Inorganic Syntheses
Volume VIII

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This volume of Inorganic Syntheses contains sixty-eight contributions. Two articles of a review nature are included, one on metal derivatives of $\beta$-keto imines ($\beta$-imino ketones) and the other on the chemistry of the noble gases.

As in the earlier volumes, each synthesis has been checked experimentally in a different laboratory than that from which it was submitted. Furthermore, each synthesis has been critically scrutinized by the members of the Editorial and Advisory Boards and, after editing, has been sent to author and checker for approval of the edited manuscript. As in previous volumes, addresses of those submitting and checking syntheses are the addresses in effect at the time the work was done. In addition, a change in address, when applicable, is indicated for the senior author for convenience in correspondence.

The Editorial and Advisory Boards of Inorganic Syntheses encourage contributions both from this country and abroad and are pleased with the increasing number of scientists of other countries who are submitting or checking syntheses. Twenty-five of the sixty-eight contributions in this volume originated in or were checked in laboratories abroad.

In accord with previous practice, the syntheses in this volume are arranged on the basis of the Mendeleev periodic classification, with subdivision into A and B groups. Inasmuch as the placing of syntheses within a given chapter is arbitrary depending upon which element of the compound is chosen for the classification, the practice of listing appropriate syntheses from other chapters at the beginning of each chapter is continued in Volume VIII.
Nomenclature, particularly for compounds containing elements of periodic groups VA and VIA, often presents problems. In some cases, general agreement has not yet been reached among experts in the field. For example, names considered for Cl$_3$P=NP(O)Cl$_2$ during the editing of synthesis 22 were trichlorophosphazophosphorus(V) oxychloride, (trichlorophosphoranylidene) amidophosphoryl dichloride, (trichlorophosphoranylidene) phosphoramidic dichloride, and (dichlorophosphinyl) phosphorimidic trichloride. The compound (PNCI)$_4$ used as a starting material in syntheses 20 and 21 and often referred to simply as "tetrameric phosphonitrile chloride" or "phosphonitrile chloride, cyclic tetramer," may alternatively be named octachlorocyclotetraphosphazatetraene or, more systematically, 1,3,5,7,2,4,6,8-tetrazatetraphosphocine 2,2,4,4,6,6,8,8-octachloride.

Emphasis has been placed on the use of systematic nomenclature consistent with recommendations of the International Union of Pure and Applied Chemistry and/or the Chemical Abstracts Service. However, in some instances, a factor such as a strong preference of the author or common usage has influenced the choice. In several such instances, an alternative name as a synonym has been included at least once within the article. For example, in synthesis 20, three names are given for the eight-membered ring compound N$_4$P$_4$(OC$_2$H$_5$)$_8$: octaethoxycyclotetraphosphazatetraene; tetrameric ethyl phosphonitrilate; and 2,2,4,4,6,6,8,8-octaethoxy-2,2,4,4,6,6,8,8-octahydro-1,3,5,7,-2,4,6,8-tetrazatetraphosphocine (the last being the name preferred by the Chemical Abstracts Service). It is hoped that until agreement is reached on a logical unambiguous system of nomenclature the names used in this volume will be adequate for complete clarity.

It is a pleasure to acknowledge the election of Professor Stanley Kirschner, Department of Chemistry, Wayne State University, Detroit, Michigan, to the new position of Secretary of the Editorial Board. Contributions to future
volumes are invited and should be submitted to Professor Kirschner. Manuscripts should be in accord with the *Notice to Contributors* section, which follows the *Preface* in this volume. Competent checkers are essential to the success of *INORGANIC SYNTHESSES*. Persons who are interested in helping with this important function should communicate with Professor Kirschner.

The editor-in-chief for Volume IX is Professor S. Young Tyree, Jr., Department of Chemistry, University of North Carolina, Chapel Hill, North Carolina, and for Volume X is Dr. Earl L. Muetterties, Central Research Department, Experimental Station, E. I. du Pont de Nemours & Company, Wilmington, Delaware.

