phate, as recommended by Dyer, and to boil for one-half hour after the solution becomes colorless, or in the case of quickly decolorized samples, for at least one hour from the time the potassium sulphate is added.

(7) The Dyer modification appears to combine the advantages of the other methods (Kjeldahl-Willfarth, Gunning and Arnold-Wedemeyer) now recommended by the Association of Official Agricultural Chemists for the determination of nitrogen in organic compounds.

[CONTRIBUTION FROM THE JOHN HARRISON LABORATORY OF CHEMISTRY, No. 88].

DERIVATIVES OF COMPLEX INORGANIC ACIDS.

SIXTH PAPER.

BY ALLEN ROGERS AND EDGAR F. SMITH.

Received September 5, 1904.

IN A previous communication[1] from this laboratory, attention was called to complexes of certain sesquioxides with tungstic acid; for example, the aluminico-tungstates and the bismuthico-tungstates, described by Balke and Smith, in which there exist the following ratios between sesquioxide and tungstic acid:

$$1Al_2O_3 : 9WO_3 \quad \text{and} \quad 2Bi_2O_3 : 11WO_3.$$

The literature on complexes reveals the fact that the sesquioxides which, in the past, have been combined with tungstic and molybdic acids are those of phosphorus, arsenic and antimony, corresponding to the chloride type RCl_3. It might well be expected that bismuth oxide, corresponding to the same chloride type, would enter into combination with tungstic acid in ratios similar to those found among the complex phosphorico-, arsenico- and antimonico-tungstates and molybdates. This surmise proved correct, for among the many derivatives of complex acids containing those oxides, synthesized by Wolcott Gibbs, appear the analogues of phosphorus, more particularly the compound

$$2Na_2O.4P_2O_3.22WO_3.37H_2O$$

with which

$$6(NH_4)_2O.4Bi_2O_3.22WO_3.20H_2O$$

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[1] This Journal, **25**, 1229.

and other salts are, without question, analogous. The harmony becomes evident upon doubling the formulas first given them by Balke and Smith.

Aluminium oxide conforms not only to the RCl_3-type of chlorides, but also to the R_2Cl_6-type. The ratio found in the aluminicotungstates was

$$1Al_2O_3 : 9WO_3.$$

By doubling this proportion so that it reads

$$2Al_2O_3 : 18WO_3,$$

complete analogy with existing tungstates is established. Thus,

$$6(NH_4)_2O.2Al_2O_3.18WO_3.36H_2O$$

would accord well with

$$7(NH_4)_2O.2As_2O_5.18WO_3.18H_2O$$

prepared by Wolcott Gibbs.

Would other sesquioxides—those generally regarded as certain analogues of the chloride type R_2Cl_6—exhibit new ratios between the sesquioxide and tungstic acid, or would they, too, incline to the ratio manifested by oxides like P_2O_3, As_2O_3 and Sb_2O_3? To answer this question, experiments were instituted with the view of combining the oxides of manganese and nickel (R_2O_3) with tungstic acid. Accordingly, Howard W. Brubaker[1] boiled 15 grams of ammonium paratungstate in a liter of water with an excess of manganic hydroxide[2] for twelve hours. The hot solution, pink in color, was filtered and reduced to a small volume upon a water-bath. After standing in a cool place for several hours large, red-colored, octahedral crystals separated. They were recrystallized and proved to be very readily soluble in water. Their analysis gave

	Per cent.
$(NH_4)_2O$	5.77
Mn_2O_3	4.48
WO_3	78.24
H_2O	11.51

from which was deduced the formula

$$4(NH_4)_2O.Mn_2O_3.12WO_3.23H_2O.$$

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[1] See Thesis, 1904.

[2] Made by passing chlorine gas through manganous carbonate suspended in water at the room temperature.

