2. Pyridinium chloride and quinolinium chloride crystallize from solutions in selenium oxychloride with two molecules of the solvent. Isoquinolinium chloride probably forms a mixture of the mono-solvate and the di-solvate. These facts indicate the possibility of disolvation of the chloride ion in selenium oxychloride.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF CORNELL UNIVERSITY]

Chlorogermanic Acid and the Chlorogermanates. Properties and Crystal Structure of Cesium Hexachlorogermanate

BY A. W. LAUBENGAYER, O. B. BILLINGS AND A. E. NEWKIRK

The tendency of the elements of Group IV, exclusive of carbon and thorium, to form complex ions with the halogens is well recognized. Germanium is known[1] to form hexafluogermanates but no other halogen complexes of germanium have been studied. Pauling[2] has shown that it is possible to predict the type of aggregate which two ions can form by considering the ratio of the ionic radii. Using his values for the radii, the ratios of the univalent ionic radius of germanium to those of fluorine, chlorine, bromine, and iodine are 0.54, 0.42, 0.39, and 0.35, respectively. Since 0.41 is the minimum radius ratio which will permit hexacoördination it is evident that germanium should form hexahalogen complex ions with fluorine and chlorine but can only have a coördination number of four toward bromine or iodine. Because the ratio in the case of chlorine is so close to the limit between hexa- and tetra-coördination, it is to be anticipated that the hexachlorogermanate ion will not form except under the most favorable conditions.

In the present investigation the formation of chlorogermanic acid and its salts has been studied.

Experimental

Formation of Chlorogermanic Acid.—Germanium tetrachloride is slightly soluble in concentrated hydrochloric acid.[3] This indicates that chlorogermanic acid may be formed, but that it is not very stable in solution since its formation to any great extent would give rise to high solubility of the tetrachloride.

Chlorostannic acid crystallizes as the hexahydrate when a solution of stannic chloride in concentrated hydrochloric acid is chilled. A similar procedure was tried in an effort to isolate chlorogermanic acid. Germanium tetrachloride was added to an equal volume of 12 *N* hydrochloric acid to give a two liquid layer system and the mixture was chilled to −49°. No crystals appeared. When gaseous hydrogen chloride was bubbled through cold anhydrous germanium tetrachloride no solid formed above −49°, the freezing point of germanium tetrachloride. If chlorogermanic acid is formed under such conditions it is present in such small amounts that it will not crystallize out.

Migration studies of solutions of various concentrations of germanium tetrachloride in 6 *N* hydrochloric acid gave evidence that the small amount of germanium in solution is present in complex ions. The solutions were electrolyzed in a migration cell which had a capacity of 60 cc. The concentration of germanium in anolyte and catholyte was determined before and after electrolysis with a given current for a definite period of time. These experiments are summarized in Table I.

TABLE I

MIGRATION OF GERMANIUM DURING ELECTROLYSIS OF SOLUTIONS OF $GeCl_4$ IN 6 *N* HCl

Expt.	Time, min.	Current, m. amp.	Grams Ge per 1000 g. solution Original	Anolyte finally	Catholyte finally
1	70	86	2.001	2.072	1.903
2	60	87	4.681	4.734	4.627

Both of these experiments show a small but significant migration of germanium toward the anode, indicating the presence of an anion of this element, presumably $GeCl_6^{=}$. The solutions contained such large concentrations of other ions that the concentration of chlorogermanate ions could not be calculated from the data.

Formation of Chlorogermanates.—The direct addition of ammonia to 12 *N* hydrochloric acid saturated with germanium tetrachloride gave only a precipitate of ammonium chloride with no evidence of chlorogermanate formation.

The reactions of the alkali chlorides with germanium tetrachloride were studied under a variety of conditions.

Anhydrous germanium tetrachloride was refluxed with a weighed amount of sodium chloride for several days, the mixture being protected from atmospheric moisture. No evidence of any reaction could be observed. Similarly the chlorides of lithium, potassium, cesium and calcium did not react when refluxed with anhydrous germanium tetrachloride.

The low solubility of germanium tetrachloride in concentrated hydrochloric acid makes it impossible to achieve any large concentration of germanium tetrachloride in an

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(1) Winkler, *J. prakt. Chem.*, **36**, 177 (1887); Müller, *Proc. Am. Phil. Soc.*, **65**, 44 (1926); Dennis and Staneslow, THIS JOURNAL, **55**, 4392 (1933).

(2) Pauling, THIS JOURNAL, **49**, 765 (1927).

