rection of decreasing field, resulting in $\delta = -0.06$ and $\delta = -0.28$ for the protons of the alpha and beta carbon atoms.

The proton magnetic resonance spectrum of pure tetrahydropyran contains two peaks of intensity ratio 2:3 at $\delta = -0.15$ and $\delta = -0.35$, the first being attributed to protons of the alpha methylenes and the second to protons of the beta and gamma methylenes.[23] Again, the spectrum of the tetrahydropyran:boron trifluoride shows two peaks similar in appearance to those of the pure ether but shifted in the direction of decreasing field, and they now appear at $\delta = -0.07$ and $\delta = -0.32$.

It is clear, shown also by Diehl and Ogg,[24] that the shifts which arise from coördination can be appreciable. Coördination affects the total electronic structure of the base, making the protons of the complexed ether less shielded or more protonic than those of the uncomplexed ether. The effect of chloroform in this respect is very small,[25] which is to be expected because of the weakness of the hydrogen bond. However, in the case of the stronger binding with boron trifluoride, the protonic character of the hydrogens of the ether is markedly increased, especially for those attached to the alpha carbon atoms. The formation of the dative bond between the oxygen atom of the ether and the boron atom of the boron trifluoride results in some shift of charge in the bonds adjacent to the oxygen atom. This in turn produces a shift in the electrons binding the alpha hydrogen atom and results in the observed increase in protonic character. Apparently, the effect falls off rapidly for atoms more removed from the oxygen. The magnitude of the effect on the alpha hydrogen upon complex formation with boron trifluoride is the same for the 5- and the 6-membered rings within experimental sensitivity.

Additional evidence for the effect of complexation upon the electronic structure of the boron trifluoride addition compound comes from studies[26,27] of the fluorine magnetic resonance in liquid boron trifluoride ($\delta = 4.6$) compared with that in the boron trifluoride diethyl etherate ($\delta = 1.4$ to 2.5), where the shifts are referred to the fluorine resonance in BeF_2 as zero. The direction of the shift shows that complexation with the ether markedly increases the shielding of the fluorine atoms.

Acknowledgment.—This research was supported in part by a grant from the Petroleum Research Fund administered by the American Chemical Society. Grateful acknowledgment is hereby made to the donors of this fund. D.E.M. wishes to express his appreciation to the Horace H. Rackham School of Graduate Studies of The University of Michigan for a University Fellowship. A separate grant from the Horace H. Rackham School made possible preliminary work on these addition compounds. We also wish to thank Mrs. Lila M. Hall and Mr. LeRoy Johnson, the latter of Varian Associates, for obtaining the NMR spectra.

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[24] P. Diehl and R. A. Ogg, *Nature*, **180**, 1114 (1957).

[25] The shift of 0.02 units in the δ-values is at the limit of the sum of the estimated experimental errors for the technique used. However, the shift seems real and may be due due in part to solvent effects other than that of hydrogen bonding. Mr. LeRoy Johnson, of Varian Associates, obtained the following results using an audio-oscillator to match peak heights with tetramethylsilane as an internal standard (on the V-4300C High Resolution NMR Spectrometer):

System	δ-Value for CH_2's (relative to H_2O)	
Tetrahydrofuran (35.6 mole % in CCl_4)	$\alpha = 0.123$	$\beta = 0.305$
Tetrahydrofuran (34.7 mole % in $CHCl_3$)	$\alpha = .112$	$\beta = .300$
Tetrahydropyran (37.1 mole % in CCl_4)	$\alpha = .135$	$\beta + \gamma = 0.330$
Tetrahydropyran (36.9 mole % in $CHCl_3$)	$\alpha = .125$	$\beta + \gamma = .325$

These samples had been run previously in this Laboratory, and the results were in excellent agreement with the more precise data of Mr. Johnson.

[26] H. S. Gutowsky and C. J. Hoffman, *Phys. Rev.*, **80**, 110 (1950).

[27] W. C. Dickinson, *ibid.*, **81**, 717 (1951).

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Coördination of Polymeric Organosilyl Amines. I. Reactions with Copper(II) Ion

BY RONN MINNÉ AND EUGENE G. ROCHOW

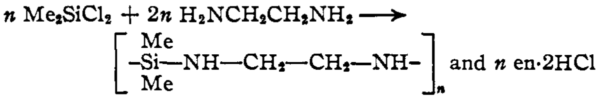
RECEIVED MARCH 12, 1960

Anhydrous ethylenediamine reacts with dimethyldichlorosilane in xylene to form a linear polymeric silylamine of the composition $(CH_3)_2SiNHCH_2CH_2NH$. Reaction of this with anhydrous $CuCl_2$ brings about rapid rearrangement to form a polymeric silazane and eliminate half of the ethylenediamine as Cu^{++} complex. Subsequent treatment of the silazane with excess $CuCl_2$ results in reversible coördination, with cross-linking. Copper-free silazane polymer hydrolyzes only $^1/_3$ as fast as the original silylamine, probably through decreased donor activity because of greater involvement of the nitrogen electron-pairs with silicon.

Numerous organosilicon compounds containing silicon–nitrogen bonds have been prepared, principally through the reaction of organochlorosilanes with ammonia or amines. In general, such compounds are thermally quite stable but hydrolyze at varying rates to form the corresponding siloxane and regenerate ammonia or the amine. Such behavior implies variable donor properties on the part of nitrogen linked to silicon in the different structures; for example, trisilylamine appears to have no donor tendency at all.[1] The purpose of the present series of investigations is to determine whether the nitrogen atoms in *polymeric* organosilazanes and organosilylamines retain any donor properties toward metal ions, and, if so, whether coördination to such metal ions affects the structure or the properties of such polymers.

