The cobalt sulfone bond seems to be weak. When water is added, the visible spectrum shifts. At 3% water (by vol.) the 687 mμ peak is shifted to 675 mμ and the extinction coefficient at the maximum increased by 4%. The spectrum is insensitive to further addition of water until the water content reaches 10%. Above this the blue color disappears and a spectrum similar to $[Co(H_2O)_6]^{++}$ in water develops. It appears that water begins to displace sulfone from the complex immediately but displaces chloride only when there is a large excess of water.

Cobalt(II) Perchlorate–Tetramethylene Sulfone Adduct.—A red complex of cobalt(II) containing tetramethylene sulfone was prepared by heating hexaaquocobalt(II) perchlorate and the sulfone to dryness in a drying pistol at 110° in the presence of P_2O_5. The solid was extremely sensitive to moisture. Analysis for cobalt was carried out as before and perchlorate was determined by conductometric titration using analytical reagent tetraphenylarsonium chloride from G. F. Smith Chemical Co. as a precipitant. Although other analyses would be more convincing, these suggest the empirical formula $Co(ClO_4)_2 \cdot (C_4H_8SO_2)_3$. *Anal.* Calcd: Co, 9.5; ClO_4, 32.3. Found: Co, 9.4; ClO_4, 32.7. Unfortunately, the instability of the complex rendered further analysis difficult.

This substance is an electrolyte in tetramethylene sulfone. The equivalent conductance of a 1.10×10^{-3} *M* solution is 18.4 ohms^{-1} cm.$^{-2}$, which should be compared[2] to values of about 12 for sodium thiocyanate and 10 for tetraphenylarsonium chloride in this solvent. Thus it appears that this substance is a 2:1 electrolyte, consistent with the formula $[Co(C_4H_8SO_2)_3](ClO_4)_2$. This is supported by the visible spectrum in the sulfone solvent. There is a maximum at 532 mμ which is similar to the maximum for hexaaquocobalt(II) perchlorate at 523 in this solvent. It is interesting that the hexaaquo complex gives a distinct spectrum in tetramethylene sulfone, indicating that water is not displaced from the coördination sphere by the sulfone.

In summary, it appears that tetramethylene sulfone may form weak complexes with Co(II) which are more easily decomposed by water than those with similar solvents. The formulations suggest that the sulfone acts as a bidentate ligand, presumably bonding through the two oxygens. It is not unlikely that the blue complex is roughly tetrahedral and the red one octahedral.

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Vinyl Derivatives of Metals. XII. Some Perchlorovinylmercury Compounds[1]

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Bis-(perchlorovinyl)-mercury has been known since 1908 through the work of Hofmann and Kirmreuther.[2] The synthesis of this compound and of related chlorovinylmercurials has been the subject of further studies.[3,4] The reactions of bis-(perchlorovinyl)-mercury have received practically no study. It has been noted that the cleavage of this compound by chlorine proceeds well only with strong illumination,[5] that its reaction with ammonium sulfide produces mercuric sulfide and trichloroethylene, and that almost no reaction is observed with hot 10% hydrochloric acid or with potassium cyanide solution.[2] We report here some further reactions of mercurials containing the perchlorovinyl group.

The cleavage of diorganomercurials by the halogens and by hydrogen halides is well-known. Bis-(perchlorovinyl)-mercury underwent carbon–mercury bond cleavage when treated with two equivalents of bromine in carbon tetrachloride or with two equivalents of iodine in refluxing xylene solution, giving the respective mercuric halide and halotrichloroethylene. When these reactions were carried out with the mercurial and the halogen in 1:1 molar ratio, the expected perchlorovinylmercuric halides were not obtained. Isolated instead was the respective mercuric halide, and *ca.* one half of the starting mercurial was recovered. This could be due either to the instability toward disproportionation of perchlorovinylmercuric bromide and iodide under the experimental conditions, or to a significantly greater rate of cleavage of the perchlorovinylmercuric halide when compared with bis-(perchlorovinyl)-mercury. This question remains unresolved, although further studies (see below) showed that perchlorovinylmercuric bromide is capable of existence, but that perchlorovinylmercuric iodide

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(1) Part XI: D. Seyferth and T. Wada, *Inorg. Chem.*, **1**, 78 (1962).

