example, the thermoluminescence of a zinc borate glass which contains a small amount of manganese is increased by small amounts of cerium, but decreased by larger amounts. A definite amount of cerium may either increase or decrease the thermoluminescence, since the effect is dependent upon the amount of manganese present.

3. The emission spectrum for zinc borate glass which contains manganese has been found to be a band.
4. Single ended absorption bands have been found in the ultraviolet spectra with zinc borate glasses which contain manganese, cerium or thorium as the solute.
5. Intensity measurements of the thermoluminescence have been used to indicate that it is probably from near the edge of these bands that the energy for thermoluminescence is drawn.
6. From the positions of the absorption bands the conclusion is drawn that the relative thermoluminescent intensities of two materials in the same solvent changes with a change of the source of excitation.
7. Absorption curves which show the effect of cerium upon glasses which contain manganese and vice versa have been obtained.
8. An anomalous absorption has been found for zinc borate glasses which contain manganese.

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[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY, UNIVERSITY OF PENNSYLVANIA]

STUDIES ON HETEROPOLY ACIDS OF GERMANIUM. I. GERMANOMOLYBDIC ACID[1]

BY CHARLES G. GROSSCUP

RECEIVED SEPTEMBER 18, 1930 PUBLISHED DECEMBER 18, 1930

In the list of elements known to form heteropoly acids with molybdenum, tungsten and vanadium, one notices the absence of three members of the fourth periodic group. These elements, carbon, germanium and hafnium are missing from an otherwise complete series of the type $H_8[X(Mo_2O_7)_6]$ aq. where X may be silicon,[2] titanium,[3] zirconium,[3] thorium,[4] tin[5] and lead.[6] Possibly this may be supplemented by hafnium, which, it is conceivable, was present in the preparations of zirconomolybdates, since this element was not recognized at the time of the investigations and has since

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[1] An extract from a thesis presented in partial fulfilment of the requirements for the degree of Doctor of Philosophy, University of Pennsylvania.

[2] A pure acid has been obtained by Scroggie, THIS JOURNAL, 51, 1057 (1929).

[3] Péchard, *Compt. rend.*, 117, 781 (1893).

[4] Barbieri, *Atti. accad. Lincei*, 221, 5, 781 (1913).

[5] Rosenheim, Pieck and Pinsker, *Z. anorg. Chem.*, 96, 139 (1916).

[6] Ephraim, "Inorganic Chemistry," English ed., 1926.

been proved to be present in specimens of supposedly pure zirconium compounds to the extent of as much as 5%. Other elements exhibiting tetravalency such as manganese,[7] platinum[6] and cerium[8] may also be included here. The elements grouped about germanium in the periodic system, especially boron, phosphorus and arsenic, are known to play the role of central atom in similar compounds, *e. g.*, the familiar ammonium phosphomolybdate, $(NH_4)_3H_4[P(Mo_2O_7)_6]$ aq.

The similarities in chemical behavior of germanium to arsenic and silicon were largely responsible for the present endeavor to prepare a heteropoly acid which would be the germanium analog of silico-duodecimomolybdic acid, $H_8[Si(Mo_2O_7)_6]\cdot 28H_2O$. That germanium would enter into such "poly acid" formation was a logical conclusion and is supported by the results of this paper. A knowledge of "complexes" is important from an analytical standpoint, since the identity of the constituents of certain compounds and mixtures may be so masked that the elements escape detection in the usual procedures and the analyst is confronted with unusual reactions. It is through a study of the formation and properties of these compounds that the unexpected behavior of certain elements in the presence of molybdic, tungstic and vanadic acids is to be anticipated and means taken to insure their detection.

Experimental

Materials.—The germanium dioxide was prepared from zinc residues which were kindly furnished by Professor J. H. Müller. It was of the highest purity and entirely free from arsenic. The molybdenum trioxide was Baker's "Special," free from arsenic and phosphorus. Lead, calcium, magnesium and ammonium salts, sodium hydroxide, hydrobromic acid and sulfuric acid (special arsenic free) were Baker chemicals. Reagent quality ether was distilled over sodium. Guanidine carbonate was obtained from the Eastman Kodak Co. Laboratory distilled water was redistilled for preparation work. Ammonium hydroxide was redistilled in pyrex vessels and used immediately.

