chromatic light are all alike and the displacement must be carefully followed on the cross hairs of a telescope.

IV. Length of Cell.—The maker of the instrument supplies cells varying in length from 0.1 cm. to 8 cm. The observation has been confirmed that the micrometer reading, that is, the displacement of the bands, is proportional to the length of the cell. The longer cell, therefore, increases the accuracy of the measurements.

In the case of benzene derivatives the longer cell increases the optical effects which have just been described. For example, using a 4cm. cell the breaks in the calibration of thymol occurred regularly with each increase in concentration of about 200 mg. per liter. When using an 8cm. cell this phenomenon occurred at about every 100 mg. per liter.

The writer wishes to express his thanks to Dr. A. L. Kibler, Chief of the Physical Chemistry Department for his advice, and to Mr. G. A. Sachs for his assistance in the laboratory.

Summary

Some observations are reported on the use of the Zeiss interference refractometer as a means of determining the concentrations of dilute solutions.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF WISCONSIN]

SELENO COMPOUNDS OF TUNGSTEN[1]

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Since selenium is similar to sulfur in many respects, it was believed to be possible to prepare some new compounds of selenium which would be analogous to known compounds of sulfur. Thus, seleno-antimonates, seleno-arsenates and seleno-stannates are known which are analogous to the thio-antimonates, thio-arsenates and thio-stannates. Many mixed compounds such as $Na_3SbSeS_3{\cdot}9H_2O$ and $Na_3AsSe_2S_2{\cdot}9H_2O$ have also been prepared. Thio-compounds of tungsten, molybdenum and vanadium such as $(NH_4)_2WS_4$, $(NH_4)_2WO_2S_2$, $(NH_4)_2MoS_4$ and $(NH_4)_3VS_4$ are known, but analogous seleno compounds have not been reported. It is the purpose of this investigation to attempt the preparation of seleno compounds which are analogous to the thio-tungstates.

Uelsmann[2] prepared tungsten triselenide by saturating a tungstate with hydrogen selenide and then acidifying the solution with sulfuric acid, when the tungsten triselenide was precipitated. It was logical to

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[1] From part of a thesis to be submitted by August Fruehan in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Wisconsin.

[2] Uelsmann, *Jahresbericht*, **1860**, 92.

believe that the solution which he had saturated with hydrogen selenide contained a seleno-tungstate and efforts were directed to crystallize a seleno-tungstate from a concentrated solution of ammonium tungstate which had been saturated with hydrogen selenide.

Preparation of Materials

Elementary Selenium.—A rapid stream of sulfur dioxide was passed into a hot hydrochloric acid solution of selenium dioxide. The selenium was filtered, washed with hot water, then with alcohol and finally with ether. It was dried at 105°.

Hydrogen Selenide.—The method of Moser and Doctor[3] was used to prepare the hydrogen selenide.

Tungstic Oxide.—Tungstic oxide, WO_3, was prepared from well-crystallized sodium tungstate. Sodium tungstate was treated with hydrochloric acid and evaporated to dryness. The sodium chloride was dissolved out of the dried mass with hot water and the tungstic oxide was filtered, washed and dried. An analysis of the sodium tungstate showed good agreement with the formula $Na_2WO_4 \cdot 2H_2O$.

Preparation of Seleno-tungstates

Procedure

A solution of ammonium tungstate was prepared by adding an excess of tungstic oxide to ammonium hydroxide of specific gravity 0.90 and filtering off the excess of the oxide. The ammonium tungstate solution was placed in a reaction chamber which consisted of a 250cc. wash bottle with an enlarged delivery tube to prevent stopping of the tube with the crystalline product. Nitrogen was used to sweep the air out of the system. Hydrogen selenide was then passed through the ammonium tungstate solution. During the course of the reaction heat was liberated, the solution changed to a dark brown color and crystals deposited on the sides of the container. Cooling of the reaction chamber caused more crystals to deposit from solution. During some of the early experiments it was noted that sometimes dark green crystals would be formed and at other times red ones would be obtained.