(2) K. A. Hofmann and H. Kirmreuther, *Ber.*, **41**, 314 (1908).

(3) M. Fitzgibbon, *J. Chem. Soc.*, 1218 (1938).

(4) H. E. Parker, British Patent 427,979 (1935); *Chem. Abstr.*, **29**, 6608 (1935).

(5) K. A. Hofmann and H. Kirmreuther, *Ber.*, **42**, 4232 (1909).

apparently is not. Hydrogen bromide cleaved bis-(perchlorovinyl)-mercury, giving mercuric bromide and trichloroethylene in high yield.

Electrophilic cleavage of diorganomercurials by mercuric halides results in organomercuric halides. Such redistribution reactions were used in the present study to prepare perchlorovinylmercuric chloride and bromide. This procedure failed when applied to the attempted preparation of perchlorovinylmercuric iodide by reaction of bis-(perchlorovinyl)-mercury with mercuric iodide in dioxane. For this reason, the preparation of the iodide was tried using the reaction of perchlorovinylmercuric chloride with sodium iodide in acetone. This reaction gave mercuric iodide and bis-(perchlorovinyl)-mercury instead of the expected perchlorovinylmercuric iodide. A similar observation was made when perchlorovinylmercuric chloride was treated with potassium thiocyanate in acetone

$$2CCl_2{=}CClHgCl + 2KSCN \longrightarrow (CCl_2{=}CCl)_2Hg + Hg(SCN)_2 + 2KCl$$

It is apparent that the intermediate $CCl_2{=}CClHgI$ and $CCl_2{=}CClHgSCN$ are unstable and disproportionate to the symmetrical compounds. Such disproportionation has been reported[6,7] when *an excess* of iodide or thiocyanate ion is used, and this is due to the large formation constants of the tetraiodo- and tetrathiocyanatomercurate ions

$$2RHgI + 2I^- \longrightarrow R_2Hg + HgI_4^{-2}$$

However, in the cases reported in the present study an excess of iodide or thiocyanate ion was not used, and the reactions were carried out by adding the sodium iodide or potassium thiocyanate solutions to the perchlorovinylmercuric chloride solution slowly with rapid stirring in order to avoid a local excess of iodide or thiocyanate reagent. Such disproportionation of RHgI compounds in acetone solution in the absence of external iodide ion seems to be limited to those compounds where R is a perhalovinyl group. Perfluorovinylmercuric chloride[8] gave mercuric iodide and bis-(perfluorovinyl)-mercury when treated with one equivalent of sodium iodide in acetone in this manner, but methylmercuric bromide, ethylmercuric chloride, vinylmercuric bromide,[9] and phenylmercuric chloride reacted under the same conditions to give the respective organomercuric iodides in good yield. The factors which affect the stability of unsymmetrical mercurials are not completely understood but, in general, the greater the difference in electronegativity between the two different substituents in an unsymmetrical mercury compound, the more stable is that compound toward disproportionation.

Bis-(perchlorovinyl)-mercury did not form an isolatable complex with triphenylphosphine. The action of triphenylphosphine on perchlorovinylmercuric chloride resulted in disproportionation

$$2CCl_2{=}CClHgCl + 2(C_6H_5)_3P \longrightarrow [(C_6H_5)_3P]_2HgCl_2 + (CCl_2{=}CCl)_2Hg$$

Alkylmercuric halides are known to disproportionate in the presence of stoichiometric amounts of triphenylphosphine,[10] but it might have been expected that perchlorovinylmercuric chloride with its two electronegative substituents might have formed a stable adduct with this phosphine.

