

**INORGANIC  
SYNTHESES**

*Volume XII*



*Editor-in-Chief*

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*University of Utah, Salt Lake City, Utah*



# **INORGANIC SYNTHESES**

*Volume XII*

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**INORGANIC SYNTHESSES, VOLUME XII**

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**To WALTER C. SCHUMB**  
**(1892–1967)**

*Dedicated teacher, researcher, and scholar  
whose many contributions to inorganic  
chemistry included distinguished service to*  
**INORGANIC SYNTHESIS.**

## PREFACE

This volume follows the organizational patterns initiated in Volumes X and XI. Syntheses are grouped according to interest area, using this criterion, we have placed in Vol. XII a chapter on Metal Complexes of Molecular Nitrogen and one on Significant Solids. More traditional chapter headings such as Nonmetal Systems and Boron Compounds also fit appropriately under the criterion of interest areas.

Inorganic Syntheses, Inc., is a nonprofit organization dedicated to the selection and presentation of tested procedures for the preparation of compounds of more than routine interest. The Editorial Board seeks the cooperation of the entire scientific community in realizing these goals. The editor for Volume XIII is F. A. Cotton; for Volume XIV, J. K. Ruff; and for Volume XV, Aaron Wold. Directions for submitting preparations are included in the section which follows this one.

The editor of Volume XII is particularly indebted to a number of people who have contributed significantly to this volume. Dr. George Parshall, Prof. A. D. Allen, Dr. Frank Bottomley, and their associates made particularly valuable contributions to Chapter One. Professor John Fackler assisted in the accumulation of syntheses on pentanedionato complexes; Prof. Aaron Wold assisted with the work on solids, and Prof. John Ruff assisted with the section on fluorine chemistry. The assistance of these men is gratefully acknowledged. Finally, every vol-

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ume of INORGANIC SYNTHESSES owes a large debt to the many scientists who willingly contribute their time and materials to the checking operation. We are particularly grateful for such help. It is a real pleasure to thank Janet Scott who has been of great help in the editing and indexing, as well as Dr. J. Richard Weaver and Mrs. Jeanne Gordus who helped willingly at crucial points in the preparation of this volume. The generous assistance of other members of Inorganic Syntheses, Inc., is also gratefully acknowledged.

R. W. Parry

## NOTICE TO CONTRIBUTORS

The INORGANIC SYNTHESSES series is published to provide all users of inorganic substances with detailed and foolproof procedures for the preparation of important and timely compounds. Thus the series is the concern of the entire scientific community. The Editorial Board hopes that all chemists will share in the responsibility of producing INORGANIC SYNTHESSES by offering their advice and assistance both in the formulation and laboratory evaluation of outstanding syntheses. Help of this type will be invaluable in achieving excellence and pertinence to current scientific interests.

There is no rigid definition of what constitutes a suitable synthesis. The major criterion by which syntheses are judged is the potential value to the scientific community. An ideal synthesis is one which presents a new or revised experimental procedure applicable to a variety of related compounds, at least one of which is critically important in current research. However, syntheses of individual compounds that are of interest or importance are also acceptable.

The Editorial Board lists the following criteria of content for submitted manuscripts. Style should conform with that of previous volumes of INORGANIC SYNTHESSES. The *Introduction* should include a concise and critical summary of the available procedures for synthesis of the product in question. It should also include an estimate of the time required for the synthesis,



an indication of the importance and utility of the product, and an admonition if any potential hazards are associated with the procedure. The *Procedure* should present detailed and unambiguous laboratory directions and be written so that it anticipates possible mistakes and misunderstandings on the part of the person who attempts to duplicate the procedure. Any unusual equipment or procedure should be clearly described. Line drawings should be included when they can be helpful. All safety measures should be clearly stated. *Sources of unusual starting materials must be given*, and, if possible, minimal standards of purity of reagents and solvents should be stated. The scale should be reasonable for normal laboratory operation, and any problems involved in scaling the procedure either up or down should be discussed. The criteria for judging the purity of the final product should be clearly delineated. The section on *Properties* should list and discuss those physical and chemical characteristics that are relevant to judging the purity of the product and to permitting its handling and use in an intelligent manner. Under *References*, all pertinent literature citations should be listed in order.

The Editorial Board determines whether submitted syntheses meet the general specifications outlined above. Every synthesis must be satisfactorily reproduced in a different laboratory other than that from which it was submitted.

