It would be surmised that the comparison method, in giving such good agreement for the N=N bond in the azobenzenes and azoparaffins, has effectively reduced the resonance and other energy differences to a minimum so that bond energies in a series of related compounds may be quantitatively evaluated by this method. However, the lower N=N bond energy terms obtained on comparison of the azobenzenes with hydrazobenzene in the standard state (for *trans*-azobenzene N=N is 59.0 kcal., for a N–H of 93.4 kcal., and 48.3 kcal., for a N–H of 88.0 kcal.; for *cis*-azobenzene N=N is 48.9 kcal., for a N–H of 93.4 kcal., and 38.2 kcal., for a N–H of 88.0 kcal.,) were not to be expected.

Calculation of the N=N bond energy term in *p*-aminoazobenzene from the combustion data of Lemoult,[31] making use of the heats of combustion of *p*-phenylenediamine[32] and of aniline, yields 104 kcal., for a N–H bond energy term of 93.4 kcal., and 82.7 kcal., for an assumed N–H bond energy term of 88.0 kcal., in agreement with that in *trans*-azobenzene calculated here by comparison with two moles of aniline.

[31] M. P. Lemoult, *Ann. chim. phys.*, [8] **14**, 184, 289 (1908).

[32] G. Kibler and H. Hunt, *J. Phys. Colloid Chem.*, **53**, 955 (1949).

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Sodium and Potassium Tungsten Bronzes[1,1a]

BY E. O. BRIMM, J. C. BRANTLEY, J. H. LORENZ AND M. H. JELLINEK

A study of the sodium tungsten bronzes, potassium tungsten bronzes and sodium–potassium tungsten bronzes has been made. Methods are presented for preparing a series of sodium–potassium tungsten bronzes of violet color and tetragonal structure. A new sodium–potassium tungsten bronze has also been prepared. It is a dark blue, needle-like crystal; the structure appears to be hexagonal. The solubility of the sodium tungsten bronzes, $NaWO_3$ to $Na_{0.8}WO_3$, in sodium tungstate has been demonstrated. New electrical properties of the tungsten bronzes as electrodes in aqueous solutions are described. They are, in general, excellent conductors of direct current when used as cathodes. As anodes, the blue sodium tungsten bronzes conduct in all electrolytes. All other tungsten bronzes conduct as anodes only in alkaline reducing electrolytes. X-Ray studies and chemical analyses of the tungsten bronzes have been used to study their structure and composition. A new value of 3.8622 Å. is reported for the lattice constant of cubic $NaWO_3$. The tetragonal potassium tungsten bronzes and sodium–potassium tungsten bronzes have lattice constants of about $a = 12.28$ Å. and $c = 3.82$ Å., there being variations from these values for varying compositions. Sodium tungsten bronze has catalytic activity in the decomposition of formic acid but not in the dehydrogenation of *n*-heptane.

Sodium tungsten bronzes were first reported by Wöhler,[2] potassium tungsten bronzes by Laurent.[3] The preparation and properties of the sodium tungsten bronzes have been studied by Hägg,[4] Straumanis[5,6] and Magnéli.[7] The properties of the potassium tungsten bronzes are not well known although several methods for their preparation have been described.[8,9,10] Recently Magnéli[11] has reported the crystal structure of tetragonal potassium tungsten bronze.

In addition to tungsten bronzes containing only sodium or potassium, a mixed sodium–potassium tungsten bronze has been described.[8,12] This bronze is reported to consist of purple-red needles, but no other properties are given. It was prepared by hydrogen or tin reduction of a mixture of sodium and potassium paratungstates.

The work of Straumanis[5,6] and Magnéli[7,11] was published soon after an investigation into the properties of the alkali metal tungsten bronzes had been started in this Laboratory. We report here on certain extensions of their work as well as some new data on the properties of the sodium and potassium tungsten bronzes and the mixed sodium–potassium tungsten bronzes.

Materials.—All of the materials used in the preparation of the tungsten bronzes were of reagent grade. Sodium tungstate dihydrate was dehydrated by heating at 120° for 24 hours. Potassium tungstate was prepared from tungsten (VI) oxide and potassium carbonate by fusing the solids, extracting the tungstate with water and recrystallizing the potassium tungstate. It was then dried at 120° for 24 hours.

Analytical Procedures.—The tungsten bronzes were analyzed by standard procedures. A weighed sample was digested with ammonium sulfate and sulfuric acid. Tungsten was precipitated with cinchonine and determined as tungsten(VI) oxide.[13] No correction was made for silica. The alkali metal content of the filtrates was determined by precipitating the sodium as sodium uranyl zinc acetate and the potassium as potassium perchlorate.[14] The error in these determinations was such that there was an uncertainty of ±0.02 in the value of x in Na_xWO_3.

Sodium Tungsten Bronzes

Preparation of the Sodium Tungsten Bronzes.—Although numerous methods have been proposed for the preparation of sodium tungsten bronzes,[2,10,15] the method of Straumanis[5] was found to produce a wider variety of tungsten bronzes

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[1] Na_xWO_3 and K_xWO_3 where x varies from 0.15 to 1.0 for the sodium tungsten bronzes and 0.40–0.55 for the potassium bronzes. In addition, $Na_xK_yWO_3$ is known in which the sum of x and y is between 0.20 and 0.55. (a) The material in this paper was originally submitted September 22, 1950.