Experimental[11]

Preparation of Bis-(perchlorovinyl)-mercury.—In a 500-cc. flask was placed 50 g. (0.2 mole) of mercuric cyanide (J. T. Baker), 23 g. (0.41 mole) of potassium hydroxide, and 200 cc of water. To this mixture was added 80 g. (0.61 mole) of trichloroethylene, and the reaction mixture was agitated on a mechanical shaker for 36 hr. The lower, oily layer was separated, and the excess of trichloroethylene removed under reduced pressure. The white residue (30.0 g., m.p. 70–73°) was recrystallized from pentane to give 28.9 g. (86%) of bis-(perchlorovinyl)-mercury, m.p. 72–73°.

Anal. Calcd. for C_4Cl_6Hg: C, 10.41; Cl, 46.11; Hg, 43.48. Found: C, 10.23; Cl, 45.97; Hg, 43.69.

Hofmann and Kirmreuther reported a m.p. of 83° for this compound,[2] while Fitzgibbon reported 141° as the m.p.[3] We are unable to explain these discrepancies. The mercurial in question was recrystallized from a variety of solvents and always had a constant m.p. of 72–73°. Furthermore, the bis-(perchlorovinyl)-mercury produced in the disproportionation of perchlorovinylmercuric iodide and thiocyanate had the 72–73° m.p.

Cleavage of Bis-(perchlorovinyl)-mercury with Bromine. (a) **1:2 Molar Ratio.**—To 15.0 g. (0.033 mole) of bis-(perchlorovinyl)-mercury[12] in 50 ml. carbon tetrachloride was added with stirring during 2 hr. a solution of 10.6 g. (0.066 mole) of bromine in 50 ml. carbon tetrachloride. The mixture was stirred for 6 hr. The white precipitate which had formed soon after the start of the bromine addition was filtered off, giving crude mercuric bromide (10.6 g., m.p. 227–234°), which was recrystallized from methanol

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[6] F. C. Whitmore and R. J. Sobatzki, *J. Am. Chem. Soc.*, **55**, 1128 (1933).

[7] R. N. Beattie and F. C. Whitmore, *ibid.*, **55**, 1567 (1933).

[8] D. Seyferth, G. Raab, and K. A. Brändle, *J. Org. Chem.*, **26**, 2934 (1961).

[9] D. Seyferth, *ibid.*, **22**, 478 (1957).

[10] G. E. Coates, "Organo-Metallic Compounds," Methuen & Co. Ltd., London, 1956, p. 48.

[11] Analyses by Dr. S. M. Nagy, M.I.T.; the Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.; and Alfred Bernhardt, Mülheim, Germany. Melting points are uncorrected.

[12] Henceforth R_2Hg.

(10.4 g., 87%, m.p. 237°; reported m.p.[13] 236°). The filtrate was shaken with 20 ml. of 10% aqueous sodium thiosulfate, dried over anhydrous magnesium sulfate, and distilled to give 8.7 g. (63%) of bromotrichloroethylene, b.p. 52° (27 mm.), n^{28}D 1.5394. An authentic sample of the latter was prepared as follows: To 65.8 g. (0.5 mole) of trichloroethylene in 100 ml. carbon tetrachloride was added dropwise with stirring a solution of 80.0 g. (0.5 mole) of bromine in 100 ml. carbon tetrachloride. The mixture was stirred at room temperature and irradiated with a 100-watt incandescent bulb for 7 hr. It then was shaken with 20 ml. of 10% aqueous sodium thiosulfate, and the organic layer was dried and distilled to give 111.6 g. (77%) of 1,2-dibromo-1,1,2-trichloroethane, b.p. 112–113° (49 mm.), n^{21}D 1.5703; lit.[14] b.p. 116.5° (50 mm.), n^{20}D 1.5710. This product (116.6 g., 0.4 mole) was added to 90 g. (0.89 mole) of triethylamine. The white precipitate which formed immediately was dissolved in water after the reaction mixture had been stirred for 1 hr. The organic layer was dried and distilled to give 61.6 g. (74%) of bromotrichloroethylene, b.p. 85–87° (118 mm.), n^{21}D 1.5396.

Anal. Calcd. for C_2Cl_3Br: C, 11.42; Cl, 50.58; Br, 38.00. Found: C, 11.35; Cl, 50.38; Br, 38.20. The infrared spectra of this product and of the product from the bromine cleavage of R_2Hg were superimposable.

(b) **1:1 Molar Ratio.**—To 15.0 g. of R_2Hg in 50 ml. carbon tetrachloride was added during 1 min. 5.3 g. of bromine in 30 ml. carbon tetrachloride. Mercuric bromide (5.9 g. crude, 5.6 g. recrystallized, m.p. 235°) was filtered off, a yield of 93%.[15] The filtrate was evaporated to dryness, leaving a white solid (7.4 g., m.p. 68–72°), which was recrystallized from pentane to give 7.2 g. (96%) of R_2Hg, m.p. 73°.

Cleavage of Bis-(perchlorovinyl)-mercury with Iodine. (a) **1:2 Molar Ratio.**—To a refluxing solution of 15 g. (0.033 mole) of R_2Hg in 50 ml. xylene was added 16.8 g. (0.066 mole) of iodine during 2 hr. The mixture was refluxed for 18 hr., cooled, and filtered. Red mercuric iodide was isolated: 14.5 g. crude, 12.3 g. (82%) recrystallized from acetone, transition to yellow at 126–127°, m.p. 259°. The filtrate was shaken with 20 ml. of 10% sodium thiosulfate in water, dried, and distilled in red light. Iodotrichloroethylene, b.p. 49–50° (4 mm.), was obtained in 48% yield (8 g.).

Anal. Calcd. for C_2Cl_3I: C, 9.34; Cl, 41.34; I, 49.33. Found: C, 9.54; Cl, 41.46; I, 49.11.

Iodotrichloroethylene, as the pure liquid or in solution, is decomposed very rapidly when exposed to light. It could be stored in the dark at room temperature for several weeks without noticeable decomposition.

(b) **1:1 Molar Ratio.**—The same procedure was used in the reaction of 0.033 mole each of R_2Hg and iodine in 50 ml. xylene. The red precipitate was filtered and recrystallized from methanol to give 6.8 g. (91%[15]) of mercuric iodide. R_2Hg was recovered in 95% yield (7.1 g.) from the filtrate; m.p. 73°.

Cleavage of Bis-(perchlorovinyl)-mercury with Hydrogen Bromide.—To 15 g. (0.033 mole) of R_2Hg in 60 ml. of chloroform was added dropwise with stirring a solution of 5.4 g. (0.066 mole) of hydrogen bromide in 40 ml. of chloroform. A white precipitate formed immediately. After 10 min. of stirring, the mixture was filtered to give 11.7 g. of mercuric bromide, m.p. 236–237°. Vapor phase chromatography of the filtrate indicated an 83% yield of trichloroethylene.

Preparation of Perchlorovinylmercuric Chloride.—A solution containing 16.8 g. (0.066 mole) of mercuric chloride and 30.0 g. (0.066 mole) of R_2Hg in 100 ml. of methanol was refluxed for 7 days. The solution was concentrated to one third of its original volume and cooled to 0°; 40.6 g. of white solid, m.p. 103–106°, crystallized. The latter was washed three times with warm pentane and recrystallized from methanol to give 38.3 g. (79%) of pure compound, m.p. 109°.

Anal. Calcd. for C_2Cl_4Hg: C, 6.55; Cl, 38.70; Hg, 54.70. Found: C, 6.70; Cl, 38.76; Hg, 54.87.

