

# INORGANIC SYNTHESES

Volume VII

# Inorganic Syntheses

Volume VII

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## PREFACE

The present volume of INORGANIC SYNTHESSES contains sixty-five contributions covering a wide range of compounds and emanating from a large number of laboratories both in this country and abroad. As in previous volumes of this series, each synthesis has been carefully checked in a laboratory other than that from which it was submitted. Also in accordance with established practice, the syntheses in Volume VII are arranged on the basis of the Mendeleev periodic classification, with subdivision into A and B groups. The author, subject, and formula indexes in this volume are cumulative for all seven volumes.

Contributions for Volume VIII of this series are invited, and manuscripts, in triplicate and in the conventional style, should be submitted to the editor-in-chief of that volume, Professor Henry F. Holtzclaw, Jr., Department of Chemistry, University of Nebraska, Lincoln, Nebraska. The services of competent checkers are always desired, and those persons interested in performing this invaluable function are urged to communicate with Professor Holtzclaw.

Since the appearance of Volume VI, four new members have been elected to the Editorial Board. They include Professor William L. Jolly of the University of California (Berkeley); Dr. Earl L. Muetterties of E. I. du Pont de Nemours and Co.; Dr. Morris L. Nielsen of the Monsanto Chemical Co.; and Professor Robert W. Parry of the University of Michigan.

The editor-in-chief is deeply grateful to his associates on the Editorial and Advisory Boards for their most valuable assistance in the preparation of Volume VII. He is par-

ticularly indebted to Miss Janet D. Scott for handling all the problems of nomenclature and indexing, and for her participation in the final editing of the manuscript. Finally, the editor wishes to acknowledge the splendid efforts of Miss Julia Jeffery, Miss Judith Ann Kleinberg, and Mrs. Alberta Rogers in typing the manuscript.

The editors welcome suggestions and criticisms pertinent to this and other volumes of INORGANIC SYNTHESSES. The comments of the readers of the series have always been most useful.

*Jacob Kleinberg*

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## CHAPTER IA

See also: Sodium hydrogen sulfide, synthesis 35

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Sodium fluoride( $F^{18}$ ), synthesis 42

Potassium hexachlororhenate(IV) and potassium hexabromorhenate(IV), synthesis 51

Sodium salts of carbonyl hydrides prepared in ethereal media, synthesis 53

### 1. LITHIUM HYDROXIDE AND LITHIUM OXIDE

SUBMITTED BY JUSTO BRAVO\*

CHECKED BY JOHAN H. DE GROOT†

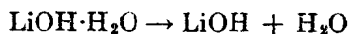
Anhydrous lithium hydroxide was first obtained by Troost<sup>1</sup> by thermally dehydrating the monohydrate in a vacuum for several weeks. De Forcrand<sup>2</sup> obtained the anhydrous product by passing pure dry hydrogen over the hydrated crystals for an hour at a temperature not exceeding 140°. By fusion of the hydrate, Gmelin<sup>3</sup> produced an anhydrous product.

The thermal decomposition of lithium hydroxide has been effected by Dittmar<sup>4</sup> by holding it at red heat under a hydrogen atmosphere for 4 hours. The decomposition pressures along with the corresponding temperatures have been published in the International Critical Tables.<sup>5</sup>

\* Foote Minerals Company, Berwyn, Pa.

† Research Associate with the Joint Committee on Chemical Analysis by Powder Diffraction Methods, American Society for Testing Materials, National Bureau of Standards, Washington, D.C.

## A. ANHYDROUS LITHIUM HYDROXIDE



## Procedure

A laboratory roaster (Fig. 1) is provided with a tube to supply a positive pressure of carbon dioxide-free dry air

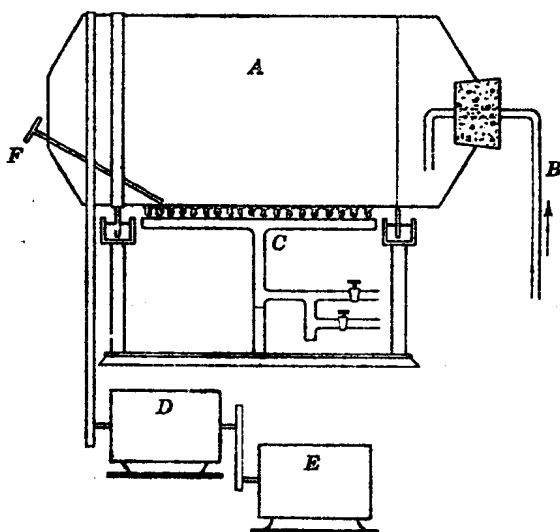


FIG. 1. Apparatus for the preparation of anhydrous lithium hydroxide.