Preparation of the Free Acid.—Five grams of germanic oxide was dissolved in 200 ml. of water containing 7 g. of sodium hydroxide and the solution brought to boiling, whereupon 70 g. of molybdic oxide was slowly added with stirring. Rapid solution of the molybdic oxide took place until about half the amount had been added. Almost complete precipitation occurred at this point, followed by re-solution with continued addition of the molybdic oxide. An intense yellow color developed after this midpoint of reaction. Gentle boiling was continued for five minutes, the solution filtered and allowed to cool. The method of extraction was that of Drechsel;[9] several hundred ml. of ether was added, followed by an excess of cold 9 *N* sulfuric acid. An intermediate turbidity disappeared when sufficient acid had been added. Heavy yellow oily drops separated and settled, forming the third layer common to such extractions. This lower layer—an ether solution of the "complex acid"—was removed and evaporated at 40°. After powdering, the residue was dissolved in a small volume of water and the extraction with ether and sulfuric acid repeated. The ether was removed as before, the residue

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[7] Péchard, *Compt. rend.*, **125**, 29 (1897).

[8] Barbieri, *Atti accad. Lincei*, **23*i***, 5, 805 (1914).

[9] Drechsel, *Ber.*, **20**, 1452 (1887).

dissolved in water, the solution filtered and then allowed to crystallize at room temperature (18–28°). The major portion of mother liquor was removed by filtration and the crystals dried as rapidly as possible by pressing between filter paper, after which they were kept in tightly stoppered weighing bottles or weighed out at once for analysis. In spite of the high solubility, the solutions crystallized well. Three separate batches of the acid were prepared.

Preparation of the Guanidine Salt.—To an aqueous solution of the acid was added a concentrated solution of guanidine carbonate, the mixture warmed and filtered. The residue was boiled with water until solution was nearly complete, then filtered and cooled. The shining greenish-yellow crystals were removed and dried at 105°. On standing for several days the filtrate deposited white crusts containing germanium and molybdenum.

Properties.—The free acid crystallizes in yellow transparent octahedra, readily efflorescing. The melting point is approximately 65°. Induration, with loss of color and transparency, invariably resulted from attempts to preserve crystals imperfectly freed of mother liquor. Such changes took place in a few days and the substance produced, in sharp contrast to the parent compound, was but sparingly soluble in water. Well-dried specimens on the other hand have been kept ten weeks, suffering no apparent deterioration and differing from fresh samples only in a slightly lower water content. Analogous to the behavior of the corresponding silicon compound, pale yellow, difficultly soluble compounds are obtained with silver, thallous, mercurous, cesium, rubidium and guanidine salts and with alkaloids.

Analysis.—Calibrated weights were used and all gravimetric determinations were brought to constant weight (±0.05 mg.).

A. **Water.**—Samples were dried in an oven at 105° for "water of hydration." Total loss on ignition was determined by heating at 400° in a resistance furnace. The residues were yellow when hot and pale blue when cold.

B. **Germanium and Molybdenum.**—A number of separations were tried but only one yielded duplicable results. The procedure finally adopted was a distillation from 9 *N* hydrobromic acid. The free acid or ignition residue was placed in a 200-ml. round-bottomed flask, to which was attached by a ground joint a 25-cm. neck with side arm. A meter length of glass tubing dipping under water in an Erlenmeyer flask served as a condenser and receiver for the germanium tetrabromide; 25 ml. of hydrobromic acid (sp. gr. 1.30) containing a small amount of bromine was added to the flask and the mixture slowly distilled. If less than two hours were consumed in this operation, a little molybdenum usually appeared in the distillate as evidenced by the brown color of the sulfide. The distillation was continued until the volume of the solution remaining in the flask was about 3 ml.; an additional 25 ml. of hydrobromic acid was introduced and the distillation repeated. The distillate was made 6 *N* in acid by adding concentrated sulfuric acid and the germanium precipitated as sulfide by saturating the hydrogen sulfide. The germanium sulfide was filtered on a König crucible and, after washing with 6 *N* sulfuric acid saturated with hydrogen sulfide, was converted to oxide by nitric acid in the usual manner. The brown solution remaining in the distilling bulb was washed into a small sillimanite crucible, ten drops of concentrated sulfuric acid added and this mixture evaporated to dryness in an air-bath. The residue was gently ignited to expel sulfur trioxide and weighed as molybdic oxide.

C. The guanidine salt was analyzed for nitrogen by the Dumas method.

Discussion

Three physical constants of the compound under investigation suggested a formula similar to silicomolybdic acid, $H_8[Si(Mo_2O_7)_6]$ aq. They are:

(1) the isomorphism of the free acids; (2) the yellow color, which is usually associated with "poly acids" containing Mo_2O_7 groups; (3) the melting point, which is comparable with the values for the silico acid, 45°, and the titano acid, 60°.

The theoretical composition of $H_8[Ge(Mo_2O_7)_6]$ aq., according as the amount of "aq." is 24, 25, 26 and 28 moles, respectively, is given in Table I.

