[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY.]

DERIVATIVES OF COMPLEX INORGANIC ACIDS; PHOSPHO-VANADO-MOLYBDATES.[1]

BY WILLIAM BLUM.

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Wolcott Gibbs[2] prepared two phospho-vanado-molybdates, assigning them the following formulas: $8(NH_4)_2O.P_2O_5.8V_2O_6.14MoO_3 + 50H_2O$ and $7(NH_4)_2O.2P_2O_6.V_2O_5.48MoO_3 + 30H_2O$.

In an attempt to reproduce these two salts by the method of Rogers,[3] ammonium molybdate, phosphate and vanadate, in varying proportions, were boiled together in aqueous solution for several hours. The liquids gradually became orange in color and finally deep red. Upon evaporation a mixture of crystals was invariably obtained. It consisted of yellow needles and small red "octahedra." The analysis of the latter proved them to be identical with the 1 : 8 : 14-salt of Wolcott Gibbs, which he made by boiling ordinary yellow ammonium phosphomolybdate with ammonium vanadate (proportions not stated) till the former dissolved, when the solution was concentrated. The attempt was made to duplicate his results, so ten grams of ammonium vanadate and twenty-five grams of ammonium phosphomolybdate were boiled together in half a liter of water. The yellow precipitate having entirely dissolved, the deep red colored solution was reduced in volume and from it there separated red octahedral crystals. Their analysis led to the formula $6(NH_4)_2O.P_2O_5.4V_2O_5.18MoO_3 + 52H_2O$, which differs from the salt sought, in the ratio of vanadium and molybdenum, although the sum of these ratios in each case equals 22.

Wolcott Gibbs thought it probable that the vanadium pentoxide, V_2O_5, in his salt might be considered as $(V_2O_2)O_3$, and as such, replace the molybdenum trioxide—MoO_3—of the phosphomolybdate. As another salt had been found, confirming this idea, the existence of other compounds containing vanadium for varying amounts of molybdenum became very probable. Accordingly, different proportions of ammonium phosphovanadate were treated in a similar manner and there resulted six new derivatives. Not more than eight molecules of vanadic oxide could be introduced into the phosphomolybdate by this procedure. The reason why Wolcott Gibbs invariably obtained but the one salt—the 1 : 8 : 14-salt—is, probably, that he always had present in the boiling mixture an excess of ammonium vanadate.

In analyzing the several products the ammonia and water content were

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[1] From author's thesis for the Ph.D. degree.

[2] *Am. Chem. J.*, 5, 391 (1883).

[3] THIS JOURNAL, 25, 298 (1903).

determined by igniting a sample of the salt with anhydrous sodium tungstate (method of Wolcott Gibbs). The ammonia was obtained by distillation with sodium hydroxide into excess of standard acid, which was then titrated. The water was obtained by difference. In estimating the phosphoric oxide the salt was dissolved in water and boiled with ammonium hydroxide until the solution became colorless. The vanadium was then removed by an excess of ammonium chloride. To the filtrate was added a magnesia mixture. The resulting ammonium magnesium phosphate was dissolved in nitric acid and reprecipitated with ammonia.[1] The vanadium and molybdenum were estimated by a combined volumetric method.[2] The results for vanadium and molybdenum, in all the analyses given, represent the average of at least two concordant determinations.

Salts.

1. Ten grams of ammonium phosphomolybdate were boiled with 1.2 grams of ammonium vanadate and 400 cc. of water for eight hours. The precipitate was almost completely dissolved. The filtrate from it was deep orange in color. Upon concentration, yellow needles separated—their analysis indicated them to be nothing more than a vanado-molybdate. In the mother liquid from them, however, there separated orange colored octahedral forms. It was extremely difficult to free them from the needles. Their analysis approximated the formula $5(NH_4)_2O.P_2O_5.2\frac{1}{2}V_2O_5.21\frac{1}{2}Mo.O_3.50H_2O$.

2. When varying amounts of ammonium phosphate, ammonium vanadate and molybdate were boiled together for several hours, two crops of deep red *colored octahedral* crystals were obtained. Their analysis indicated them to be $6(NH_4)_2O.P_2O_5.4V_2O_5.18MoO_3.52H_2O$, which would require:

	Calculated.	Found.	
Water	19.87	19.89	19.53
$(NH_4)_2O$	6.62	6.25	6.36
P_2O_5	3.01	3.04	2.93
V_2O_5	15.46	14.93	15.47
MoO_3	55.04	55.96	55.71

3 and 4. Here 10 grams of phosphomolybdate and 4.8 grams of ammonium vanadate were boiled together for almost eight hours. As the salts were not recrystallized and merely dried between filter paper their difference in composition may be due to the presence of occluded mother liquor or to other undiscovered conditions.

3. $8(NH_4)_2O.P_2O_5.5V_2O_5.18MoO_3.45H_2O$.

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[1] Gooch, *Proc. Am. Acad.*, **15**, 53.

[2] Edgar, *Am. J. Sci.*, **25**, 2332 (1908).

Analysis:

	Calculated.	Found.
H_2O	16.63	16.93
$(NH_4)_2O$	8.54	8.09
P_2O_5	2.92	3.07
V_2O_5	18.69	18.37
MoO_3	53.22	53.54

4. $7(NH_4)_2O.P_2O_5.5\frac{1}{2}V_2O_5.16\frac{1}{2}MoO_3.50H_2O$.

Analysis:

	Required.	Found.
H_2O	18.84	18.50
$(NH_4)_2O$	7.61	7.17
P_2O_5	2.97	2.64
V_2O_5	20.93	21.09
MoO_3	49.67	50.60

5. Two preparations were obtained by boiling 10 grams of phosphomolybdate with 6 and 7.5 grams of ammonium vanadate. Red crystals separated, were recrystallized and gave analytical results pointing to identity and the formula $8(NH_4)_2O.P_2O_5.7V_2O_5.15MoO_3.50H_2O$.

Analysis:

	Calculated.	Found.	
H_2O	18.40	18.53	17.72
$(NH_4)_2O$	8.50	8.11	7.93
P_2O_5	2.90	3.12	3.08
$7V_2O_5$	26.05	26.65	27.04
$15MoO_3$	44.15	44.35	43.78

6. A salt similar to that of Wolcott Gibbs was obtained on boiling together equal amounts of the two constituents. The results indicated the formula $8(NH_4)_2O.P_2O_5.8V_2O_5.14MoO_3.50H_2O$.

Analysis:

	Calculated.	Gibbs.	Found.	
H_2O	18.25	18.14	17.80	17.45
$(NH_4)_2O$	8.44	8.36	7.99	8.55
P_2O_5	2.88	3.44	3.45	3.27
$8V_2O_5$	29.53	29.51	29.81	30.91
$14MoO_3$	40.89	40.54	40.95	40.12

7. In two preparations, 10 grams of ammonium molybdate, 2 cc. of sirupy phosphoric acid and 400 cc. of water were boiled respectively with two and three grams of vanadic oxide. When these solutions were concentrated black crystals separated. Their analysis gave the formula $8(NH_4)_2O.P_2O_5.10\frac{1}{2}V_2O_5.11\frac{1}{2}MoO_3.50H_2O$, which would require:

Analysis:

	Calculated.	Found.	
H_2O	17.91	17.92	18.07
$(NH_4)_2O$	8.28	8.37	8.10
P_2O_5	2.83	3.59	3.36
V_2O_5	38.03	37.38	37.74
MoO_3	32.96	32.46	32.73

8. In a preliminary trial a mixture of red and black crystals was obtained by boiling together 10 grams of ammonium molybdate, 5 grams of ammonium vanadate and 5 grams of ammonium phosphate in 700 cc. of water for eight hours. The black crystals were present in larger amount and after recrystallization from water were analyzed and the following formula deduced: $8(NH_4)_2O.P_2O_5.11V_2O_5.11MoO_3.50H_2O$.

