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DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[THIRD PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

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BY REFERENCE to the American Chemical Journal, 7, 413, there will be found a classification of the various groups of "complex inorganic acid" derivatives obtained by Wolcott Gibbs—the pioneer in this field of research. There will not be observed in that grouping any derivatives in which there are four different acid radicals acting as a compound anion. It has been the purpose of the present investigation to ascertain whether dioxides could be introduced into complexes consisting of sesquioxides, pentoxides and trioxides. It was hoped that by boiling ammonium vanadico-phospho-tungstate with an excess of silicic hydrate such a result would be reached, but combination did not ensue. The various constituents were then separately brought together and boiled with an excess of ammonium hydroxide for a period of six hours. Some dioxide did enter the combination, but it was concluded to operate in neutral solution; accordingly, 30 grams of ammonium paratungstate, in 700 cc. of water, were boiled ten hours in the presence of an excess of the hydrate of the particular dioxide which it was desired to introduce, after which 2 grams of ammonium phosphate were added, the solution being then boiled two hours longer, when 8 grams of ammonium metavanadate, reduced to the hydrate of the trioxide,[1] were added and the whole boiled for two hours more. This was the general method of preparation; hence, it will not be repeated in connection with the several derivatives which are described later.

In studying the behavior of these products, no tests were discovered which would differentiate one body from another. The following observations apply equally well to all. The salt separated from a concentrated aqueous solution in large, brilliant, black, octahedral crystals. These were very soluble in water, but were insoluble in organic reagents. Nitric acid, added to the solid salts, served to decompose them, a yellow-colored body resembling tungsten trioxide separating, but disappearing completely on the addition of water, and yielding a yellow-colored solution.

Dilute or concentrated nitric acid, added to the solution of the salts, merely caused a change in its color, without producing a precipitate. Hydrochloric acid caused a color change in the solution very slowly only on boiling.

Ammonium hydroxide did not alter the salt solutions. Sodium hydroxide produced a gray precipitate, which dissolved, on boiling, with the evolution of ammonia. A dark brown precipitate was produced by silver nitrate. It dissolved, to some extent, in boiling water. Ammoniacal silver nitrate produced an olive-green colored precipitate. It dissolved completely when the solution was boiled.

The precipitate, light green in color, formed by mercurous nitrate, was insoluble in water, but readily dissolved upon the addition of a few drops of nitric acid. The lead precipitate acted similarly. Mercuric chloride caused no precipitation. The same was true of copper sulphate, while a solution of ammoniacal copper sulphate produced a dirty gray precipitate, insoluble in boiling water. Cadmium chloride gave no reaction. Ammoniacal cadmium chloride threw out a dirty gray precipitate, insoluble in boiling water, but dissolved by water containing a few drops of hydrochloric acid. Cobalt nitrate, in ammoniacal solution, produced a bottle-green colored precipitate, which changed to an

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[1] The hydrate of the trioxide is produced when ammonium meta-vanadate is boiled for half an hour with hydrochloric acid, then evaporating to dryness upon a water-bath. The residue, taken up in water, imparts to the latter a copper-green color. Ammonium hydroxide was added to the solution. The resulting precipitate (hydrate of vanadium trioxide), after being washed once or twice with dilute ammonium hydroxide, was introduced into the tungstate solution.

olive-green on boiling. Barium chloride, in neutral solution, was without any action, but in the presence of ammonia and upon boiling, threw down a heavy insoluble precipitate. In the analysis of the salts mentioned below, the method described in previous communications proved inadequate. The difficulties met in this portion of the investigation were great. They were, in the main, surmounted. After much search, with frequent failures, the following course was adopted and gave, it is believed, reliable results.

In each case the air-dried salt was gently and gradually heated to dull redness. The loss represented water and ammonium oxide. The residue was then fused with equal parts of sodium carbonate and potassium nitrate. The fusion was taken up with water containing ammonium hydroxide and ammonium nitrate, boiled for several minutes and then filtered. The insoluble portion was thoroughly washed, dried, ignited and weighed as MeO_2. A "magnesia mixture" was added to the cold filtrate and washings. The magnesium ammonium phosphate was dissolved and reprecipitated. The tungstic acid, in the filtrate from the phosphoric acid precipitate, was determined according to the method of Gibbs, modified by Friedheim.[1] The vanadium was obtained by difference. The ammonium oxide was estimated in the usual manner.

