydrate.

Analyses. Calc. for $Hg(ClO_4)_2.6H_2O$ (mol. wt., 507.6): Hg, 39.52; ClO_4, 39.19. Calc. for $Hg(ClO_4)_2.6.5H_2O$ (mol. wt., 516.6): Hg, 38.83; ClO_4, 38.50. Found: Hg, 39.94; ClO_4, 38.51.

All three forms are very deliquescent.

Mercury Mercaptide.—This compound was prepared by Claesson[32] from mercuric cyanide and ethyl mercaptan; but it can be prepared more cheaply, and with less danger, from mercuric oxide.

A 25% solution of ethyl mercaptan, in alcohol, was added to an alcoholic suspension of the equivalent amount of red oxide of mercury, and the mixture warmed and stirred. After completion of the action, the mixture was allowed to cool and settle, and the clear alcoholic layer was decanted from the solidified mercaptide. The mercaptide was extracted from a residue of mercuric oxide, sulfide, etc., with about five times its weight of boiling carbon tetrachloride; the filtered hot solution was poured into a suitable volume of boiling alcohol; and the mixture was filtered from the precipitated impurities. On cooling, the mercaptide separated in the form of pure, glistening white plates, melting at 78°.[33]

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[30] Chablay, *Ann. chim.*, [9] **1,** 469 (1914).

[31] Chikashige, *J. Chem. Soc.*, **67,** 1013 (1895). This salt was originally described by Sérullas, *Ann. chim. phys.*, [2] **46,** 306 (1831), who noted its existence in two crystalline forms. He recorded no analytical data for these.

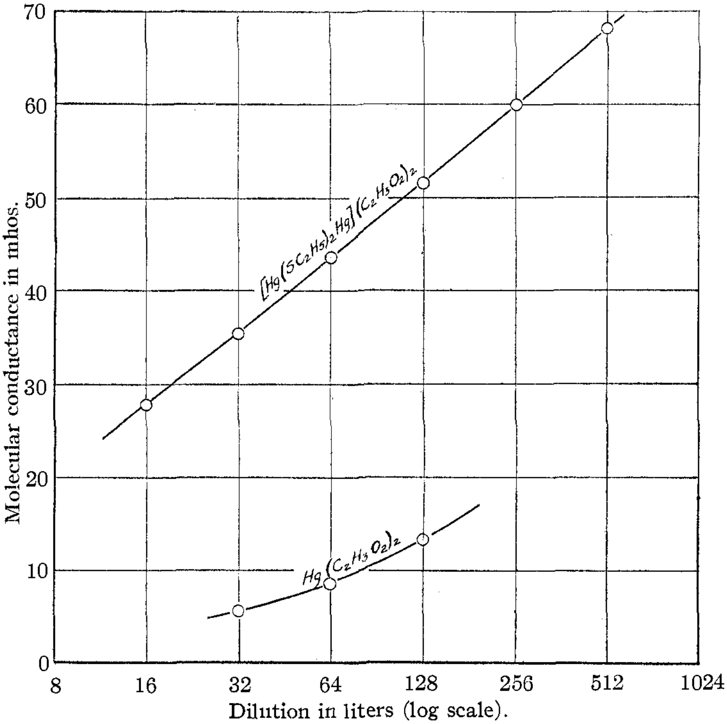
[32] Claesson, *J. prakt. Chem.*, [2] **15,** 193 (1887).

[33] In the *Chemiker-Kalender* for 1911, 60° is recorded as the melting point of this compound; and in that for 1923, 76°. Our material, therefore, would seem to exceed the latter in purity.

IV. Organic Sulfur Complexes of Mercury. *Dieththiol-dimercurio acetate,*[34] $[Hg(SC_2H_5)_2Hg](C_2H_3O_2)_2$.—This compound was made by Sachs,[21a] by the interaction of ethyl thiolacetate and mercuric acetate in acetic anhydride, and also by mixing mercuric acetate and ethyl mercaptan in the same solvent. Influenced, however, by the work of others, he erroneously assigned to it the "half-formula," $C_2H_5S—Hg—OCOCH_3$.

The compound may readily be prepared by mixing 16.14 g. of mercuric mercaptide with 15.94 g. of mercuric acetate in 60 cc. of warm water. Upon stirring, a clear solution is formed, from which, upon slow evaporation, the pure salt is deposited in large crystals.

