

Inorganic Syntheses

Volume IV

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PREFACE

The reception which has been accorded the earlier volumes of INORGANIC SYNTHESSES has been most gratifying to the Board of Editors and has encouraged them to continue the series at an accelerated rate. The resurgence of interest in inorganic chemistry and the rapidly increasing number of its applications lead the editors to hope that these volumes will find increasing usefulness. Conversely, they hope that the publication of INORGANIC SYNTHESSES will stimulate interest in inorganic chemistry still further.

The policy of having each synthesis carefully checked in at least one independent laboratory has been continued, as it has been found that the efficiency and usefulness of the syntheses are often greatly increased by the checker. After checking and revision, the syntheses have been edited and then returned to the authors and checkers for final approval.

As in the earlier volumes, the syntheses in Volume IV are arranged on the basis of the Mendeleev periodic classification, with subdivision into A and B groups. The nomenclature is that used in Volumes II and III. Cross references have been used liberally, and the index has been made as complete as possible. The index is cumulative for all four volumes.

Contributions are now being accepted for forthcoming volumes, two of which are in preparation. Manuscripts describing syntheses of a general nature should be sent to Prof. Therald Moeller of the University of Illinois, who will serve as editor of the next general volume. Manuscripts concerning syntheses of hydrides should be sent to Prof. W. C. Johnson of the University of Chicago, who, with Prof. H. I. Schlesinger, is preparing a volume on that subject. All manuscripts should be submitted in triplicate

and should follow, as nearly as possible, the style used in the earlier volumes. After a brief introduction, the procedure should be described in detail. This should be followed by a brief description of the chemical and physical properties of the substance under discussion and by analytical data. If the analytical methods are sufficiently distinctive to warrant description, they should be presented in detail. Pertinent references should be placed at the end of the synthesis.

The editors wish, again, to call attention to the fact that *INORGANIC SYNTHESIS* is a periodical publication and that references to articles appearing in it should include the names of the authors of the articles in addition to the name of the editor of the volume.

In dedicating this volume to Prof. Harold S. Booth, the editors wish to acknowledge the invaluable help which Dr. Booth rendered to *INORGANIC SYNTHESIS*. Not only was he one of the founders of the project and the first editor, but he continued to contribute generously of his talents, time, and energy to ensure its continued success. He was an outstanding chemist, an inspiring leader, and best of all, a beloved friend.

The editor-in-chief takes pleasure in thanking his colleagues on the Editorial and Advisory Boards for their help in preparing this volume. Miss Janet D. Scott has been particularly helpful, as she has handled all the problems of nomenclature and indexing. The editor wishes also to thank Mrs. John Maisch for her help in preparing the manuscript, and Daryle H. Busch, without whose excellent help this project could not have been completed for many months.

The editors will consider it a favor if users of *INORGANIC SYNTHESIS* will call to their attention any errors or omissions.

John C. Bailar, Jr.

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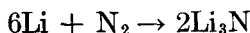
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CHAPTER IA

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1. LITHIUM NITRIDE



SUBMITTED BY E. MASDUPUY* AND F. GALLAIS*

CHECKED BY T. R. P. GIBB† AND H. O. WARREN†

Lithium nitride was first prepared by Ouvrard,¹ who heated metallic lithium to dull redness in a stream of nitrogen. Guntz² observed shortly afterward that the preparation can be realized with but slight heating, while Deslandres³ found that the metal absorbs nitrogen even at room temperature. Other early experimental work^{4,5} has determined that the compound may best be obtained either at room temperature or at approximately 450°. In the first case, the preparation proceeds slowly; the substance produced is very hygroscopic and retains uncombined nitrogen. When lithium nitride is prepared at the higher temperature, the process is completed in a short time; the substance so obtained is more compact, less hygroscopic, and more easily preserved. For these reasons the second method is preferred.

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† Metal Hydrides, Beverly, Mass.