A—Stainless-steel rotating drum, 8 in. in diameter and 14 in. long.

B—Tube supplying carbon dioxide-free dry air.

C—Air-blast gas burner.

D—Reducer drive.

E—110-voltmeter.

F—Metal thermometer.

inside the drum. The drum is heated by an air-blast gas burner. It is charged with 876.8 g. (20.9 mols) of lithium hydroxide 1-hydrate (99.5%  $\text{LiOH} \cdot \text{H}_2\text{O}$ , 0.50%  $\text{Li}_2\text{CO}_3$ ). The gas burner is lighted and the drum is rotated. A temperature of 130 to 150°, measured by a metal thermometer inserted at the front end of the drum, is maintained by adjusting the gas and air pressure. Within one

hour the disappearance of the water vapor is observed, and a granulated dry lithium hydroxide is obtained. The drum is cooled by shutting off the gas. When the temperature reaches about  $50^{\circ}$ , the product is scooped into a bottle. (NOTE: The transfer of all material is carried out in a dry-box which contains carbon dioxide-free dry air.) The bottle is sealed and a sample analyzed. The yield of 500.0 g. is nearly quantitative. *Product analysis:* 99.0% LiOH, 1.0%  $\text{Li}_2\text{CO}_3$ .

### Properties

Anhydrous lithium hydroxide is white, granular, and free flowing. It readily absorbs both carbon dioxide and water from the atmosphere. Both the hydroxide and the monoxide have a marked irritating effect on the skin. The hydroxide has a density of 2.54 g./cc.

### B. LITHIUM OXIDE\*



### Procedure

In a carbon dioxide-free dry-box, 200.0 g. (8.35 mols) of anhydrous lithium hydroxide is placed in a nickel trough, 12 in. long,  $3\frac{1}{2}$  in. in diameter,  $\frac{1}{8}$  in. thick, lined with silver foil 16 in. long, 6 in. wide, and 0.002 in. thick. The trough is placed in a tube furnace (Fig. 2). The furnace is heated to  $675^{\circ} \pm 10^{\circ}$  and maintained at this temperature by a temperature controller. The open end of the furnace is closed with a rubber stopper connected with a glass tube and rubber tubing to a Dry Ice-acetone trap, which is directed to a vacuum pump. The pressure is maintained at about 0.5 in. The process is allowed to proceed for half an hour at the temperature indicated, after which

\* An alternative method for the preparation of this compound has been given by A. J. Cohen, *INORGANIC SYNTHESIS*, 5, 5 (1957).

the pump and heat are shut off. The rubber tubing is clamped for vacuum tightness. When the temperature is about  $50^{\circ}$ , the vacuum is released by the introduction of carbon dioxide-free dry air. The stopper is removed and the trough quickly transferred into the dry-box. The

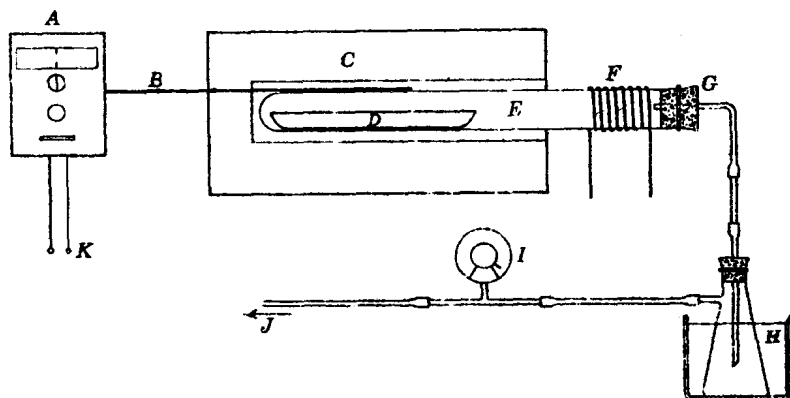


FIG. 2. Apparatus for the preparation of lithium oxide.