Several new members of the Editorial Board have been elected to the Editorial Board since the publication of Volume VII:

Professor L. Malatesta, Universita Di Milano, Milano, Italy
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Professor Richard H. Holm, University of Wisconsin, Madison, Wisconsin
Dr. John K. Ruff, Rohm and Haas Company, Huntsville, Alabama

Professor Malatesta begins his term of service with Volume IX; the other four new members, with Volume X.

This volume is dedicated to the late Professor Francis P. Dwyer, who at the time of his death was a member of the Editorial Board. The Boards acknowledge with respect and appreciation the fine contributions Professor Dwyer made to the work of *INORGANIC SYNTHESSES* and in a broader sense to the field of inorganic chemistry.

The editor-in-chief takes pleasure in expressing his appreciation to his colleagues on the Editorial and Advisory
Boards for their fine help in the preparation of this volume. He is especially grateful to Miss Janet D. Scott for her work on nomenclature and indexing. Appreciation is expressed also to Professor Roy M. Adams, Chairman of the Committee on Inorganic Nomenclature for the Division of Inorganic Chemistry of the American Chemical Society, and to Dr. Kurt L. Loening, Director of Nomenclature for the Chemical Abstracts Service, for advice on several specific questions with respect to nomenclature. The editorial help of Mr. Theodore A. Michelfeld and Dr. John R. Demuth of the University of Nebraska is gratefully acknowledged. The editor wishes also to thank Miss Corrine Newton, Miss Camilla Connell, Miss Connie Svolopoulos, and Miss Georgianne Kozisek for their capable assistance in typing the manuscript.

The editors hope that users of Inorganic Syntheses will call to their attention any errors or omissions. The suggestions and criticisms of readers are helpful and are much appreciated.

Henry F. Holtzclaw, Jr.
NOTICE TO CONTRIBUTORS

The Inorganic Syntheses 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 Syntheses 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 Syntheses. 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 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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To
Francis Patrick Dwyer
(1910–1962)
CHAPTER IA

ALKALI METAL COMPOUNDS

See: Complex carbonates of beryllium, synthesis 2
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1. BIS(4-IMINO-2-PENTANONATO)COPPER(II) AND BIS(3-PHENYLIMINO-1-PHENYL-1-BUTANONATO)-COPPER(II)

Submitted by Arthur W. Struss* and Dean F. Martin†
Checked by Norman E. Griswold‡

This synthesis is an example of chelate exchange, the advantages of which are noted later.1 Attempts to prepare bis(3-phenylimino-1-phenyl-1-butanonato)copper(II) by direct combination of the β-keto imine (β-imino ketone) and ammoniacal copper(II) nitrate have not been successful.2 However, the compound can be obtained from reaction of the β-keto imine and bis(4-imino-2-pentanonoato)copper(II) [bis(4-amino-3-penten-2-onato)copper(II)] prepared by the method of Holtzclaw, Collman, and Alire.3

* University of Illinois, Urbana, Ill.
† Present address: University of South Florida, Tampa, Fla.
‡ University of Nebraska, Lincoln, Neb.
Procedure

A. BIS(4-IMINO-2-PENTANONATO) COPPER(II)

\[2\text{CH}_3\text{COCH}_2\text{C}(\equiv\text{NH})\text{CH}_3 + \text{Cu(NO}_3\text{)}_2\cdot3\text{H}_2\text{O} + 2\text{NH}_4\text{OH} \rightarrow \]
\[[\text{CH}_3\text{COCHC}(\equiv\text{NH})\text{CH}_3]_2\text{Cu} + 2\text{NH}_4\text{NO}_3 + 5\text{H}_2\text{O}\]