Preparation of Perchlorovinylmercuric Bromide.—A mixture of 11.9 g. (0.033 mole) of mercuric bromide and an equimolar quantity of R_2Hg in 60 ml. of methanol was refluxed for 2 days. The solution was concentrated to *ca.* 25 ml. and cooled to −40° to crystallize 25.2 g. of white solid, m.p. 87–89°, which was recrystallized from methanol to give 24.8 g. (92%) of perchlorovinylmercuric bromide, m.p. 99–100°.

Anal. Calcd. for C_2Cl_3BrHg: C, 5.85; Cl, 25.89; Br, 19.45; Hg, 48.82. Found: C, 6.14; Cl, 25.66; Br, 19.22; Hg, 48.52.

Attempted Preparation of Perchlorovinylmercuric Iodide.—A solution containing 6 mmoles each of mercuric iodide and R_2Hg in 60 ml. dioxane was refluxed for 20 hr. Evaporation of the solvent left an orange-red residue (5.2 g.). Extraction with pentane gave 2.6 g. of red mercuric iodide. Evaporation of the pentane extracts resulted in a quantitative recovery of R_2Hg, m.p. 70–71°.

Reaction of Sodium Iodide in Acetone with Organomercury Chlorides and Bromides.—A solution of the respective mercurial in anhydrous acetone was prepared, and a solution containing a molar equivalent of sodium iodide in acetone was added dropwise with rapid stirring. The precipitated sodium chloride or bromide was filtered, and the organomercury products isolated from the filtrate by evaporation of the solvent. These experiments are summarized in Table I. In the case of perchlorovinylmercuric chloride, the R_2Hg was separated from mercuric iodide by extraction with hot pentane. With perfluorovinylmercuric chloride the filtrate was distilled rapidly into a receiver cooled with liquid nitrogen, leaving mercuric iodide as a residue. The distilled acetone solution was treated with one-half molar equivalent of mercuric chloride for 2 hr. at reflux. Evaporation of the mixture left a white-brown residue from which perfluorovinylmercuric chloride, m.p. 104–106°, could be sublimed (80° at 1 mm.).

Reaction of Perchlorovinylmercuric Chloride with Potassium Thiocyanate.—Potassium thiocyanate (1.36 g., 0.014 mole) in 25 ml. anhydrous acetone was added dropwise with rapid stirring to 5.0 g. (0.014 mole) of R_2Hg in 25 ml. of acetone. The white precipitate formed (0.71 g.) was filtered, and the filtrate evaporated to dryness, leaving a white residue (6.3 g., 149–154°). This solid was washed with five 10-ml. portions of hot pentane. The white crys-

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(13) "Handbook of Chemistry and Physics," C. D. Hodgman, ed., 41st edition, Chemical Rubber Publishing Co., Cleveland, Ohio, 1959, p. 607.

(14) M. S. Kharasch, J. A. Norton, and F. R. Mayo, *J. Org. Chem.*, **3**, 48 (1938).

(15) Based on the equation $R_2Hg + X_2 \rightarrow {}^1/_2HgX_2 + {}^1/_2R_2Hg + RX$.

TABLE I

THE REACTION OF ORGANOMERCURY CHLORIDES AND BROMIDES WITH MOLAR EQUIVALENTS OF SODIUM IODIDE IN ACETONE

RHgX			
R	X	Wt., g. (mmoles)	Product Wt., g. (% yield)
CH_3	Br	0.96 (3.3)	CH_3HgI, 0.94 (83); m.p. 150–152°[a]
$CH_2{=}CH$	Br	1.69 (5.5)	$CH_2{=}CHHgI$, 1.68 (86); m.p. 150–152°[b]
C_2H_5	Cl	1.35 (5.1)	C_2H_5HgI, 1.6 (83); m.p. 183–185°[c]
C_6H_5	Cl	1.73 (5.6)	C_6H_5HgI, 1.20 (95); m.p. 265°[d]
$CCl_2{=}CCl$	Cl	5.0 (14)	HgI_2, 2.8 (88) $(CCl_2{=}CCl)_2Hg$, 2.8 (88); m.p. 73°
$CF_2{=}CF$	Cl	1.2 (3.8)	HgI_2, 0.7 (90) $(CF_2{=}CF)_2Hg$ (33%, identified as described in experimental section)

