

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, CORNELL UNIVERSITY]

Germanium. XLI. Some New Salts of Fluogermanic Acid¹

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WITH MICROSCOPICAL STUDIES BY W. D. FORGENG

The fluogermanates of the alkali metals and of silver, thallium and barium are already known. The present article describes compounds of this acid with several nitrogen bases.

Experimental

The preparation and purification of the several salts were carried out entirely in platinum apparatus. The purity of each salt was confirmed by spectroscopic examination.

Fluogermanic acid was prepared from pure germanium dioxide and Baker's "c. p." 40% hydrofluoric acid. The bases were Kahlbaum purest grade except ammonia, which was purified in the laboratory.

Ammonium Fluogermanate.—Purified ammonia was passed through a platinum tube into a cooled solution of fluogermanic acid; a white, gelatinous solid formed. This was collected on a filter, dissolved in a small amount of water, was then slightly acidulated with hydrofluoric acid and reprecipitated with ethyl alcohol. The precipitate was dissolved in a very dilute solution of hydrofluoric acid, and was fractionally crystallized from this solution. The end fractions were discarded. The middle fractions were combined and again fractionally crystallized.

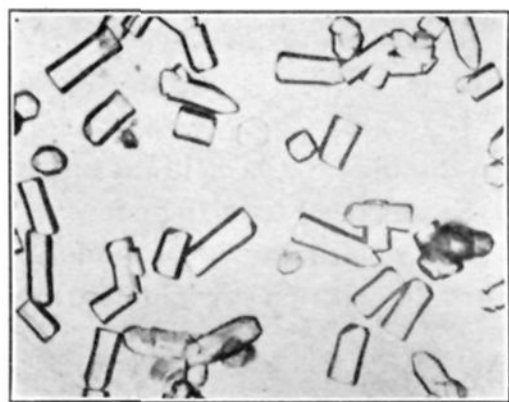


Fig. 1.—Ammonium fluogermanate
($\times 86$).

Optical Properties.—The crystals of ammonium fluogermanate (Fig. 1) are apparently combinations of hexagonal prisms and bipyramids. Occasional hexagonal plates also occur.

The prismatic views show parallel extinction with very weak double refraction. The plate-like crystals are isotropic and give a good uniaxial interference figure. The material is optically negative. Refractive indices: (ϵ) = 1.425; (ω) = 1.428.

This salt is crystallographically similar to the hexagonal modifications of ammonium and potassium fluosilicate.

Hydroxylamine Fluogermanate.—In one synthesis, hydroxylamine, and in another, hydroxylamine hydrochloride, was added to a cooled solution of fluogermanic acid. The clear solution was fractionally crystallized as for the ammonium salt. A sample from the middle fractions, dried by pressing between filter paper, was found on analysis to be the dihydrate, $(\text{NH}_2\text{OH})_2 \cdot \text{H}_2\text{GeF}_6 \cdot 2\text{H}_2\text{O}$.

Optical Properties.—The tabular crystals of hydroxylamine fluogermanate dihydrate are monoclinic prisms 110, and orthopinacoids 100 terminated by clinodomes 011 (Fig. 2).

Observed perpendicular to 100, the crystals show parallel or symmetrical extinction,

(1) This article is based upon the thesis presented to the Faculty of the Graduate School of Cornell University by B. J. Staneslow in partial fulfilment of the requirements for the degree of Master of Chemistry.

with weak double refraction. The interference figure for the view indicates that the acute bisectrix is approximately perpendicular to this face.

Crystals lying on 110 show slightly oblique extinction, with strong double refraction. Clinopinacoidal views of the crystals are rare. They show an angle β of about 80° , and an extinction angle of about 35° .

The material is biaxial, negative, with $2V$ about 60° , and fairly strong dispersion, $r > v$. $B_{xa} \wedge a = 80^\circ$. The axial plane is 010. Refractive indices: $(\alpha) = 1.418$; $(\beta) = 1.438$; $(\gamma) = 1.443$.

Hydrazine Fluogermanate.—A 50% solution of hydrazine hydrate was added to a cooled solution of fluogermanic acid. On addition of 95% ethyl alcohol the salt separated out in colorless plates. The compound was purified by repeatedly dissolving it in water that was slightly acidified with hydrofluoric acid, and throwing out the salt from this solution by ethyl alcohol. The

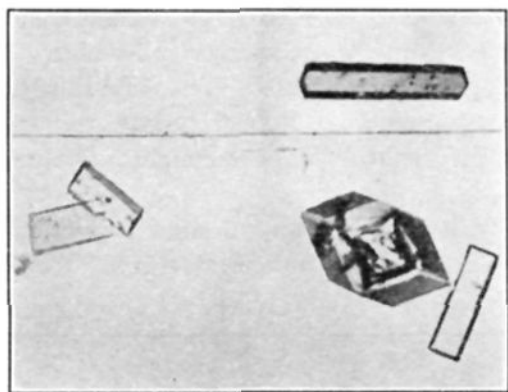


Fig. 3.—Hydrazine fluogermanate ($\times 86$).