Analyses. Calc. for $[Hg(SC_2H_5)_2Hg](C_2H_3O_2)_2$ (mol. wt., 641.5): $C_2H_3O_2$, 18.42. Found: 18.52%.



The salt is very soluble in water, alcohol and carbon tetrachloride, and slightly soluble in ether and benzene. The aqueous solution yields precipitates of the corresponding salts with hydrochloric acid, nitric acid, potassium chloride, bromide and iodide and sodium nitrite. It gives no precipitate with sulfuric acid, and only a slight one with sodium sulfate or disodium phosphate.

The salt is more soluble in cold than in hot water.[35] A solution saturated at 25°,

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[34] According to the systematic nomenclature of A. Werner, "Neuere Anschauungen," Friedr. Vieweg und Sohn, Braunschweig, **1913**, p. 92.

[35] A very striking experiment illustrating retrograde solubility consists in placing a sealed tube of the solution, saturated at room temperature, in a beaker of boiling water. The liquid in the tube becomes milky, but quickly clears up upon being cooled. This can be repeated indefinitely.

when warmed becomes milky and finally separates into two layers, a lower viscous one and an upper aqueous one. The viscous layer crystallizes upon cooling, if kept separate from the aqueous layer. At first, it was thought likely that the lower layer consisted of mercuric mercaptide, from the dissociation of the salt; but this is not the case. A rough determination showed the weight ratio, $C_2H_3O_2/Hg$, to be 0.27 in the viscous layer, and 0.30 in the aqueous layer, while the ratio calculated for the compound is 0.294.

Cryoscopic molecular-weight determinations showed the compound to have the "double molecular" formula, and to be ionized to a very appreciable degree.

Subs., 0.8173, 1.0133, 1.0133: water, 29.2, 25.0, 25.0; Δt, 0.094°, 0.134°, 0.131°. Calc. for $[Hg(SC_2H_5)_2Hg](C_2H_3O_2)_2$: mol. wt., 641.5. Found: 554, 564, 576; mean, 565.

The behavior of the salts of this series upon treatment with liquid ammonia, to be described below, is in full harmony with the molecular formulas herein ascribed to them.

The following conductance data were obtained with this salt, at 25°, dissolved in water having a specific conductance = 1.3×10^{-6} mhos. They are followed by data on mercuric acetate, at 25°, taken from Abegg's *Handbuch*.[36] The dilution curves of the two salts are shown in the accompanying figure.

Dilution (L. per formula wt.).....	16	32	64	128	256	512
Specific cond. $\times 10^3$............	1.74	1.11	0.680	0.404	0.234	0.133
Mol. cond......................	27.9	35.5	43.5	51.7	60.0	68.1
Mol. cond. of $Hg(C_2H_3O_2)_2$.......	..	5.72	8.61	13.2	...	...

Dieththiol-dimercurio Perchlorate, $[Hg(SC_2H_5)_2Hg](ClO_4)_2$.

Mercury mercaptide, dissolved in carbon tetrachloride, was treated with an excess of saturated mercuric perchlorate solution. After a vigorous reaction, the aqueous portion solidified. To this, water was added to a pasty consistence, and the mixture heated and stirred. Next morning, the white amorphous precipitate was filtered off, and dried over sulfuric acid in a vacuum.

Analyses. Calc. for $[Hg(SC_2H_5)_2Hg](ClO_4)_2$ (mol. wt., 722.3): Hg, 55.5; ClO_4, 27.8. Found: Hg, 55.0; ClO_4, 27.8.

The salt is slightly soluble in water. When dry it is explosive, but if touched with the flame of a match, the explosion is local and the main portion is blown away undecomposed.

Dieththiol-dimercurio Nitrite $[Hg(SC_2H_5)_2Hg](NO_2)_2$.—This compound has been prepared by Ray,[21e] by adding ethyl mercaptan to a solution of sodium mercuric nitrite. Nitrous fumes were evolved in a violent reaction, with possible oxidation of mercaptan, and the formation of by-products. Ray's product contained 4.78% of nitrogen according to his analysis.

Upon adding sodium nitrite to a well-cooled solution of dieththiol-dimercurio acetate, however, we readily obtained a yellowish precipitate of this nitrite, which became crystalline upon standing.

