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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[1] J. P. Phillips and F. J. O'Hara, THIS JOURNAL, **73**, 583 (1951).

[2] E. Lippman and F. Fleissner, *Monatsh.*, **10**, 798 (1889).

[3] A. Claus and M. Posselt, *J. prakt. Chem.*, [2] **41**, 33 (1889).

[4] G. A. Vaisman, *Ukrain. Gosudarst. Inst. Eksptl. Farm.* (*Kharkov*) *Konsul'tats. Materialy*, 143 (1940); *C. A.*, **36**, 3117 (1942).

greenish-yellow fluorescence. Hence it may be concluded that this fluorescence must originate in the formation of the complexes of the metal ions with the substituted 8-hydroxyquinoline, as in the case with 8-hydroxyquinoline itself.

(B) **Resolution of Zinc Derivative of 8-Hydroxyquinoline-5-sulfonic Acid.**—A conclusive proof that the zinc derivative of 8-hydroxyquinoline-5-sulfonic acid is covalent and has a tetrahydral configuration lies in the resolution of the complex salt into its optically active isomers. Strychnine was found to be a satisfactory resolving agent. It gave nice crystals from a boiling aqueous solution.

Strychnine (0.01 mole or 3.344 g.) and the complex zinc acid (0.01 mole or 5.14 g.) were dissolved in 300 ml. of hot water. The solution was concentrated to 100 ml. and allowed to cool, whereupon crystals slowly formed. These were dissolved in pyridine and fractionally precipitated by the addition of ether. After each ether addition, the solution was allowed to stand overnight, the resulting light yellow crystals were filtered, washed with ether, and dried. In this manner, five fractions were obtained.

Fraction no.	Observed rotation (α_D) of 0.5% soln. in pyridine	Specific rotation $[\alpha]_D$	Dec. temp., °C.
1	−0.22	−44	258–262
2	− .27	−54	235–240
3	− .32	−64	233–238
4	− .35	−70	222–228
5	− .36	−72	178–185

The rotation of the solutions did not change on standing for two days at room temperature.

X-Ray diffraction patterns of these fractions did not coincide exactly, indicating them to be of a different nature.

The removal of strychnine from the complex salt was accomplished by grinding the dry salt in a mortar with a slight excess of potassium iodide, followed by extraction with enough water to give 0.5% solutions. Such solutions, prepared from the first, fourth and fifth fractions gave specific rotations ($[\alpha]_D$) of −10, −40 and −35°, respectively. The slightly smaller value obtained from the fifth fraction, in comparison with the fourth, is attributed to slight decomposition during recrystallization, as shown by its heterogeneous shade. The value of 40° (fourth fraction) is probably close to the specific rotation of the levo form of the zinc complex.

After a four-hour digestion at 100°, 0.5% solutions of the fourth and fifth fractions of the strychnine complex salt gave a specific rotation of −32° which was doubtless contributed by the strychnine itself. An aqueous solution of the potassium salt, obtained from the fourth fraction, completely lost its optical activity when digested for four hours.

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[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND CHEMICAL ENGINEERING AT THE UNIVERSITY OF WASHINGTON]

Thermodynamic and Structural Characteristics of the Iron(III) Phase Formed by Bromination of Iron(II) Chloride

BY N. W. GREGORY

X-Ray powder patterns indicate that the iron(III) phase ($FeBrCl_2$) formed by bromination of $FeCl_2$ is essentially isostructural with $FeCl_3$ and $FeBr_3$, closely approximating that expected for a solid solution of the two. Thermodynamic properties, determined from equilibrium studies, are also reasonably consistent with those anticipated for such a solid solution. The sublimation of $FeCl_3$ in a bromine atmosphere at relatively low temperatures has been observed.

Introduction

Preparation of iron(III) monobromodichloride by bromination of $FeCl_2$ was reported by Lenormand in 1893.[1] The behavior of ionic substances such as the alkali halides (sodium chloride and sodium bromide form a complete series of solid solutions with essentially random distribution of the halide ions) suggests that metallic compounds of the mixed halide type may not be clearly defined. Whereas the bonds in $FeCl_3$ and $FeBr_3$ undoubtedly possess considerable covalent character, their crystal structures are very similar[2,3] and one would anticipate formation of solid solutions in this system. Both structures are of the layer type, typified by BiI_3, in which the crystal parameters are effectively determined by close packing of the halogens with the metal atoms (ions) in the interstices.

The relationship of thermodynamic and structural properties of the mixed halide phase to those of the simple halides has been investigated to determine whether these properties indicate $FeBrCl_2$ to be a distinct compound or a phase indistinguishable from a solid solution of $FeCl_3$ and $FeBr_3$. The equilibrium between $FeCl_2$ and bromine has been studied in the temperature interval between 30 and 97°, and X-ray powder patterns from the mixed halide phase compared with those of the simple halides.

Experimental Part

(a) **Preparation of Materials.**—Lenormand[1] reported complete conversion of $FeCl_2$ into $FeBrCl_2$ by reaction with bromine in a sealed tube at 100° for a period of five days. This observation was essentially confirmed in the present work. It was found difficult, however, to ensure complete separation of excess bromine from the product without some decomposition. This is to be anticipated as the equilibrium decomposition pressure of bromine over the solid is quite large even at room temperature (35 mm.). It was also observed that larger crystals of $FeCl_2$ were not completely brominated in this period of time.

Two of the samples used in the equilibrium studies were prepared directly in the apparatus. Others were prepared independently by Lenormand's method and transferred to the apparatus or powder tubes in a carbon dioxide dry-box. Excess bromine was removed by subjecting the samples to high vacuum at −20°. The composition of Sample III (treated in this manner) did not correspond to complete bromination; however, it was desired to ensure absence of excess adsorbed bromine before undertaking equilibrium measurements.

Analyses were performed by heating samples slowly in vacuum, eventually at 200°, and collecting the liberated bromine in a trap cooled with liquid air. The quantity of $FeCl_2$ remaining was determined by standard analytical methods and its identity confirmed by X-ray powder patterns. The amount of bromine released was determined by dissolving the condensed material in KI solution and titrating the liberated iodine with standard thiosulfate.

(b) **Determination of Equilibrium Pressures of Bromine.**—Pressures were measured by means of a thin glass membrane manometer. The gage was a modification of the Daniels type[4] in which the membrane was arranged to support a mirror. With a suitable beam of light the null position of the membrane could be established with an uncertainty of less

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(1) M. C. Lenormand, *Compt. rend.*, **116**, 820 (1893).

(2) Nora Wooster, *Z. Krist.*, **83**, 35 (1932).

(3) N. W. Gregory, THIS JOURNAL, **73**, 472 (1951).

(4) F. Daniels, *ibid.*, **50**, 1115 (1928).