- A—Temperature controller.
- B—Thermocouple connection.
- C—Tube furnace.
- D—Nickel trough lined with silver foil.
- E—Four-inch-diameter quartz tube.
- F—Cooling coil (water circulation).
- G—Rubber stopper.
- H—Dry Ice-acetone trap.
- I—Vacuum gage.
- J—To vacuum pump.
- K—220-volt power source

lithium oxide is removed by peeling off the silver foil. The product is crushed, bottled, and sealed. The yield of 125 g. is quantitative. *Product analysis*: 98%  $\text{Li}_2\text{O}$ , 2.0%  $\text{Li}_2\text{CO}_3$ .

### Properties

Lithium oxide is obtained as a white crusty material. It readily absorbs both carbon dioxide and water from the atmosphere. At elevated temperature it attacks glass,

silica, and many metals. The high-temperature heat content and entropy have been evaluated.<sup>6</sup>

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2. R. DE FORCRAND: *Compt. rend.*, **146**, 802 (1908).
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## CHAPTER IB

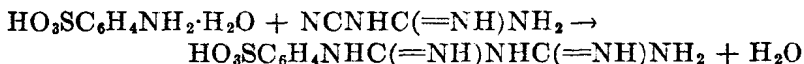
### 2. 1-PHENYLBIGUANIDE-*p*-SULFONIC ACID COMPLEXES OF COPPER(II)

SUBMITTED BY PRIYADARANJAN RÂY\*

CHECKED BY SAM N. HOLTER† AND W. CONARD FERNELIUS†

Two modifications (green and red) of the copper derivative of phenylbiguanide-*p*-sulfonic acid (*N*-(amidinoamidino)sulfanilic acid) are known.<sup>1,2</sup> Both are formed by the careful neutralization of the acid by ammonia in the presence of copper ion. The two modifications have almost the same magnetic moment and they dissolve in alkali to give the same red solution. Although only a few *cis-trans* isomers of copper(II) are known, infrared spectra indicate that the two forms of the present complex are *cis-trans* isomers.<sup>3</sup>

#### A. 1-PHENYLBIGUANIDE-*p*-SULFONIC ACID



Phenylbiguanide-*p*-sulfonic acid is prepared by the usual reaction for the synthesis of *N*-substituted biguanides: i.e., the addition of dicyanodiamide (cyanoguanidine) to an amine.<sup>1</sup>

#### Procedure

A mixture of 2.0 g. (0.0104 mol) of sulfanilic acid, 1.2 g. (0.0142 mol) of dicyanodiamide, and 30 ml. of water is

\* University College of Science, Calcutta, India.

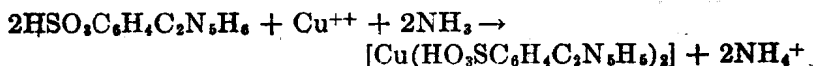
† The Pennsylvania State University, University Park, Pa.

heated at reflux for about 2 hours, during which a silky white solid separates. When the mixture has cooled, the solid is filtered and washed with 50 ml. of water. Yield (based on sulfanilic acid): 2.0 g. (74%). For purification, the product is recrystallized from 170 ml. of boiling water. Yield; 1.8 g. (67%); m.p. 265 to 268° (decomp.). *Anal.* Calcd. for  $\text{HO}_2\text{SC}_6\text{H}_4\text{C}_2\text{N}_5\text{H}_6$ : N, 27.20; S, 12.45. Found: N, 26.90; S (by peroxide fusion), 12.60.

### Properties

Phenylbiguanide-*p*-sulfonic acid forms silky white crystals which are very slightly acid to litmus. The substance is nearly insoluble in cold water and organic solvents such as alcohol, ether, and acetone, but is soluble in strong acids as well as dilute alkalies and ammonia.

#### B. COPPER COMPLEXES OF 1-PHENYLBIGUANIDE-*p*-SULFONIC ACID



1. **Red-violet modification.** A mixture of 2.05 g. (0.008 mol) of phenylbiguanide-*p*-sulfonic acid and 150 ml. of water is acidified with 1.5 ml. of concentrated hydrochloric acid (35%) and warmed to 60°. To this solution is added 1 g. (0.004 mol) of copper(II) sulfate 5-hydrate dissolved in 10 ml. of water. The resulting solution is then treated with dilute (12%) ammonia water drop by drop until the solution becomes just alkaline and the red-violet crystals of the copper complex separate. About 4 ml. of ammonia is required. The crystals are filtered, washed first with 100 ml. of water and finally with 15 ml. of ethanol, and dried in air. Yield: 2.2 g. (93% based on copper taken). *Anal.* Calcd. for  $[\text{Cu}(\text{HO}_2\text{SC}_6\text{H}_4\text{C}_2\text{N}_5\text{H}_6)_2]\cdot\text{H}_2\text{O}$ : N, 23.59; Cu, 10.71;  $\text{H}_2\text{O}$ , 3.04. Found: N, 23.66; Cu, 10.61, 10.64;  $\text{H}_2\text{O}$  (loss at 90°), 3.0.