Analysis:

	Calculated.	Found.
H_2O	17.84	17.74
$(NH_4)_2O$	8.25	8.51
P_2O_5	2.82	3.50
V_2O_5	39.69	39.93
MoO_3	31.40	30.32

It may be said of the crystallography of all these salts that their habit was that of the octahedron truncated by a cube, but it was noticed that in most cases only two cubical faces were present, or at least that four were very minute. The same was true of the crystals having the rhombohedral aspect. Accurate measurement of the angles was somewhat difficult, owing to the efflorescence of the crystals. Observations on a number of crystals indicated that they were all tetragonal, although the axial ratio differed from unity by less than 0.01. There was no evidence of regularity in this ratio, the angles on different crystals of the same compound varying as much as did those of different compounds. The optical properties point decidedly to the tetragonal system. When convergent polarized light was passed through a section cut parallel to the basal pinacoid, uniaxial figures were obtained, although after efflorescence there was a slight tendency to form a biaxial figure. Unfortunately only a few of the salts were sufficiently transparent for this purpose.

All of these salts are soluble in water, the solutions ranging in color from orange to dark red. The effects produced by a number of reagents upon these solutions fail to show any marked differences in behavior. Sodium hydroxide produced colorless solutions, from which ammonia was expelled by boiling. Ammonium hydroxide formed orange-colored precipitates, which dissolved on boiling, with the formation of colorless solutions. Silver nitrate produced precipitates varying in color from orange to reddish-brown, these precipitates being somewhat soluble in water, and readily so in dilute nitric acid. Mercurous and lead nitrates formed yellow to orange-red precipitates. Copper sulphate caused green precipitates, while cadmium sulphate had no action. Barium chloride had no immediate effect, but there gradually separated reddish crystalline precipitates with usually an orange colored fluorescent precipitate in the supernatant liquid.

The silver salts corresponding to the ammonium salts in 2, 5 and 7 were made and analyzed. The ratios of the acid oxides were preserved in these new compounds.

No study of the limits of concentration leading to the formation of any single member of the series was made. Such a study should be preceded by a systematic investigation of each of the three and four component systems which may be present in this very complicated five-component system. It is proposed to begin such an extended research of the many complexes which have already been prepared.

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DOUBLE FLUORIDES OF TITANIUM.[1]

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In the course of a study of titanium the following double fluorides with certain alkaloids were prepared. It was thought a knowledge of them would prehaps lead to better methods than now exist of separating titanium from columbium and tantalum.

Quinine Titanium Fluoride, $(C_{20}H_{24}N_2O_2)(H_2TiF_6)_2.H_2O$.—This salt separated on mixing an alcoholic solution of quinine with a hydrofluoric acid solution of titanium hydroxide. It was recrystallized three times from alcohol and dried in the air. It had a white, velvety appearance. It dissolved readily in water, showing a slight opalescence. In its analysis the titanium was precipitated with ammonium hydroxide and weighed as dioxide. To obtain the fluorine content the water solution of the salt was boiled and titrated with a 0.2 normal solution of sodium hydroxide. Phenolphthalein was the indicator. Fairly concordant results in the estimation of the water were obtained by drying the salt to constant weight at 120°.

Calculated: Ti, 9.67; F, 22.93; H_2O, 1.81.
Found: Ti, 9.53; F, 23.55; H_2O, 1.80, 1.92.

Strychnine Titanium Fluoride, $(C_{21}H_{22}N_2O_2)_2H_2TiF_6.3H_2O$.—It consisted of small lustrous white needles when recrystallized from water. The crystals retained their luster for months. They were quite soluble in

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[1] From the author's thesis for the Ph.D. degree.