(3) Allison and Müller, THIS JOURNAL, **54**, 2833 (1932).

aqueous solution containing sufficient acid to prevent hydrolysis. Also the alkali chlorides are all rather insoluble in concentrated hydrochloric acid. It is impossible, therefore, to prepare the aqueous solution presumably the most ideal for the formation of chlorogermanates, namely, one high in concentration of chloride ion, germanium tetrachloride, and alkali ion. All attempts to obtain chlorogermanates from such systems failed.

Cesium chloride, however, is quite soluble in a mixture of one volume of ethyl alcohol and two volumes of 12 *N* hydrochloric acid. When germanium tetrachloride was added to such a solution a flocculent yellowish-white precipitate was formed. This was filtered off, washed with 12 *N* hydrochloric acid, and dried in air to a light yellow powder. It was found advisable to use less than the equivalent amount of germanium tetrachloride for the precipitation to avoid contamination of the precipitate by the tetrachloride. Analysis of the dry powder showed it to be cesium hexachlorogermanate, Cs_2GeCl_6. In the analysis the chlorine was determined as silver chloride and the germanium by precipitation as the sulfide and conversion to the oxide.[4] Cesium was determined by heating the cesium chlorogermanate with a low flame. The compound decomposes into cesium chloride and germanium tetrachloride and the latter volatilizes. The residual cesium chloride was finally heated to its melting point, 646°, and then cooled and weighed. It was found to retain only very slight traces of germanium.

Anal. Calcd. for Cs_2GeCl_6: Cs, 48.21; Ge, 13.18; Cl, 38.62. Found: Cs, 48.77; Ge, 12.54; Cl, 38.62.

Properties of Cesium Hexachlorogermanate.—Cesium hexachlorogermanate dissolves readily in water, undergoing rapid hydrolysis. It is insoluble in 12 *N* hydrochloric acid and in absolute ethyl alcohol, but 100 cc. of a 1:2 mixture dissolves 1.5 g. at 0° and 4.3 g. at 75°. It may readily be recrystallized from this mixed solvent.

Cesium chlorogermanate is stable in dry air at room temperature. Passage of a slow stream of nitrogen over it at various temperatures and then through a dilute solution of silver nitrate showed that decomposition, without melting, to cesium chloride and germanium tetrachloride became appreciable at 160° and was very rapid and in some hours complete at 200°.

The density of the compound at 25° was found to be 3.45 ± 0.01 by the pycnometric method, using toluene as the immersion liquid.

The crystals are well formed and are isotropic and, for the most part, octahedral. Their refractive index is 1.68.

Crystal Structure of Cesium Hexachlorogermanate.—A powder X-ray diffraction pattern for the compound was obtained, using Cu Kα radiation. The data fitted a face-centered cubic lattice, since only lines having all odd or all even indices appeared. The structure is probably of the ammonium chloroplatinate type, and the intensity calculations have been made on this basis. This type of structure is also shown by cesium fluogermanate.[5]

A value of a_0 was calculated for each line. The values for the last 20 lines were plotted against $\cos^2 \theta$, and the best straight line through the points was extrapolated to $\cos^2 \theta = 0$ to obtain $a_0 = 10.21$ Å. In this manner, correction was

TABLE II

h k l	*I*-obsd.	*I*-calcd.	*h k l*	*I*-obsd.	*I*-calcd.
111	20	28	10, 00	0	1.2
200	19	14	860		
220	105	91	10, 20	5	13
311	3	7	862		
222	86	77	951	0.8	4
400	75	72	773		
331	0	1	10, 22	1.6	6
420	8	11	666		
422	58	68	953	0.8	2
511	7	8	10, 40	.7	2
333			864		
440	46	49	10, 42	3	8
531	5	6	11, 11	0	0.04
600	5	6	775		
442			880	0.7	4
620	19	12	11, 31	.6	2
533	0	1	971		
622	17	28	955		
444	16	16	10, 44	.6	1.5
711	3	5	882		
551			10, 60	2.4	3.5
640	0.9	2	866		
642	13	24	11, 33	0	0.3
731	1.6	2.5	973		
553			10, 62	2.3	7
800	1.4	8	12, 00	3.4	8
733	0	1	884		
820	1.4	4	11, 51	0	0.2
644			777		
822	5	8	12, 20	0	1
660			12, 22	5	6.5
751	0.6	2	10, 64		
555			11, 53	0	3
662	5	12	975		
840	7	21	12, 40	1.5	5
911	0.6	2	991	0.5	0.9
753			12, 42	1.4	3
842	1.1	4	10, 80		
664	4	7	886		
931	1	2	10, 82	1.3	6.5
844	6	15	13, 11	0	0.5
933	0	1	11, 71		
771			11, 55		
755			993		
			10, 66	1	2.3

( ) Dennis and Johnson, THIS JOURNAL, 47, 790 (1925).