Analyses. Calc. for $[Hg(SC_2H_5)_2Hg](NO_2)_2$ (mol. wt., 615.3): N, 4.55. Found: 4.68.

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[36] Abegg, "Handbuch der anorg. Chemie," S. Hirzel, Leipzig, **2,** part 2, 628 (1905).

Dieththiol-dimercurio Chloride, Bromide and Iodide, $[Hg(SC_2H_5)_2Hg]X_2$.—These salts have previously been prepared, by various methods, as noted earlier in this paper. Owing largely to the work of Hofmann and Rabe,[37] however, the so-called half formula, $C_2H_5S—Hg—X$, has been generally assigned to them. This we have shown to be erroneous.

Samples of these compounds were prepared by treating an alcoholic solution of mercuric mercaptide with the proper mercuric halide. These were analyzed for their halogen contents, with the following results.

Analyses. Calc. Cl, 11.94; Br, 23.4; I, 32.6. Found: Cl, 11.89; Br, 21.7; I, 32.9.

Dieththiol-dimercurio chloride is a white microcrystalline substance, which decomposes on heating, without melting. It is insoluble in water, alcohol, ether, carbon tetrachloride, glacial acetic acid, and many other organic solvents. However, it is very sparingly soluble in boiling xylene, from which it may be crystallized. It dissolves in concd. hydrochloric acid, with the evolution of mercaptan. Heated with aniline, it gives a beautifully crystalline product, yet to be investigated.

A solution of hydrogen sulfide in acetone or alcohol transforms the white chloride into a deeply orange-colored material, still containing chlorine, and the mother liquid contains mercaptan. More hydrogen sulfide converts the orange-colored substance into black mercuric sulfide. These transformations are accompanied by various color changes, but attempts to isolate an intermediate product of definite molecular composition were unsuccessful.

Although the properties of dieththiol-dimercurio bromide and iodide have been very fully described by Hofmann and Rabe,[37] there is one reaction of the salts of this series which seems to have been hitherto overlooked. *The dieththiol-dimercurio salts are dissolved by anhydrous liquid ammonia, with more or less complete dissociation into their simpler molecular constituents.*

The Behavior of Dieththiol-dimercurio Salts Towards Liquid Ammonia. *Chloride.*—A 1.00-g. sample of this chloride, placed in a beaker, was treated with 50 cc. of anhydrous liquid ammonia. The salt dissolved to a yellowish liquid, which upon evaporation of the solvent left a solid consisting of two varieties of crystals. Upon extracting these with carbon tetrachloride and distillation of the solvent a residue weighing 0.377 g. was obtained; and this, after one recrystallization from alcohol, was found to melt at 76°. It was mercuric mercaptide. The water-soluble portion of the residue left on extraction with carbon tetrachloride contained 0.0449 g. of chlorine; and the water-insoluble portion, by means of a Kjeldahl determination, contained the equivalent of 0.0126 g. of ammonia. These figures indicate that upon treatment with carbon tetrachloride about 70% of the products of dissociation, as represented by the equation, $[Hg(SC_2H_5)_2Hg]Cl_2 \rightleftharpoons Hg(SC_2H_5)_2 + HgCl_2$, had failed to recombine.[38]

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[37] Hofmann and Rabe, *Z. anorg. Chem.*, **14**, 293 (1892).

[38] However, the entire action is not so simple as that indicated, since the mercuric chloride produced is itself acted upon by liquid ammonia. In an excess of this solvent, it behaves as represented by the equations: $HgCl_2 + 12NH_3 \rightleftharpoons HgCl_2.12NH_3$; and $HgCl_2 + 2NH_3 \rightleftharpoons Cl—Hg—NH_2 + NH_4Cl$. [(a) E. C. Franklin, *Am. Chem. J.*, **47**, 368 (1912)].

Bromide.—The same procedure was followed, with a 1.00-g. sample, as in the case of the chloride. The salt gave with liquid ammonia a colorless solution, from which also a mixed residue remained after evaporation. This, upon extraction with carbon tetrachloride, yielded 0.143 g. of the mercaptide, melting at 78°. In the aqueous extract was found 0.046 g. of bromine, and in the insoluble residue 0.006 g. of ammonia. The lower percentage of mercaptide obtained in this case may be ascribed either to a different ammonolytic tendency[39] of mercuric bromide, or to a greater tendency of the bromide to recombine with the mercaptide under the conditions of extraction with carbon tetrachloride. In this connection, compare with the behavior of the iodide.

