# Synthesis of Guanidine Compounds by the Cyanamide Condensation Method I. Preparation of Ethylenediguanidine and Tetramethylenediguanidine.* ** (Studies on some derivatives of calcium cyanamide. XI.⁽¹⁾)

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## Introduction and Outline of the Research.

In the previous communication, one of the authors⁽²⁾ (K. Sugino) studied the reaction of amine salts with dicyandiamide for guanidine preparation and the mechanism of this reaction was perfectly determined. For ammonium salt, this mechanism was outlined as follows:—

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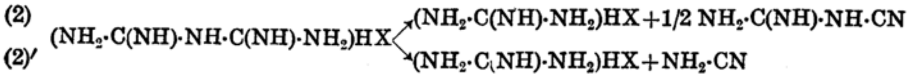
* A part of this report was given in the lecture at the general meeting of the Chemical Society of Japan, held in April, 1941.

** A part of this paper is one (Part II) of the papers of the series "Studies on Raw Materials of Synthetic Fiber". (Part I: *J. Soc. Chem. Ind. Japan*, **44** (1941), 706.)

(1) The earlier papers of this series: I. Y. Kato, K. Sugino and K. Koizumi; *J. Electrochem. Assoc. Japan,* **2** (1934), 187; *Bull. Tokyo Univ. Eng.*, **3** (1934), 684; *Chem. Abst.*, **28** (1934), 7250. II. K. Sugino: *J. Electrochem. Assoc. Japan,* **4** (1936), 396. III. K. Sugino, T. Kobayashi and Y. Shibazaki: *J. Electrochem. Assoc. Japan,* **5** (1937), 390. IV. K. Sugino and M. Ogawa: *J. Electrochem. Assoc. Japan,* **6** (1938), 292; *Chem. Abst.*, **34** (1940), 7704. V. K. Sugino: *J. Chem. Soc. Japan,* **60** (1939), 111; *Bull. Tokyo Univ. Eng.*, **8** (1939), 84; *Chem. Abst.*, **34** (1940), 2795. VI. VII. K. Sugino: *J. Chem. Soc. Japan,* **60** (1939), 267, 351; *Bull. Tokyo Univ. Eng.*, **8** (1939), 99; *Chem. Abst.*, **34** (1940), 2273; **35** (1941), 5097. VIII. K. Sugino: *J. Chem. Soc. Japan,* **60** (1939), 411; *Bull. Tokyo Univ. Eng.*, **8** (1939), 151; *Chem. Abst.*, **35** (1941), 5097. IX. K. Sugino: *J. Chem. Soc. Japan,* **60** (1939), 507; *Bull. Tokyo Univ. Eng.*, **8** (1939), 195; *Chem. Abst.*, **35** (1941), 5098; *Chem. Zentr.*, (1939) II, 2638. X. K. Sugino and M. Kanayama: *J. Electrochem. Assoc. Japan,* **8** (1940), 250.

(2) Report VII of this series: *loc. cit.* (Foot note 1.)

(1) $NH_2\cdot C(NH)\cdot NH\cdot CN + NH_3\cdot HX = (NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX$



$$(NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HX \begin{array}{ll} \nearrow (NH_2\cdot C(NH)\cdot NH_2)HX + 1/2\ NH_2\cdot C(NH)\cdot NH\cdot CN & (2) \\ \searrow (NH_2\cdot C(NH)\cdot NH_2)HX + NH_2\cdot CN & (2)' \end{array}$$

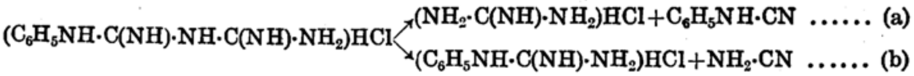
(3) $^1/_2 NH_2\cdot C(NH)\cdot NH\cdot CN + {}^1/_2 NH_3HX = {}^1/_2 (NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)\cdot HX \longrightarrow$ reaction (2)

(3)′ $NH_2\cdot CN + NH_3\cdot HX = (NH_2\cdot C(NH)\cdot NH_2)HX$

The formation of biguanide monosalt, its thermal decomposition into guanidine salt and dicyandiamide or cyanamide and the reaction of latter compounds with parent ammonium salt take place successively and 2 mols of guanidine salt is obtained from 1 mol of dicyandiamide and 2 mols of ammonium salt.

