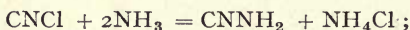


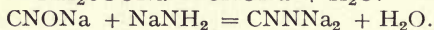
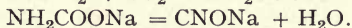
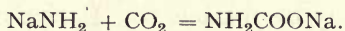
CHAPTER II

CYANAMIDE AND ALLIED COMPOUNDS

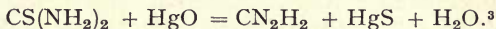
NORMAL CYANAMIDE, $\text{H}_2\text{CN}_2 = \text{N} : \text{C.NH}_2$, may be prepared by the action of cyanogen bromide, chloride, or iodide, on ammonia : ¹



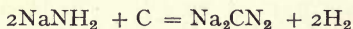
it may also be prepared by the action of carbon dioxide on sodium amide :



By the action of mercuric oxide on thiourea :



As the sodium salt as the intermediate product in the manufacture of cyanides from sodium amide :



And as the calcium salt by the action of nitrogen on calcium carbide at high temperatures.

The compound may be prepared from thiourea by gradually adding freshly precipitated and well washed mercuric oxide to a cold but not saturated solution of thiourea, avoiding excess, otherwise mercuric cyanamide will be precipitated. The end of the

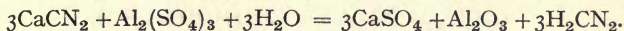
¹ Bineau, *A. Ch.* [2], 67, 368 ; 70, 251 ; Cloez a Cannz-zauro, *A.*, 78, 228.

² Beilstein and Geuther, *A.*, 108, 93 ; Drechsel, *J. pr.* [2], 16, 203.

³ Volhard, *J. pr.* [2], 9, 24 ; Baumann, *B.*, 6, 1371.

reaction can be determined by adding a drop of the clear liquor to a few c.c. of an ammoniacal solution of silver nitrate, the addition of mercuric oxide is continued until the test shows no black coloration. The liquid is filtered from the mercuric sulphide and concentrated as quickly as possible under a vacuum over sulphuric acid, to avoid polymerization into dicyandiamide. The cyanamide is separated from the dicyandiamide which is always formed to a certain extent by treatment with ether, in which the former is soluble, but the latter insoluble. This reaction proceeds more readily if the thiourea is impure.

Cyanamide may be prepared from the sodium salt by adding the latter to well-cooled, concentrated hydrochloric acid, distilling in a vacuum, and dissolving the cyanamide out of the residue with ether; but it may be more conveniently prepared from the commercial calcium salt, by adding a solution of aluminium sulphate to the aqueous solution of calcium cyanamide :



The solution is filtered from the precipitated calcium sulphate and aluminium hydroxide, and concentrated in a vacuum with the usual precautions, to prevent polymerization as much as possible to the dicyandiamide; and the cyanamide separated, and purified by solution in, and crystallization from ether.¹

Cyanamide forms colourless crystals melting at 41° to 42° C. It is readily soluble in water, alcohol, and ether, but sparingly soluble in carbon disulphide, benzene, chloroform, and other organic solvents; the compound is deliquescent and attacks the skin like caustic alkalis. When heated above its melting-point it polymerizes with ease to dicyandiamide :



And when heated to 150° C. a further polymerization

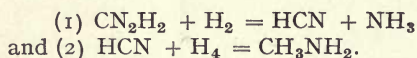
¹ N. Caro, *Z. angew. chem.* (1910), 23, 2405-17; *J.S.C.I.*, 30, 23.

takes place with formation of tricyantriamide or melamine : ¹



The solution slowly polymerizes in the cold to dicyandiamide and the change takes place more quickly on boiling, particularly in the presence of ammonia, or other alkali.