Iodide.—The procedure was again the same. The solution in ammonia was colorless, and the residue on evaporation consisted of red crystals, evidently of mercuric iodide[40] and white plates of mercuric mercaptide. Upon seeking to extract the mercaptide with carbon tetrachloride, or other solvents, the two substances recombined, apparently to give the original compound.

Acetate.—Here again the same procedure was followed. The solution in ammonia was of a grayish tinge, and left upon evaporation two varieties of crystals. When an attempt was made to extract the mercaptide, however, recombination took place as in the case of the iodide.

V. Inorganic Sulfur Complexes of Mercury.—*Evidence of the Existence of Thio-dimercurio Perchlorate.*[41]

A measured volume of 0.1 *M* mercuric perchlorate, diluted somewhat, was titrated with freshly prepared hydrogen sulfide water. (It should be noted that hydrogen sulfide and perchloric acid do not interact in aqueous solution.) Each portion of hydrogen sulfide added produced locally a flocculent black precipitate, *which quickly redissolved on stirring, to a clear, colorless solution, with no trace of opalescence.* As the addition of the reagent continued, however, the clear, colorless liquid soon began to acquire a brownish opalescence, but nevertheless it remained practically transparent and continued to redissolve the precipitate, more and more slowly, as produced, until a point was reached at which the further addition of hydrogen sulfide yielded a permanent black precipitate. This point, while difficult of exact location by direct observation, could nevertheless be very closely approximated. The permanent precipitate showed no tendency to settle, as the titration proceeded, *until finally a single drop of hydrogen sulfide water suddenly flocculated the colloid.* Somewhat beyond this point, free hydrogen sulfide could be detected in the liquid. The precipitate was filtered off, washed and treated with a quantity of the mercuric perchlorate solution exactly equal to that originally taken, whereupon the precipitate just redissolved and yielded a transparent solution with

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[39] The ammonolytic action in this case is represented by the equation: $2HgBr_2 + 4NH_3 \rightleftharpoons Hg{:}N{-}Hg{-}Br + 3NH_4Br$. (Ref. 38 a, p. 371.) It might be mentioned that $HgBr_2$ is more soluble in CCl_4 than is $HgCl_2$ or HgI_2.

[40] White $HgI_2.2NH_3$, upon standing in air, readily loses ammonia and yields red HgI_2. (Ref. 38 a, p. 373.)

[41] Concerning more or less analogous hydroxy complexes of lead, see Weinland and Stroh, *Ber.*, **55B**, 2706 (1922).

only a slight brownish opalescence. Upon standing for several hours, this solution (as well as a similar one obtained by the addition of hydrogen sulfide to a solution of mercuric perchlorate) deposited a white, almost colloidal precipitate of dithio-trimercurio perchlorate, $[Hg(SHg)_2](ClO_4)_2$. After this deposition was complete, the mercury and perchlorate present in the filtrate were determined.

The data in Table I show that, upon the addition of hydrogen sulfide to mercuric perchlorate solution, a soluble product is formed, containing one equivalent of sulfur to two of mercury: $2Hg(ClO_4)_2 + H_2S \longrightarrow [HgSHg](ClO_4)_2 + 2HClO_4$; that from this the mercury is precipitated by hydrogen sulfide in excess, say as mercuric sulfide: $[HgSHg](ClO_4)_2 + H_2S \longrightarrow 2HgS + 2HClO_4$; and that the freshly precipitated sulfide is soluble in an equivalent amount of aqueous mercuric perchlorate, to form the same soluble compound, thio-dimercurio perchlorate: $HgS + Hg(ClO_4)_2 \longrightarrow [HgSHg](ClO_4)_2$. Upon prolonged standing, this compound decomposes in solution, with the separation of a very much less soluble compound, dithio-trimercurio perchlorate: $2[HgSHg](ClO_4)_2 \longrightarrow [Hg(SHg)_2](ClO_4)_2 + Hg(ClO)_2$.