A few words regarding the nomenclature, used in this communication, may not be out of place. An inspection of the literature relating to "complex inorganic acids" will disclose confusion on this point. After reflection, it was concluded to terminate the names of the dioxides, MeO_2 in *oso;* those of the type of Me_2O_3 in *ico*, and those of the form of Me_2O_5 in *o* or *io*. It is admitted that this system is not satisfactory and is contradictory to our generally accepted ideas on the subject, yet it seems to be the only means of indicating a differentiation in the types of oxides in these complexes.

AMMONIUM SILICOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.42	5.37	5.40
SiO_2	0.56	0.67	0.68
V_2O_3	15.83	15.77	15.80
P_2O_5	1.33	1.35	1.34
WO_3	60.32	60.58	60.45
H_2O	16.41	16.26	16.32

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[1] *Ber. d. chem. Ges.* (1890), p. 353.

AMMONIUM TITANOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.48	5.55	5.48	5.45
TiO_2	0.66	0.65	0.72	0.50
V_2O_3	18.98	19.10	18.89	18.87
P_2O_5	2.45	2.44	2.75	2.52
WO_3	56.29	56.08	56.50	56.42
H_2O	16.14	16.18	16.01	16.24

AMMONIUM ZIRCONOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(NH_4)O_2$	5.35	5.43	5.39
ZrO_2	0.63	0.59	0.61
V_2O_3	14.28	14.22	14.25
P_2O_5	2.49	2.55	2.52
WO_3	62.29	62.18	62.24
H_2O	14.96	15.03	14.99

AMMONIUM THOROSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.42	5.40	5.41
ThO_2	0.77	0.80	0.79
V_2O_3	16.03	16.31	16.17
P_2O_5	2.52	2.71	2.61
WO_3	59.31	58.94	59.13
H_2O	15.95	15.84	15.89

AMMONIUM STANNOSO-VANADICO-PHOSPHO-TUNGSTATE.

	Per cent.	Per cent.	Per cent.	Per cent.
$(NH_4)_2O$	5.34	5.40	5.38	5.37
SnO_2	0.25	0.23	...	0.24
V_2O_3	12.33	12.47	...	12.40
P_2O_5	2.34	2.38	2.36	2.36
WO_3	65.51	65.29	65.20	65.40
H_2O	14.23	14.23	....	14.23

The reactions of ammonium vanadico-phospho-tungstate are vastly different from those obtained after the introduction of a dioxide into its composition, even if the quantity of that dioxide be small. In mineral analysis the influence of such minute amounts of supposedly adventitious constituents is too often disregarded and not considered in the deduction of formulas.

The reader will grant that there is in the above analytical results satisfactory concordance. The dioxide was extremely difficult to eliminate entirely from the remaining components of the anion, so that while it is thought the percentages given are correct, yet, if there be an error in this factor, when corrected, it will prove to be above rather than below the amount here given.

The formulas deduced from the preceding figures of analysis are imposing and appear rather improbable, so that, for the present, they can be omitted, as the introduction of other dioxides is projected. Efforts, too, are being made to find other means of arriving at the molecular magnitudes of these bodies.

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DERIVATIVES OF COMPLEX INORGANIC ACIDS.

[FOURTH PAPER.]

BY ALLEN ROGERS AND EDGAR F. SMITH.

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IT may be observed that in those bodies containing vanadium but two oxides of the latter element appear—the trioxide and pentoxide. No derivatives of vanadicotungstic acid ($H_2O.V_2O_3WO_3$) have yet been prepared. In the classification of Wolcott Gibbs they are lacking. Further, the question had arisen whether by reduction of vanadic acid with hydrochloric acid the resulting oxide was really not the same as that produced on reducing vanadic acid with sulphur dioxide. If the stages of reduction were identical, then the hydroxides corresponding to these oxides—V_2O_3 and V_2O_4—if combined with tungstic acid, would yield one and the same complex acid. As will be seen, the products were dissimilar.

AMMONIUM VANADICO-TUNGSTATE,

$3(NH_4)_2O.V_2O_3.8WO_3.10H_2O$.

Thirty grams of ammonium paratungstate were boiled for six hours, when 6 grams of vanadium trioxide were introduced and the boiling continued for two hours longer. The filtered solution was reduced to a small volume and allowed to crystallize. Frequently, ammonium tungstate separated first and mixed with the vanadico-tungstate derivative. The crystals were treated several times with ice-water, which did not dissolve the ammonium tungstate, and, on evaporating the solution, ammonium vanadico-tungstate crystallized out in thin crusts, very soluble in water, but insoluble in organic solvents. The addition of nitric acid