[2] F. Wöhler, *Pogg. Ann.*, **2**, 350 (1824).

[3] A. Laurent, *Ann. chim. phys.*, **67**, 215 (1838).

[4] G. Hägg, *Z. physik. Chem.*, **B29**, 192 (1935); *Nature*, **135**, 874 (1935).

[5] M. E. Straumanis, THIS JOURNAL, **71**, 679 (1949).

[6] M. E. Straumanis and A. Dravnieks, *ibid.*, **71**, 683 (1949).

[7] A. Magnéli, *Arkiv Kemi*, **1**, 269 (1949).

[8] G. v. Knorre, *J. prakt. Chem.*, **27**, 49 (1883).

[9] E. Zettnow, *Pogg. Ann.*, **130**, 240 (1867).

[10] O. Brunner, Dissertation, Zurich, 1903.

[11] A. Magnéli, *Arkiv Kemi*, **1**, 213 (1949).

[12] W. Feit, *Ber.*, **21**, 134 (1888).

[13] I. M. Kolthoff and E. B. Sandell, "Textbook of Quantitative Inorganic Analysis," The Macmillan Company, New York, N. Y., 1946, p. 728–729.

[14] *Ibid.*, p. 414–418.

[15] J. Phillip, *Ber.*, **15**, 506 (1882); V. Spitzin, *Z. anorg. allgem. Chem.*, **148**, 69 (1925); D. van Duyn, *Rec. trav. chim.*, **61**, 669 (1942); L. Kahlenberg and H. H. Kahlenberg, *Trans. Am. Electrochem. Soc.*, **46**, 188 (1924).

and more reproducible results than could be obtained with the other preparative procedures. This method is based on the reaction

$$3x\text{Na}_2\text{WO}_4 + (6 - 4x)\text{WO}_3 + x\text{W} \rightleftarrows 6\text{Na}_x\text{WO}_3 \quad (1)$$

which takes place at 800–1000° in an inert atmosphere.

However, reaction (1) represents only the stoichiometry of the reaction and not necessarily the actual ratios of reactants. The ratios required are determined by other reactions which can occur in the melt (see following section). Only for the lowest values of x does the equation give the proportions of reactants which are required. Thus, when sodium tungstate, tungsten(VI) oxide and tungsten were used in a mole ratio of 3:26:1 (calculated $x = 0.2$), the resulting bronze had an x value of 0.20. Variations in the ratios of reactants from 3:26:1 to 3:2:1, the stoichiometric ratio for $x = 1$, produced bronzes which varied in x from 0.2 to 0.6, representing a range in colors from dark blue to orange. To prepare the orange to yellow bronzes in which x was 0.6 to 0.9 it was necessary to use an excess of sodium tungstate over that required by reaction (1) for $x = 1$, *i.e.* from about 4:2:1 to 9:2:1 mole ratios of reactants. Bronzes with still higher values of x could be prepared by fusing a yellow sodium tungsten bronze with about four times its weight of sodium tungstate at temperatures over 850°. The products of this fusion included metallic tungsten which remained as an impurity in the bronze after the usual purification steps were taken. No method was found to remove this free tungsten without destroying the bronze.

The bronze crystals were recovered from the reaction mass by leaching the solid in boiling water, sodium hydroxide solution and concentrated hydrofluoric acid in the order named. Contrary to previous reports[2,16] none of the bronzes was attacked by hydrofluoric acid at room temperature.

Properties of the Sodium Tungsten Bronzes.

Solubility in Sodium Tungstate.—Although Straumanis[5] already had found that an excess of sodium tungstate in the reaction mixture promoted the growth of yellow tungsten bronze crystals, he reported the bronzes to be insoluble in sodium tungstate even at temperatures over 1000°. However, three observations made in this Laboratory in determining the optimum conditions for the preparation of sodium tungsten bronzes suggested that the bronzes were soluble in sodium tungstate. (1) When yellow sodium tungsten bronzes were prepared from reaction mixtures containing excess sodium tungstate, well-defined cubes, visible to the naked eye, were obtained only when the reaction temperature was greater than 900°. (2) The size of the crystals was a function of the time taken to cool the melt from 1000 to 700°. If the temperature was lowered at a uniform rate for 18 hours, the crystals of bronze were single cubes up to 5 mm. on an edge. Cooling periods of 2–4 hours produced very fine powders of the bronzes. (3) The sizes of the bronze crystals decreased with decreasing ratios of sodium tungstate to tungsten(VI) oxide in the reaction melt if the same temperatures and cooling times were employed.

Further investigation of the Na_2WO_4–Na_xWO_3 system produced more evidence for the solubility of sodium tungsten bronze in sodium tungstate. (1) When large crystals of a yellow bronze were heated with anhydrous sodium tungstate at 800° in argon for 16 hours, the sodium tungstate melted, but the crystals were unchanged and lay in their original positions after cooling. At a temperature of 900° under the same conditions, the bronze was found dispersed as smaller crystals throughout the mass after it was rapidly cooled. (2) It was found that sodium tungsten bronze could be recrystallized from a sodium tungstate melt with an increase in the size of the crystals. A quantity of light orange tungsten bronze powder was heated *in vacuo* at 1000° for 5 hours with three times its weight of sodium tungstate. The melt was cooled to 700° at a uniform rate over a period of 11 hours. The resulting yellow crystals were imperfect cubes about 5 mm. on an edge. When the same orange tungsten bronze was heated to 1000° for 2 hours *in vacuo* and cooled in the same way, there was no change in the crystal size nor did X-ray patterns show any change in the crystal structure.