The green crystals were found to be ammonium seleno-tungstate $(NH_4)_2WSe_4$, as will be shown later, and the red ones ammonium diseleno-tungstate $(NH_4)_2WSe_2O_2$. When the ammonium tungstate solution was saturated with hydrogen selenide, the green crystals were obtained, and the red crystals deposited from the solution when it was incompletely saturated with hydrogen selenide.

From the knowledge of the ease of oxidation of other seleno compounds it was anticipated that the preparation, filtration and washing of the crystals would necessitate the process being carried out in the absence of oxygen. Both crystalline compounds were treated in the same manner after removal from the chamber.

The crystals, together with enough of the mother liquor to cover them, were transferred to the filter as rapidly as possible to avoid oxidation. The small amount of oxidation which occurred during the transfer was confined to the mother liquor. The crystals were washed first with alcohol, then with ether to displace the alcohol and finally with carbon disulfide to dissolve traces of selenium which might cling to the crystals from the mother liquor. The carbon disulfide was purified by shaking it with phosphorus pentoxide and mercury and then distilling it. The crystals were finally dried for several hours in a current of hydrogen. Oxygen was removed from the hydrogen by passing the gas over hot copper gauze and moisture was removed by passing the gas through sulfuric acid and phosphorus pentoxide.

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[3] Moser and Doctor, *Z. anorg. Chem.*, **118**, 284–292 (1921).

Methods of Analysis

Determination of Ammonia.—Ammonia was determined by adding an excess of sodium hydroxide and distilling the liberated ammonia. Tenth normal acid was used to collect the ammonia and the excess acid was titrated with tenth normal alkali, using methyl orange as an indicator.

Determination of Tungsten.—Tungsten was determined by igniting the sample in a porcelain crucible over a Bunsen burner. The tungstic oxide, WO_3, which remained after the ignition was weighed.

Determination of Hydrogen.—Although the analysis of the red crystals showed good agreement with the formula $(NH_4)_2WSe_2O_2$, it was thought advisable to determine the hydrogen. Such a determination would necessarily reveal the presence of water. Combustion of the compound was carried out in the ordinary manner with the exception that a plug of potassium chromate was placed in the combustion tube to retain selenium dioxide.[4] The sample in the boat was also covered with potassium chromate.

Determination of Selenium.—The determination of selenium required an oxidation of the compounds, a separation of the tungsten from the selenium and a precipitation of selenium as the element. Oxidation was carried out in a Parr sulfur bomb. The charge was made up in the following manner. Approximately 14.0 g. of sodium peroxide was mixed with 0.60 g. of starch and the mixture divided into two equal parts. The sample was mixed in the bomb with one of these parts and the second part placed on top of the mixture containing the sample. The fuse wire was arranged so that it was suspended in the upper mixture. After firing the charge, the material in the bomb was dissolved out with water and the solution boiled for a few minutes to decompose the hydrogen peroxide. The solution was then cooled and strongly acidified with hydrochloric acid. Tungstic acid was precipitated in the acid solution. Precipitation and coagulation were completed by adding a few cubic centimeters of a hydrochloric acid solution of cinchonine. The precipitate was filtered on a Gooch crucible and washed with a cinchonine solution. Repeated tests for selenium in the precipitate containing the tungsten showed that a good separation of tungsten from selenium was obtained with a single precipitation.

To one volume of the filtrate containing the selenium in the form of selenic acid were added one volume of hydrochloric acid (sp. gr. 1.20) and one volume of the same acid which had been saturated with sulfur dioxide. The solution was allowed to stand until most of the selenium had settled to the bottom of the beaker. The supernatant liquid was poured through a Gooch crucible and the sodium chloride which had precipitated with the selenium from the strong hydrochloric acid solution was dissolved with water. Before transferring the selenium to the Gooch crucible it was washed with strong hydrochloric acid and then changed to

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[4] Julien, This Journal, **47**, 1799 (1925).

the black variety by treatment with hot water. The selenium was washed first with hot water, then with alcohol and finally with ether. It was dried at 105° and weighed.

Results

The results of the analysis are given in the following tables.