TABLE I

THEORETICAL COMPOSITIONS

	24 aq.	25 aq.	26 aq.	28 aq.
Ignition loss	21.58	22.18	22.77	23.92
GeO_2	4.48	4.44	4.41	4.34
MoO_3	73.94	73.38	72.82	71.74
	100.00	100.00	100.00	100.00
"aq."	18.48	19.02	19.72	21.58
Molecular weight	2336.6	2354.6	2372.6	2408.6

The tendency of the crystals to effloresce made it difficult to obtain samples of exactly the same composition, although the deviation and variance of results is not great, as is evident from the analyses.

TABLE II

"AQ." AND IGNITION LOSSES

No.	Sample, g.	Loss at 105°, %	Ignition loss, %
1	0.46224	19.26	22.41
2	.37547	19.10	22.65
3	.20490		22.20
4	.17245		22.31
5	.17857		22.19
6	.59183		22.47
7	.45747		22.62
8	.57261		22.32
9	.38234		21.77
10	.30670	18.70	21.88
11	.31427		22.15
12	.25630		22.08
13	.18382		22.08
14	.11287		21.18
15	.14546		21.22
16	.13040		21.20

Samples 1–5 from Preparation A; samples 6–10 from Preparation B; samples 10–16 from Preparation C; samples 14, 15, 16 were kept for ten weeks before analysis.

It will be seen that the ignition losses predicate an "aq." content of 24–26 moles and that the values for loss at 105° are in proportionate agreement. The molecular formula for silicomolybdic acid is accepted as $H_8[Si(Mo_2O_7)_6]\cdot 28H_2O$ but the analysis of the germanium compound failed to reveal a water content of the same magnitude. Five of the above samples were analyzed by the hydrobromic method and gave the following values.

TABLE III

ANALYSIS OF THE FREE ACIDS

No.	2	6	12	8	9
Wt. of sample, g.	0.37547	0.59183	0.25630	0.57261	0.38234
MoO_3 found, g.	.27177	.43085	.18761	.42087	.28217
MoO_3, %	72.38	72.80	73.20	73.50	73.80
GeO_2 found, g.	0.01633	0.02604	0.01164	0.02548	0.01759
GeO_2, %	4.35	4.40	4.54	4.45	4.60
Ignition loss, g.	22.65	22.47	22.08	22.32	21.77
Total	99.38	99.67	99.82	100.27	100.17
Ratio $GeO_2:MoO_3$	1:12.07	1:12.01	1:11.72	1:12.00	1:11.65
Ratio GeO_2 $MoO_3:H_2O$	1:30.10	1:29.68	1:28.92	1:29.25	1:28.22

Since vapor pressure measurements were not made, the existence of lower hydrates is not postulated. By efflorescence, however, it is conceivable that samples could have compositions agreeing with those selected in Table I.

Because of the simplicity of procedure we may use the ignition loss as a standard in the critical examination of results. Comparing, for example, Analyses 2 and 6, we see that lower ignition loss in No. 6 is compensated for by a higher metallic oxide content and, by reference to Table I, that the values for ignition loss, MoO_3 and GeO_2, agree proportionately within the limits of experimental error.

North and Beal[10] made use of a titration with sodium hydroxide as a means of analysis for silicomolybdic acid. Scroggie[2] repeated the work, using chlor phenol red as indicator. The complete decomposition of the germanium compound by alkalies may be expressed by the equation

$$GeO_2 \cdot 12MoO_3\text{ aq.} + 24\text{ NaOH} = GeO_2\text{ aq.} + 12\text{ Na}_2MoO_4 + \text{aq.}$$

if the germanic acid is not attacked under the conditions of the experiment. A sample, No. 13, after ignition was titrated with 0.2920 *N* sodium hydroxide and chlor phenol red. The water content, 22.08%, corresponds closely with that of $H_8[Ge(Mo_2O_7)_6]\cdot 25H_2O$, with a molecular weight of 2355. On this basis the titration required 23.93 moles of sodium hydroxide per mole of acid. Calculated from the weight of ignited oxides the value is 23.95. Another sample, No. 17, wt. 0.15717 g., was weighed out at the same time as samples No. 6 and No. 7, the water content of which gave a mean value of 22.54%, approximately equivalent to $H_8[Ge(Mo_2O_7)_6]\cdot 26H_2O$. Assuming then a molecular weight of 2373, the titration showed a consumption of 23.80 moles of the base.

That progressive decomposition with the intermediate formation of "unsaturated" compounds—those with lower MoO_3 content—took place was indicated by the fact that upon the addition of a drop of the base the basic color of the indicator persisted several minutes and then gradually

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[10] North and Beal, *J. Am. Pharm. Assn.*, **13**, 889 (1924).

faded. The titration was necessarily extended over a period of several hours before a permanent "end-point" was reached.

The analysis of the guanidine salt gave 7.97% nitrogen. The theoretical value for the tetrabasic salt, $(CN_3H_5)_4H_8[Ge(Mo_2O_7)_6]$ is 7.84%.