To a solution of 11.5 g. (0.116 mol) of acetylacetone imide (4-imino-2-pentanone)* in 100 ml. of 95% ethanol is added 14.5 g. (0.06 mol) of copper(II) nitrate 3-hydrate in 300 ml. of water containing 13.5 ml. of concentrated (15 N) aqueous ammonia. The reaction mixture is shaken vigorously until a gray precipitate forms, and the mixture is allowed to stand at room temperature overnight. After filtration, the crude material (yield, about 14.3 g.; m.p. 190 to 192°, decomp.) may be recrystallized if desired from about 200 ml. of 95% ethanol. In this way, about 12 g. of dark needles results, and additional material (1 g.) may be obtained by heating the filtrate to boiling and adding enough water (about 100 ml.) to initiate crystallization. The total yield of purified material is at least 13 g. (87%), m.p. 190 to 192°, decomp. Anal. Calcd. for C_{15}H_{16}N_2O_2Cu: C, 46.23; H, 6.21; N, 10.78. Found: C, 45.61; H, 6.03; N, 10.87. By checker: C, 46.10; H, 6.41; N, 10.75.

B. BIS(3-PHENYLIMINO-1-PHENYL-1-BUTANONATO)-COPPER(II)

\[[\text{CH}_3\text{CO} \equiv \text{CHC}(\equiv\text{NH})\text{CH}_3]_2\text{Cu} + \]
\[2\text{C}_6\text{H}_5\text{COCH}_2\text{C}(\equiv\text{NC}_6\text{H}_5)\text{CH}_3 \rightarrow \]
\[[\text{C}_6\text{H}_5\text{CO} \equiv \text{CHC}(\equiv\text{NC}_6\text{H}_5)\text{CH}_3]_2\text{Cu} + \]
\[2\text{CH}_3\text{COCH}_2\text{C}(\equiv\text{NH})\text{CH}_3\]

A solution of 2.37 g. (0.01 mol) of 3-phenylimino-1-phenyl-1-butanalone and 1.3 g. (0.005 mol) of bis(4-imino-2-pentanonato)copper(II) in 75 ml. of 95% ethanol is heated at

* Acetylacetone imide is available from the Aldrich Chemical Company, Milwaukee, Wis.
reflux for one hour. During this time, dark green platelets form. The reaction mixture is cooled in an ice-water bath and the green platelets collected by filtration (1.6 to 2.1 g.). Additional material (0.5 to 0.8 g.) is obtained by heating the filtrate to boiling, adding water (about 50 ml.) to initiate crystallization, and allowing the mixture to cool slowly. The crude material is recrystallized from 95% ethanol (in the proportion of 325 ml. of 95% ethanol for 2.4 g. of the crude material). The yield is about 1.7 g. (64%) of green platelets, m.p. 180 to 182°. Anal. Calcd. for \( \text{C}_{32}\text{H}_{22}\text{O}_2\text{N}_2\text{Cu} \): C, 71.69; H, 5.26; N, 5.23. Found: C, 71.58; H, 5.17; N, 5.30. By checker: N, 5.40.

**Properties**

Bis(4-imino-2-pentanonato)copper(II) is obtained as short dark gray, almost black, needles from 95% ethanol. The compound melts with decomposition at 190 to 192°. Prominent bands in the infrared absorption spectrum of the compound have been listed and discussed.³

Bis(3-phenylimino-1-phenyl-1-butanonato)copper(II) crystallizes as green platelets (from 95% ethanol) which melt at 180 to 182°. The compound has been partially resolved into optical enantiomers by means of a chromatographic technique.⁵

**References**

CHAPTER II A

2. COMPLEX CARBONATES OF BERYLLIUM

Submitted by A. K. Sengupta*
Checked by S. von Winbush†

Beryllium hydroxide and the rather complex compounds obtained by the addition of ammonium carbonate, or the carbonates or hydrogen carbonates of the alkali metals, to solutions of beryllium salts are soluble in an excess of these reagents.1 Debray2 reported the isolation of compounds with formulas $3K_2Be(CO_3)_2\cdot Be(OH)_2$ and $3(NH_4)_2Be(CO_3)_2\cdot Be(OH)_2$ from solutions prepared by dissolving beryllium hydroxide in solutions of potassium carbonate and ammonium carbonate, respectively. Atterberg3 considered these compounds to be mixtures, and Humpidge4 later assigned the formula $2(NH_4)_2Be(CO_3)_2\cdot Be(OH)_2$ to the ammonium compound. Recently, Pirtea5 reported the isolation of the complex compound $[Co(NH_3)_6][(H_2O)_2\cdot Be_2(CO_3)_2(OH)_4]\cdot 3H_2O$.