When reduced in solution by means of zinc and hydrochloric acid, ammonia and methylamine are produced. The formation of the latter body is probably due to secondary reaction by reduction of the hydrocyanic acid first formed ; the reaction taking place in two stages, thus :

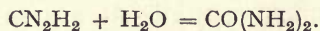


Cyanamide unites directly with glycocoll to form glycocamine ; and with methyl glycocoll to form creatine. Heated to a high temperature with ammonium chloride it forms guanidine hydrochloride :



With ammonium thiocyanate guanidine thiocyanate is obtained in a similar manner.

By the action of mineral acids, and certain organic acids, cyanamide combines with the elements of water to form urea :



Nitric acid added to an ethereal solution of the compound forms a crystalline precipitate of urea, which is insoluble in ether.

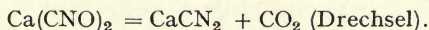
Dicyandiamidine sulphate may be obtained by adding commercial calcium cyanamide with good stirring to sulphuric acid mixed with twice its volume of water, and treating the product with hot water.

Additional compounds are formed with the haloid acids : thus when dry hydrochloric acid is passed into an ethereal solution of cyanamide, the compound

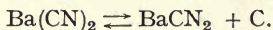
¹ Drechsel, *J. pr Chem.* [2], 13, 331.

$\text{CN}_2\text{H}_2\text{HCl}$ is obtained, which may be crystallized from water in large plates.¹ With hydrogen sulphide, or ammonium sulphide, thiourea is formed; and it also combines with potassium cyanate to form monopotassium amidodicyanate,² and with guanidine to form diguanide.

Metallic monoderivatives may be prepared by the action of alkalis or alkaline earths on the cyanamide. Metallic diderivatives may be obtained by heating certain metallic cyanates:



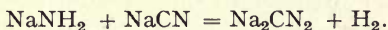
By heating dry barium cyanide, when part of the cyanide is converted into cyanamide:



And by heating calcium carbide in an atmosphere of nitrogen to a high temperature; or by gently igniting calcium ferrocyanide:



The sodium salt may be prepared by the action of sodium amide on fused sodium cyanide:



This salt may be obtained as a crystalline powder, very soluble in water and alcohol, but insoluble in ether. It absorbs carbon dioxide from the air to form cyanamide carboxylic acid $\text{CO} \begin{smallmatrix} \text{NHCN} \\ \text{ONa} \end{smallmatrix}$. The compounds Hg_3CN_2 ; PbCN_2 ; CuCN_2 ; and Ag_2CN_2 , have been described. The latter body is an amorphous yellow precipitate, insoluble in ammonia but easily soluble in nitric acid, and when heated it explodes violently³ with formation of metallic silver, nitrogen, and cyanogen.

Silver cyanamide is easily soluble in alkaline cyanides, and if silver nitrate be added to the solution, a crystal-

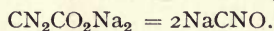
¹ Drechsel, *J. pr Chem.* [2], 9, 284.

² Mulder, *Ber.*, 6, 1236.

³ H. R. Ellis *Chem. News*, 100, 154-55.

line double salt of silver cyanamide and cyanide is obtained ; pure normal silver cyanamide is, however, only prepared by the precipitation of very dilute solutions, with stronger solutions a precipitate containing varying amounts of silver is obtained.¹

By passing carbon dioxide through a boiling solution of sodium cyanamide in alcohol, an amorphous precipitate separates of the sodium salt of cyanamide carboxylic acid, $\text{CN}_2\text{NaCO}_2\text{Na}$, and the potassium, and other salts may be prepared in a similar manner thus : $(\text{CN}_2\text{CO}_2)\text{Ca}5\text{H}_2\text{O}$ white needles sparingly soluble in water and $(\text{CN}_2\text{CO}_2)\text{Sr}2\frac{1}{4}\text{H}_2\text{O}$. The acid when liberated splits into cyanamide and carbon dioxide ; and the sodium salt when fused is converted into sodium cyanate : ²



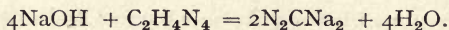
DICYANDIAMIDE, $\text{H}_4\text{C}_2\text{N}_4$, a polymeric compound of cyanamide, from which it may be readily obtained by boiling the aqueous solution with an alkali, preferably ammonia.³

It crystallizes from its aqueous solution in broad laminae, and is soluble also in alcohol, but is insoluble in ether, in which property it is distinct from cyanamide which is very soluble.

On heating to 150°C . normal malamine is formed together with melam and ammonia.

When heated with ammonium carbonate solution to 120°C . or with water, ammelide (melanurenic acid) is produced.

When heated with concentrated ammonia in sealed tubes to 120°C . for three hours, melamine and ammeline are produced ; and when fused with alkali hydroxide at 500°C . dialkali cyanamides are produced :

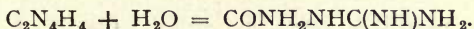


Guanylurea is formed when dicyandiamide is heated

¹ N. Caro, etc., *J.S.C.I.*, **30**, 23.

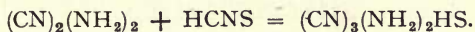
² G. Meyer, *J. pr. Chem.*, **126**, 417. ³ Haag, *A.*, **122**, 22.

with dilute acids by combination with the elements of water :



Concentrated sulphuric acid acts on dicyandiamide liberating carbon dioxide, and ammonia, and forming guanidine ;¹ and guanythiourea is produced by heating with hydrogen sulphide. On reduction with nascent hydrogen in acid solutions, melamine, and ammonia, are produced.²

When heated with ammonium chloride to 150° C. carbon dioxide and ammonia are evolved, and guanidine hydrochloride formed, and it combines with hydrothiocyanic acid to form thioammeline :



Heated on the water bath with hydrazine hydrate guanazole is obtained, which when heated to 270° C. for half an hour is converted into pyroguanazole with evolution of ammonia. The pyroguanazole separates from solution in strong hydrochloric acid with two molecules of acid, and from dilute solutions, with one molecule of HCl.³

Diguanides may be obtained by heating dicyandiamide with the hydrochlorides of aromatic amines in aqueous solutions. When heated with aniline hydrochloride, phenyl diguanide is produced.⁴

β -methylguanidine dicyandiamide is produced by the action of thiocarbamide and methylamine in presence of mercuric oxide.⁵

A sodium salt of dicyandiamide is produced by mixing an alcoholic solution of the compound with sodium ethylate, as a crystalline precipitate.⁶ It forms the compounds $\text{C}_2\text{N}_4\text{H}_4\text{AgNO}_3$; $(\text{C}_2\text{N}_4\text{H}_4)_2\text{AgNO}_3$; $(\text{C}_2\text{N}_4\text{H}_4)_3\text{AgNO}_3$; when mixed with silver nitrate solution in the molecular proportions of 1 : 1 ; 2 : 1 ;

¹ H. Lidholm, *Ber.* (1913), 46, 156-160.

² Ralhke, *Ber.* 18, 3607.

³ K. A. Hofmann and O. Ehrhard, *Ber.* (1912), 45, 2731-40.

⁴ Luminère and Parrin, *A.* (1905), i. 249.

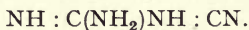
⁵ *J.C.S.*, i. 842, 1911.

⁶ Bamberger, *Ber.*, 16, 1461.

3 : 1. The first compound is converted by caustic soda solution into the silver salt, $C_2H_3N_4Ag$, while the second, and third, yield the same compound together with silver oxide. On boiling the silver salt with water, it is converted first into silver cyanamide and ultimately into cyanamide.¹

Dicyandiamide (cyanoguanidine) does not possess the poisonous properties of cyanamide and is said to be harmless to mice. The nitrocompound is used in the manufacture of explosives.

From a study of the reactions and decompositions of the compound, H. Lidholm² considers it to possess the structure of guanidinoformonitrile:



DICYANDIAMIDINE (guanyl carbamide), $C_2H_6ON_4$, may be prepared by evaporating a solution of dicyandiamide with a moderately strong solution of sulphuric acid, or by treating calcium cyanamide with the acid diluted with twice its volume of water.

