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Symmetrical and Mixed Bisalkylmercuric Sulphides

M. Dadić and D. Grdenić

Laboratory of General and Inorganic Chemistry, Faculty of Science,
University of Zagreb, Zagreb, Croatia, Yugoslavia

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A simple method for the preparation of bisalkylmercuric sulphides, based on the reaction of alkylmercuric bromide with sodium sulphide in alcoholic solution, is proposed. The preparation and the properties of the symmetrical sulphides $(\text{RHg})_2\text{S}$, where $\text{R} = \text{Me}$, Et , $n\text{-Pr}$, $n\text{-Bu}$ and $i\text{-Pr}$, are described. The synthesis of the mixed sulphides $\text{R}'\text{HgSHgR}''$ was performed over the formation of the corresponding sodium alkylmercuric sulphide $\text{R}'\text{HgSNa}$ as an intermediate. The preparation and the properties of mixed sulphides where $\text{R}' = \text{Me}$ and $\text{R}'' = \text{Et}$, $n\text{-Pr}$, are described. All compounds prepared are well defined crystalline substances which decompose slowly on exposure to light.

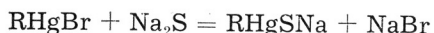
Recent results in the field of onium compounds, which proved the existence of trisalkylmercurioxonium¹ and trisalkylmercurisulphonium² salts, have stimulated the investigation on bisalkylmercuric oxides³ and sulphides. In the present paper the methods of the preparation as well as the properties of alkylmercuric sulphides are described, while the investigations concerning the electric dipole moment measurements, will be published in due course⁴.

Bismethylmercuric sulphide was described first by Frankland⁵ as an amorphous yellow powder, which was obtained by the action of ammonium sulphide on methylmercuric iodide. The pure product was obtained first by Hilpert and Ditmar⁶ by treating an alcoholic solution of methylmercuric chloride with hydrogen sulphide. The same product was prepared later by Perret and Perrot⁷ in the form of bright crystalline leaflets (m. p. 143°C). According to these authors the compound could be, like mercuric sulphide, converted to sulphosalt, the hydrosulphide CH_3HgSH should be thus considered as a weak acid, capable of giving salts with strong bases. In the Russian edition of Whitmor's book on organomercurials⁸ a reaction of hydrogen sulphide with n -butylmercuric hydroxide leading to the formation of $n\text{-C}_4\text{H}_9\text{HgSH}$ is mentioned, but no particular reference is given. In the same monograph bisethylmercuric sulphide is described as a yellow powder⁹. These products were probably impure. The pure sulphides, as isolated in the course of our investigation, are well defined colourless crystalline substances.

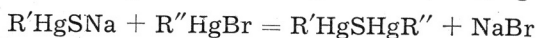
We have established that the preparation of bisalkylmercuric sulphides by means of hydrogen sulphide is not satisfactory, since it gives impure products in a poor yield. Namely, alkylmercuric bromide reacts with hydrogen sulphide by giving hydrogen bromide, which in turn dissolves the precipitated sulphide until an equilibrium is established. This disadvantage can be avoided by the addition of pyridine or another similar base. However, the simplest and most successful method consists in the use of sodium sulphide. This

method is especially suitable in the case of methylmercuric sulphide, which is poorly soluble in alcohol or acetone so that the addition of sodium sulphide can be stopped just in the moment when the molar ratio of the reagents is reached². The higher alkyl homologues are more soluble and the equivalent ratio cannot be obtained in the same way. Therefore, it is more suitable to apply a sodium sulphide solution of the known concentration.

The fact that the equimolar amounts of the reagents give a soluble product can be explained by the following equation:



This equation shows that a method analogous to Williamson synthesis of mixed ethers can be adopted for the preparation of mixed alkylmercuric sulphides. As a matter of fact the mixed alkylmercuric sulphides were prepared in the course of our investigation according to the following equation:



All the sulphides prepared possess a characteristic disgusting odour. *n*-Alkyl homologues represent colourless leaflets, whereas *i*-propyl derivative crystallises in colourless needles. Bisalkylmercuric sulphides turn brown to black on exposure to light. The sensitivity to light increases with the number of carbon atoms. The solubility in organic solvents is increased by the length of the alkyl-chain while the melting point decreases as it is seen from Table I.