The preparation of hydrated complex carbonatoberyllates of the form $M_6[Be_4O(CO_3)_6]$, where $M$ is either $\frac{1}{2}[Co(NH_3)_6]^{3+}$ or $K^+$, is described in the following procedure. Inasmuch as the potassium compound can be completely dehydrated at ordinary temperatures, the formulation of the carbonatoberyllate anion with a single oxygen atom is preferred to writing the formula with two hydroxyl groups.

* University College of Science, Calcutta, India. Present address: Kalyani University, Kalyani, West Bengal, India.
† The Agricultural and Technical College of North Carolina, Greensboro, N.C.
Procedure

A. HEXAAMMINECOBALT(III) OXOHEXACARBONATOTETRA-
BERYLLATE 10- AND 11-HYDRATES,

\[ [\text{Co(NH}_3\text{)}_6]\text{Be}_4\text{O(CO}_3\text{)}_6\cdot x\text{H}_2\text{O} \]

\( (x = 10 \text{ or } 11) \)

By varying the concentration of the solution of alkali metal hydrogen carbonate or of ammonium carbonate, the salt can be obtained as either a 10- or 11-hydrate and in any of three crystalline modifications best described as being needle-like, tetrahedral, or polyhedral in character.

1. Needle-like modification: \([\text{Co(NH}_3\text{)}_6]\text{Be}_4\text{O(CO}_3\text{)}_6\cdot 11\text{H}_2\text{O}\). A solution composed of 3 g. (0.02 mol) of beryllium sulfate 4-hydrate dissolved in 10 ml. of water is added with constant stirring to a solution of 10 g. (0.1 mol) of ammonium carbonate in 35 ml. of water. When the precipitate that appears when the solutions are mixed has redissolved, the resulting solution is added with constant mechanical stirring to 170 ml. of an aqueous solution which contains 6 g. (0.02 mol) of hexaamminecobalt(III) chloride and 13 g. (0.14 mol) of ammonium carbonate. A voluminous mass of fine, slender, reddish-yellow crystals separates immediately. After a few minutes, the crystals are filtered by suction, are washed successively with water and ethanol, and are air-dried. The yield of \([\text{Co(NH}_3\text{)}_6]\text{Be}_4\text{O(CO}_3\text{)}_6\cdot 11\text{H}_2\text{O}\) is 3.9 g. (98%). Anal. Calcd. for \([\text{Co(NH}_3\text{)}_6]\text{Be}_4\text{O(CO}_3\text{)}_6\cdot 11\text{H}_2\text{O}\): N, 18.03; H, 6.27; C, 7.72; Be, 3.87. Found: N, 17.88; H, 6.18; C, 7.72; Be, 3.78. By checker: N, 18.70; H, 6.21; C, 7.82; Be, 3.83.