TABLE I

THE FORMATION AND DECOMPOSITION, AT 25°, OF THIO-DIMERCURIO PERCHLORATE

	No. 1	No. 2
Volume taken of 0.1036 *M* $Hg(ClO_4)_2$, cc.	25.00	25.00
a. Titration with H_2S water		
Required for incipient opalescence, cc.	14.0	18.5
For appearance of permanent suspensoid, cc.	24.0	26.0
For flocculation of suspensoid, cc.	44.7	44.2
Total H_2S water added, cc.	50.0	50.0
b. Precipitate treated with 0.1036 *M* $Hg(ClO_4)_2$		
Volume of solution added, cc.	25.00	25.00
c. Found in filtrate from $Hg(ClO_4)_2.2HgS$		
Mercury equivalent to HgS, g.	0.2561	0.2606
Perchlorate equivalent to 0.0998 *N* NaOH, cc.	24.65	27.70
H_2S added in terms of that required to produce flocculation, %		
For incipient opalescence: (this point has no especial significance)	31.3	41.8
For appearance of permanent suspensoid	53.7	58.8
For flocculation of suspensoid	100.0	100.0
Quantitative relationships		
Moles of HgS formed in *a*	0.00259	0.00259
Moles of $Hg(ClO_4)_2$ added to this HgS in *b*	.00259	.00259
Gram-atoms of Hg in Filtrate *c;* calc.	.00173	.00173
Found	.00110	.00112
Gram-equivalents of ClO_4 in Filtrate *c;* calc.	.00346	.00346
Found	.00246	.00278
On basis of Hg in Filtrate *c*, calc.	.00220	.00224

Now, according to Table I slightly less mercury, and in comparison a greater amount of perchlorate, are found in the filtrate than would be indicated by this last equation. Remembering, however, as has already been demonstrated, that the freshly precipitated sulfide, to which an equivalent amount of mercuric perchlorate was added, contained not only mercuric sulfide but also the hydrosulfide in proportions depending upon the freshness of the precipitate, etc., these apparent discrepancies are readily accounted for on the basis of side reactions such as are represented by the equations: $Hg(SH)_2 + 2Hg(ClO_4)_2 \longrightarrow [Hg(SHg)_2](ClO_4)_2 + 2HClO_4$, and $2[HgSHg](SH)_2 + 5Hg(ClO_4)_2 \longrightarrow 3[Hg(SHg)_2](ClO_4)_2 + 4HClO_4$.

Dithio-trimercurio Perchlorate, $[Hg(SHg)_2](ClO_4)_2$.—The solution of thio-dimercurio perchlorate, obtained as described above, gave upon standing overnight a precipitate, which according to Analysis 1 corresponds in composition to the formula, $Hg(ClO_4)_2.2HgS$. This compound was more conveniently prepared in large quantities by treating freshly precipitated mercuric sulfide with a concentrated solution of mercuric perchlorate. After several days, for complete action, the mixture was centrifuged, and the precipitate washed by decantation until it began to assume a colloidal condition. It was then air-dried *in small portions*, and finally dehydrated in a vacuum over sulfuric acid. Analyses 2 were made on this preparation.

Analyses. Calc. for $[Hg(SHg)_2](ClO_4)_2$ (mol. wt., 864.9): Hg, 69.58; S, 7.41; ClO_4, 23.01. Found: Hg, (1) 69.0, (2) 68.25, 68.57; S, (1) 6.94, (2) 6.89, 6.91; ClO_4, (1) 24.40, (2) 23.06, 23.00. Total: Analysis 1, 100.34; analyses 2, 98.20, 98.48.

Dithio-trimercurio perchlorate is a white, amorphous powder, which undergoes a partial dissociation in water, with the separation of black mercuric sulfide in small amount. This is accompanied by a tendency to assume the colloidal condition. The presence of perchloric acid, or of mercuric perchlorate, prevents this dissociation.