TABLE I

AMMONIUM SELENO-TUNGSTATE, $(NH_4)_2WSe_4$

	Found, %			Calcd., %
	1	2	3	$(NH_4)_2WSe_4$
W	34.22	34.04	34.38	34.27
NH_3	6.34	6.44	6.50	6.33
Se	59.45	58.85	58.90	59.01

TABLE II

AMMONIUM DISELENO-TUNGSTATE, $(NH_4)_2WSe_2O_2$

	Found, %			Calcd., %
	1	2	3	$(NH_4)_2WSe_2O_2$
W	44.92	44.91	44.73	44.83
NH_3	8.40	8.38	8.45	8.30
Se	38.30	38.45	38.60	38.50
H_2	1.97	1.99	...	1.96

The experimental values are seen to be in close agreement with the calculated ones. The results for the hydrogen show that the compound contains no water of crystallization.

Properties of Seleno-tungstates

Crystals of ammonium seleno-tungstate and ammonium diseleno-tungstate which have been carefully washed and dried do not show any discoloration when kept in a calcium chloride desiccator for several months. However, a slight odor which resembles hydrogen selenide can be detected.

Both the seleno-tungstate and the diseleno-tungstate are readily soluble in water, somewhat soluble in alcohol, but insoluble in ether, benzene and carbon disulfide. The seleno-tungstate yields a red aqueous solution which is slowly decomposed in the air, giving a brown precipitate. The precipitate is probably a mixture of selenium and tungsten triselenide, WSe_3. The diseleno-tungstate gives an aqueous solution which is similar in color to a solution of potassium dichromate but the color of concentrated solutions is also red. Aqueous solutions of the diseleno-tungstate are slowly decomposed in the air and a precipitate of red selenium is formed.

Green crystals of ammonium seleno-tungstate are reddish-brown in a finely pulverized state. In order to minimize oxidation, the crystals were pulverized under benzene.

Through the kindness of Professor A. N. Winchell of the Department of Geology of the University of Wisconsin we are publishing the following optical study which he has made of these new compounds.

Crystals of ammonium seleno-tungstate are yellowish-green in color with bright metallic luster; they gradually tarnish to a dark purple. The streak is reddish-brown which alters to black in a few days' time. The crystals are not entirely opaque under the microscope, although they are very dark and are opaque except with maximum illumination, high power and very thin flakes, which transmit a deep red color. The crystals seem to be rectangular parallelopipeds; they are not isotropic and are, therefore, not isometric; a thin flake probably parallel with a cleavage seems to be normal to a bisectrix, but the mineral is so dark-colored that greater precision is not possible. If these properties are correctly determined, the crystals are biaxial and orthorhombic and are bounded by 001, 010 and 100. They are probably isomorphous with the analogous sulfur compound $(NH_4)_2WS_4$.

The indices of refraction seem to be higher than 1.74.

Crystals of ammonium diseleno-tungstate have a brownish-red color and an adamantine luster; they are complex with numerous small faces, but have a short prismatic habit. Under the microscope a fragment nearly normal to an optic axis shows very little curvature of the isogyre; consequently the optic angle (2V) is nearly 90°; the optic sign is positive. The birefringence is extreme and the dispersion is very strong; in both of these characters the mineral resembles titanite, though quantitative measures have not been made. One optic axis is nearly normal to a cleavage, which may be taken for a basal cleavage, since one such fragment shows four very low pyramid faces, nearly symmetrical; in this case the optic axis is out of center about one-third the radius of the field and roughly in the 100 plane. The angle between the prism faces (110 to $1\bar{1}0$) measured in this fragment and therefore presumably in the 001 plane is 109°. The dispersion seems to be unsymmetrical, and extinction in white light is incomplete in some cases because the dispersion is so strong.

In thin plates, probably about .03 mm. in thickness, the pleochroic colors are as follows: X = light (yellowish) green; Y = greenish-yellow; Z = brownish-yellow. All the indices of refraction are above 1.74.

Assuming a thickness of .03 mm. in one plate, the interference colors indicate that $N_m - N_p = 0.045$.

All these properties make it probable that these crystals are triclinic and isomorphous with crystals of $(NH_4)_2WS_2O_2$.

Summary

Ammonium seleno-tungstate, $(NH_4)_2WSe_4$, and ammonium diseleno-tungstate, $(NH_4)_2WSe_2O_2$, have been prepared and analyzed. Some of their properties, including the crystal form, have been studied.

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