Procedure

The nitrogen employed should be perfectly dry and free from oxygen and hydrogen. In order to prevent contamination with hydrogen, which may be formed by reduction of water vapor by the hot copper, the nitrogen is passed through a U-tube *A* (Fig. 1) containing Drierite or phosphorus(V) oxide prior to removal of the oxygen. To eliminate the oxygen which the gas contains, it is passed successively

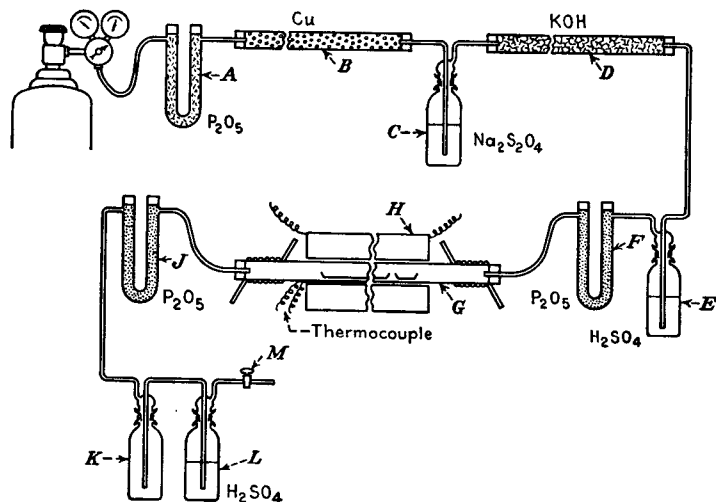


FIG. 1. Apparatus for the preparation of lithium nitride.

over hot powdered copper *B* and through an alkaline solution of sodium dithionite *C*, which is cooled in an ice bath. It is then dried by passing over potassium hydroxide pellets *D*, through sulfuric acid *E*, and then over phosphorus (V) oxide *F*, after which it enters the reaction apparatus *G*. This consists of an iron tube 90 cm. in length and approximately 5 cm. i.d., the ends of which are surrounded by a few turns of lead or copper tubing which surround by a few turns of water as a coolant. The central portion of the iron tube is placed in an electric tube furnace *H* about 50 cm. long. This iron tube is fitted with two one-hole rubber stoppers which hold pyrex gas inlet and outlet tubes. The reaction

tube is preceded in the nitrogen path by the purification train described above and followed by a phosphorus(V) oxide drying tube *J*, a safety flask *K*, a gas-washing bottle containing sulfuric acid *L*, and a glass stopcock *M*, in that order. The sulfuric acid serves both as a washing medium for the gas and as a flowmeter. The external temperature of the reaction tube is determined by means of a thermocouple placed between the tube and the furnace.

Two flat, iron boats are located in the central part of the reaction tube; the boat nearest the point of entry of the nitrogen holds only a small quantity of lithium and serves as a final protection against oxygen and water-vapor contamination, while the second vessel contains the amount of lithium required for the preparation. The apparatus must be thoroughly dried, and all the air must be displaced before the reaction is initiated. Therefore, the reaction tube is first heated gently (200°) for some time in a stream of nitrogen. It is then allowed to cool, and lithium which has been freshly cut into lumps of approximately 0.5 cc. volume is placed in the vessels (1 lump in the first vessel, 10 or 12 lumps in the second). The nitrogen is then allowed to flow for 1 hour to eliminate any air which may have entered the apparatus when the boats were introduced. The temperature is gradually increased to a maximum of 450°. The reaction is most rapid at 370°, at which temperature a sudden strong absorption of nitrogen takes place. In order to prevent air from entering the apparatus during this phase of the preparation (suckback), it is advisable to close the stopcock *M* near the exhaust end of the train. The flow of nitrogen may also be increased. If care is taken, the pressure regulator on the nitrogen tank may be set up to about 4 p.s.i. without causing undue hazard. The gas-washing bottles must be equipped with "horns" which are wired to prevent popping when the pressure builds up after the reaction subsides.* When the absorption is no longer

* As an additional safety precaution, a T-tube with a long vertical arm may be incorporated in the train between wash bottle *E* and tube *F*. The

vigorous, the pressure regulator is set back and the stopcock is *slowly* opened. The temperature is maintained at 450° until nitrogen is no longer absorbed, after which the furnace is allowed to cool while nitrogen still passes through the system.

The lithium nitride produced in the second vessel will be 95 to 99% pure, depending on the purity of the lithium that was used in the reaction. On the basis of ammonia obtained by hydrolysis, the ratio Li:N is very nearly 3:1. Pure lithium nitride may also be produced in the first vessel if the purification of the nitrogen is complete, but this sample of nitride is sometimes contaminated with small quantities of lithium oxide or hydroxide.