2. Polyhedral modification: \([\text{Co(NH}_3\text{)}_6]\text{Be}_4\text{O(CO}_3\text{)}_6\cdot 10\text{H}_2\text{O}\). A solution containing 1 g. (0.006 mol) of beryllium sulfate 4-hydrate dissolved in 65 ml. of water is saturated with potassium hydrogen carbonate and filtered. A solution of 1 g. (0.004 mol) of hexaamminecobalt(III) chloride in 15 ml. of water is added dropwise to the mechanically stirred solution. After approximately...
one-half of the reagent has been added, light orange-colored crystals of hexaamminecobalt(III) oxohexacarbonatotetraberyllate 10-hydrate, \([\text{Co(NH}_3\text{)}_6\text{][Be}_4\text{O(CO}_3\text{)}_6\text{]·10H}_2\text{O}\), begin to separate from the solution. When the addition of the reagent is complete, the solution is allowed to stand for a few minutes; the crystals are then collected by suction filtration, are washed successively with water and ethanol, and are air-dried. The yield is 0.85 g. (65%). *Anal.* Calcd. for \([\text{Co(NH}_3\text{)}_6\text{][Be}_4\text{O(CO}_3\text{)}_6\text{]·10H}_2\text{O}\): N, 18.38; H, 6.17; C, 7.87; Be, 3.94. Found: N, 18.30; H, 6.18; C, 7.79; Be, 3.81. By checker: N, 18.89; H, 6.12; C, 8.58; Be, 3.93.

3. Tetrahedral modification: \([\text{Co(NH}_3\text{)}_6\text{][Be}_4\text{O(CO}_3\text{)}_6\text{]·10H}_2\text{O}\). A solution of any soluble beryllium salt (sulfate, nitrate, or chloride) is prepared in such concentration that approximately 140 ml. of the solution will contain 0.1 g. (0.01 mol) of beryllium. This solution is saturated with potassium hydrogen carbonate (about 38 g. of potassium hydrogen carbonate will be required) and is separated by filtration from the undissolved solid. The solution is stirred mechanically and to it is added, in one installment, 125 ml. of a solution containing 6 g. (0.02 mol) of hexaamminecobalt(III) chloride and 8 g. (0.08 mol) of potassium hydrogen carbonate. Precipitation of tetrahedral crystals of hexaamminecobalt(III) oxohexacarbonatotetraberyllate 10-hydrate, \([\text{Co(NH}_3\text{)}_6\text{][Be}_4\text{O(CO}_3\text{)}_6\text{]·10H}_2\text{O}\), reddish cream in color, is immediate. The solution is allowed to stand for a few minutes, is filtered, washed successively with water and ethanol, and air-dried. The yield is 2 g. (87%). *Anal.* Calcd. for \([\text{Co(NH}_3\text{)}_6\text{][Be}_4\text{O(CO}_3\text{)}_6\text{]·10H}_2\text{O}\): N, 18.38; H, 6.17; C, 7.87; Be, 3.94. Found: N, 18.26; H, 6.15; C, 7.78; Be, 3.91. By checker: N, 18.50; H, 6.16; C, 7.80; Be, 3.94.

**B. POTASSIUM OXOHEXACARBONATOTETRABERYLLATE,**

\(\text{K}_4[\text{Be}_4\text{O(CO}_3\text{)}_6]\)

Pure beryllium hydroxide, freshly prepared from 12 g. (0.06 mol) of beryllium nitrate 4-hydrate, is dissolved by
heating it in 100 ml. of an aqueous solution containing 16 g. (0.16 mol) of potassium hydrogen carbonate. The solution is cooled to room temperature and is filtered.

The clear solution is placed in a glass-stoppered Erlenmeyer flask, and to it ethanol is added gradually and with frequent shaking until a heavy oily liquid separates. Portionwise addition of ethanol and agitation of the flask are continued until no further increase in the volume of the heavy layer is apparent or precipitation of potassium hydrogen carbonate begins.

The heavy oily liquid is separated from the rest of the solution and is placed in another glass-stoppered flask. Water is added dropwise to the oily emulsion until it becomes clear. To this solution is added a volume of ethanol equal to approximately one-third the volume of the solution itself. After the mixture has been shaken and allowed to stand for a few minutes, two immiscible phases again result. The heavy oily liquid is again drawn off, and further extractions with water and with ethanol, respectively, are made (about 10 times*) until the dropwise addition of water causes a white flocculent precipitate to form. After the solution has stood several minutes, it is filtered through dry fine-textured filter paper (S & S 589\(^3\) or Whatman 42) and placed in a desiccator.