Here the ratio of sesquioxide to tungstic acid is in perfect accord with the ratios observed in the aluminico-, ferrico-, and chromico-molybdates of Struve,[1] and by doubling the above formula so that it would read

$$8(NH_4)_2O.2Mn_2O_3.24WO_3.46H_2O$$

its analogue is found in Wolcott Gibbs

$$4(NH_4)_2O.2P_2O_3.24MoO_3.31H_2O.$$

That is, in this manganico-tungstate there is reason to believe that the manganic oxide betrays a kinship to acid oxides, like those of phosphorus, arsenic and antimony

In making the nickel derivatives the hydrated sesquioxide of nickel was boiled in an ammoniacal solution of ammonium paratungstate for eight hours. The filtered solution was blue in color. It acquired a green tint upon concentration when the ammonia was driven out. There was also a simultaneous separation of a green powder which, however, redissolved on the addition of ammonium hydroxide, the blue color being at the same time restored to the liquid. By keeping it ammoniacal during the evaporation, there separated at last a greenish white crystalline powder. This compound was prepared repeatedly and showed the same characteristics. After freeing it from any contaminating ammonium paratungstate it was analyzed, giving results corresponding to the formula

$$3(NH_4)_2O.Ni_2O_3.16WO_3.22H_2O.$$

	Found.				Theory.
	I.	II.	III.	IV.	
$(NH_4)_2O$	3.59	3.53	3.52	3.53	3.52
Ni_2O_3	3.97	3.93	3.68	4.06	3.73
WO_3	82.90	82.94	83.58	82.88	83.80
H_2O	8.95	9.54	9.60	9.53	8.95

This salt was very sparingly soluble in water after it had once separated from its solution so that to obtain other derivatives, *e. g.*, the barium salt, barium chloride was added to the liquid remaining after filtering out the ammonium salt. In this way a white, very insoluble precipitate was procured which, after washing, was dried and analyzed, giving results corresponding to the formula

$$19BaO.Ni_2O_3.16WO_3.$$

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[1] *Am. Chem. J.*, 7, 417.

	Found.			
	I.	II.	III.	Theory
BaO	43.29	42.95	43.12	42.91
Ni_2O_3	2.53	2.86	2.69	2.44
WO_3	54.18	54.19	54.19	54.65

It may be worth while to observe here that another ammonium salt was obtaind by conducting ammonia through the solution of ammonium nickelico-tungstate during evaporation. The second salt was dark blue in color when moist, but on drying became light blue. Its analysis gave results approximating those required by the formula

$$(NH_4)_2O.Ni_2O_3.4WO_3.7H_2O.$$

	Found.		
	I.	II.	Theory.
$(NH_4)_2O$	4.27	4.27	4.09
Ni_2O_3	13.82	13.95	13.09
WO_3	71.75	71.93	72.99
H_2O	10.16	9.85	9.92

It is needless to add that the perfect removal of nickel from tungstic acid is difficult to accomplish.

Two ratios, then, are present in the nickelico-tungstates:

$$1Ni_2O_3 : 16WO_3 \text{ and } 1Ni_2O_3 : 4WO_3.$$

If the formula of the second salt be doubled, it becomes

$$2(NH_4)_2O.2Ni_2O_3.8WO_3.14H_2O,$$

which has its analogue in

$$3BaO.2As_2O_3.8MoO_3,$$

prepared by Wolcott Gibbs. In other words, in this derivative the nickel oxide is in harmony with the oxides of phosphorus, arsenic and antimony. In the salts

$$3(NH_4)_2O.Ni_2O_3.16WO_3.22H_2O$$

and

$$19BaO.Ni_2O_3.16WO_3$$

there exists a ratio not previously noticed among the complex tungstates, but present in several of Struve's molybdates:

$$5K_2O.Mn_2O_3.16MoO_3.21H_2O,$$

$$5(NH_4)_2O.Mn_2O_3.16MoO_3.12H_2O.$$

It would appear, therefore, taking into consideration also molybdates, that the sesquioxides of manganese and nickel not only imitate P_2O_3, As_2O_3 and Sb_2O_3 in their ratio combinations with tungstic and molybdic acids, but that they show another ratio

$$1Ni_2O_3 : 16WO_3 \text{ and } 1Mn_2O_3 : 16MoO_3,$$

in which they perhaps follow the other type of chloride, assumed by many sesquioxides.

In one of the admirable contributions[1] of Wolcott Gibbs upon complexes, that investigator remarks: "It still remains to study the relations of the oxides of the cerium and yttrium groups to molybdic and tungstic oxides, since these correspond to chlorides of the type RCl_3, and yet differ in a very marked degree from oxides like As_2O_3, Sb_2O_3, etc., etc."