Each manuscript should be submitted in duplicate to the Secretary of the Editorial Board, Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A. The manuscript should be typewritten in English. Nomenclature should be consistent and should follow the recommendations presented in "The Definitive Rules for Nomenclature of Inorganic Chemistry," *J. Am. Chem. Soc.*, **82**, 5523 (1960). Abbreviations should conform to those used in publications of the American Chemical Society, particularly *Inorganic Chemistry*.

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**INORGANIC  
SYNTHESES**

*Volume XII*

## Chapter One

# METAL COMPLEXES OF MOLECULAR NITROGEN AND RELATED SPECIES

*(Assembled through the cooperation of Dr. George W. Parshall.)*

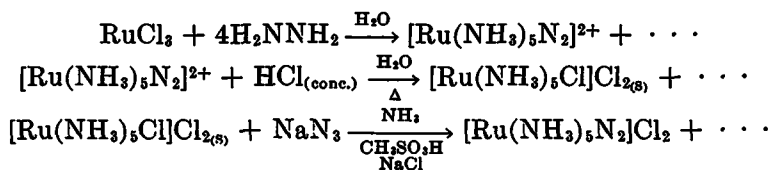
Metal complexes containing coordinated carbon monoxide have been known for years. Some speculation about the existence of related compounds containing the isoelectronic nitrogen molecule appeared in the earlier literature, but all attempts at the synthesis of these nitrogen analogs were unsuccessful until 1965. In December of that year, a highly significant communication by A. D. Allen and C. V. Senoff (see reference 1, synthesis 1) described the first successful synthesis of a family of nitrogen complexes of the form  $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$  (where  $\text{X}^-$  was  $\text{Br}^-$ ,  $\text{I}^-$ ,  $\text{BF}_4^-$ , and  $\text{PF}_6^-$ ). Since the initial report of Allen and Senoff, interest in these compounds has been high, partly because of the apparent relationship between these substances and the nitrogen-fixation process. A number of significant compounds containing coordinated molecular nitrogen or a closely related molecule are described herein.

Synthesis 4 describes a well-characterized substance which will pick up elementary nitrogen under carefully controlled conditions. Procedures described in these pages have all been verified in at least two independent laboratories. In every case, however, checkers reported that *all details* of each synthesis had to be



carried out as indicated. Care is required. ■ **Caution.** *In cases where azides are used, the explosive nature of heavy metal azides should always be kept in mind.*

### 1. PENTAAMMINE(NITROGEN)RUTHENIUM(II) SALTS AND OTHER AMMINES OF RUTHENIUM



Submitted by A. D. ALLEN,\* F. BOTTOMLEY,\* R. O. HARRIS,\*  
V. P. REINSALU,\* AND C. V. SENOFF\*  
Checked by DAVID W. BADGER†

Solutions of pentaammine(nitrogen)ruthenium(II) have been prepared from ruthenium(III) chloride and hydrazine hydrate.<sup>1,2</sup> These solutions have been used to prepare pentaammine-haloruthenium(III) salts:  $[\text{Ru}(\text{NH}_3)_5\text{X}]\text{X}_2$  ( $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).  $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$  has been converted to pure pentaammine-(nitrogen)ruthenium(II) salts— $[\text{Ru}(\text{NH}_3)_5\text{N}_2]\text{X}_2$  ( $\text{X}^- = \text{Cl}^-, \text{Br}^-, \text{I}^-, \text{BF}_4^-, \text{PF}_6^-$ )—via the reaction between azide ion and aquopentaammineruthenium(III).<sup>2</sup> Hexaammineruthenium(III) salts— $[\text{Ru}(\text{NH}_3)_6]\text{X}_3$  ( $\text{X} = \text{I}^-, \text{BF}_4^-$ )—have been prepared by the reaction between pentaamminechlororuthenium(III) chloride and hydrazine monohydrochloride.

Syntheses of the ammine complexes of ruthenium(III) have appeared in the literature,<sup>3</sup> but the methods given here offer advantages in time and yield over the earlier procedures.

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#### 4 Inorganic Syntheses

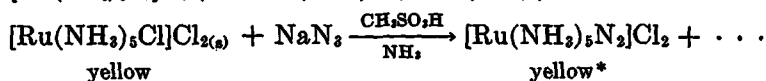
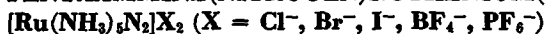
paper). Vigorous gas evolution takes place. The solution is *boiled, with stirring, and becomes yellow, slowly precipitating the yellow product*. When no further precipitation is observed, the mixture is cooled to room temperature, and the crude pentaamminechlororuthenium(III) chloride is collected by filtration, washed once with 6 *M* hydrochloric acid, alcohol, and acetone, and then air-dried. The yield of crude product is 3 g., 46% based on  $\text{RuCl}_3$ .