Properties

When prepared at high temperature, lithium nitride forms as porous, puffy lumps which are a dark violet in color. Its crystalline nature is apparent on viewing a section of the substance. It is quickly altered by air and must be preserved in an atmosphere of nitrogen. It melts between 840 and 845°. Lithium nitride is extremely reactive at temperatures near its melting point, attacking iron, nickel, copper, and even platinum, silica, and porcelain. It begins to react with iron at 500°, and for this reason the preparation outlined here must be carried out at temperatures of 450° or lower. Its high reactivity may be related, to some extent, to the fact that it exists in an ionic lattice.⁶ It evolves nitrogen when electrolyzed.⁷

References

1. OUVARD: *Compt. rend.*, **114**, 120 (1892).
2. GUNTZ: *ibid.*, **120**, 777 (1895).

open end of the vertical arm is immersed in a test tube, 70 to 100 cm. in length, filled with sulfuric acid or mercury. The flow of nitrogen through the horizontal arm of the T-tube is kept adjusted so that some of it bubbles out of the bottom opening. A coarse sintered-glass disk sealed near the top of the vertical arm serves as a further safety device since it prevents, or at least greatly impedes, suckback.

3. DESLANDRES: *ibid.*, **121**, 886 (1895).
4. GUNTZ: *ibid.*, 945.
5. DAFERT and MIKLAUZ: *Monatsh.*, **31**, 981 (1910).
6. ZINTL and BRAUER: *Z. Elektrochem.*, **41**, 102 (1935).
7. GALLAIS and MASDUPUY: *Compt. rend.*, **227**, 635 (1948).

2. EXTRACTION OF CESIUM FROM POLLUCITE

Although cesium may be recovered from minerals such as lepidolite¹ and beryl,² the chief source of this metal is the relatively rare mineral pollucite.* The isolation of a pure compound of cesium usually depends upon the insolubilities of the "double salts" such as the chloroplatinates, the alums, and the double chlorides with tin, lead, and antimony.³⁻⁵ Of these, the compound having the composition $(\text{CsCl})_3(\text{SbCl}_3)_2$ is most commonly employed.⁶ Use of this material is based upon the observations first recorded by Setterberg⁷ and elaborated by the work of Wells^{8,9} and others.¹⁰⁻¹² Procedure A outlined below is based primarily upon the work of Wells with $(\text{CsCl})_3(\text{SbCl}_3)_2$.^{4,5,8}

Pollucite contains enough aluminum to form an alum when treated with sulfate, and the use of this sparingly soluble alum as a means of recovering the cesium value is well known.^{13,14} Procedure B given here uses sulfuric acid for the treatment of the mineral, giving the alum directly, eliminating the usual preliminary decomposition of the mineral with hydrochloric acid or hydrofluoric acid.

Other methods which have been suggested for the separation of cesium from pollucite include the conversion of the mineral to carbonates, followed by the extraction of cesium carbonate with ethanol,¹⁵ and the precipitation of cesium iododichloride. The use of cesium iododichloride was first suggested by Wells.⁸ This provides the basis for procedure C.

* Approximately $\text{Cs}_4\text{Al}_4\text{H}_2\text{Si}_9\text{O}_{27}$.

Procedure A*

Cesium Antimony(III) Chloride Method and Preparation of Cesium Nitrate

SUBMITTED BY GEORGE W. WATT†

CHECKED BY WM. C. SMITH‡

One hundred grams of pollucite§ is ground to -100 mesh in a ball mill, placed in a 600-ml. beaker together with 100 ml. of concentrated hydrochloric acid (12*N*), covered with a watch glass, and digested at the boiling temperature for 4 hours. The mixture is stirred at frequent intervals, and concentrated hydrochloric acid is added from time to time to keep the volume at approximately 100 ml. over the entire digestion period. The hydrochloric acid solution is decanted through a fritted-glass filter, and the residue is covered with 100 ml. of 12 *N* hydrochloric acid and again extracted as described above. The second extract is combined with the first, and the residual solid is collected on the filter and washed twice with 25-ml. portions of water. The residue is dried and weighed in order to determine the total weight of ore dissolved during the two extractions. For most samples of pollucite the extraction is complete when 40 to 50% has been dissolved. If the weight loss is not within the range indicated, the digestion is repeated. The solid residue is finally discarded.