TABLE I
Melting points of alkylmercuric sulphides

Alkyl	Me	Et	<i>n</i> -Pr	<i>i</i> -Pr	<i>n</i> -Bu
m. p.	145 ^o	105 ^o	70 ^o	59.5 ^o	59 ^o

Melting point of mixed sulphides is lower than that of both corresponding symmetrical sulphides and amounts to 73.5^oC and 51^oC for the methyl-ethyl and the methyl-propyl-compound, respectively.

EXPERIMENTAL

All melting points are uncorrected.

Alkylmercuric bromides were prepared according to Slotta and Jacobi¹⁰ by the reaction of mercuric bromide with the appropriate Grignard reagent in ethereal solution. Melting points of the alkylmercuric bromides obtained were as follows: CH₃HgBr 161^oC; C₂H₅HgBr 190^oC; *n*-C₃H₇HgBr 136^oC; *i*-C₃H₇HgBr 92^oC; *n*-C₄H₉HgBr 132^oC.

The sodium sulphide used was enneahydrate of the analytical grade. A fresh alcoholic solution of the reagent had to be prepared before use and filtered if necessary. Owing to the high deliquescence of sodium sulphide enneahydrate, the commercial product is usually a mixture of crystals and saturated aqueous solution. In this case the crystals have to be separated from the liquor and dried by pressing between filter-paper before dissolved in alcohol. The sodium sulphide crystals when treated in this way, correspond nearly exactly to the formula Na₂S · 9H₂O.

The analytical determination of mercury and sulphur content was carried out in the usual way. The sample (0.15–0.20 g.) was refluxed with *aqua regia* and the mercury content determined gravimetrically as mercuric sulphide. Sulphur was determined as barium sulphate after refluxing the sample with *aqua regia*.

Methylmercuric sulphide

A warm alcoholic solution of sodium sulphide enneahydrate (0.5 g. in 10 ml.) was mixed with a saturated alcoholic solution of methylmercuric bromide (1 g. in 10 ml.) and the reaction mixture cooled with running water. Bright leaflets were

collected (0.7 g., yield 90% calculated on methylmercuric bromide). The product was recrystallized from alcohol (or chloroform) m. p. 145°C (lit. 143°).

Anal. 0.1238 g. subst.: 0.1246 g. HgS
 0.1809 g. subst.: 0.0901 g. BaSO₄
 C₂H₆Hg₂S (463.35) calc'd.: Hg 86.59; S 6.93%
 found: Hg 86.78; S 6.88%

Bisethylmercuric sulphide

A warm alcoholic solution of sodium sulphide enneahydrate 1.6 g. was gradually added with stirring to a warm solution of ethylmercuric bromide (4.0 g.) in alcohol. The reaction mixture was cooled with running water, and the crude grey product collected (3.0 g., yield 94% calculated on C₂H₅HgBr). Two recrystallizations from benzene gave bright nacreous leaflets; m. p. 105°C.

Anal. 0.1283 g. subst.: 0.1218 g. HgS
 0.2302 g. subst.: 0.1054 g. BaSO₄
 C₄H₁₀Hg₂S (491.41) calc'd.: Hg 81.44; S 6.53%
 found: Hg 81.82; S 6.32%

Bis-n-propylmercuric sulphide

n-Propylmercuric sulphide was prepared analogously from *n*-C₃H₇HgBr (4.0 g.) and Na₂S · 9H₂O (2.0 g.). Yield: 3.0 g. (93%). Bright leaflets from alcohol; m. p. 70°C.

Anal. 0.1015 g. subst.: 0.0913 g. HgS
 0.2103 g. subst.: 0.0909 g. BaSO₄
 C₆H₁₄Hg₂S (519.46) calc'd.: Hg 77.26; S 6.17%
 found: Hg 77.53; S 5.95%

Bis-i-propylmercuric sulphide

i-Propylmercuric sulphide was prepared in the same way from alcoholic solution of *i*-propylmercuric bromide (15.0 g.) and Na₂S · 9H₂O (8.0 g.). Yield: 12.0 g. (98%). After two recrystallizations from alcohol the pure product was obtained as bright needle-like crystals; m. p. 59.5°C.