[5] Wyckoff and Müller, *Am. J. Sci.*, 13, 347 (1927).

made for incorrect centering of the specimen and for absorption in the powder rod.[6]

The density of cesium chlorogermanate as determined pycnometrically was 3.45. From this figure and the value of a_0 the number of molecules in the unit cell was calculated to be 3.96. The number of molecules in the unit cell is therefore four, and the density calculated from X-ray data is 3.48.

The values for the intensities of the powder lines were calculated from the formula

$$I = \text{constant}\left(\frac{1 + \cos^2 2\theta}{\sin 2\theta \sin \theta}\right) jS^2 \text{ where}$$

$$S = f_{\text{Ge}} + 2f_{\text{Cs}} \cos 2\pi\left(\frac{h + k + l}{4}\right) + 2f_{\text{Cl}}(\cos 2\pi hx + \cos 2\pi kx + \cos 2\pi lx)$$

The atomic f-values of Pauling and Sherman[7] were used throughout these calculations. In order to determine the chlorine parameter, values of 0.22, 0.23 and 0.24 were used to calculate the intensities for the first ten lines. The value x = 0.23 gave the best agreement with the observed and was therefore used in the calculation of the remaining intensities. The observed intensities were corrected for absorption in the powder rod in the usual manner. The values for the observed and calculated intensities are given in Table II. The agreement is reasonable.

From the chlorine parameter of 0.23, the germanium–chlorine distance was calculated to be 2.35 Å. This is in good agreement with the value 2.34 Å. calculated from the ionic radii of Pauling.[2]

The authors wish to acknowledge the assistance of Professor J. L. Hoard who made available X-ray equipment and helped with the interpretation of the X-ray data.

Summary

1. The formation of chlorogermanic acid and its salts has been studied under a variety of conditions.

2. Evidence for the formation of negatively charged complex ions, presumably $GeCl_6^=$, when germanium tetrachloride is dissolved in concentrated hydrochloric acid has been obtained by migration experiments.

3. Cesium hexachlorogermanate has been prepared and its properties and crystal structure have been studied. It has a face-centered cubic lattice.

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(6) "Internationale Tabellen zur Bestimmung von Krystallstrukturen," Gebrüder Borntraeger, Berlin, 1935, pp. 581–582.

(7) Pauling and Sherman, *Z. Krist.*, **81**, 1 (1932).

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The Dielectric Constants of Some Pairs of Diastereomers

BY SAUL WINSTEIN AND REUBEN E. WOOD

Pairs of diastereomeric substances show no very characteristic differences in physical properties such as boiling point, polarizability, etc.[1] However, owing to the lack of free rotation about carbon–carbon single bonds[2] there is the possibility that the dipole moments and thus the dielectric constants of *meso* and *dl* compounds or *erythro* and *threo* compounds may differ sufficiently to be useful analytically. Also, there is the possibility that there may be enough regularity in these differences to allow the formulation of rules for the assignment of configuration to diastereomers on the basis of dielectric constant measurements. To study these possibilities and in some cases to obtain data immediately useful in analysis and identification we have determined the dielectric constants of some pairs of diastereomers available to us.

Materials

***meso*- and *dl*-2,3-Diacetoxybutanes.**—The *meso* isomer, m. p. 2.5°, b. p. (13 mm.) 83.6°, was prepared[3] from *meso*-2,3-butanediol, m. p. 34.0°, and distilled through a 40-cm. Weston column.[4] The *dl* isomer, m. p. 42.1°, was prepared[3] from the *dl*-2,3-butanediol from pure *cis*-2,3-epoxybutane.[5]

***dl-erythro*- and *dl-threo*-2,3-Diacetoxypentanes.**—These materials were kindly furnished us by Professor H. J. Lucas and Mr. M. J. Schlatter of these Laboratories.

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(1) Hückel, "Theoretische Grundlagen der organischen Chemie," Vol. II, Akademische Verlagsgesellschaft m. b. H., Leipzig, 1935, p. 125.

(2) See Weissberger, *J. Org. Chem.*, **2**, 245 (1937), for a review of configuration about single bonds.

(3) Wilson and Lucas, THIS JOURNAL, **58**, 2396 (1936).

(4) Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).

(5) Winstein and Lucas, THIS JOURNAL, **61**, 1576 (1939).