Cesium is precipitated as $(\text{CsCl})_3(\text{SbCl}_3)_2$ by diluting the combined filtrate and washings with an equal volume of water and adding a solution that is 20 *M* in antimony(III) chloride and 6 *M* in hydrochloric acid until no further precipitation occurs.|| The precipitate is filtered through a

* This procedure is readily amenable to being scaled up by at least a factor of 10.

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‡ University of Illinois, Urbana, Ill.

§ Most of the pollucite samples used by the author were obtained from the A. D. Mackay Co., New York, N.Y.

|| The solubility of the double salt with antimony(III) chloride is about 10 g./l.⁶ On the basis of this solubility, 14.2 ml. and 44.4 ml. of the anti-

fritted-glass funnel and washed three times with 10-ml. portions of water. The filtrate and washings are discarded.

A gross separation of cesium and antimony is accomplished by transferring the precipitate to 2500 ml. of boiling distilled water contained in a 4-l. beaker and agitated vigorously with a motor-driven stirrer. The resulting precipitate of antimony(III) oxychloride is digested for 30 minutes, washed with three 25-ml. portions of water, and discarded. The separation from antimony is completed by saturating the hot filtrate with hydrogen sulfide. If a precipitate of antimony sulfide forms, the solution is cooled to room temperature, and the precipitate is removed by filtration and washed with three 25-ml. portions of water. The washings are added to the filtrate, and the precipitate is discarded.

The filtrate from the antimony separation is boiled to expel hydrogen sulfide and to reduce the total volume by approximately one-half. One hundred milliliters of concentrated nitric acid (16 *N*) is added to this solution. The resulting solution is evaporated to a volume of approximately 150 ml. and filtered. The precipitate is washed once with 10 ml. of distilled water, and the combined filtrate and washing are collected in a 250-ml. beaker. This solution is concentrated by evaporation until the formation of crystals is first evident. It is then cooled in an ice-salt bath. The resulting crystals of cesium nitrate 1-hydrogen nitrate¹⁶ are separated by filtration, washed twice with 10-ml. portions of cold 50% ethanol, and air-dried. Complete conversion of the 1-hydrogen nitrate to the unsolvated salt is ensured by heating the air-dried product for 1 hour in a vacuum oven at 110°. If a product of exceptionally high purity is desired, the nitrate may be recrystallized from water.

Although additional crops of crystals may be obtained from the original mother liquor, either by further concen-

mony(III) chloride solution will precipitate 99% and 99.9% of the cesium, respectively.

tration and cooling or by dilution with ethanol, these products are usually relatively impure. It is preferable to collect these residues (and the mother liquors from any recrystallizations) and recycle them during the extraction of the next batch of ore.

By the above procedure a sample of average pollucite gives a yield of cesium nitrate of about 19 g. This is a convenient starting material for the preparation of other cesium compounds.

Procedure B

Cesium Alum Method

SUBMITTED BY ROBERT WEST* AND ROBERT P. ANDERSON*

CHECKED BY LEWIS I. KRIMEN† AND THERALD MOELLER†

Pollucite is broken into pea-sized lumps with a hammer and then ground in a ball mill until fine enough to pass through a 120-mesh sieve. One hundred grams of the screened pollucite‡ is mixed with 400 ml. of 50% sulfuric acid (7.1 *M*) in a 1-l. round-bottomed flask and refluxed gently for 30 hours. The mixture is diluted with 250 ml. of water, heated to boiling, and filtered with suction, using a large, coarse, sintered-glass funnel. The silica residue is washed well with hot water.

The hot solution is cooled to 0°, and the well-defined octahedra of cesium alum are collected on a sintered-glass funnel and washed with cold water. A small second crop of crystals is obtained when the filtrate is concentrated to about 450 ml. and cooled. The yield is about 110 g., or nearly 90% (for Varuträsk pollucite).

Properties

Cesium alum crystallizes in colorless octahedra which melt at 117°. This compound is more insoluble than the other alkali-metal alums and is remarkable for its high

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‡ Swedish pollucite obtained from Ward's Natural Science Establishment was used in both procedures B and C.