The product is recrystallized by heating an aqueous slurry (3 g. in 10 ml. of water) to 60°C. and adding concentrated ammonia dropwise until the yellow complex dissolves to give a wine-red solution. The solution is *filtered hot* and then cooled in an ice bath. To the cold solution concentrated hydrochloric acid is added dropwise to reprecipitate the mustard-yellow pentaamminechlororuthenium(III) chloride. The product is collected by filtration, washed once with 6 *M* hydrochloric acid, and then quickly washed with water, alcohol, and acetone. Finally it is dried at 78°C. over  $\text{P}_2\text{O}_5$  *in vacuo*. Yield is 1.1 g., 39%. *Anal.* Calcd. for  $\text{Cl}_3\text{H}_{15}\text{N}_5\text{Ru}$ : H, 5.19; N, 23.98; Cl, 36.35. Found: H, 5.30; N, 24.53; Cl, 34.84.

#### C. PENTAAMMINEIODORUTHENIUM(III) IODIDE, $[\text{Ru}(\text{NH}_3)_5\text{I}]\text{I}_2$ , AND PENTAAMMINEBROMORUTHENIUM(III) BROMIDE, $[\text{Ru}(\text{NH}_3)_5\text{Br}]\text{Br}_2$

These complexes are prepared from the solution prepared in Sec. A by methods similar to those described for pentaamminechlororuthenium(III) chloride in Sec. B, using *hydriodic* or *hydrobromic acid* as a reagent, and 6*M* HI or HBr as a wash liquid. Yields are  $[\text{Ru}(\text{NH}_3)_5\text{I}]\text{I}_2$ , 2.7 g., 49%;  $[\text{Ru}(\text{NH}_3)_5\text{Br}]\text{Br}_2$ , 1.25 g., 31%; based on  $\text{RuCl}_3$ . *Anal.* Calcd. for  $\text{H}_{15}\text{I}_3\text{N}_5\text{Ru}$ : H, 2.67; I, 67.19; N, 12.35. Found: H, 2.95; I, 67.60; N, 11.80. Calcd. for  $\text{Br}_3\text{H}_{15}\text{N}_5\text{Ru}$ : Br, 56.33; H, 3.88; N, 16.44. Found: Br, 56.10; H, 3.50; N, 16.92.

## D. PENTAAMMINE(NITROGEN)RUTHENIUM(II) SALTS,

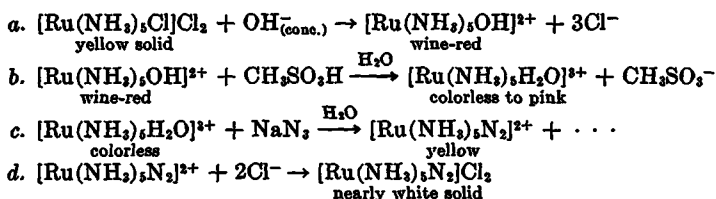
**Procedure**

A slurry of pentaamminechlororuthenium(III) chloride (1.0 g., 3.4 mmoles), in water (25 ml.) is heated to 60°C. Concentrated ammonia is added *dropwise*, and the temperature is kept at 60°C. until all the yellow complex dissolves to give a wine-red solution. This solution is cooled in an ice bath; it is then stirred vigorously while methanesulfonic acid is added *dropwise* to the ice-cold solution until the pH is 2. The solution becomes colorless to pale pink.†

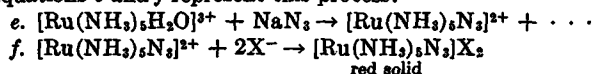
To the solution is added sodium azide, 5 g. (77 mmoles).

■ **Caution.** From the reaction between azide and aquopentaammineruthenium(III), it is possible to precipitate a red solid

\* *Editor's note:* The equations shown below are proposed by the editor to represent the various color changes reported.



■ **Warning.** If the azide group is coordinated in step c without an accompanying oxidation-reduction reaction, the resulting red azide complex is dangerously explosive. Equations e and f represent this process:



† If, on adding methanesulfonic acid to the wine-red solution of  $[\text{Ru}(\text{NH}_3)_5\text{OH}]^{2+}$ , a fluffy, white precipitate is produced, ice-cold water may be added to redissolve it. If a yellow precipitate which is insoluble in water is produced, hydrochloric acid (6 M) should be added, the mixture refluxed for 10 minutes, the precipitated pentaamminechlororuthenium(III) chloride recovered, and the procedure started again.