After several days the potassium salt crystallizes from the syrupy solution as large transparent rhombohedra. The crystals are filtered by suction and quickly dried between folds of filter paper. After the crystals have been powdered and dried to constant weight over \(\text{P}_4\text{O}_{10}\) the composition corresponds to that of the anhydrous salt, \(\text{K}_6[\text{Be}_4\text{O}(_\text{2}\text{CO}_3)_4]\). \textit{Anal.} Calcd. for \(\text{K}_6[\text{Be}_4\text{O}(_\text{2}\text{CO}_3)_4]\): K, 36.28; Be, 5.57; CO\(_2\), 40.82. Found: K, 36.46; Be, 5.51; CO\(_2\), 41.06. By checker: K, 36.17; Be, 5.50.

* The checker reports that a minimum of 10 extractions is essential if the compound is to crystallize in a reasonable length of time.
Properties

Hexaamminecobalt(III) carbonatoberyllates are generally insoluble in water, but complete precipitation of beryllium is obtained only in procedures A-1 and A-3. Although potassium oxohexacarbonatotetraberyllate dissolves in water to form a clear solution, a white flocculent precipitate separates after a few minutes, indicating that the complex carbonate anion must be unstable in aqueous solution.

The sodium and ammonium analogs of the potassium compound can be prepared by the same procedure as described for the synthesis of the potassium compound. Both of the alkali metal compounds are hygroscopic in nature. The ammonium derivative cannot be obtained in a pure condition, because of its continuous evolution of ammonia and carbon dioxide.

Anhydrous potassium oxohexacarbonatotetraberyllate is thermally stable up to a temperature of 100°; the hexaamminecobalt(III) salts decompose at temperatures above 50°.

References

CHAPTER IIB

3. DICHLORO(2,2'-IMINODIPYRIDINE)ZINC, DIAcETATO(2,2'-IMINODIPYRIDINE)ZINC, AND DICYANO(2,2'-IMINODIPYRIDINE)ZINC

\[
\begin{align*}
\text{ZnCl}_2 + \text{NH}(&\text{C}_6\text{H}_4\text{N})_2 \rightarrow [\text{Zn}\{\text{NH}(&\text{C}_6\text{H}_4\text{N})_2\}\text{Cl}_2] \\
\text{Zn}(&\text{OOCCH}_3)_2 + \text{NH}(&\text{C}_6\text{H}_4\text{N})_2 \rightarrow [\text{Zn}\{\text{NH}(&\text{C}_6\text{H}_4\text{N})_2\}(\text{OOCCH}_3)_2] \\
\text{Zn}(\text{CN})_2 + \text{NH}(&\text{C}_6\text{H}_4\text{N})_2 \rightarrow [\text{Zn}\{\text{NH}(&\text{C}_6\text{H}_4\text{N})_2\}(\text{CN})_2]
\end{align*}
\]

Submitted by Joseph Simkin* and B. P. Block*
Checked by John A. Broomhead†

In Volume V of this series, syntheses were presented for coordination compounds of 2,2'-iminodipyridine [di-2-pyridylamine, \text{NH}(&\text{C}_6\text{H}_4\text{N})_2] with copper(II)\(^1\) and cobalt(II). Nickel(II) has also been shown to coordinate with this ligand.\(^3\) A similar behavior is exhibited by zinc salts, which form 1:1 derivatives if a 1:1 mol ratio of reactants is used. The specific choice of a solvent medium for synthesis is dictated by the solubility of the zinc compound. Either acetone or methanol may be used with zinc chloride, methanol with zinc acetate, and pyridine with zinc cyanide.