**2. Green modification.** A mixture of 3 g. (0.0117 mol) of phenylbiguanide-*p*-sulfonic acid and 150 ml. of water is acidified with 2.5 ml. of concentrated hydrochloric acid (35%) and warmed to 60°. To this solution is added 1 g. (0.004 mol) of copper(II) sulfate 5-hydrate dissolved in 10 ml. of water. The resulting mixture is then treated with concentrated ammonia water (24%) until the red-violet precipitate first formed goes into solution with a deep blue color. About 200 ml. of ammonia solution is required. The blue solution is heated with stirring on a water bath (80°) for 10 minutes with the addition of concentrated ammonia water from time to time to replace what has boiled off. During the latter part of the heating dark green crystals begin to separate on the side of the container. After heating for about an hour, the crystals are filtered and washed with water. They may be purified by dissolution in 15 ml. of warm dilute hydrochloric acid (5.8%), reprecipitation from hot solution with 100 ml. of concentrated ammonia water, and digestion on the water bath as before. Yield: 2.2 g. (93% based on copper taken). *Anal.* Calcd. for  $[\text{Cu}(\text{HO}_3\text{SC}_6\text{H}_4\text{C}_2\text{N}_5)_2] \cdot 1.5\text{H}_2\text{O}$ : N, 23.23; Cu, 10.54. Found: N, 23.56; Cu, 10.68.

### Properties

Both modifications of the copper derivative of phenylbiguanide-*p*-sulfonic acid are insoluble in water but dissolve in alkali to form a red solution from which red-violet crystals separate on neutralization with acid in the cold. The red form changes to the green form on warming with ammonia solution. The magnetic moments are: red-violet,  $\mu = 1.85$  Bohr magnetons; green,  $\mu = 1.84$  Bohr magnetons.

### References

1. P. RAY and S. K. SIDDHANTA: *J. Indian Chem. Soc.*, **20**, 250 (1943).
2. P. RAY and R. K. DUTT: *ibid.*, **25**, 563 (1948).
3. P. RAY: unpublished observations.



### 3. TETRAKIS[iodo(tri-*n*-butylphosphine)-copper(I)] AND IODO-(2,2'-bipyridine)-(tri-*n*-butylphosphine)copper(I)

SUBMITTED BY GEORGE B. KAUFFMAN\* AND LARRY A. TETER\*

CHECKED BY T. C. ICHNIOWSKI† AND A. F. CLIFFORD†

Tertiary alkylphosphines or -arsines combine in equimolar amounts with gold(I) chloride, silver(I) iodide, or copper(I) iodide to form crystalline nonelectrolytic compounds insoluble in water but very soluble in most organic solvents. X-ray diffraction of the solids as well as ebullioscopic and cryoscopic measurements of solutions have shown the copper(I) iodide derivatives to be tetramers which dissociate only slightly in solution.<sup>1</sup> In these structures the four copper atoms are situated at the apexes of a regular tetrahedron with the iodine atoms at the centers, but above the planes of the tetrahedral faces, while each phosphorus or arsenic atom lies beyond each copper atom on a line extending from the center of the tetrahedron through the corresponding copper atom. The stability of these compounds can thus be attributed to the attainment by copper of a coordination number of four and an effective atomic number equal to the atomic number of the nearest inert gas, krypton. When acetone solutions of tetrakis[iodo(tri-*n*-butylphosphine)copper(I)] and 2,2'-bipyridine (dipyridyl) are mixed, the tetrameric structure is ruptured, yielding iodo-(2,2'-bipyridine)(tri-*n*-butylphosphine)copper(I), in which the monomolecular structure is stabilized by chelation of 2,2'-bipyridine with consequent achievement of a coordination number of four by copper.

The stabilities and melting points of the copper(I) iodide derivatives of tertiary phosphines fall rapidly, and their solubilities in organic solvents increase as the size

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