Upon being heated or struck, the dry salt explodes violently, a few milligrams being sufficient to completely shatter a test-tube. Dynamite caps, each loaded with 0.25 g. of this compound, in place of fulminate of mercury, sufficed to set off ten different commercial varieties of dynamite. Blasting powders not containing nitroglycerol, however, were not exploded. One g. of the substance, when run by the improved sand test,[42] cracked 12.3 g. of 20–30-mesh sand. Of this, 8.0 g. passed an 80-mesh sieve, 5.2 g. a 100-mesh sieve, and 3.0 g. passed a 200-mesh sieve. This shows that the salt cracks only one-seventh as much sand as does an equal weight of mercury fulminate, but the sand that is cracked is much more finely pulverized than with the latter.[42]

Dithio-trimercurio perchlorate gives with ammonium or sodium hydroxide an orange-red or yellow solid, too impure to yield a definite formula on analysis; and with hydrochloric or nitric or sulfuric acid, or with sodium chloride or nitrate solution, the salt enters into double decomposition with the formation of a corresponding, less soluble dithio-trimercurio salt. These reactions, which indicate that the dithio-trimercurio complex behaves as a radical in double decompositions, may be represented by the following general equation: $[Hg(SHg)_2](ClO_4)_2 + 2MX \rightleftharpoons [Hg-$

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[42] Dehn, *Chem. Met. Eng.*, **27**, 784 (1922).

$(SHg)_2]X_2 + 2MClO_4$. On the other hand, however, there is evidence which may be interpreted to indicate that these transformations, in part at least, may be due to reactions more complicated than the above. For example, it has already been stated that dithio-trimercurio perchlorate undergoes dissociation in water, to a slight extent, with the separation of black mercuric sulfide. Now, since the filtrate from the aqueous mixture yields with nitric or hydrochloric acid a white precipitate of the corresponding dithio-trimercurio salt, this filtrate must contain in solution either thio-dimercurio perchlorate (formed in accordance with the equation $[Hg(SHg)_2](ClO_4)_2 \longrightarrow HgS + [HgSHg](ClO_4)_2$) or dithio-trimercurio perchlorate; possibly it contains both. At any rate, just as thio-dimercurio perchlorate decomposes in solution slowly to yield a deposit of dithio-trimercurio perchlorate, so also do thio-dimercurio nitrate and chloride appear to decompose, much more rapidly, to yield precipitates of the corresponding, less soluble dithio-trimercurio salts.[43] *This behavior, in the case of the nitrate is described in the next paragraph.* It should be noted that, since these precipitates consist of the decomposition products of complicated unstable substances, and are more or less amorphous as ordinarily obtained, the samples for analysis are generally somewhat contaminated with mixed or adsorbed materials.

A solution of thio-dimercurio perchlorate, $[HgSHg](ClO_4)_2$, prepared as already described, was treated with one of sodium nitrate, with the instantaneous precipitation of dithio-trimercurio nitrate, as a white powder. This was centrifuged, washed and dried. It was analyzed with the following results:

Analyses. Calc. for $[Hg(SHg)_2](NO_3)_2$ (mol. wt., 790.0): Hg, 76.2; N, 3.55. Found: Hg, 75.0; N, 3.38.

In conclusion, it may be stated that the dithio-trimercurio salts are readily dissociated upon treatment with liquid ammonia, with the separation of (insoluble) black mercuric sulfide. In this respect, they are similar in behavior to the dieththiol-dimercurio salts described in the previous section.

Discussion

Before entering upon the enumeration and discussion of the conclusions which we feel to be justified by our work, it would seem worth while to consider briefly a few suggestions of the same nature which have been advanced by others in the past. For it is a striking fact that, dating at least

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[43] Compare this behavior with the analogous behavior of the basic perchlorates of lead, $[Pb(OH)_2.Pb](ClO_4)_2$, $[2Pb(OH)_2.Pb](ClO_4)_2$, etc.; Ref. 41.

Of course this precipitation might be explained in terms of the removal of dithio-trimercuric perchlorate, by direct precipitation with nitrate or chloride, from the equilibrium mixture, $2[HgSHg](ClO_4)_2 \rightleftharpoons [Hg(SHg)_2](ClO_4)_2 + Hg(ClO_4)_2$, with the consequent completion of the action from left to right; but this is unlikely, since dithio-trimercurio perchlorate is not dissolved by even a large excess of concentrated mercuric perchlorate solution, that is, since the reaction does not appear to be reversible.

from 1887, the birth year of the ionic theory, chemical literature contains accounts of at least a few important observations which seem to unequivocally indicate the occurrence of just such reactions as those advanced in the present paper.