The material is biaxial, negative, with $2V$ near 90° . The axial plane is 010.

Refractive indices: $(\alpha) = 1.452$; $(\beta) = 1.460$; $(\gamma) = 1.464$.

Aniline Fluogermanate.—A solution of fluogermanic acid was run into a solution of aniline in 95% ethyl alcohol, the latter being in slight excess. On cooling the solution in ice, fine, white crystals separated. These were collected on a filter, were washed with cold alcohol to remove the excess of aniline, and purified by recrystallization from hot alcohol. The solubility in alcohol was lowered by the addition of ether. The pure salt is white, but gradually turns light yellow on exposure to air.

Optical Properties.—The tabular crystals of aniline fluogermanate are monoclinic prisms

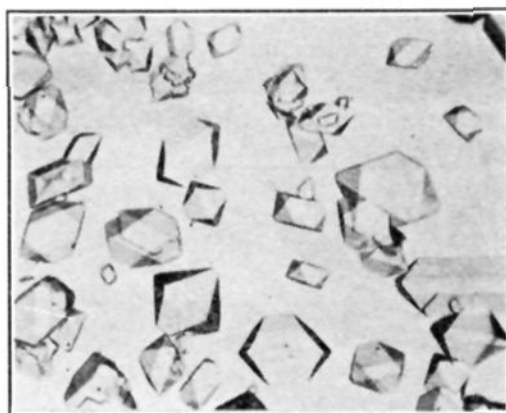


Fig. 2.—Hydroxylamine fluogermanate dihydrate ($\times 80$).

compound separates in the anhydrous form.

Optical Properties.—Hydrazine fluogermanate crystallizes as monoclinic prisms with basal and orthopinacoids (Fig. 3). Crystallized on a slide, they lie on either pinacoid face 001 or 100, or on a prism face 110. Clinopinacoid faces are occasionally developed, and when lying on these faces, the crystals show an angle β of about 80° .

Observed perpendicular to 001 or 100, the crystals exhibit parallel or symmetrical extinction, with very weak double refraction. Interference figures of these views indicate that 010 is the axial plane.

Crystals lying on 110 show oblique extinction, the angle being about 30° .

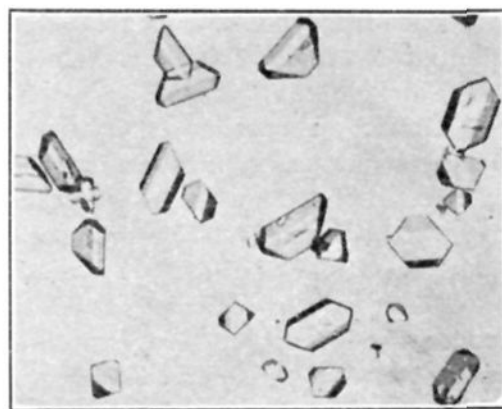


Fig. 4.—Aniline fluogermanate ($\times 80$).

110, with ortho 100 and basal pinacoids 001. Clinopinacoid and hemipyramid faces are also developed (Fig. 4).

When lying on 001, the crystals show parallel extinction with very weak double refraction. The interference figure for this view shows the optic normal to be approximately perpendicular to the C axis.

Observed perpendicular to 100, the crystals show parallel extinction with weak double refraction. Interference figures show an optic axis at an angle of about 30° to the perpendicular of this face.

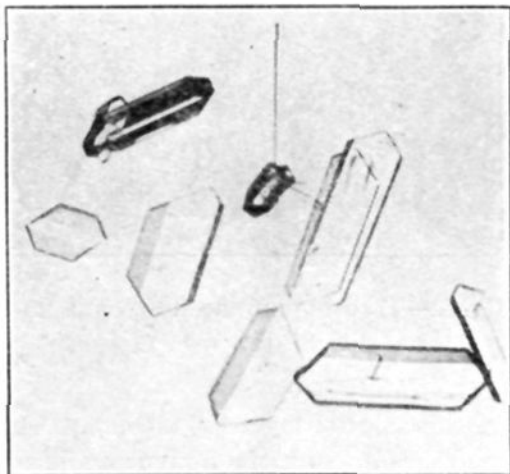


Fig. 5.—Monomethylaniline fluogermanate ($\times 100$).