The following paragraphs contain the results reached by combining such oxides with tungstic acid. The new compounds were prepared in practically the same way so that a general description will apply to all. Ammonium paratungstate in aqueous solution was boiled with the respective hydroxides in excess for eight hours (as in the case of nickel). After filtration the solution was evaporated to dryness on a water-bath. In every case a salt separated as the concentration proceeded. This was examined and found to vary in composition, due, no doubt, to its instability. If it was not removed, it dissolved, becoming later an oil, which finally dried down to a transparent gum.

All of the salts to be described proved quite insoluble after they had become dry, so that very little could be learned regarding their chemical behavior.

Ammonium Praseodymico-tungstate,

$$2(NH_4)_2O.Pr_2O_3.16WO_3.16H_2O.$$

—This salt was obtained in the form of a green transparent gum. It was very sparingly soluble in water. Alkalies and acids quickly decomposed it. The method of analysis was practically that pursued in former cases with complexes. The ammonia and water were obtained by heating a portion of the salt. The ammonia itself was determined by distillation of the salt with potassium hydroxide and subsequent titration of the acid in which the gas had been collected.

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[1] *Am. Chem. J.*, 7, 412.

To estimate the praseodymium a portion of the salt was decomposed by digestion with nitric or hydrochloric acid. After filtering out the tungstic acid the praseodymium was precipitated with ammonia water. The praseodymium hydroxide was again treated with acid, filtering out any tungstic acid which might separate. Even then the praseodymium hydroxide was white in color, totally unlike its usual appearance. This was due to adherent tungstic acid which could only be eliminated by fusing the impure praseodymium oxide with sodium carbonate and potassium nitrate. The tungstic acid was determined by difference.

	Found.			
	I.	II.	III.	Theory.
$(NH_4)_2O$	2.63	2.41	2.39	2.34
Pr_2O_3	7.59	7.56	7.48	7.42
WO_3	83.17	83.47	83.62	83.73
H_2O	6.61	6.56	6.51	6.51

Barium Praseodymico-tungstate,

$$4BaO.Pr_2O_3.16WO_3.7H_2O.$$

—This salt was made by adding barium chloride to the solution poured off from the ammonium salt. It was a white precipitate, insoluble in water. It was washed by decantation, dried and analyzed.

	Found.		
	I.	II.	Theory.
BaO	12.96	12.41	12.80
Pr_2O_3	6.84	....	6.88
WO_3	77.51	78.68	77.67
H_2O	2.69	....	2.65

Attempts to prepare it a second time failed, but no trouble was experienced in making the following compound:

$$6BaO.Pr_2O_3.16WO_3.9H_2O,$$

the analyses of which agree very well and give it definiteness.

	Found.			
	I.	II.	III.	Theory.
BaO	17.54	17.36	17.45	17.92
Pr_2O_3	6.61	6.52	6.45	6.42
WO_3	72.70	72.97	73.35	72.48
H_2O	3.15	3.15	3.15	3.18

Silver Praseodymico-tungstate,

$4Ag_2O.Pr_2O_3.16WO_3.8H_2O$.

—This was prepared like the barium salt. Its color was greenish white. It was insoluble in water. Its analysis proved troublesome.

	Found.	Theory.
Ag_2O	18.43	18.15
Pr_2O_3	6.38	6.43
WO_3	72.48	72.59
H_2O	2.71	2.83

Ammonium Neodymico-tungstate,

$3(NH_4)_2O.Nd_2O_3.16WO_3.20H_2O$.

—This salt is pink in color. It dissolved in water with great difficulty. Its analysis proved difficult. The removal of the last traces of tungstic acid could only be effected by fusing the neodymium oxide with a mixture of sodium carbonate and potassium nitrate. The neodymium was weighed as Nd_4O_7.

	Found.			
	I.	II.	III.	Theory.
$(NH_4)_2O$	2.80	2.92	2.86	3.42
Nd_2O_3	6.82	7.22	7.02	7.34
WO_3	82.78	82.24	82.51	81.35
H_2O	7.60	7.62	7.61	7.89

Barium Neodymico-tungstate,

$6BaO.Nd_2O_3.16WO_3.17H_2O$.