Anal. 0.1401 g. subst.: 0.1256 g. HgS
 0.2037 g. subst.: 0.0887 g. BaSO₄
 C₆H₁₄Hg₂S (519.46) calc'd.: Hg 77.26; S 6.17%
 found: Hg 77.31; S 6.01%

Bis-n-butylmercuric sulphide

n-Butylmercuric sulphide was obtained analogously from *n*-butylmercuric bromide (5.0 g.) and Na₂S · 9H₂O (2.0 g.). Yield: 4.0 g. (97%). Bright leaflets from alcohol; m. p. 59°C.

Anal. 0.1089 g. subst.: 0.0928 g. HgS
 0.2834 g. subst.: 0.1178 g. BaSO₄
 C₈H₁₈Hg₂S (547.51) calc'd.: Hg 73.35; S 5.87%
 found: Hg 73.45; S 5.72%

Methylmercuric-ethylmercuric sulphide

A warm alcoholic solution of Na₂S · 9H₂O (5.0 g. in 50 ml.) was added to a solution of methylmercuric bromide (5.0 g.) in alcohol (about 50 ml.). A warm saturated alcoholic solution of ethylmercuric bromide (5.0 g. in about 50 ml.) was added and the reaction mixture was heated again. A quick hot filtration followed, the filtrate cooled and a greyish product collected (7.0 g., 89%). Bright leaflets from chloroform, m. p. 73.5°C.

Anal. 0.1064 g. subst.: 0.1036 g. HgS
 0.1987 g. subst.: 0.0952 g. BaSO₄
 C₃H₅Hg₂S (477.38) calc'd.: Hg 84.05; S 6.72%
 found: Hg 83.90; S 6.62%

Methylmercuric-n-propylmercuric sulphide

A warm saturated solution of methylmercuric bromide (2.0 g.) in alcohol (20 ml.) was mixed with an alcoholic solution of $\text{Na}_2\text{S} \cdot 9\text{H}_2\text{O}$ (2.0 g.). The primarily formed precipitate was redissolved. A warm alcoholic solution of *n*-propylmercuric bromide (2.0 g.) was added to the reaction mixture. A greyish precipitate was collected after cooling. An additional amount of the crude product could be obtained from the mother liquor by precipitation with water. The overall product was dried (2.5 g., 78%) and recrystallized from chloroform. Bright tiny leaflets; m. p. 51°C.

Anal. 0.1080 g. subst.: 0.1023 g. HgS
 0.2707 g. subst.: 0.1229 g. BaSO_4
 $\text{C}_4\text{H}_{10}\text{Hg}_2\text{S}$ (491.41) calc'd.: Hg 81.66; S 6.53%
 found: Hg 81.68; S 6.24%

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IZVOD

Simetrični i mješoviti bisalkilmerkurisulfidi

M. Dadić i D. Grdenić

Predložena je jednostavna metoda preparacije bisalkilmerkurisulfida, bazirana na reakciji između alkilmerkuribromida i natrijeva sulfida u alkoholnoj otopini. Opisan je način dobivanja kao i svojstva simetričnih sulfida opće formule $(\text{RHg})_2\text{S}$, gdje R predstavlja metilnu, etilnu, *n*-propilnu, *izo*-propilnu, odnosno *n*-butilnu grupu. Sinteza mješovitih sulfida opće formule $\text{R}'\text{HgS}\text{HgR}''$ provedena je preko odgovarajućeg natrijeva alkilmerkurisulfida $\text{R}'\text{HgSNa}$, koji nastaje u toku reakcije kao intermedijer. Također je opisan postupak dobivanja i svojstva mješovitih sulfida, gdje u spomenutoj općoj formuli R' označuje metilnu, a R'' etilnu odnosno *n*-propilnu grupu. Svi priređeni spojevi su dobro definirane kristalinične supstance, koje se na svijetlu polagano raspadaju.

LABORATORIJ ZA OPĆU I ANORGANSKU KEMIJU
 PRIRODOSLOVNO-MATEMATIČKI FAKULTET
 ZAGREB

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