[1] S. Sujishi and S. Witz, THIS JOURNAL, **79**, 2447 (1957).

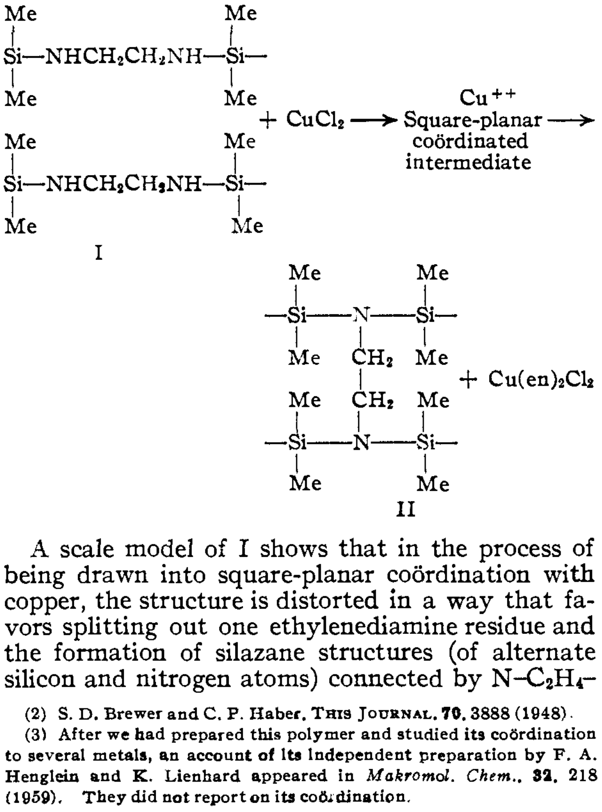
It is known that dimethylsilazane, $[(CH_3)_2SiNH]_n$, has much more tendency to form rings (especially where $n = 3$ or 4) than the corresponding siloxanes.[2] Such cyclic structures have not been excluded from our study, but it is obvious that cyclization imposes handicaps (steric and otherwise) on possible coördination. For this reason we have sought to prepare *linear* polymers containing Si–N bonds. We have found that a very useful and interesting reagent for coördination studies may be obtained from the reaction of dimethyldichlorosilane with ethylenediamine in xylene.[3] The polymer normally was used in xylene



$$n\ Me_2SiCl_2 + 2n\ H_2NCH_2CH_2NH_2 \longrightarrow \left[\begin{array}{c} Me \\ -Si-NH-CH_2-CH_2-NH- \\ Me \end{array}\right]_n \text{ and } n\ en{\cdot}2HCl$$

solution, but to obtain the yield and molecular weight, an aliquot was freed of solvent under reduced pressure, leaving a nearly colorless oil.

The silylamine polymer in xylene solution, when refluxed with copper (II) chloride under nitrogen, undergoes a rearrangement to give a ladder-type structure. During the rearrangement, ethylenediamine is split out. It is postulated that the nitrogen atoms in the linear polymer coördinate to copper ions to form a square-planar intermediate in which each copper ion acts as a bridge between two chains. Ethylenediamine is then split out to form a ladder-type structure in which the silicon-nitrogen ratio is now 1:1 instead of 1:2 as it was in the linear polymer. A substantial portion of the ethylenediamine is recovered as the copper complex, and the remainder must remain in xylene solution



A scale model of I shows that in the process of being drawn into square-planar coördination with copper, the structure is distorted in a way that favors splitting out one ethylenediamine residue and the formation of silazane structures (of alternate silicon and nitrogen atoms) connected by $N-C_2H_4-N$ links. There then is competition between the liberated ethylenediamine and the rearranged polymer for the copper ions, and the ethylenediamine proves itself the better donor by appearing as the copper complex. The ability of the resulting silazane chain to take up additional copper ions has been demonstrated, and the new polymer-held copper has in turn been removed (without affecting the polymer structure) by treatment with fresh ethylenediamine.

Three products actually are isolated from the reaction of I with anhydrous copper(II) chloride: a xylene-soluble fraction, a xylene-insoluble fraction which will be designated as III and a dark-brown residue. The xylene-soluble fraction contains the ladder-type polymer (II), which is isolated by evaporating the xylene at reduced pressure. This substance is a firm, waxy material, in contrast to the mobile oil that was the linear polymer (I). It contains no copper. The xylene-insoluble fraction III is a bluish jelly which is a cross-linked polymer of higher molecular weight. It contains 1.9% of coördinated copper by weight, and the increase in molecular weight may be due to cross-linking of the chains by copper. This material forms a powder, bluish-white in color, when the xylene is washed out with petroleum ether. When the powder is replaced in xylene, it swells to give back the gelatinous material III. The powder melts at 240° to a yellowish liquid which hardens to a solid resinous material. These facts are consistent with the view that the xylene-insoluble gel is a swelled polymer, probably cross-linked by the copper. The brown solid contains all of the copper dichloride except the small fraction that was coordinated in polymer III, principally as ethylenediamine complex.

Since the framework of the polymer was changed from a -Si-N-C-C-N-Si- sequence to a -Si-N-Si- sequence by reaction with copper chloride, it might be expected that the product would be a less active donor to hydrogen ion and hence would hydrolyze less readily. