

307. *The Chemistry of Bivalent Germanium Compounds. Part II.**
Some Complex Compounds of Bivalent Germanium.

By D. A. EVEREST.

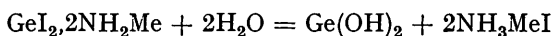
The following new complex compounds of bivalent germanium have been prepared: $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$; $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$; $3\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeBr}_2$. They resemble the corresponding tin compounds. Germanium dioxide, in contrast to stannic hydroxide, is reduced to the bivalent state when heated alone with hypophosphorous acid.

THE best-defined complexes of bivalent germanium which were known at the start of this work were of the type MGeX_3 , where M was a univalent cation, and X was chlorine, bromine, or iodine (Tchakarian, *Compt. rend.*, 1931, **192**, 233; Karantassis and Capatos,

* *J.*, 1950, 2282, is regarded as Part I of this series.

ibid., 1934, **199**, 64; 1935, **201**, 74). Transport experiments (Tchakarian, *ibid.*, 1937, **204**, 117), supported by observations of Raman spectra (Tchakarian, Volklinger, and Freymann, *ibid.*, 1934, **199**, 292; Tchakarian and Volklinger, *ibid.*, 1935, **200**, 1758), showed that in halogen acids bivalent germanium was present as complex anions, e.g., GeCl_3^- . It is noteworthy that there is no evidence for the existence of the simple Ge^{++} ion in solution. The existence in hydrochloric acid solution of a complex tartrate of bivalent germanium has also been reported by Robinson (*Ann. Reports*, 1944, **41**, 112).

Germanous Iodide-Methylamine System.—Since bivalent germanium only formed stable solutions in an excess of acid it was considered that complex formation would be more readily observable if the complexing agent was added under anhydrous conditions. In preliminary experiments gaseous ammonia was used as complexing agent, being allowed to react with solid germanous iodide. The pressure-composition curves obtained were irregular and not reproducible, possibly owing to ammonolysis. Reaction readily occurred when germanous iodide was treated with liquid ammonia, germanous imide being formed (Johnson, Morey, and Kott, *J. Amer. Chem. Soc.*, 1932, **54**, 4278). It has been pointed out by Fernelius and Bowman (*Chem. Reviews*, 1940, **26**, 6) that for any given substance the extent of aminolysis was less than that of ammonolysis. Gaseous methylamine was therefore chosen as the complexing agent; the pressure-composition curves obtained indicated the formation of the compound $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$. It was observed that as the solid phase approached the composition $\text{GeI}_2 \cdot \text{NH}_2\text{Me}$ it became bright red, the colour reaching maximum intensity at that point. When this composition was passed, the solid phase changed from red to yellow, and was entirely yellow at the composition $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$. There was, however, no break in the pressure-composition curves corresponding to a compound $\text{GeI}_2 \cdot \text{NH}_2\text{Me}$. This may have been due to the dissociation-pressure difference between $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$ and $\text{GeI}_2 \cdot \text{NH}_2\text{Me}$ being so small (less than 5 mm.) that the apparatus used was too insensitive to detect it. The maximum pressure of methylamine measured in these experiments was about 200 mm. so that the possible existence of higher methylamine compounds, with a dissociation pressure greater than this, cannot be ruled out. $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$ was insoluble in most solvents but dissolved in hydrochloric acid after the momentary formation of a bright red solid, possibly $\text{GeI}_2 \cdot \text{NH}_2\text{Me}$. When heated, $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$ decomposed in the range 190–200°; when warmed with aqueous sodium hydroxide, it evolved methylamine; with water hydrolysis took place according to the equation:



Repetition of these experiments with stannous halides and methylamine indicated the formation of $\text{SnI}_2 \cdot 2\text{NH}_2\text{Me}$ and $\text{SnCl}_2 \cdot 2\text{NH}_2\text{Me}$ analogous to $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$; the pressure-composition curves also indicated the existence of the monomethylamine compounds $\text{SnI}_2 \cdot \text{NH}_2\text{Me}$ and $\text{SnCl}_2 \cdot \text{NH}_2\text{Me}$ (Everest, Thesis, London, 1949).

Compounds of Germanous Hypophosphite and Germanous Halides.—Two compounds have been prepared: $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$ and $3\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeBr}_2$, the latter being the less soluble. These were the only compounds isolated, whatever the relative proportions of the hypophosphorous and halogen acids. The compounds were fairly stable in air but were hydrolysed by water, giving germanous hydroxide. Warm concentrated sulphuric and nitric acids rapidly decomposed them, giving germanium dioxide. They dissolved in concentrated halogen acids, hypophosphorous or phosphoric acid, the last two being new solvents for bivalent germanium compounds. Both $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$ and $3\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeBr}_2$ had sharp melting points (124° and 129° respectively); no other germanous compound has been reported to have a melting point with the exception of germanous bromide (m. p. 122°) (Brewer and Dennis, *J. Phys. Chem.*, 1927, **31**, 1526). The reported properties of germanous bromide were exceptional (e.g., it was soluble in alcohol and acetone) and differed sharply from those of the other germanous halides. $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$ and $3\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeBr}_2$ resembled the corresponding bivalent tin compounds (Everest, *J.*, 1951, 2903) in their reactions, in possessing analogous formulæ, and in having sharp melting points. This possibly indicated that these compounds had similar structures.

If germanium dioxide was heated alone with hypophosphorous acid it was dissolved to give a clear yellowish-green solution which gave the reactions of bivalent germanium, reduction having occurred. This behaviour was in contrast to that of stannic hydroxide, which, although soluble in hypophosphorous acid, was not reduced to the bivalent state in absence of hydrochloric acid (Everest, *loc. cit.*).

EXPERIMENTAL

Germanous Iodide-Methylamine System.—Germanous iodide was prepared by the method of Powell and Brewer (*J.*, 1938, 197) and carefully dried before use. Methylamine was prepared by heating methylamine hydrochloride with calcium oxide and condensing the methylamine in a freezing mixture. It was then dried over metallic sodium. The pressure-composition curves were followed by adding gaseous methylamine to germanous iodide in successive small portions, allowing 24–36 hours for the system to attain equilibrium, and measuring the vapour pressure of methylamine. The amount of methylamine absorbed was followed by weighing the reaction mixture. The apparatus used was based on that described by Hart and Partington (*J.*, 1943, 104), and was kept in a thermostat within $\pm 0.1^\circ$. The vapour pressure of methylamine over $\text{GeI}_2 \cdot 2\text{NH}_2\text{Me}$ was 7 mm. at 25° and 15 mm. at 75° .

Analytical Procedures.—Germanium. After reduction to the bivalent state by an excess of boiling hypophosphorous acid and 6*N*-hydrochloric acid for 30 minutes, the cooled solution was titrated in an inert atmosphere with 0.1*N*-iodine (standardised with pure germanium dioxide). The end-point was sharp but slowly faded, the germanium values obtained tending to be higher than the theoretical.

Halogens. The sample was dissolved in aqueous sodium hydroxide in presence of hydrogen peroxide and heated for 2 hours to oxidise the hypophosphite. Halogens were then precipitated with silver nitrate.

Phosphorus. The sample was dissolved in 6*N*-hydrochloric acid in presence of the minimum amount of hydrogen peroxide needed to oxidise the germanium to the quadrivalent state. The germanium was then precipitated as disulphide and removed. The solution was then treated with bromine to oxidise the hypophosphite to phosphate and, after evaporation nearly to dryness to drive off all the hydrochloric acid, the phosphate was determined gravimetrically with ammonium molybdate.

Double Salt, $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$.—This salt (m. p. 124°) was prepared by heating activated germanium dioxide (0.5 g.), formed by dissolving the normal oxide in alkali and reprecipitating it with acid, in 6*N*-hydrochloric acid (4.5 ml.) and 50% hypophosphorous acid (2.5 ml.) under reflux for 30 minutes; on storage for 12 hours crystals separated. These were washed with dilute hypophosphorous acid and absolute alcohol and dried in a vacuum at room temperature [Found: Ge, 42.1; Cl, 20.9; P, 18.4. $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$ requires Ge, 41.95; Cl, 20.5; P, 17.9%]. If too concentrated solutions were used, or if the solution was cooled too quickly, an amorphous precipitate of $\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeCl}_2$ was obtained.

Double Salt, $3\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeBr}_2$.—This salt (m. p. 129°) was prepared similarly from activated germanium dioxide (0.5 g.), 35% hydrobromic acid (4 ml.), and 50% hypophosphorous acid (2 ml.); on slow cooling crystals separated. A better method, which more readily gave a crystalline precipitate, was to reduce a solution of activated germanium dioxide (0.4 g.) in 35% hypophosphorous acid (3.5 ml.) by heating it at 100° for 40 minutes; 46% hydrobromic acid (0.5 ml.) was then added and on cooling for 12 hours crystals were obtained [Found: Ge, 35.2; Br, 19.0; P, 22.3. $3\text{Ge}(\text{H}_2\text{PO}_2)_2 \cdot \text{GeBr}_2$ requires Ge, 34.6; Br, 19.0; P, 22.1%]. In the above two preparations an inert atmosphere was maintained although these compounds were sufficiently resistant to oxidation to permit their isolation in the presence of gaseous oxygen.

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UNIVERSITY COLLEGE, GOWER STREET, LONDON, W.C.1.
BATTERSEA POLYTECHNIC, LONDON S.W.11.

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