Procedure

A. DICHLORO(2,2'-IMINODIPYRIDINE)ZINC

Commercial 2,2'-iminodipyridine\(‡\) is purified by recrystallization from ethanol (20 g. of 2,2'-iminodipyridine in 30

* Pennsalt Chemicals Corporation Technological Center, King of Prussia, Pa.
† University of Queensland, St. Lucia, Brisbane, Australia.
‡ Available from Reilly Tar and Chemical Corp., Indianapolis, Ind.
DICYANO(2,2'-IMINODIPYRIDINE)ZINC

A solution of 17.12 g. (0.10 mol) of the purified 2,2'-iminodipyridine in 280 ml. of reagent-grade acetone is added dropwise with vigorous stirring to a filtered solution of 13.63 g. (0.10 mol) of reagent-grade anhydrous zinc chloride in 30 ml. of reagent-grade acetone. (Granular anhydrous zinc chloride is preferable because of its ease of solution; if it is not available, sticks of zinc chloride should be powdered and weighed rapidly. Anhydrous zinc chloride powder may be obtained commercially or may be prepared by the method of Pray.4) The white precipitate which forms almost immediately is removed by vacuum filtration, washed with three successive 30-ml. portions of acetone, and dried to constant weight at 90 to 95°. The yield is 29.5 to 30.5 g. (96 to 99%). Anal. Calcd. for [Zn(NH(C_5H_4N)_2]Cl_2]: C, 39.06; H, 2.95; N, 13.67; Cl, 23.06; Zn, 21.26. Found: C, 39.1; H, 3.0; N, 13.9; Cl, 23.4; Zn, 21.2. By checker: C, 39.11; H, 3.22; N, 13.72.

B. DIACETATO(2,2'-IMINODIPYRIDINE)ZINC

NOTE: Parts B and C include modifications suggested by the checker and checked independently by the submitters.

A solution of 17.56 g. (0.08 mol) of zinc acetate 2-hydrate in 100 ml. of absolute methanol is filtered into a 250-ml. flask. To this solution is added with stirring a solution of 13.70 g. (0.08 mol) of 2,2'-iminodipyridine in 20 ml. of hot methanol. The solution is heated to boiling and then allowed to cool. White crystals are deposited. The mixture is cooled in ice and the product filtered off, washed with acetone, and dried at 90 to 95°. The yield is 20.1 g. (71%). Anal. Calcd. for [Zn(NH(C_5H_4N)_2](CH_3CO_2)_2]: C, 47.41; H, 4.26; N, 11.85; Zn, 18.43. Found: C, 47.7; H, 4.1; N, 11.8; Zn, 18.4. By checker: C, 47.51; H, 4.57; N, 11.91.

C. DICYANO(2,2'-IMINODIPYRIDINE)ZINC

A solution of 3.51 g. (0.030 mol) of zinc cyanide in 250 ml. of pyridine is heated to boiling on a hot plate and
filtered while hot. The solution obtained by dissolving 7.7 g. (0.045 mol) of 2,2'-iminodipyridine in the filtrate is heated to boiling and evaporated to dryness on a steam bath. The white residue is then finely ground, washed four times with 100-ml. portions of boiling absolute ethanol, and dried at 90 to 95° at 20 mm. pressure. The yield is 6.4 g. (74%). *Anal.* Calcd. for [Zn(NH(CsH4N)2)(CN)2]: C, 49.94; H, 3.14; N, 24.27; Zn, 22.65. Found: C, 49.4; H, 3.0; N, 24.1; Zn, 22.9. By checker: C, 49.33; H, 3.31; N, 23.99.

**Properties**

All three compounds are white solids. The acetato derivative melts at 254 to 259°, but the other two decompose on heating. All three are insoluble in carbon tetrachloride, acetone, ether, and benzene and soluble in *N,N*-dimethylformamide, *N,N*-dimethylacetamide, and pyridine. The acetato derivative is soluble in water, methanol, and ethanol. The chloro derivative is sparingly soluble in boiling water and insoluble in methanol and ethanol, whereas the cyano derivative is somewhat soluble in boiling ethanol and methanol and insoluble in water.

**References**