Crystals lying on the clinopinacoidal faces 010 are flattened. They show an angle β of about 85° and an extinction angle of about 80° . No interference figure is obtained for this orientation.

The substance is biaxial, negative, with $2V$ about 35° , dispersion strong $r > v$. Axial plane is 010.

Refractive indices: $(\alpha) = 1.471$; $(\beta) = 1.532$; $(\gamma) = 1.541$.

Monomethylaniline Fluogermanate.—

The method was similar to that used for the aniline salt. Recrystallized from hot 85% ethyl alcohol, washed with 95% alcohol and ether: crystals, white needles, anhydrous.

Optical Properties.—The crystals of monomethylaniline fluogermanate are ap-

parently orthorhombic prisms 110 terminated by domes 011. The terminal angle between two dome faces is about 100° (Fig. 5). Prismatic views show parallel extinction with fairly strong double refraction. The axial plane is parallel to 001. The acute bisectrix is perpendicular to 100. Good interference figures are obtainable.

The material is biaxial, negative, with $2V$ about 60° , $r > v$ strong; optical orientation: $X = a$; $Y = c$; $Z = b$; $B_{x_a} = a$.

Refractive indices: $(\alpha) = 1.472$; $(\beta) = 1.562$; $(\gamma) = 1.565$.

Dimethylaniline Fluogermanate.—The method of preparation was similar to that used for aniline fluogermanate. Recrystallized from hot 95% ethyl alcohol with precipitation from the alcoholic solution by the addition of ether; white, crystalline, stable in the air.

Optical Properties.—Dimethylaniline fluogermanate crystallizes in the monoclinic system as clinodomes 011, clinopinacoids 010, orthopinacoids 100, and occasional basal pinacoids 001 (Fig. 6).

Observed perpendicular to 100, the crystals are rhomb-shaped in outline with acute angles of about 35° . This view shows symmetrical extinction with strong double refraction, the slower component vibrating parallel with the acute diagonal. Interference figures for this view show the axial planes to be roughly parallel with 010.

Crystals developed so as to lie on 100 are flattened and show parallel extinction with

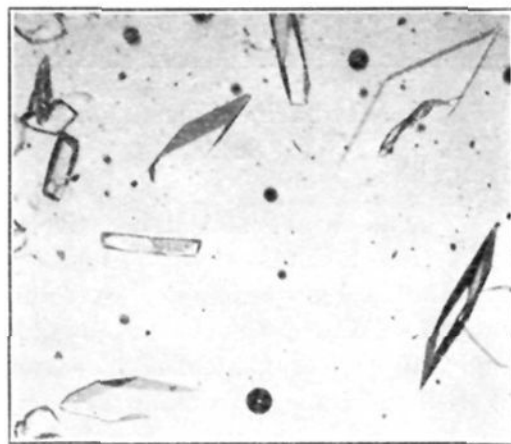


Fig. 6.—Dimethylaniline fluogermanate ($\times 80$); (see summary)

weak double refraction. The interference figure indicates an optic axis at an angle of about 45° to the normal for this view.

Clinopinacoidal views show an angle β of about 30° and an extinction angle of about 40° . Both optic axes lie outside this view.

The material is biaxial, positive or negative, with $2V$ about 90° . Axial plane is 010. Refractive indices: (α) = 1.445; (β) = 1.53 ± 0.005 ; (γ) = 1.617.

The analyses, densities and solubilities of the six salts are given in the table.

No.	d_{25}^{25}	Water	Solubilities		Other organic solvents
			CH ₃ OH	C ₂ H ₅ OH	
1 (NH ₄) ₂ GeF ₆	2.564	s.	i.	i.	i.
2 (NH ₂ OH) ₂ ·H ₂ GeF ₆	2.492 ^a	s. hyd.	s. absol.	v. sl. s.	v. sl. s.
3 (N ₂ H ₄) ₂ ·H ₂ GeF ₆	2.406	s. hyd.	v. sl. s.	v. sl. s.	v. sl. s.
4 (C ₆ H ₅ ·NH ₂) ₂ ·H ₂ GeF ₆	1.579	s. hyd.	s.	s. hot	i.
5 (C ₆ H ₅ ·NHCH ₃) ₂ ·H ₂ GeF ₆	1.631	s. hyd.	s.	sl. s. hot	i.
6 (C ₆ H ₅ ·N(CH ₃) ₂) ₂ ·H ₂ GeF ₆	1.548	s. hyd.	s.	s.	i.