Commercial calcium cyanamide is gradually added to a solution of 33 per cent. sulphuric acid, a vigorous action sets in with evolution of gas. The cooled product is then treated with hot water, and the filtered aqueous solution concentrated. Sulphate of calcium first separates out and then crystals of dicyandiamidine sulphate, $(C_2H_6ON_4)_2H_2SO_4 \cdot 2H_2O$, contaminated with the sulphates of calcium and ammonium; but may be purified by recrystallization from alcohol.

The crystals are soluble in water, and alcohol, but are insoluble in ether, and lose all water at $110^\circ C$. By treating the solution with barium chloride dicyandiamidine chloride $(C_2H_6ON_4)HCl \frac{1}{2}H_2O$, may be obtained³ in thin colourless leaflets.

The sulphate is decomposed by barium hydroxide forming dicyandiamidine or guanyl carbamide, which, when crystallized from alcohol, forms lustrous prisms,

¹ N. Caro and B. Schüick, *Z. angew. Chem.* (1910), **23**, 2405.

² *Ber.* (1913), **46**, 156-60.

³ T. Jona, *Gazz.* (1907), **37** [ii], 558-62.

which rapidly absorb carbon dioxide from the air. The free base melts at 105° C. and gives off ammonia on boiling with water, or at 160° C.

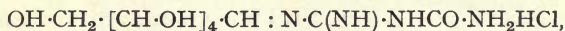
The addition of an ammoniacal solution of cupric sulphate produces first a violet colour and then precipitates a rose red cupric compound, $C_4H_5O_2N_4Cu$. This precipitate is also formed when a solution of a copper salt is added to a solution of the dicyandiamidine containing sodium hydroxide. An insoluble precipitate with nickel is also formed, but not with the other metals of the same group, and may, therefore, be used in the quantitative determination and separation of nickel.¹

The picrate crystallizes in yellow plates, melting-point 265° C., and is used for the quantitative determination of the compound.² Dicyandiamidine chloroplatinate, $(C_2H_5ON_4)_2H_2PtCl_6$, is crystalline, and the palladium dicyandiamidine, $Pd(C_2H_5ON_4)_2 \cdot 2H_2O$, is obtained by the reaction of dicyandiamidine sulphate, caustic potash, and palladium chloride, as a yellow crystalline powder³ soluble in ammonia.

The sulphate heated with acetic anhydride yields $C_2H_5ON_4SO_3H$ guanylcarbamidesulphonic acid, which crystallizes in prisms; the ammonium salt forms short thick prisms. Melting-point, 165° to 167° C.

When heated with acetic anhydride and sulphuric acid it is converted into acetylguanylcarbamide, or acetyldicyanodiamidine.⁴

Dicyandiamidine chloride condenses with dextrose in alcoholic solutions to form dicyandiamidine dextrose,



in slender microscopic needles, melting-point 107° C., at which temperature it begins to decompose.⁵

NORMAL MELAMINE, $C_3H_6N_6$ (cyanuramide), is

¹ H. Grosmann and B. Schück, *Ber.*, **43**, 674-6.

² *J.C.S.* (1910), i. 14. ³ Grossman and Schück, *l.c.*

⁴ T. Jona, *Gazz.* **38** [ii], 480-84.

⁵ L. Radlberger, *J.C.S.* (1913), i. 450.

obtained when dicyandiamide is heated to 150°C ., and like the latter body it is a polymeride of cyanamide :



It is also found among the products formed by the action of heat on ammonium thiocyanate.¹ And by the action of ammonia on cyanogen chloride at 100°C .²

Melamine is obtained in monoclinic prisms which may be sublimed unchanged by gentle heating. It is very slightly soluble in hot or cold water, or alcohol, but dissolves in glycerine ; it is a powerful base and forms salts with acids. When heated to redness it is converted into mellen, and by boiling with dilute nitric acid it is ultimately converted into cyanuric acid.³

The carbonate crystallizes in needles and forms the platinochloride, $(\text{C}_3\text{H}_6\text{N}_6\text{HCl})_2\text{PtCl}_4\cdot 2\text{H}_2\text{O}$.⁴ The sulphate, $(\text{C}_3\text{H}_6\text{N}_6)_2\text{H}_2\text{SO}_4\cdot 2\text{H}_2\text{O}$, is very sparingly soluble in cold water.⁵ The crystalline compound, $\text{C}_3\text{H}_6\text{N}_6\text{AgNO}_3$, may be obtained by the addition of silver nitrate, which is soluble in hot water, and by treatment with ammonia, the compound, $(\text{CN})_3(\text{NHAg})_2\text{NH}_2$, is said to be obtained.⁶

Melamine and dextrose heated in 30 per cent. alcoholic solution on the water-bath condense, yielding a product consisting of two molecules of melamine to one of dextrose :



The compound crystallizes in lustrous crystals which do not reduce Fehling's solution, and melt at 281°C .⁷

When melamine is heated with a large proportion of hydrazine hydrate for five hours under pressure at 150°C . microscopic needles of triaminomelamine are

¹ Liebig, *A.*, **10**, 18 ; **53**, 242 ; Volhard, *J. pr Chem.* [ii], 929 ; Claus, *A.*, **179**, 121 ; *B.*, **9**, 1915.

² Hofmann, *Ber.*, **18**, 2765.

³ Knapp, *A.*, **21**, 256.

⁴ Hofmann, *Ber.*, **18**, 2760.

⁵ Dreschsel, *J. pr Chem.* [ii], **13**, 322. ⁶ Zimmermann.

⁷ L. Radlberger, *Chem. Zentr.* (1913), i. 2110 ; *J.C.S.* (1913) i. 960.

obtained, this product rapidly reduces warm ammoniacal silver nitrate solution.¹

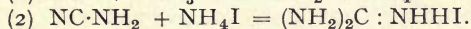
Of the four isomeric melamines theoretically possible only two alkylmelamines are known: the normal melamine, derivatives of the compound described above, and isomelamine. According to Hans Krall² this latter body may be isolated by heating guanidine carbonate at 180° C. for three hours when a mixture is obtained of ammeline and isomelamine, the latter is separated by treatment with a cold aqueous solution of sodium hydroxide in which the ammeline dissolves.

ISOMELAMINE is said to crystallize in ill-defined crystals. With strong acids isomerization takes place, with formation of the corresponding salt of ordinary melamine; and when isomelamine is heated to 260° C. normal melamine is formed.

GUANIDINE, $\text{CN}_3\text{H}_5 = \text{NH} \cdot \text{C}(\text{NH}_2)_2$, is formed when ammonium thiocyanate is heated to 190° C. Thiourea is first formed which is then converted into guanidine thiocyanate. It may also be produced by the interaction of ammonia and cyanamide:



And by the action of cyanogen chloride, bromide or iodide on alcoholic ammonia, cyanamide being first formed, thus: ³



Guanidine salts may be obtained by heating together dicyandiamidine, or melamine, with the corresponding ammonium salt; ⁴ or by heating dicyandiamide in presence of water under pressure.⁵

Guanidine nitrate may be obtained in good yield by treating dicyandiamine with an acid mixture

¹ Stollé and Krauch, *Ber.* (1913), **46**, 2337-39.

² *P.C.S.* (1913), p. 377. ³ Erlenmeyer; M. Schenck.

⁴ G.P. 222,552 (30.10.08), Stickstoffwerke.

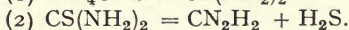
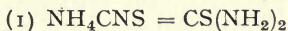
⁵ E.P. 815 (12.1.10), S. J. Gelhär.

containing 25 per cent. hydrochloric acid (sp. gr. 1.19), and 35 per cent. nitric acid (1.38 sp. gr.).¹

Guanidine is most conveniently prepared as the thiocyanate by heating dry ammonium thiocyanate. The method usually applied is to heat the dry salt to 180° to 190° C. for twenty to twenty-four hours. According to Hans Krall,² the best method for the preparation of the compound is to heat the ammonium thiocyanate to 200°C. when a yield of 60 per cent. may be obtained in four hours. It is suggested that the guanidine thiocyanate is formed by the interaction of cyanamide and some unchanged ammonium thiocyanate :



And that the cyanamide is formed by the decomposition of the thiourea which is first formed, with evolution of hydrogen sulphide :



The guanidine thiocyanate may be purified by recrystallization from alcohol, or water.

Guanidine is a strongly alkaline crystalline substance which absorbs carbon dioxide from the air, and forms crystalline salts with acids. It is found among the products resulting from the oxidation of certain proteid substances such as egg albumen.

Guanidine perchromate³ may be prepared by heating guanidine carbonate and chromic acid in water, and then treating the mixture with hydrogen peroxide at 0° C. The perchromate separates out in brownish yellow prisms which are very stable when dry, and do not explode. When boiled with water the chromate, $(\text{CN}_3\text{H}_5)_2\text{H}_2\text{CrO}_4\cdot\text{H}_2\text{O}$, is formed in thin yellow monoclinic crystals.

Guanidine carbonate, when treated with cobaltisodium nitrite solution at 50° C. yields guanidinium

¹ N. Caro and others, *J.S.C.I.*, 30, 25.

² *P.C.S.* (1913), 166 ; *T.C.S.*, 150, 1913, 1375.

³ K. A. Hofmann, *Ber.*, 62, 2773-76.

trihydroxotrinitrocobaltate, $[\text{Co}(\text{HO})_3(\text{NO}_2)_3](\text{C}_2\text{H}_5\text{N}_3)_3$, in long red prisms, which are decomposed by water at 80°C . As guanidine can be produced by the action of cyanogen iodide on alcoholic ammonia, so also may guanidine derivatives be obtained by substituting organic ammonias. Thus with cyanogen iodide and alcoholic methylamine s-dimethylguanidine is obtained and in a similar manner the compounds, ethylene-guanidine, propyleneguanidine, etc., may be prepared.¹

Mono and s-dimethylguanidine may be obtained by the action of methyl iodide on guanidine sulphate and potassium hydroxide.² Guanidine reacts with the esters of monobasic acids forming simple acylguanidines;³ thus formylguanidine, $\text{H}_2\text{NC}(:\text{NH})\text{NHCHO}$, may be prepared by adding to ethyl formate, a dilute alcoholic solution of guanidine. It is obtained in crystalline granules; in cold aqueous solution bromine converts it into formylbromoguanidine, $\text{C}_2\text{H}_4\text{ON}_3\text{Br}$. From ethyl acetate in a similar manner acetylguanidine may be obtained.

Aminoguanidine nitrate when diazotized in aqueous solution at 0°C . with sodium nitrite yields aminoguanidine diazohydroxide, $\text{C}_2\text{H}_7\text{N}_{10}\text{OH}$, in colourless crystals which explode when struck, or on heating to 135° to 140°C . The chloride, $\text{C}_2\text{H}_7\text{N}_{10}\text{Cl}$, is obtained in colourless silky needles which explode at 140°C ., and couples slowly with aromatic amines.⁴

If the compound is diazotized in acid solutions, using nitrous vapour carbamideimidazide $\text{H}_2\text{NC}(:\text{NH})\text{N}_3$, is formed;⁵ by the action of strong reducing agents it is converted into tetrazylhydrazine, $\text{H}_2\text{NNHCHN}_4$.

Amidoguanidine diazonitrate reacts with excess of silver nitrate to form $\text{C}_2\text{H}_7\text{N}_{10}\text{OAg} \cdot \text{AgNO}_3 \cdot 3\text{H}_2\text{O}$ in light yellow needles or prisms. It reacts with hydriodic acid to form the compound $\text{C}_2\text{H}_7\text{N}_{10}\text{I}$, in light yellow

¹ M. Schenck, *Arch. Pharm.* (1909), **247**, 490–506.

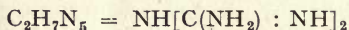
² M. Schenck. ³ W. Traube, *Ber.*, **43**, 3586–90.

⁴ K. Hofmann and R. Roth, *Ber.* (1910), **43**, 682.

⁵ Thiele, *Ann.*, **270**, 46.

explosive needles, and $C_2H_7N_{10}I_4$, in almost black crystals with a dark green lustre.¹

DIGUANIDE (guanylguanidine),



may be prepared by heating an intimate mixture of dicyandiamide and ammonium chloride.² The substitution of ammonium bromide, or better still ammonium iodide is recommended by O. Ostrogovich,³ whereby the yield of diguanide is said to be raised from 21 to 45 per cent.

Finely powdered and dry dicyandiamide and ammonium iodide are intimately mixed and heated to $173^\circ C.$ for five minutes, the cooled product is dissolved in water, filtered and made alkaline with aqueous ammonia and then ammoniacal copper sulphate solution added so long as the rose-coloured precipitate of the copper compound of dicyandiamidine is precipitated. Further addition of the copper solution precipitates a violet compound of the diguanide.

The diguanide may be obtained from the copper derivative, by treatment with dilute sulphuric acid, and the pure base from the latter solution by barium hydroxide. The salt may be purified by crystallization from alcohol in glistening prisms which melt at $130^\circ C.$, but the aqueous solution of the compound decomposes gradually on heating.

The following salts have been described by K. Rackmann.⁴ The carbonate, $C_2H_7N_5H_2CO_3$, crystallizes in prisms sparingly soluble in alcohol; the hydrochloride, $C_2H_7N_5 \cdot 2HCl$, in glistening needles which melt at $248^\circ C.$; the nitrate, $C_2H_7N_5HNO_3$, in large glistening prisms, melting-point $192^\circ C.$; the acetate, $C_2H_7N_5CH_3CO_2H$, melting-point $268^\circ C.$; and the oxalate, $C_2H_7N_5C_2O_4H_2$, melting-point $210^\circ C.$

When the chloride is treated with dextrose in

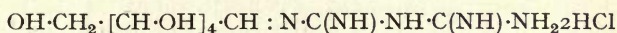
¹ K. Hofmann, *Ann.*, **380**, 131, 47.

² Bamberger and Dieckmann, *Ber.*, **25**, 545.

³ *Chem. Zentr.* (1910), **11**, 1890.

⁴ *Annalen* (1910), **376**, 163.

alcoholic solutions condensation takes place and guanylbisguanidine dextrose :



is obtained in small needles, which yield red needles of cuprobisguanide sulphate with ammoniacal copper sulphate.

By substituting the hydrochloride of aromatic amines for the ammonium salt in the preparation of diguanide, aromatic diguanides may be obtained ; thus aniline hydrochloride and dicyandiamide yield phenyldiguanide, etc., etc.¹

NORMAL AMIDO DICYANIC ACID. This compound is formed when dicyandiamide is heated with barium hydroxide solution, one of the amido group, of the dicyandiamide is replaced by hydroxyl. It may also be formed by the direct combination of potassium cyanate and cyanamide, when a solution of these two bodies is left for some time,² the acid being obtained as its potassium salt.

The acid is monobasic and crystallizes in needles. It is decomposed when its solution is heated alone, or with sulphuric acid by combination with a molecule of water to form biuret :



With ammonium sulphide thiobiuret is produced.³

MELAM. When dry ammonium thiocyanate is heated to 300° C. hydrogen sulphide, carbon disulphide, and ammonia are evolved. If the heating is continued until the evolution of gas ceases, crude melam thiocyanate is formed together with other products. The residue is first washed with hot water, then with a cold dilute solution of potassium hydroxide, and finally dissolved in dilute hydrochloric acid and reprecipitated by potassium hydroxide solution.