The reaction of aniline hydrochloride with dicyandiamide was also found to take place according to this mechanism. But in this case, two reactions take place in the thermal decomposition of phenylbiguanide hydrochloride(3). It is decomposed to (a) guanidine hydrochloride and phenylcyanamide and to (b) phenylguanidine hydrochloride and cyanamide.

$$NH_2\cdot C(NH)\cdot NH\cdot CN + C_6H_5NH_2\cdot HCl = (C_6H_5NH\ C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HCl$$



$$(C_6H_5NH\cdot C(NH)\cdot NH\cdot C(NH)\cdot NH_2)HCl \begin{array}{ll} \nearrow (NH_2\cdot C(NH)\cdot NH_2)HCl + C_6H_5NH\cdot CN & \ldots\ldots\ (a) \\ \searrow (C_6H_5NH\cdot C(NH)\cdot NH_2)HCl + NH_2\cdot CN & \ldots\ldots\ (b) \end{array}$$

The cyanamides formed in nascent state react again immediately with aniline hydrochloride and the salts of diphenylguanidine and phenylguanidine are formed. (A part of cyanamides reacts together to give the phenyl derivatives of melamine.)

$$C_6H_5NH\cdot CN + C_6H_5NH_2\cdot HCl = (C_6H_5NH\cdot C(NH)\cdot NHC_6H_5)HCl$$

$$NH_2\cdot CN + C_6H_5NH_2\cdot HCl = (C_6H_5NH\cdot C(NH)\cdot NH_2)HCl$$

From these results, it was found that several kinds of guanidines were necessarily formed by the reaction of amine salt with dicyandiamide. Therefore, in order to convert the amine into corresponding simple guanidine, the older cyanamide method must be applied if calcium cyanamide is used as the starting material.

It has been well known that guanidine salt can be obtained by the action of cyanamide with amine salt. General methods of guanidine preparation using cyanmide may be summarized as follows:—

(1) $RNH_2 + NH_2\cdot CN \xrightarrow[\text{cold}]{H_2O} RNH\cdot C(NH)\cdot NH_2$

(2) $RNH_2\cdot HX + NH_2\cdot CN \xrightarrow[\text{boiling or in sealed tube}]{C_2H_5OH} (RNH\cdot C(NH)\cdot NH_2)HX$

But recent guanidine literature indicates the popularity of methylisothiourea sulphate method (3) over the cyanamide condensation method.

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(3) Report VIII of this series: *loc. cit.* (Foot note 1.)

$$RNH_2+(NH_2\cdot C(NH)\cdot SCH_3)1/2\ H_2SO_4 \xrightarrow[\text{hot or cold}]{\substack{H_2O \text{ or} \\ C_2H_5OH}} (NH_2\cdot C(NH)\cdot NHR)1/2\ H_2SO_4+CH_3SH \tag{3}$$

This reason is not clearly known by the authors. But many disadvantages are found in the older cyanamide method. In that process, side reactions are possible in each instance. The three most common side reactions are the polymerisation of cyanamide to dicyandiamide (a), the condensation of this latter compound with the parent amine salt to give a biguanide salt (b) and the hydration of cyanamide to urea (c) (in aqueous solution). These may be outlined as follows:—

(a) $2NH_2\cdot CN = NH_2\cdot C(NH)\cdot NH\cdot CN$

(b) $NH_2\cdot C(NH)\cdot NH\cdot CN+RNH_2\cdot HX = (NH_2\cdot C(NH)\cdot NH\cdot C(NH)\cdot NHR)HX$

(c) $NH_2CN+H_2O = NH_2\cdot CO\cdot NH_2$

Therefore the yield of guanidines is very poor and the separation of guanidine salt from by-products and unchanged amine salt looks very difficult.

The cause of the above side reactions are probably due to the slowness of the rate of condensation for the guanidine salt. And it would appear that this method becomes practical when the rate of condensation absolutely exceeds that of side reactions.

The authors undertook to study this problem using the reactions of cyanamide with diamine salts. And it was found that corresponding diguanidine dihydrochloride was quantitatively obtained when diamine dihydrochloride was fused with the excess of cyanamide. At about 140°C, this reaction was completed for a short time and the probable side reaction was only the polymerisation of excess of cyanamide to dicyandiamide.

The reaction product contained diguanidine dihydrochloride and dicyandiamide. The separation of these two compounds was easily performed when the reaction product was refluxed with acetone. Dicyandiamide was soluble in hot acetone, but diguanidine dihydrochloride was not soluble. By this extraction, almost pure diguanidine dihydrochloride was obtained. If melamine (polymerisation product of 3 mols of cyanamide) existed, it was separated by the recrystallisation of diguanidine salt from alcohol.

From pure diguanidine dihydrochloride thus obtained, various salts of diguanidine were prepared and the properties of these compounds were compared with that cited in the literature.

Free alkylene diguanidines are not obtainable and not described in the literature. These compounds were also prepared by the action of metallic sodium with diguanidine dihydrochloride suspended in absolute alcohol and by evaporating the resulting alcoholic solution to almost dryness under the reduced pressure at low temperature. Beautiful crystals of alkylene diguanidine could be obtained when the concentrated alcoholic solution of diguanidine was mixed with a large amount of acetone and the resulting turbid mixture was allowed to stand for a long time. From the free alkylene diguanidine, many salts were also prepared.

**Literature.** About the synthesis of these diguanidine salts, only two literatures have as yet been published. Schenck⁽⁴⁾ prepared ethylenediguanidine dihydroiodide in alcoholic solution at room temperature from ethylenediamine hydrate and methylisothiourea hydroiodide and many salts of ethylenediguanidine were also derived from the dihydroiodide. Tetramethylenediguanidine salts were prepared by Kiesel⁽⁵⁾ by the reaction of cyanamide with tetramethylenediamine in aqueous solution at room temperature. (34% of the diamine could be converted to diguanidine and agmatine.) Tetramethylenediguanidine was also found by Kutscher, Ackermann u. Flössner⁽⁶⁾ in the muscle of Arca Noae and was named as Arcain.

**Experimental materials.** 1. *Ethylenediamine.* Commercial sample (Ethylenediamine hydrate) was used without purification. Its picrate melted at 230°C. From this, the hydrochloride was prepared. (Found Cl, 53.3. Calculated for $C_2H_8N_2 \cdot 2HCl$: Cl, 53.3%.)

2. *Tetramethylenediamine* (*Putrescine*). Tetramethylenediamine was prepared from ethyl alcohol by the following procedure.

Ethylene, made by passing the vapour of ethyl alcohol over Japanese acid clay at 380–390°C, was absorbed in bromine and the resulting ethylene dibromide (Yield: 90%) in alcoholic solution was refluxed with a slight excess of saturated aqueous solution of potassium cyanide according to the direction of Fauconnier⁽⁷⁾. Ethylene dinitrile (M.p. 53–54°C, B.p. 158–159°C/19 mm, 124°C/5 mm, yield: 52%) was obtained by distilling the reaction product under the reduced pressure. This was dissolved in absolute alcohol saturated with dry $NH_3$ gas and was reduced by metallic sodium. (The temperature was maintained below 20°C.) The reduction product was neutralized by conc. HCl and after removal of insoluble substances (NaCl, $NH_4Cl$ etc.), the filtrate was evaporated to dryness to give the crude tetramethylenediamine dihydrochloride. For separation of ammonia from tetramethylenediamine, the crude diamine salt was converted to free diamine by the fractional distillation of the former compound with NaOH. Free tetramethylenediamine distilled was again neutralised by conc. HCl and evaporated to dryness. The residue was recrystallised from 85% alcohol. M.p. 317°C. (Found Cl. 43.8; N, 17.7. Calculated for $C_4H_{12}N_2 \cdot 2HCl$: Cl, 44.0; N, 17.4%.)

3. *Cyanamide.* Cyanamide was prepared from commercial calcium cyanamide according to the direction of one of the authors (K. Sugino) and M. Kanayama⁽⁸⁾ which was described in the previous paper. M.p. 44°C.

**Reaction of cyanamide with alkylenediamine dihydrochloride.** 1/100 mol of ethylenediamine- or tetramethylenediamine dihydrochloride (1.33 g, 1.61 g respectively) was thoroughly mixed with 2/100 mols (0.84 g, equimolecular amount) or 3/100 mols (1.26 g) of cyanamide and

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(4) *Z. physiol. Chem.*, **155** (1926), 306.
(5) *ibid.*, **118** (1921), 277.
(6) ibid., **199** (1931), 273.
(7) Bull. soc. chim., [2], **50** (1888), 214.
(8) Report X of this series: *loc. cit.* (Foot note 1.)

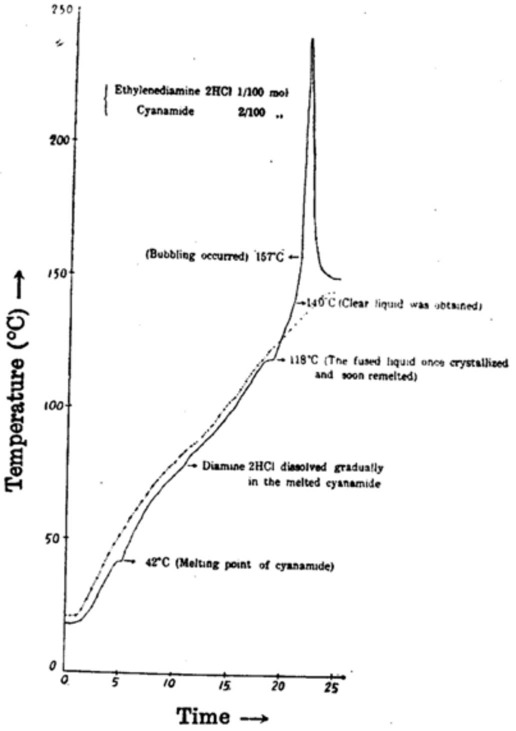

Fig. 1.

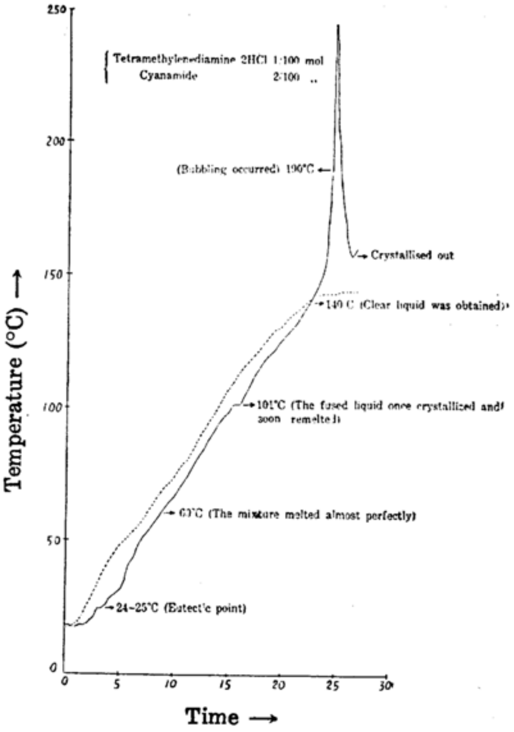

Fig. 2.

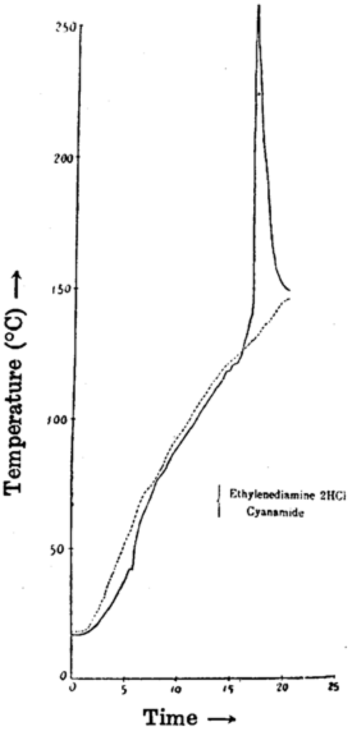

Fig. 3.

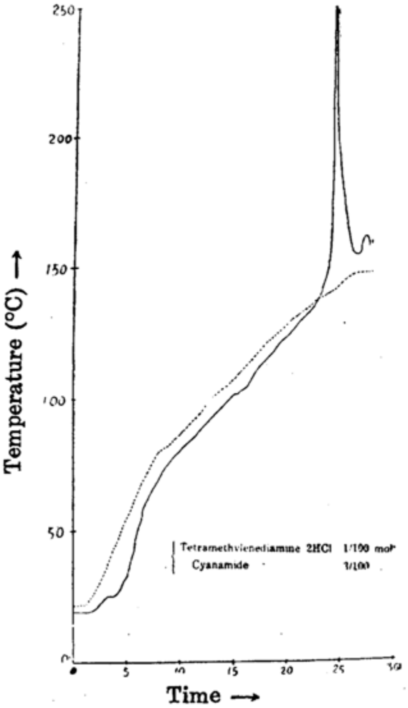

Fig. 4.

the mixture was heated in an oil-bath under fused state. The detail of the reactions was shown in the heating curves. (Fig. 1, 2, 3 and 4).

The evolution of heat due to the increase of the rate of condensation began at 135°C (ethylene-) and 155°C (tetramethylene) respectively and the temperature of the mixture reached about 240°C even if as small an amount of sample as 1/100 mol was used. This rise of the temperature induced the decomposition of diguanidine salts. In the case of ethylenediamine dihydrochloride, ethylenediguanidine dihydrochloride was obtained with a fair yield even at a high temperature. But in the case of putrescine dihydrochloride, the properties of the reaction product according to the heating curve (Fig. 2 or 4) was not identified with that of tetramethylenediguanidine dihydrochloride. So, for obtaining the alkylenediguanidine salt in pure state, it is essential that the temperature of the reaction is seriously regulated not to rise above 150°C at the highest. The influence of the reaction temperature and of the quantity of cyanamide on the yield of diguanidine was shown in Table 1.

Analytical method: Total reaction product (from 1/100 mol of diamine 2HCl and 2/100–3/100 mols of cyanamide) was dissolved in distilled water and the solution was made up to 250 c.c.. 50 c.c. of the aliquot portion was transferred to a beaker and about 150 c.c. of the saturated solution (20°C) of ammonium picrate and a few drops of conc. $NH_4OH$ ($NH_4OH$ dissolved the dipicrate of diamines) were added to it with constant stirring. (In the case of tetramethylenediguanidine, conc. $NH_4OH$ was previously added to the ammonium picrate solution.) The precipitate was filtered off by suction with a gooch crucible of known weight and dried for 2–3 hrs. at 110°C and finally weighed as diguanidine dipictrate. The filtrate should be tested by adding more ammonium picrate solution. The solubility of ethylenediguanidine dipicrate in saturated ammonium picrate solution was found to be 0.0144 g./100 c.c. at 25°C.

Table 1.

| Quantity of samples (mol) | | Condition of the reaction | Yield of Diguanidine (%) | |
|---|---|---|---|---|
| Diamine 2HCl | Cyanamide | | Ethylene | Tetramethylene |
| 1/100 | 2/100 | Fig. 1 & 2 | 71 | 77* |
| 1/100 | 2/100 | 140∼150°C, 30 mins | 80 | — |
| 1/100 | 3/100 | Fig. 3 & 4 | 87 | 91* |
| 1/100 | 3/100 | 140∼150°C, 30 mins | 103 | 95 |

* In these cases, pure tetramethylenediguanidine could not be obtained as above mentioned. Therefore these data were calculated from the quantity of dipicrate which was assumed to be pure tetramethylenediguanidine dipicrate.

In the case of tetramethylenediamine dihydrochloride, agmatine (aminotetramethyleneguanidine) salt was not found in the reaction product even if 1 mol of cyanamide was used for 1 mol of diamine salt.

From these results, it is demonstrated that for converting the alkylenediamine dihydrochloride perfectly to corresponding diguanidine dihydrochloride, it is most favorable for 1 mol of diamine dihydrochloride, to be fused with 3 mols (1.5 times of equivalent amount) of cyanamide and the temperature of the reaction mixture cautiously maintained at about 140°C for less than 30 mins. This reaction is an exothermic one as above mentioned, so the regulation of the temperature is quite difficult if a large amount of sample is used practically. But for small scale experiment, this is performed by a simple cooling.* In the case of large scale experiment, it is favorable that a small amount of water is previously used in the mixture of samples (or a small amount of water is added into the fused mass (140°C) from time to time) or an extremely concentrated aqueous solution of diamine dihydrochloride (1 mol) and cyanamide (3 mol) is heated in an autoclave at 140°C for 30–60 mins.

Ethylenediguanidine dinitrate and dihydroiodide were also prepared by fusion of 1/100 mol of ethylenediamine dinitrate and dihydroiodide with 3/100 mols of cyanamide according to the heating curves of Fig. 5 and 6. The yields of diguanidines were 60% and 70% of the theory respectively. The decomposition of the dinitrate at higher temperature was more rapid than that of the dihydrochloride. At 135–145°C, the yield of the dinitrate reached to 84% of the theory.

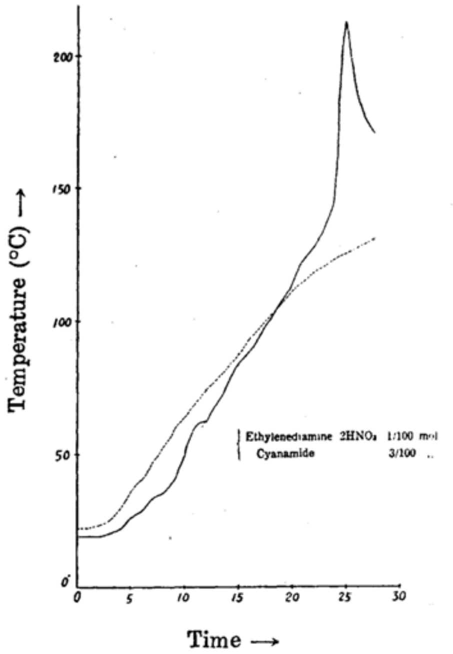

Fig. 5.

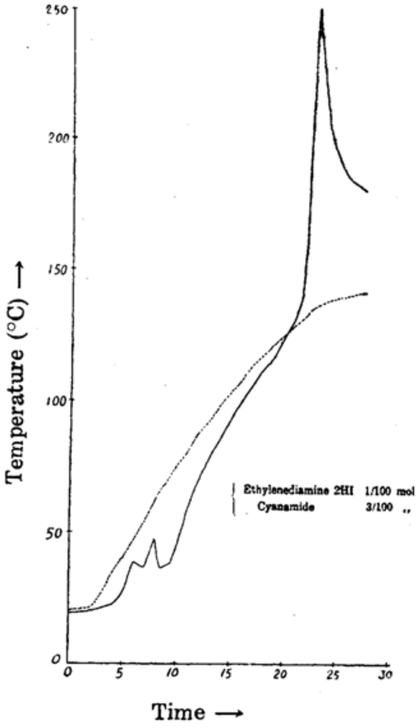

Fig. 6.

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* The method of cooling in these experiments was as follows:—The reaction mixture was first heated according to the heating curves (Fig. 1 and 2) and when the temperature of the reaction reached 140°–150°C, the reaction vessel was taken away quickly from the oil bath. The temperature continued to rise by the heat of reaction, so the vessel was cooled by air or water. And when the temperature was depressed below 140°C by cooling, the vessel was again heated in the oil bath. These methods were repeated several times and after the evolution of heat ceased, the vessel was heated at about 140°C for a time.

**Isolation of pure diguanidine dihydrochloride from the reaction product.** By the above method, ethylenediamine- or tetramethylenediamine dihydrochloride could be converted perfectly to the corresponding diguanidine dihydrochloride. The possible impurities may be dicyandiamide and melamine due to the polymerisation of excess of cyanamide. For removal of dicyandiamide, the fused mass was pulverised by rubbing with a glass rod in a small portion of absolute alcohol and the powdered reaction product was refluxed with acetone for about 3 hrs. (100 c.c. of acetone was used for 5 g. of the crude diguanidine 2HCl.) Almost pure diguanidine dihydrochloride was obtained by a single extraction with acetone. Melamine probably does not exist when the reaction takes place at about 140°C, but if it exists, it is separated by the recrystallisation of the residue of acetone extract from alcohol. The properties and analytical results of pure alkylenediguanidine dihydrochloride were as follows:— Ethylenediguanidine dihydrochloride. M.p. 225°C. M.p. of its dipicrate 284°C. (Found Cl, 31.6; N, 39.6; $C_4H_{12}N_6$ (ethylenediguanidine, determined as dipicrate), 67.6. Calculated for $C_4H_{12}N_6 \cdot 2HCl$: Cl, 32.7; N, 38.7; $C_4H_{12}N_6$, 66.4%.)

Tetramethylenediguanidine dihydrochloride.

(1) Residue of acetone extraction. M.p. 228°C. M.p. of its dipicrate 253°C. (Found N, 34.8; $C_6H_{16}N_6$ (determined as dipicrate), 70.7. Calculated for $C_6H_{16}N_6 \cdot 2HCl$: N, 34.3; $C_6H_{16}N_6$, 70.2%.)

(2) 1 g. of sample (1) was refluxed with 20 c.c. of absolute alcohol. Soluble part (0.25 g.): M.p. 227–228°C. (Found N, 34.1. Calculated for $C_6H_{16}N_6 \cdot 2HCl$: 34.3%.) Insoluble part (0.70 g.): M.p. 233–234°C. (Found N, 35.0. Calculated for $C_6H_{16}N_6 \cdot 2HCl$: 34.3%.)

Ethylenediguanidine dinitrate was also purified by this method but not the dihydroiodide. For the salts of diguanidines which dissolve in acetone, this method cannot be applied.

**Free alkylenediguanidines.** Free alkylenediguanidines could be obtained in crystal form. The procedure was as follows:

In an alcoholic suspension of pulverised diguanidine dihydrochloride, a slightly less amount of clean sodium cuttings was added piece by piece with frequent shaking. (For example, 2.17 g. of ethylenediguandine dihydrochloride (2.45 g. of tetramethylenediguanidine dihydrochloride) was suspended in 30–50 c.c. of absolute alcohol and 0.45–0.46 g. of metallic sodium was added.) After removal of the precipitate, the solution was evaporated under the reduced pressure at low temperature to a syrupy mass which was allowed to crystallise in a vacuum desicator. In order to prepare a pure and beautiful crystal, absolute acetone was added to the concentrated solution until white turbidity occurred and was allowed to stand for 2 or 3 days. A beautiful and large crystal of ethylene- and tetramethylenediguanidine could be obtained.

Ethylenediguanidine. M.p. 163°C. M.p. of its dipicrate 285.5°C. (Found N, 59.1. Calculated for $C_4H_{12}N_6$: N, 58.3%.)

Tetramethylenediguanidine. M.p. 172°C. M.p. of its dipicrate 253°C. (Found N, 48.3. Calculated for $C_6H_{16}N_6$: N, 48.8%.)

**Preparation of various salts of ethylenediguanidine and tetramethylenediguanidine.** 1. *From the dihydrochloride* the dinitrate was prepared by the addition of the theoretical amount of $AgNO_3$ to the solution of dihydrochloride. The dipicrate was precipitated from an aqueous solution of the dihydrochloride. The chloroplatinate and dichloroaurate were also precipitated from the dihydrochloride in aqueous solution. The melting point and other properties are shown in table 2.

Table 2.

1. Salts of ethylenediguanidine

| Salts | M.p. (°C) | M.p. (given by Schenck) (°C) | Crystal form (under microscope) |
|---|---|---|---|
| $C_4H_{12}N_6 \cdot 2HCl$ ........ | 225 | | Aggregate of small cubic crystal |
| $C_4H_{12}N_6 \cdot 2$ picrate ..... | 287* | 284–285* | Long needlelike prism (brownish yellow) |
| $C_4H_{12}N_6 \cdot 2HNO_3$ ....... | 252 | 252 | Thin plate |
| $C_4H_{12}N_6 \cdot H_2PtCl_6$ ...... | 253 | 255–258 | Small granules (orange yellow) |
| $C_4H_{12}N_6 \cdot 2HAuCl_4$ ..... | 255 | 258 | Large plate (golden yellow) |

* Schenck reported that this dipicrate decomposed without melting. But the dipicrate obtained by the authors melts at this temperature.

2. Salts of tetramethylenediguanidine

| Salts | M.p. (°C) | M.p. (given by Kiesel) (°C) | Crystal form (under microscope) |
|---|---|---|---|
| $C_6H_{16}N_6 \cdot 2HCl$ ...... | 228, 234 | | Aggregate of small plate-shaped crystals |
| $C_6H_{16}N_6 \cdot 2$picrate .... | 253 | 253–254 | Long needle (brownish yellow) |
| $C_6H_{16}N_6 \cdot 2HNO_3$ ..... | 242 | · | Plate |
| $C_6H_{16}N_6 \cdot H_2PtCl_6$ .... | 224 | 224 | Small platelike granule (deep yellow) |
| $C_6H_{16}N_6 \cdot 2HAuCl_4$ ... | 173 | 173 | Small needlelike granule (light yellow) |

2. *From free diguanidine* the carbonate was precipitated by passing $CO_2$ saturated with water vapour in the absolute alcoholic solution of diguanidine. The carbonate was converted to the sulphate by the addition of dil. $H_2SO_4$. The dihydroiodide, adipate and sebacate were also prepared from the absolute alcoholic solution of diguanidine by the addition of HI and the alcoholic solution of adipic acid or sebacic acid. The melting point and other properties are described in table 3.

Polymerisation of ethylene- and tetramethylenediguanidine adipate or sebacate.

Table 3.

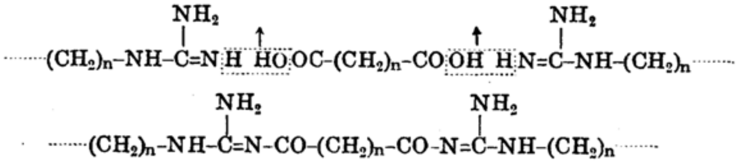
1. Salts of ethylenediguanidine

| Salts | M.p. (°C) | M.p. (given by Schenck) (°C) | Crystal form (under microscope |
|---|---|---|---|
| $C_4H_{12}N_6 \cdot H_2CO_3$ ...... | 193 | | Long needle |
| $C_4H_{12}N_6 \cdot H_2SO_4$ ...... | 278 | | Plate |
| $C_4H_{12}N_6 \cdot 2HI$ ....... | 216 | 218–220 | Large plate |
| $C_4H_{12}N_6 \cdot$adipate .... | 263 | | Small granules |
| $C_4H_{12}N_6 \cdot$sebacate .... | 217 | | Small granules |

2. Salts of tetramethylenediguanidine

| Salts | M.p. (°C) | M.p. (given by Kiesel) (°C) | Crystal form (under microscope) |
|---|---|---|---|
| $C_6H_{16}N_6 \cdot H_2CO_3$ ........ | 202 | | Aggregate of small needlelike crystals |
| $C_6H_{16}N_6 \cdot H_2SO_4$ ........ | 297 | 291 | Spheric aggregate of small needle-shaped crystals |
| $C_6H_{16}N_6 \cdot 2HI$ .......... | 199.5 | | Large plate |
| $C_6H_{16}N_6$·adipate ...... | 274 | | Fine blanching needle |
| $C_6H_{16}N_6$·sebacate ...... | 227 | | Small granules |

Further, it was tested whether these diguanidine-dicarboxylic acid salts are able to form a fiber-forming polymer just as diamine-dicarboxylic acid salts by removal of the water formed in the reaction or not.



$$\cdots(CH_2)_n-NH-\overset{\overset{NH_2}{|}}{C}=N\boxed{H\ \overset{\uparrow}{HO}}OC-(CH_2)_n-CO\boxed{\overset{\uparrow}{OH}\ H}N=\overset{\overset{NH_2}{|}}{C}-NH-(CH_2)_n\cdots$$

$$\cdots(CH_2)_n-NH-\overset{\overset{NH_2}{|}}{C}=N-CO-(CH_2)_n-CO-N=\overset{\overset{NH_2}{|}}{C}-NH-(CH_2)_n\cdots$$

And it was found that this dehydration was difficult and imperfect compared with the case of diamine-dicarboxylic acid salts under same conditions and the thermal decomposition of diguanidine salt (into diamine salt and other comps.) occurred. (Heating in the absence of a solvent or diluent (fusion method) to reaction temperature (180–250°C) under the extremely reduced pressure (1 mm) or $H_2$. $N_2$ atmosphere.)

The cause of this difficulty is probably due to the existence of the double bonds between carbon and salt-forming nitrogen in guanidine groups. According to preliminary experiments, the resulting polymers had fiber-forming property, but were somewhat soluble in hot water. (Ethylenediguanidine sebacate gave a polymer which was almost insoluble in water). These experiments are now being continued.

## Summary.

(1) Ethylenediguanidine- and tetramethylenediguanidine dihydrochloride were prepared by the reaction of 3 mols of cyanamide with 1 mol of corresponding diamine dihydrochloride in fused state at about 140°C. The yield was about 100% of the theory.

(2) The dihydrochlorides were purified by the extraction with acetone which dissolved dicyandiamide.

(3) The method for preparing free diguanidines in crystal form is described.

(4) Various salts of these diguanidines were prepared from dihydrochlorides and free diguanidines and the melting point and other properties of these salts are also described.

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