To determine whether the red and blue bronzes of high tungsten(VI) oxide content exhibited similar properties, a quantity of each of these bronzes was heated with sodium tungstate *in vacuo* at 1000° for one-half hour and cooled slowly. After removing the excess sodium tungstate, only yellow bronze crystals were found; the red and blue bronzes had reacted with sodium tungstate to produce a yellow bronze of much lower tungsten(VI) oxide content.

X-Ray patterns of the bronzes recovered from the tungstate melts showed that at temperatures over 850° and in the presence of large excesses of sodium tungstate the tungsten(VI) oxide content was reduced markedly (see following section). The value of x was always in the range 0.8 to 1.0. Metallic tungsten, present as an impurity, was also identified from these X-ray patterns. At temperatures below 850° there was no reaction with the tungstate and no evidence of solution, nor was there any change in the bronze when it was heated to temperatures over 850° with only enough sodium tungstate to react with the excess tungsten(VI) oxide according to reactions (2) and (4) below.

In view of these results it is concluded that tungsten bronzes are soluble in molten sodium tungstate, but the process of solution may be accompanied by reaction with the solvent.

These observations might be explained by three reactions

$$\text{Na}_x\text{WO}_3 \rightleftarrows x\text{NaWO}_3 + (1 - x)\text{WO}_3 \quad (2)$$

$$6\text{NaWO}_3 \rightleftarrows 3\text{Na}_2\text{WO}_4 + 2\text{WO}_3 + \text{W} \quad (3)$$

$$\text{Na}_2\text{WO}_4 + \text{WO}_3 \rightleftarrows \text{Na}_2\text{W}_2\text{O}_7 \quad (4)$$

According to these equations, when excess sodium tungstate is present in the melt with the bronzes, reactions (2) and (3) can be displaced to the right by the removal of tungsten(VI) oxide to form the ditungstate by reaction (4). This results in a lower tungsten(VI) oxide content of the bronze by reaction (2) and in the formation of metallic tungsten by reaction (3). The formation of tungsten by a combination of reactions (3) and (4) has been reported by Brunner.[10] These considerations also apply to the excess sodium tungstate required in the preparation of the tungsten bronzes of high x values. The excess tungstate apparently acts as a solvent for the reactants and as a reactant in determining the position of the equilibrium in reaction (2).

The Lattice Constant of Cubic Sodium Tungsten Bronzes. The crystal structures of the sodium tungsten bronzes have been determined.[4,5,7] Two crystal forms have been reported. When the value of x in Na_xWO_3 is 1.0 to about 0.3, the crystals are cubic of the perovskite type. The bronzes become tetragonal when the value of x drops below 0.3. However, there may be an overlap on these limits, the structure being somewhat dependent upon the method of preparation.[5] In addition, there is a variation in the lattice constant of the crystals corresponding to variations in the sodium content; the lattice constant increases with increasing values of x. The highest value reported[5] for a has been 3.8598 Å., and it was assumed that this material was essentially NaWO_3.

To check this value the lattice constants were determined for the bronzes prepared by recrystallization from sodium tungstate melts at 950–1000°. The precision X-ray patterns were made with a symmetrical back-reflection focusing camera. Cohen's method[17] of analytical extrapolation was used to calculate the a value. The camera and calculations were checked on quartz.[18] The bronzes used in this study contained metallic tungsten which could not be removed. However, since there is no interference between the X-ray powder patterns of tungsten metal and the sodium tungsten bronze, the precise determination of the lattice constant was possible. The lattice constants of some pure bronzes were also determined.

Four samples of sodium tungsten bronzes were found to have a values larger than the highest reported by Straumanis.[5] The a values were 3.8622, 3.8620, 3.8620 and 3.8613 Å. It is probable that the bronzes of $a = 3.8622$ and 3.8620 Å. were very nearly NaWO_3. The presence of the tungsten metal prevented the chemical determination of their composition. However, extrapolation of the straight line obtained from the plot of lattice constant *versus* composition of bronzes free of tungsten metal indicates that an a value of 3.8622 Å. would be reasonable for pure NaWO_3. The slope of this line is the same as that reported by Straumanis.[5]

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(16) C. Scheibler, *J. prakt. Chem.*, **83**, 321 (1861).

(17) M. U. Cohen, *Rev. Sci. Instruments*, **6**, 68 (1935); **7**, 155 (1936).

(18) A. J. Bradley and A. H. Jay, *Proc. Phys. Soc.* (*London*), **45**, 507 (1933); A. H. Jay, *Proc. Roy. Soc.* (*London*), **145A**, 237 (1933).

The Temperature Coefficient of Resistance.—The sodium tungsten bronzes are electrical conductors, but the type of conductance has never been definitely established. Both a negative[4] and a positive[6] temperature coefficient of resistance have been reported. We have found the temperature coefficient of resistance to be positive.

A single crystal (3.68 mm. × 3.58 mm. × 3.78 mm.) of a yellow sodium tungsten bronze was mounted between platinum contacts under pressure. The specific resistivity was found to be 3.9×10^{-3} ohm-cm. at 26° in a neon atmosphere. This compares to Straumanis' value of 2.9×10^{-3} ohm-cm. at 20° in vacuum or air. The specific resistivity of this same crystal was 3.3×10^{-3} ohm-cm. at −195° and 4.5×10^{-2} ohm-cm. at 100°, indicating a positive temperature coefficient of resistance.

The Sodium Tungsten Bronzes as Electrodes.—The electrical conductivity of the sodium tungsten bronzes and their high resistance to attack by acid and salt solutions suggested their possible use as electrodes. Tungsten bronze electrodes were prepared in two ways. A yellow tungsten bronze was crystallized in a porcelain boat, the crystals forming in a mass adhering to the bottom of the boat. Excess sodium tungstate was removed by leaching with water and sodium hydroxide solution, and the sides of the boat were cut away leaving a porcelain-backed plate of bronze which was 70 mm. × 10 mm. × 5 mm.

Electrodes of other bronzes were prepared by pelletization. Purified orange and blue tungsten bronze powders were moistened with water and compressed into cylindrical pellets, 20 mm. in diameter by 10 mm. in thickness. After sintering at 700° *in vacuo* the pellets were reasonably hard and compact and could be used as electrodes.

A simple cell was used for the tests of these electrodes in various electrolytes. The other electrode in the cell was platinum, and the d.c. circuit included a reversal switch so that the polarity of the electrodes could be changed rapidly.

After an initial momentary surge of current, the crystalline, yellow bronze electrode did not conduct as an anode in dilute sulfuric acid, dilute sodium chloride solution, or dilute potassium permanganate solution. The color of the electrode seemed to become brighter yellow as the current ceased flowing. In reducing electrolytes, such as hydroquinone in dilute sulfuric acid, or in alkaline electrolytes the bronze conducted as an anode. However, in alkaline solutions the electrode was rapidly dissolved. This is in contrast to the inertness of the bronzes to concentrated alkaline solutions when no potential is applied. In the purification procedure described above, concentrated sodium hydroxide solution was used to remove unreacted tungsten(VI) oxide. Even after several hours only a slight dulling of the surface of the bronze was observed.

As a cathode the yellow bronze electrode was an excellent conductor in all these electrolytes except the potassium permanganate solution, in which the conductivity was greatly reduced. If the electrode had been previously polarized at the anode, it developed a deep red-blue color when used as a cathode. This color did not develop if the electrode had been cleaned in sodium hydroxide solution before being used as a cathode. In alkaline electrolytes no color change took place on the cathode at any time, and the electrode was rapidly dissolved.

The color change of the bronze cathode was readily reversible on changing the polarity of the electrodes. It was possible to maintain a transition color on the bronze if the current was interrupted before the color change was complete. This series of colors was significant in that it followed the same order as that observed in reducing tungsten(VI) oxide, *i.e.*, yellow through green to blue. These colors were due to thin surface films which could be dissolved by dilute sodium hydroxide solutions leaving a fresh surface of the bronze.

Thus, it appears that the non-conducting character of the bronze as an anode and the colors of the conducting cathodes are due to the formation of surface films of tungsten oxides in varying oxidation states. The film of yellow tungsten(VI) oxide on the anode causes it to become non-conducting. If this layer is present when the bronze is used as a cathode, the film is reduced to conducting lower oxides of tungsten.

A cell in which both electrodes were yellow tungsten bronze plates did not conduct direct current although a reversal of the polarity resulted in a momentary flow of current. In such a cell the anode was bright yellow and the cathode red-blue. The colors were reversed on reversing the polarity. In a 60-cycle alternating current circuit a cell with a bronze electrode and a platinum electrode showed no rectifying action as observed on a cathode ray oscilloscope.

The sintered, orange, tungsten bronze pellet was such a poor conductor that no current flow could be measured on the apparatus used. The specific resistivity of a pellet of this material was found to be 3.76×10^{6} ohm-cm. compared to 3.9×10^{-3} ohm-cm. for a bronze crystal.

On the other hand, the pellet of sintered blue bronze was an excellent conductor. Although the specific resistivity of this pellet was not determined, Straumanis[6] reports the blue bronzes to be much better conductors than the yellow bronzes. The blue bronze pellet conducted both as an anode or cathode in the following electrolytes: dilute sodium chloride solution, dilute sulfuric acid solution, dilute sodium hydroxide solution and a dilute aqueous solution of hydroquinone and sulfuric acid. In sodium hydroxide solution, the pellet was rapidly dissolved both as the anode or cathode. No attack at the electrode was observed in other electrolytes. The excellent conductivity of this pellet was not due to free tungsten. X-Ray powder patterns showed the presence of lower oxides of tungsten but no free metal. No explanation for the lack of polarization at the anode has been found.

Catalytic Properties of Sodium Tungsten Bronze.—In order to determine whether sodium tungsten bronzes possess catalytic activity, their action on the decomposition of formic acid was studied.[19] Schwab and Schwab-Agallidis[20] have shown that the decomposition of formic acid proceeds by either dehydrogenation or dehydration according to the catalyst which is employed.

The catalytic activity of the yellow sodium tungsten bronzes (free of metallic tungsten) was determined in the following manner. A bed of 5 g. of sodium tungsten bronze was placed in a 10-mm. diameter Pyrex tube which was supported vertically in a tube furnace so that it could be held at any desired temperature. Mercury displacement was used to deliver 1.5 cc. per hour of 90% formic acid solution. The liquid vaporized in the heated zone above the bed. The off-gases were passed through a water-cooled condenser and an ice-trap, and the volume of gas was measured by a wet drum meter which had been previously saturated with carbon dioxide. Analysis of the off-gases and the volume of these gases then indicated the extent and type of decomposition. When no catalyst was used in this apparatus, 2% of the formic acid was decomposed at 325°. In the presence of the catalyst at 325° 62% of the formic acid decomposed, primarily by dehydrogenation.

The same apparatus was used to test the activity of the tungsten bronze in the dehydrogenation of *n*-heptane. Analysis of the off-gas and correlation with the amount of *n*-heptane collected were used to calculate the per cent. dehydrogenation. No reaction was observed at 400°, 0.2% dehydrogenation at 500° and 3.6% at 550°. Compared to a catalyst such as chromic oxide, the activity is very low for this reaction.

Potassium and Sodium–Potassium Tungsten Bronzes

Preparation of Potassium Tungsten Bronzes.—Pure potassium tungsten bronzes could only be prepared by exercising great care to exclude sodium from the reaction mixtures. They were prepared by Straumanis'[5] method for the sodium tungsten bronzes. Thus, potassium tungstate, tungsten(VI) oxide and tungsten were mixed in varying ratios in a vitreous silica boat and heated for one hour at 1050° in argon in a vitreous silica tube. The melts were cooled over a two-hour period; increased cooling periods did not affect the crystal size. The cooled masses were purified by washing in water, potassium hydroxide solution and concentrated hydrofluoric acid.

Using this general procedure, variations were made in the molar proportions of potassium tungstate, tungsten(VI) oxide and tungsten over a range of 3:74:1 to 4.5:2:1. These ratios correspond to values of x in equation (1) from 0.078 to 1.0 at a ratio 3:2:1. Therefore, higher ratios corresponded to excess potassium tungstate. Reactant ratios of 3:14:1 to 3:2:1 gave mixtures of blue needles and a blue powder. The blue powder was produced in the smallest

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[19] This test was carried out at the suggestion of Dean H. S. Taylor of Princeton University.

[20] G. M. Schwab and E. Schwab-Agallidis, This Journal, **71**, 1806 (1949).

amounts at a ratio of 1:1:1, a mixture which gave the best needles of bronze.

The blue needles of potassium tungsten bronze could only be separated from the blue powder by hand picking the needles. These needles were always small, usually only a few millimeters in length and less than $^1/_{10}$ mm. square. The products of the various preparations were in the range $K_{0.40}WO_3$ to $K_{0.45}WO_3$. Since these values of x in K_xWO_3 are lower than those reported by Magnéli[11] for bronzes prepared by electrolysis, it is probable that the lower limit of x for tetragonal bronzes is 0.40 rather than 0.475.

The blue powder was never obtained in sufficient quantity to establish its composition. Its X-ray powder pattern showed it was not tetragonal or cubic. The properties of this material and its similarities to the hexagonal sodium-potassium tungsten bronzes described below suggest that it might be a hexagonal potassium bronze of low potassium content.

The need for careful exclusion of any source of sodium in the preparation of the potassium bronzes is shown by experiments in which porcelain boats were used instead of silica. The fusion of 1:1:1 mixtures of reactants was carried out at 1050° *in vacuo*. The products appeared to be pure potassium tungsten bronzes, but the sodium content of the needles varied from 1.2–0.5% in a random manner. Potassium tungsten bronzes which were prepared in silica equipment had sodium contents of less than 0.02%.

The Sodium–Potassium Tungsten Bronzes.—The sodium–potassium tungsten bronzes were studied to determine if a cubic tungsten bronze containing both sodium and potassium could be prepared. It was soon found that the incorporation of any potassium in the structure led to tetragonal bronzes only. A study was then made to find the best conditions for preparing the tetragonal sodium–potassium bronzes and to investigate their properties.

Preparation.—Three methods were used to prepare the sodium–potassium bronzes. (1) Straumanis' procedure was used to prepare most of the bronzes. A mixture of sodium tungstate, potassium tungstate, tungsten(VI) oxide and tungsten was fused for one hour at 1000° in a vacuum or argon atmosphere. Either silica or porcelain boats were used. The melt was cooled to room temperature over a period of two hours. (2) Attempts to prepare bronzes of high sodium content were carried out by fusing a tetragonal potassium tungsten bronze with about three times its weight of sodium tungstate at 950–1000° for one hour in an inert atmosphere. However, the products were always cubic sodium tungsten bronzes. (3) Another method consisted of fusing a mixture of a cubic sodium tungsten bronze and potassium chloride at 900° in a vacuum. This method was unsuccessful as a possible means of replacing some of the sodium in a cubic bronze by potassium and retain the cubic structure. It did prove to be a suitable method for preparing tetragonal sodium–potassium bronzes.

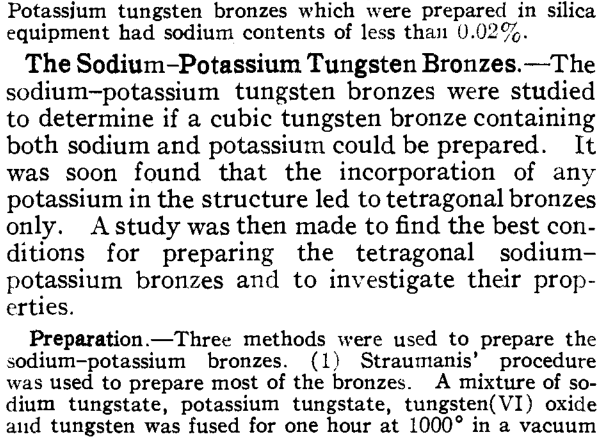

Fig. 1.—Relationship between starting ratios of reactants and the nature of the product. Values of x and corresponding ratios of reactants calculated from equation: $3M_2WO_4 + \left(\frac{6-4x}{x}\right)WO_3 + W \rightleftarrows 6/x\ Na_xWO_3$.

The cooled masses from all these reactions were purified by washing with water, concentrated potassium hydroxide solution, and concentrated hydrofluoric acid. Some of the crystals which were made in reaction melts containing large amounts of sodium tungstate were gold in color before the mass was purified. The true color proved to be red or red-violet.

Results.—Method (1) proved to be the most versatile reaction for preparing a series of sodium-potassium tungsten bronzes. To determine the composition limits of these bronzes variations were made over a wide range of reactant proportions, *i.e.*, $M_2WO_4:WO_3:W$, and over a range of sodium to potassium ratios within any given amount of alkali metal tungstate. Figure 1 represents graphically the relationships between the starting ratios of reactants and the nature of the final product. Although the boundaries are probably not as sharp as shown, they do show the approximate limits of the areas. The x values used as ordinates on the right side of the figure are those which would be realized if the reaction were stoichiometric. As was true of the other bronzes, the products did not contain the same ratios of elements as were present in the preparation mixture.

Ratios of reactants of 3:2:1 to 10:1:1—a region not shown in Fig. 1—gave mixtures of cubic sodium tungsten bronzes and tetragonal sodium–potassium tungsten bronzes. The cubic bronzes were found to be spectroscopically free of potassium. Such mixtures were obtained for all ratios of sodium to potassium when the alkali metal tungstates were in excess. Area A (Fig. 1) represents another range of starting ratios from which such mixtures were prepared.

If the ratio of sodium to potassium were lowered (Area B), only tetragonal sodium–potassium bronzes were prepared. These bronzes ranged in color from blue-violet to red. Bronzes which were red-violet in color resulted from starting ratios containing larger amounts of tungsten(VI) oxide (Area C) and a sodium to potassium ratio over 2:1. The bronzes were well formed needles which had the typical tetragonal structure. Lowering the sodium to potassium ratio (Area D) gave dark blue needles which were like the tetragonal bronzes in appearance and properties but were of different crystal structure. This structure appears to be hexagonal.

Analyses of these various bronzes showed a limited range of compositions. A plot of these compositions is given in Fig. 2. Line AB represents the limits of stability of the tetragonal sodium tungsten bronzes. The corresponding limits for the tetragonal potassium bronzes are given by line CD. When the value of $y/x + y$ was over 0.4, the $x + y$ values of the tetragonal sodium–potassium bronzes were between 0.38 and 0.56, the approximate limits on x for K_xWO_3. For $y/x + y$ values of less than 0.4, $x + y$ for the tetragonal bronzes was within the limits of stability of the

TABLE I

COMPOSITIONS AND PROPERTIES OF SOME SODIUM-POTASSIUM TUNGSTEN BRONZES

Preparation no.	Starting ratios $M_2WO_4:WO_3:W$	Starting ratio Na:K	Analysis of product	Na:K ratio in product	Structure	Size of crystal (relative)	Colo
1	6:6:1	1:1	$Na_{0.24}K_{0.17}WO_3$	1.4:1	Tetragonal	Large	Violet
2	2 KCl:$Na_{0.72}WO_3$	0.55:1	$Na_{0.20}K_{0.36}WO_3$	0.55:1	Tetragonal	Small	Red
3	3:6.5:1	0.5:1	$Na_{0.21}K_{0.28}WO_3$	0.75:1	Tetragonal	Medium	Violet
4	3:6.9:1	0.25:1	$Na_{0.16}K_{0.32}WO_3$	0.50:1	Tetragonal	Small	Blue-violet
5	3:11:1	10:1	....	Mixture of cubic Na_xWO_3 and tetragonal $Na_xK_yWO_3$			
6	3:26:1	9:1	$Na_{0.17}K_{0.04}WO_3$	4.2:1	Tetragonal	Small	Red-violet
7	3:26:1	4:1	$Na_{0.17}K_{0.05}WO_3$	3.4:1	Tetragonal	Small	Red-violet
8	3:26:1	1:1	$Na_{0.08}K_{0.13}WO_3$	0.61:1	Hexagonal (?)	Small	Blue
9	3:26:1	0.72:1	$Na_{0.07}K_{0.13}WO_3$	0.53:1	Hexagonal (?)	Small	Blue

tetragonal sodium bronzes. Tetragonal bronzes which were mechanically separated from mixtures of sodium bronzes and sodium–potassium bronzes fell within a range for $x + y$ of 0.4 to 0.55 and for $y/x + y$ of 0.4 to 0.8.

Points E and F show the compositions of two samples of the dark blue needles. These points represent the only two samples of this new form of tungsten bronze which were obtained in sufficient quantity for accurate analysis. Materials of similar structure and appearance were found in preparing the potassium tungsten bronzes. The properties of this new crystal form would appear to class it as a true tungsten bronze, *i.e.*, its intense color, exceptionally high inertness to acids and bases, and its electrical conductivity. The inertness of this bronze is demonstrated by the fact that it is insoluble in boiling hydrofluoric acid. Its electrical conductivity is similar to that of the blue tetragonal sodium bronzes.

Some typical preparations of the sodium–potassium bronzes are listed in Table I. Here are shown the changes in color and size with variations in composition and the correlation between starting ratios and the final compositions.

Results of X-Ray Studies.—X-Ray powder patterns and single crystal rotation photographs of the potassium tungsten bronzes established the unit cell as tetragonal with a = 12.28 Å. and c = 3.82 Å. The computed and observed X-ray diagrams and zero layer line from the single crystal exposure were in excellent agreement. These data and the measured density of 7.57 g./cc. at 25° indicate that there are probably 10 molecules per unit cell. This is in agreement with data published by Magnéli.[11]

The X-ray powder patterns of the one form of sodium–potassium tungsten bronzes showed it to have the same structure as the potassium bronzes. Although the patterns were not indexed to determine the lattice constants, there was some evidence of contraction of the lattice with increasing amounts of sodium in the structure. The bronzes with low sodium to potassium ratios appeared to have about the same lattice constants as the pure potassium bronzes.

The blue powder which was found in the reaction products in the preparation of pure potassium tungsten bronzes and the dark blue needles of preparations 8 and 9 in Table I had identical X-ray powder patterns. These patterns were different from those of the tetragonal or cubic bronzes. They did not match those of any of the tungsten oxides from $WO_{3.00}$ to $WO_{2.00}$.[21] The data from these films were insufficient for any positive statement of the structure. However, the best correlation between calculated and observed d values was found for a hexagonal structure with a = 7.44 Å. and c = 22.80 Å.

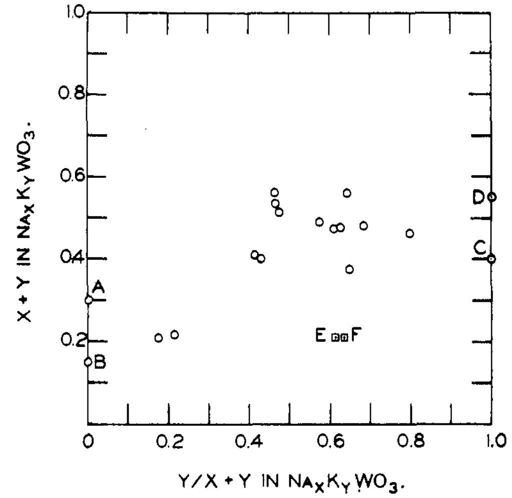

Fig. 2.—Plot of compositions of various sodium–potassium tungsten bronzes showing the relationshp between the composition and the sodium to potassium ratios.

Optical Crystallography.[22]—The potassium tungsten bronze and sodium–potassium bronze needles are reddish-violet, iridescent needles by reflected light, indigo blue when powdered and appear blue by transmitted light. The crystals are anisotropic with parallel extinction and appear to be strongly doubly refractive. The slow component (*i.e.*, high index of refraction) is at right angles to the axis indicating that the crystals are optically negative. Cleavage tends to take place along the long edge of the crystals. Because of the color and opacity of the crystals, a determination of the refractive indices was difficult, but they both appear to be greater than 2.0.

The blue powder which was separated from the potassium tungsten bronzes consisted of three crystalline materials. The principal constituent was blue-violet and optically very similar to the potassium tungsten bronzes. The data indicated

(21) O. Glemser and H. Sauer, *Z. anorg. allgem. Chem.*, **252**, 147 (1943).

(22) The studies were made by Dr. W. D. Forgeng of the Union Carbide and Carbon Research Laboratories, Niagara Falls, New York.

that it was either tetragonal or hexagonal. Thus, this information substantiates the X-ray data on the possible hexagonal structure of this material.

The second crystal type occurred as pale green to colorless needles which showed parallel extinction with a moderate degree of double refraction. The crystals were optically positive, and the refractive indices were about 2.0. The third crystal type was plate-like and weakly doubly refractive. The crystals were pale green to colorless and either orthorhombic or monoclinic. An interference figure indicated a biaxial, negative character with an optical axial angle, 2V, of about 35 degrees. The refractive indices were also about 2.0.

Electrode Properties.—The potassium and sodium–potassium tungsten bronzes show identical properties of conductance when a pelletized mass of either of them is used as an electrode in aqueous electrolytic solutions. They conduct direct current only as cathodes in dilute sulfuric acid or sodium chloride solutions. As cathodes, the bronzes are a dark violet color; as non-conducting anodes, they assume a lighter blue color. Both bronzes will conduct direct current as anodes or cathodes when a reducing solution such as hydroquinone in dilute sulfuric acid is used as the electrolyte. In sodium carbonate or sodium hydroxide solution both bronzes conduct as anodes or cathodes but are rapidly dissolved by the electrolyte.

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[CONTRIBUTION FROM THE NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS]

The Stereochemistry of Complex Inorganic Compounds. XI. The Resolution of Bis-(8-quinolinolo-5-sulfonic Acid) Zinc(II)

BY JENNIE C. I. LIU AND JOHN C. BAILAR, JR.

8-Hydroxyquinoline-5-sulfonic acid, like 8-hydroxyquinoline itself, forms stable coördination compounds with several metal ions. The zinc and cadmium derivatives of 8-hydroxyquinoline-5-sulfonic acid are fluorescent in aqueous solution as well as in the solid state while the nickel and copper derivatives are not. The covalent nature and tetrahedral distribution of the bonds in $Zn(C_9H_6SO_4N)_2$ was proved by the resolution of its strychnine salt in pyridine solution.

Although 8-hydroxyquinoline has been extensively investigated and widely used as an analytical reagent, little attention has been devoted to the structure of its metallic derivatives and especially those of substituted 8-hydroxyquinolines.

Substituents in the ring do not markedly change the coördinating properties of 8-hydroxyquinoline, though they have some influence on the strength of the coördinate bonds between the organic molecule and the metal ion.[1] Polar substituents, such as hydroxy, amino and sulfonic and carboxylic groups in the five position, tend to lower the stability of the complex. It will be evident from the work reported here, however, that this effect is not great. The major influence of such substituents is to render the complexes soluble in water and other polar solvents. The increased solubility makes it possible to study the structure, stereochemistry, and stability of these metal derivatives independently of their crystal form. This article reports such a study, using the zinc derivative of 8-hydroxyquinoline-5-sulfonic acid.

Description of Experiments and Discussion of Results

I. Preparation.—8-Hydroxyquinoline-5-sulfonic acid can be prepared by heating 8-hydroxyquinoline with sulfuric acid at 180°[2] or, better, by mixing 8-hydroxyquinoline with cold fuming sulfuric acid.[3]

One part of 8-hydroxyquinoline was dissolved gradually in seven parts of fuming sulfuric acid with mechanical stirring at a temperature not exceeding 10°. After standing for 24 hours at 8–10°, the mixture was poured over excess crushed ice. A copious yellow crystalline precipitate was formed. It was filtered off, washed with cold water, recrystallized from hot dilute hydrochloric acid (about 2% by weight) and dried.

8-Hydroxyquinoline-5-sulfonic acid does not have a definite melting point but was found to decompose at 305° and turn to black completely at 320–323°. It is slightly soluble in cold alcohol and water but more soluble in boiling alcohol, water and mineral acids. It is insoluble in ether, acetone, chloroform, carbon tetrachloride and benzene.

Some Metallic Derivatives of 8-Hydroxyquinoline-5-sulfonic Acid.—The zinc derivative of 8-hydroxyquinoline-5-sulfonic acid was prepared by a modification of Vaisman's procedure.[4] Zinc sulfate heptahydrate (11 g.) was dissolved in 50 ml. of water and treated with 10 g. of sodium tartrate and 20 ml. of 1 *N* sodium hydroxide. Then 17 g. of 8-hydroxyquinoline-5-sulfonic acid, dissolved in 100 ml. of water containing 8.5 g. of potassium hydroxide, was added slowly. Acetic acid was then added until the solution was slightly acidic. After digesting the mixture at 70–80° for ten minutes, the yellow precipitate was filtered, washed with 1% sodium tartrate solution and dried at 110–120°.

Anal. Calcd. for $Zn(C_9H_6SO_4N)_2$: C, 42.07; H, 2.36; N, 5.45; Zn, 12.73. Found: C, 41.51; H, 2.56; N, 5.36; Zn, 12.47.

The cadmium, nickel and copper derivatives of 8-hydroxyquinoline-5-sulfonic acid were prepared similarly from weakly acidic solutions of the corresponding salts with the organic molecule.

II. Examination of Some Metallic Derivatives of 8-Hydroxyquinoline-5-Sulfonic Acid. (A) Fluorescence.—Yellow fluorescence which was excited by the radiation from an ordinary filtered ultraviolet lamp was observed distinctly in the cases of both the zinc and cadmium complexes of 8-hydroxyquinoline-5-sulfonic acid, while the nickel and copper complexes were found to be not fluorescent at all.

The aqueous solutions of 8-hydroxyquinoline-5-sulfonic acid, cadmium chloride and zinc chloride, examined on a Coleman electronic fluorometer, did not exhibit fluorescence by themselves, but an aqueous mixture of 8-hydroxyquinoline-5-sulfonic acid and cadmium or zinc chloride showed

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