^a Density of (NH₂OH)₂·H₂GeF₆·2H₂O is d_{25}^{25} 2.229.

No.		Analyses					
		Found		% F		% Ge	
1	NH ₃	16.22	16.20	51.41	51.20	32.59	32.61
2	NH ₂ OH	25.93	25.94	44.93	44.76	28.55	28.51
3	N ₂ H ₄	25.35	25.36	44.84	45.11	28.8	28.73
4	N	7.31	7.48	30.33	30.42	19.47	19.37
5	N	7.00	6.96	28.2	28.30	18.01	18.03
6	N	6.38	6.50	26.42	26.46	17.01	16.85

In the analyses, ammonia was determined by distillation with sodium hydroxide and titration of the distillate; fluorine by the method of Starck;² hydroxylamine by titration with potassium permanganate,³ hydrazine by the method of Kolthoff;⁴ nitrogen in (C₆H₅·NH₂)₂·H₂GeF₆, (C₆H₅·NHCH₃)₂·H₂GeF₆ and (C₆H₅·N(CH₃)₂)₂·H₂GeF₆, by the modified Kjeldahl-Gunning-Arnold method with absorption of the ammonia in 4% solution of boric acid.⁵ Copper sulfate was used instead of mercuric oxide.

Germanium was determined by direct precipitation of GeS₂⁶ except that in the analyses of the hydrazine, aniline, monomethylaniline and dimethylaniline salts, it was found necessary first to expel the base by boiling the solution of the salt with an excess of potassium carbonate, or fusing the salt with an excess of potassium hydroxide.

Densities were determined by the pycnometric method, with toluene as the immersion liquid.

The melting points could not be determined with the apparatus of Dennis and Shelton⁷ because of dissociation.

(2) Starck, *Z. anorg. Chem.*, **70**, 173 (1911).

(3) Bray, Simpson and MacKensie, *THIS JOURNAL*, **41**, 1363 (1919).

(4) Kolthoff, *ibid.*, **46**, 2009 (1924).

(5) Markley and Hann, *J. Assoc. Off. Agr. Chem.*, **8**, 455 (1925).

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

(7) Dennis and Shelton, *ibid.*, **52**, 3128 (1930).

Summary

This article presents details concerning the preparation, analysis, properties and optical characteristics of certain salts of fluogermanic acid with nitrogen bases. All of these salts are soluble in water, but are hydrolyzed with separation of hydrated germanium dioxide. Hydrolysis is especially pronounced in the case of dimethylaniline fluogermanate as is evidenced by the round spots in the photomicrograph of the salt.

The analogy between fluogermanates and fluosilicates is shown by the formation of a dihydrate in the case of the hydroxylamine salts whereas the ammonium and hydrazine salts are anhydrous.

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x-Ray Studies of Fatty Acids^{1,2}

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Introduction

The long spacings of normal fatty acids have been measured by a series of investigators.³ However, most of this work is not reliable, due in part to insufficient purity of the acids used. Due to the fact that we had a series of acids of exceptional purity available, it seemed worth while to repeat such measurements with increased accuracy. This was especially desirable in view of the study of mixtures of such acids which will be reported in a following paper.

Experimental Procedure

A. Spectrograph.—In all the work reported here a Bragg spectrograph (made in the Seeman Laboratory, Freiburg, i. Br.) with the approximate radius of 16.79 cm. was used. The adjustable front slit was set at 0.1 mm. during all of this work. Most of the measurements of the fatty acids were made by rotating the crystal at constant speed through the angle from 0 to $\approx 10^\circ$, since we were only interested in the lower order reflections. The reflections were registered on Eastman x-ray films.

B. x-Ray Source.—x-Rays were obtained from a Seeman metal tube, using a tungsten filament and a copper target, the operating peak voltage being 40 kilovolts at 20 milliamperes. A nickel filter of 0.02 mm. thickness was used over the window of the tube at all times to cut out the β -radiation from the copper. The target of the tube was periodically cleaned, thus avoiding tungsten radiation, which under the worst conditions was found by spectrographic measurements to be less intense than the β -radiation from the copper after passing through the nickel filter. The β -radiation was never observed for the fatty acid reflections.

(1) From a thesis submitted by F. B. Slagle, in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

(2) Emil Ott and F. B. Slagle, compare preliminary note, *J. Phys. Chem.*, **37**, 257 (1933).

(3) Compare P. P. Ewald and C. Hermann, "Strukturbericht (1913-1928)," Akademische Verlagsgesellschaft, Leipzig, 1931, pp. 691-700.