For example, in discussing the addition compound, $2C_3H_5Cl.PtCl_4.3(C_3H_5)_2S.3PtS_2$, formed in absolute alcohol by the interaction of platinic chloride and allyl sulfide,[44] Semmler made this significant statement: "*Although analogous platinum addition compounds are at present unknown in inorganic chemistry, there nevertheless occur during the passage of hydrogen sulfide into platinum salt solutions, especially in the cold, reactions characterized by such striking color changes both in the solution and in the precipitate, that here also without doubt the presence of similar addition compounds between chloride and sulfide is to be assumed.*"

Only a year later, Blomstrand,[45] in his memorable researches on the interaction of alkyl sulfides and platinous salts, pointed out that the second of the following reactions might be regarded as a transition from the first to the third: $PtCl_2 + 2(C_2H_5)_2S = PtCl_2.2(C_2H_5)_2S$; $PtCl_2.2(C_2H_5)_2S + 2C_5H_{11}SH = Pt(SC_5H_{11})_2 + 2(C_2H_5)_2S + 2HCl$; $PtCl_2 + H_2S = PtS + 2HCl$. He further intimated that, although neither $Pt(SR)_2$ nor PtS adds hydrogen chloride directly, $Pt(SR)_2$ does apparently add 2RI, with the probable formation of $PtI_2.2R_2S$. *In connection with the formation of the sulfides ordinarily met in analytical practice, and with their behavior towards aqueous acid solutions, these remarks, as well as those already cited of Semmler, were worthy in their day of far more consideration than they appear to have received.* They even seem to contain the germ of a satisfactory interpretation of the anomalous behavior of cobalt and nickel, for which no adequate explanation has yet been offered.[26]

And finally, referring to solutions in anhydrous acetonitrile, Naumann[46] made the following statements: "The liberation of hydrogen chloride from cupric chloride,. . . . by hydrogen sulfide, might be ascribed to the slight degree of ionization in acetonitrile of even the hydrogen halides. But still more striking is the non-precipitation of cupric sulfide by excess hydrogen sulfide in cupric chloride solution, as well as the entrance into solution of (suspended) cupric sulfide upon the passage of hydrogen chloride,. . . . and further several color changes. *These phenomena indicate the existence of complex compounds in and with acetonitrile, more complicated in structure than the observed solvates of the salts with acetonitrile.*"

Turning now to the consideration of our own work, there are certain general conclusions which may be drawn concerning the action of hydrogen sulfide upon aqueous salt solutions of the heavy metals, as follows.

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[44] Semmler, *Ann.*, **241,** 132 and following (1887). The double sulfide, $(C_2H_3)_2S.PtS_2$, was also observed by Semmler (p. 139).

[45] Blomstrand and others, *J. prakt. Chem.*, **38,** 497 (1888).

[46] Ref. 19e, p. 255.

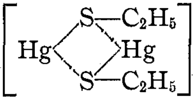
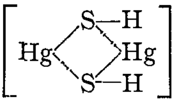
1. The excess of hydrogen sulfide contained in the freshly precipitated sulfides is at least partially present in the hydrosulfide form, probably often in decomposition products of hypothetical, very unstable and apparently soluble intermediate hydrosulfide complexes.

2. The assumption of these hydrosulfide complexes is supported by the existence of analogous hydroxide complexes of lead and other metals, as $[Pb(OH)_2.Pb](ClO_4)_2$ and $[2Pb(OH)_2.Pb](ClO_4)_2$.[41] In the latter complexes, as we should expect, the hydrogen is less mobile than in the corresponding hydrosulfide compounds.

3. Definite indications concerning these hypothetical thiol complexes may be obtained from the study of their organic analogs. Taking the latter as types to which the former are assumed to correspond, the unsubstituted thiol complexes are compounds containing mobile hydrogen in place of the alkyl radicals, and therefore they should readily lose hydrogen sulfide with the formation of intermediate types corresponding to those actually observed, in the case of mercury, in this investigation.

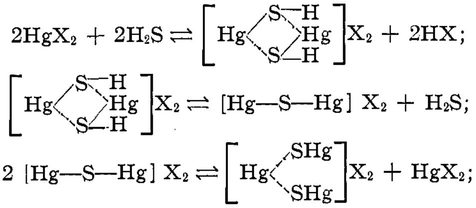
4. The relationship assumed to exist between the organic complexes and the hypothetical intermediate compounds is clearly indicated, moreover, by the fact that the organic sulfides of the complexes are capable of displacement by hydrogen sulfide, as evidenced by methods employed in their analysis in this investigation.