The product resulting from the deterioration of the undried crystals was washed with hot water, air dried and analyzed.

TABLE IV

ANALYSIS OF WHITE INSOLUBLE COMPOUND

Water at 105°, %	0.00
Ignition loss, %	11.20
MoO_3, %	86.50

Lack of material prevented a further study. Disruption of the original molecule apparently took place and a portion of the germanium was removed in the washing operation.

While the deviations from theoretical values are at times large, yet the results indicate the existence of a heteropoly acid of germanium and molybdenum with the formula $GeO_2 \cdot 12MoO_3 \cdot$aq., which may be written, after the fashion of the Miolati system of constitution, as $H_8[Ge(Mo_2O_7)_6]$aq., a member of the series $H_{12-n}[X_n(Mo_2O_7)_6]$aq. The coefficient for the "aq." has an apparent maximum of 26. The seriousness of the deviations is somewhat mitigated if one considers that ammonium phosphomolybdate, used since the time of Berzelius in analytical procedures, is, because of somewhat indefinite composition, still unsuited for gravimetric work.

In accordance with the present system of nomenclature the new compound may be called 12-germanomolybdic acid or germano-duodecimomolybdic acid.

The ease of formation of germanomolybdic acid and its salts makes the compound susceptible to qualitative and perhaps quantitative application for the detection and determination of germanium. To this purpose, germanium sulfide—the usual form in which the element is isolated—can be converted into the oxide and this boiled with a small volume of water and some molybdic oxide. The presence of the germanomolybdic acid thus produced may be confirmed by color or precipitation reactions. A yellow color is easily seen when 0.00183 g. of the free acid (corresponding to approximately 0.000082 g. of germanic oxide) is dissolved in 5 ml. of water. This may prove of particular value since no colorimetric determination of germanium has been reported.

Summary

1. The preparation and properties of a heteropoly acid of germanium and molybdenum of the type $H_8[Ge(Mo_2O_7)_6]$ aq. is outlined.

2. The use of the new acid and its salts for the colorimetric determination of germanium is suggested.

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[CONTRIBUTION FROM THE GEORGE HERBERT JONES LABORATORY OF THE UNIVERSITY OF CHICAGO]

NITROGEN COMPOUNDS OF GERMANIUM. I. THE PREPARATION AND PROPERTIES OF GERMANIC NITRIDE

BY WARREN C. JOHNSON

RECEIVED OCTOBER 2, 1930 PUBLISHED DECEMBER 18, 1930

According to the literature silicon[1] combines directly with nitrogen, when heated at 1300 to 1450°, to form the normal nitride, Si_3N_4. A similar reaction takes place when this element is heated in an atmosphere of ammonia at high temperatures. Analogous reactions in the case of germanium, tin and lead are lacking.

Carbonic anammonide, $(C_3N_4)_x$, has been obtained[2] as a highly polymerized, orange powder by heating mercuric thiocyanate. Pauly[3] has reported $(C_3N_2)_x$, carbonous nitride or anammonide, as being obtained by the thermal decomposition of tetra-iodo-imidazole. This has since been shown[4] in all probability to be a mixture of carbon and paracyanogen, $(C_2N_2)_x$. Bergstrom[5] prepared stannous imide, SnNH, by reacting potassium ammono stannite, SnNK, with a solution of ammonium bromide in liquid ammonia. The imide was deammonated by heating in a vacuum at 340°. The reaction resulted in the formation of stannous anammonide or nitride, Sn_3N_2. This nitride is the only definite one known of the fourth outer group elements exhibiting a valence of two. Carbonic nitride and silicic nitride are the only representatives of these elements functioning with a valence of four.

Recently Schwarz and Schenk[6] studied the ammonolysis of germanium tetrachloride in liquid ammonia solution. Their results indicate that the hexammonate described by Thomas and Pugh[7] may not exist in liquid ammonia. Schwarz and Schenk allowed germanium tetrachloride to ammonolyze, separated the ammonium chloride and found a definite combination in the imide, $Ge(NH)_2$. At 150° the imide was found to lose ammonia with the formation of the germanam, Ge_2N_3H. This latter

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[1] Weiss and Engelhardt, *Z. anorg. Chem.*, **65**, 78 (1910); Funk, *ibid.*, **133**, 67 (1924).

[2] King and Chamberlain, "Theses," Stanford University, **1924**, and **1930**, respectively.

[3] Pauly, *Ber.*, **43**, 2243 (1910).

[4] Wenzel, "Dissertation," Stanford University, **1927**.

[5] Bergstrom, *J. Phys. Chem.*, **32**, 433 (1928).

[6] Schwarz and Schenk, *Ber.*, **63**, 296 (1930).

[7] Thomas and Pugh, *J. Chem. Soc.*, 1051 (1926).