—This salt was also pink in color and quite insoluble in water. Its analysis showed:

	Found.		
	I.	II.	Theory.
BaO	17.16	17.18	17.44
Nd_2O_3	6.40	6.74	6.33
WO_3	69.43	69.22	70.39
H_2O	7.01	7.09	5.84

The discrepancies here are due to the extreme difficulty in obtaining the salt pure because of its insolubility, and also to troubles which arose in the analysis, simple though it would seem.

Ammonium Lanthanico-tungstate,

$2(NH_4)_2O.La_2O_3.16WO_3.16H_2O.$

—This salt was prepared like its analogues. It was white in color and showed the same great insolubility as the other complexes of this group.

	Found.			
	I.	II.	III.	Theory.
$(NH_4)_2O$	2.59	2.59	2.59	2.35
La_2O_3	7.06	6.49	7.06	7.29
WO_3	84.56	84.68	84.11	83.87
H_2O	6.29	6.24	6.24	6.49

Barium Lanthanico-tungstate,

$5BaO.La_2O_3.16WO_3.16H_2O.$

—A white salt, made by precipitation of the extremely dilute solution of the preceding salt with barium chloride.

	Found.			
	I.	II.	III.	Theory.
BaO	....	15.84	....	15.03
La_2O_3	6.52	6.21	6.92	6.34
WO_3	....	72.63	73.67	72.97
H_2O	5.42	5.32	6.08	5.66

Silver Lanthanico-tungstate,

$5Ag_2O.La_2O_3.16WO_3.4H_2O.$

—This salt was made like the preceding barium salt. It was white in color and very insoluble.

	Found.				
	I.	II.	III.	IV.	Theory.
Ag_2O	....	22.43	....	22.28	22.04
La_2O_3	6.57	6.70	6.63	6.27	6.13
WO_3	....	69.38	....	70.18	70.47
H_2O	1.49	1.49	1.49	1.49	1.36

Ammonium Cerico-tungstate,

$2(NH_4)_2O.Ce_2O_3.16WO_3.2H_2O.$

—The solution of ceric hydroxide in ammonium paratungstate was at first colorless, but upon concentration it became yellow and finally red. From this, on standing, was obtained a red transparent glass, which, once dry, would not dissolve in water and on boiling with it sustained decomposition.

	Found.				
	I.	II.	III.	IV.	Theory.
$(NH_4)_2O$	2.70	2.56	2.59	2.63	2.31
Ce_2O_3	7.55	7.19	7.23	6.97	7.28
WO_3	81.96	82.56	82.51	82.78	82.41
H_2O	7.79	7.69	7.67	7.62	8.00

Wolcott Gibbs,[1] in his last published paper on the derivatives of complex inorganic acids, mentions briefly a molybdate in which cerium oxide was present. No analyses are given.

As frequently observed in the earlier sections of this communication the products therein described were extremely insoluble. It proved to be one of the obstacles in the path of eliminating all possible contaminating bodies. When, however, a pentoxide was introduced into any one of these compounds the resulting, new derivative proved to be exceedingly readily soluble in water. This was especially true of the ammonium salts of lanthanico-vanado-tungstic acid and praseodymico-phospho-tungstic acid.

Klein studied four series of borico-tungstates. In one series he found the ratio

$$2R_2O.B_2O_3.9WO_3.$$

Here again is the ratio 1 : 9, the same ratio which Balke and Smith found in the aluminico-tungstates; but, as noted in the earlier portion of this paper, by doubling the formula so that it became

$$2Al_2O_3 : 18WO_3$$

harmony with an existing arsenico-tungstate was found; hence, there would now be

$4R_2O.2B_2O_3.18WO_3$	Klein,
$6R_2O.2Al_2O_3.18WO_3$	Balke and Smith,
$7R_2O.2As_2O_3.18WO_3$	Gibbs.

Attention, too, was called in previous paragraphs to the analogy evident in the nickelico-tungstates and the arsenico-molybdates, as well as to that between the bismuthico- and phosphorico-tungstates, also the manganico-tungstates and the phosphorico-molybdates, which would arrange in a series the oxides

B_2O_3, Al_2O_3, P_2O_3, Mn_2O_3, Ni_2O_3, As_2O_3, Sb_2O_3, and Bi_2O_3,

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[1] *Am. Chem. J.*, 17, 1895.

harmonizing with the chloride type RCl_3, and yet there is proof in the compound—

$$3(NH_4)_2O.Ni_2O_3.16WO_3—$$

and in the molybdate—

$$5(NH_4)_2O.Mn_2O_3.16MoO_3—$$

that the sesquioxides—Ni_2O_3 and Mn_2O_3—point to a possible ratio between oxides of that constitution and tungstic and molybdic acids, which had not previously been observed except in the case of Struve's manganico-molybdate, but which ratio, from the results obtained in the study of the complexes resulting from the union of the rare earth oxides with tungstic acid, is evidently a definite and important ratio, *viz.*:

$$1R_2O_3 : 16WO_3 ;$$

otherwise it would scarcely be expected to appear so well marked in such a series of derivatives as that presented above.

If it were permissible to arrange the oxides which have been combined with tungstic and molybdic acids in groups, they would appear thus:

I.		II.		III.
B_2O_3				
Al_2O_3				Nd_2O_3
P_2O_3	2 : 24	Mn_2O_3	1 : 16	Pr_2O_3
As_2O_3	2 : 8	Ni_2O_3		La_2O_3
Sb_2O_3				Ce_2O_3
Bi_2O_3				

Under I would occur the oxides which are credited with decided acid character. The ratios they exhibit in their combinations with tungstic and molybdic acids are more numerous than has been noticed with the oxides under II and III. Those under II—manganic and nickelic oxides—may be viewed as transitional oxides. In Wolcott Gibbs' interpretation of Struve's salts,[1] ferrico-, aluminico- and chromico-molybdates exist in which the ratio of the oxides Al_2O_3, Cr_2O_3 and Fe_2O_3 to molybdic acid is as 1 : 12. There is no evidence of other ratios. This one ratio, however, would be sufficient, as in the case of Mn_2O_3, to ally them with P_2O_3, As_2O_3 and Sb_2O_3. Whether other ratios will show themselves in their combinations with tungstic acid remains to be

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[1] *Am. Chem. J.*, 7, 417.

seen. In one instance an aluminico-tungstate (1 : 12 or 2 : 24) was noticed together with the usual 2 : 18-compound. Its quantity was never very great.

The ferrico-, chromico- and cobaltico-tungstates are being investigated.

In conclusion, the writers would here acknowledge their indebtedness and extend thanks to Dr. H. S. Miner, of the Welsbach Lighting Co., for the generous gift of rare earth salts, and to Messrs. Dox, Masland and Poole, for valuable and patient assistance in the analytical work connected with this study.

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AN INVESTIGATION OF SODAMIDE AND OF CERTAIN OF ITS REACTION-PRODUCTS.[1]

BY W. PHILLIPS WINTER.

Received June 10, 1904.

THE history of the preparation of sodamide dates from 1809, when Sir Humphry Davy,[2] in England, and Gay-Lussac and Thénard,[3] in France, almost simultaneously discovered the amides of sodium and of potassium. They were carrying on investigations to determine the composition of ammonia and they led a strong current of the latter gas, for several hours, over the pure metal heated in a glass retort to about 300°. The glass of the retort was considerably etched, and the semicrystalline mass of sodamide obtained was olive-green in color.

They investigated and sought to analyze it. Davy plunged pieces of sodamide under the mouths of jars filled with water, transferred the unabsorbed gas to a eudiometer and determined that hydrogen was formed in the decomposition of sodamide by water. Gay-Lussac and Thénard, by strongly heating the substance, obtained two-fifths of the ammonia that had disappeared in the reaction; at a higher temperature nitrogen and hydrogen gases were formed in the ratio of 2.5 of the former to 1 of the latter in quantities to account for one-fifth more of the ammonia. Decomposition of the residue by water yielded the remaining portions of ammonia.

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[1] The work herein described is abstracted from a dissertation for the degree of Doctor of Philosophy in the Johns Hopkins University. It was carried on under the guidance of Professor E Renouf.

[2] *Phil. Trans.*, **1**, 39 (1809).

[3] *Recherches Physico-chimiques*, **1**, 337-356.