5. The conclusions drawn from the study of the intermediate compounds observed in the precipitation of mercuric salts by hydrogen sulfide can be applied with more or less accuracy to the precipitation of other metallic salts by hydrogen sulfide.

6. Upon treating a mercuric salt with ethyl mercaptan, the product is the *dieththiol-dimercurio salt*,  X_2. By analogy, in the case of hydrogen sulfide, a corresponding product, resulting from the union of mercuric salt with mercuric hydrosulfide, the *dithiol-dimercurio salt*,  X_2, is assumed to be formed which, owing to the presence of mobile hydrogen, should readily lose hydrogen sulfide and yield the *thio-dimercurio salt*, $[Hg—S—Hg]X_2$. The latter type of compound, observed in the case of the perchlorate, in aqueous solution, has been found to decompose according to the equation, $2[Hg—S—Hg](ClO_4)_2 \longrightarrow [Hg(SHg)_2](ClO_4)_2 + Hg(ClO_4)_2$, yielding a product analogous to the white intermediate compound, $HgCl_2.2HgS$, so commonly observed in the precipitation of mercury by hydrogen sulfide, from chloride solutions.

7. Disregarding a possible hydration of the compounds, the mechanism of the interaction of mercuric salts and hydrogen sulfide, in so far as we can

conclude at present, would seem to be that represented by the equations which follow; and there are many indications that salts of other metals, as platinum, lead and cadmium, for example, behave in a more or less analogous manner:[47]



(a) $2HgX_2 + 2H_2S \rightleftharpoons \left[Hg\begin{smallmatrix}S-H\\ S-H\end{smallmatrix}Hg\right]X_2 + 2HX;$

(b) $\left[Hg\begin{smallmatrix}S-H\\ S-H\end{smallmatrix}Hg\right]X_2 \rightleftharpoons [Hg-S-Hg]\,X_2 + H_2S;$

(c) $2\,[Hg-S-Hg]\,X_2 \rightleftharpoons \left[Hg\begin{smallmatrix}SHg\\ SHg\end{smallmatrix}\right]X_2 + HgX_2;$

(d) $[Hg(SHg)_2]X_2 + 2H_2S \rightleftharpoons [Hg(SHg)_2](SH)_2 + 2HX;$

(e) $[Hg(SHg)_2](SH)_2 \rightleftharpoons [Hg(SHg)_2]S + H_2S.$

8. After a careful consideration of the evidence, including that offered in the experimental part, the writers do not hesitate to draw the conclusion that the considerations advanced in this paper give good promise of furnishing a consistent, comprehensive, and truthful interpretation of the interactions of hydrogen sulfide and metallic salt solutions; and that the precipitation of the heavy metals with hydrogen sulfide, both in acid and in alkaline solutions, will eventually be regarded in the light of the coördination theory of Werner, as are already so many of the subjects of chemistry.

SEATTLE, WASHINGTON

[CONTRIBUTION FROM THE CHEMICAL INSTITUTE OF CHARLES UNIVERSITY, PRAGUE]

A REVISION OF THE ATOMIC WEIGHT OF ALUMINUM. II.[1] THE ANALYSIS OF ALUMINUM CHLORIDE

BY HENRY KREPELKA

RECEIVED MARCH 3, 1924

In the table of the International Committee on Atomic Weights for 1921 the value 27.0 for the atomic weight of aluminum was adopted. This new value, replacing the older value of 27.1, which was evidently too high, is based on a preliminary determination by T. W. Richards and H. Krepelka[2] who obtained 26.963 as a mean of four analyses of aluminum bromide, and is rounded for the International Table to 27.0.

In the present investigation upon this subject pure aluminum chloride was prepared and analyzed by comparison with silver. The properties of aluminum chloride are, of course, less suitable both for synthesis and analysis than those of the bromide. Since the chloride does not melt under ordinary conditions, we have to deal with a material obtained by

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[47] Concerning the probable existence of a compound $Mn_3S_4H_2$, analogous to the product in (*d*), see "A Study of the Green Sulfide of Manganese," by Mickwitz and Landesen, *Z. anorg. allgem. Chem.*, **131,** 101–118 (1923).

[1] Presented before the Bohemian Academy of Prague.

[2] Richards and Krepelka, THIS JOURNAL, **42,** 2221 (1920).