[a] M.p. 152° given in ref. 16. [b] M.p. 150–151.5° given in ref. 9. [c] M.p. 186° given in ref. 16. [d] M.p. 266° given in ref. 16.

tals which remained (2.4 g., m.p. 140–150°) were recrystallized from water to give 2.0 g. (91%) of mercuric thiocyanate, dec. 175°, identified further by its characteristic band in the infrared spectrum at 2105 cm.$^{-1}$.[17] The pentane washings were evaporated; R_2Hg, m.p. 72–73°, was obtained in 88% yield (2.8 g.) after recrystallization from pentane.

Preparation of Perfluorovinylmercuric Chloride.—A solution containing 6.0 g. (0.021 mole) of triethylperfluorovinyltin[8] and 5.7 g. (0.021 mole) of mercuric chloride in 25 ml. of diethyl ether was heated at reflux for 18 hr. Two-thirds of the ether was distilled away, and 75 ml. of pentane was added to the residue. The white solid which precipitated was filtered (4.0 g., m.p. 93–97°) and then sublimed at 70° and 10 mm. to give 3.4 g. (51%) of perfluorovinylmercuric chloride, m.p. 106°.

Anal. Calcd. for C_2F_3ClHg: C, 7.58; F, 17.98; Cl, 11.18; Hg, 63.27. Found: C, 7.49; F, 17.73; Cl, 10.85; Hg, 63.00.

It had been reported previously that a recrystallized, unsublimed sample of this compound began to soften at 96° and was completely molten at 103–104°.[8] The infrared spectra of our present product and of the latter material were identical.

Reaction of Perchlorovinylmercuric Chloride with Triphenylphosphine.—To 5.0 g. (0.014 mole) of perchlorovinylmercuric chloride in 50 ml. ethanol was added 3.7 g. (0.014 mole) of triphenylphosphine in 350 ml. ethanol. A white precipitate (5.0 g., m.p. 270–273°) formed immediately; this was washed twice with 10 ml. of hot ethanol, leaving 4.8 g. (86%) of bis-(triphenylphosphine)-mercuric chloride, m.p. 274–276°. The ethanol washings and the filtrate were combined and concentrated to *ca.* one-tenth of the original volume to give 2.8 g. (88%) of R_2Hg, m.p. 72–73°.

An authentic sample of bis-(triphenylphosphine)-mercuric chloride was prepared by combination of the two components of the complex in ether solution. The solid which precipitated was washed with ethanol, giving pure material, m.p. 274–277°, in 87% yield. A mixed m.p. of the two samples showed no depression, and their infrared spectra were superimposable.

Anal. Calcd. for $C_{36}H_{30}Cl_2P_2Hg$: C, 53.22; H, 3.72; Cl, 8.73; Hg, 24.70. Found: C, 53.46; H, 3.98; Cl, 8.82; Hg, 24.92.

Infrared Spectra.—The perchlorovinylmercury compounds prepared in this study all are characterized by a strong, sharp band at 1545 cm.$^{-1}$ (KBr pellet), presumably the $C{=}C$ stretching frequency of the $CCl_2{=}CCl$ group. Similar absorption was observed at 1547 cm.$^{-1}$ for iodotrichloroethylene and at 1565 cm.$^{-1}$ for bromotrichloroethylene.

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[16] E. Krause and A. von Grosse, "Die Chemie der metallorganischen Verbindungen," Borntraeger, Berlin, 1937.

[17] C. N. R. Rao, J. Ramachandran, and P. S. Shankar, *J. Sci. Ind. Research* (India), **18B**, 169 (1959); *Chem. Abstr.*, **53**, 19568 (1959).