It is an insoluble white powder, which evolves

¹ G. Cohn, *J. pr Chem.* (1911) [ii], 84, 394-400 ; *J.C.S.* (1911), i. 928.

² Hallwack, *A.*, 153, 295.

³ Baumann, *Ber.*, 8, 709.

ammonia when heated; when boiled with dilute acids or alkalis it yields ammonia and ammeline, with concentrated nitric acid cyanuric acid is formed. Mellem, $C_6H_6N_{10}$, is a constituent of crude melam formed by heating dry ammonium thiocyanate as described above. It may be separated from the melam by boiling with a 5 per cent. solution of potassium hydroxide for twenty-four hours, when the melam is converted into ammeline, but the mellen is left unacted on.

Mellen is a white odourless insoluble powder, which when boiled with concentrated potash solution is converted into ammeline and ammonia.

AMMELINE is obtained by boiling melam for some time with potassium hydrate solution. It is also formed together with melamine when dicyandiamine is heated with concentrated ammonia solution in sealed tubes for three hours at $120^\circ C$.¹

It is very sparingly soluble in water, alcohol, or ether, and when heated with equal quantities of hydrazine hydrate for five hours under pressure to $130^\circ C$. diaminoammeline is obtained in prisms which melt above $340^\circ C$.²

AMMELIDE (melanurenic acid). Liebig considered ammeline and melanurenic acid as two distinct bodies to which he gave the formulæ,

$C_6N_9H_9O_2 : 3(CNH_2N : CNHO)$ and $C_3N_4H_4O_2(CNH_2N.2CNHO)$ respectively. Gerhardt, however, considered them to be identical, an observation that was afterwards confirmed by Klasson,³ who proved the identity of these bodies.

Ammeline may be prepared by heating melam with concentrated sulphuric acid to $190^\circ C$. for a short time, and pouring the product into a large excess of water, from which the sulphate slowly separates. It may also be formed as the principal product by the

¹ R. Stollé and K. Krauch, *Ber.* (1913), **46**, 2337.

² R. Stollé and K. Krauch, *l.c.*

³ *J. pr Chem.* [2], **33**, 295.

action of fuming sulphuric acid at 190° C. on melamine, $(C_3N_3NH_2)_2(NHNH)_2H_2O$, obtained by the action of hydrazine sulphate on dicyandiamide.¹

It is a white powder, sparingly soluble in cold water, rather more so in hot water.

ISOAMMELINE and **ISOAMMELIDE** are known only as their alkyl derivatives, but have never yet been isolated, nor have any metallic derivatives been formed.

AZULMIC ACID. When cyanogen is passed into aqueous ammonia a dark brown flocculent precipitate rapidly forms together with oxamide and oxamic acid. The formula, $C_4H_5N_5O$, has been given to the compound.

A similar, and probably identical, product is obtained when a little alkaline cyanide (particularly potassium cyanide) is dissolved in an aqueous solution of hydrocyanic acid: the solution turns first yellow, then dark brown, and ultimately deposits dark brown flocks of the compound.

It is more rapidly formed by keeping a solution of calcium cyanide of over 20 per cent. strength for a few days. The cyanide solution is prepared by passing hydrocyanic acid into milk of lime, a solution of 30 per cent. turns brown in a few hours and rapidly deposits the compound together with a basic calcium cyanide.

But little is known of the constitution and properties of the compound. It is converted into an insoluble orange powder by nitric acid. It is soluble in concentrated sulphuric acid, and is very slightly soluble in water, but is soluble in alkalis, the solution exhibiting fluorescence, and is reprecipitated by acids.

When dry distilled ammonia and hydrocyanic acid are given off amongst other products.

Dry gaseous cyanogen and ammonia form a black body called hydrazulmin, which water is said to convert into azulmic acid with liberation of ammonia.

¹ K. Hofmann, etc., *Ber.* (1911), **44**, 2713.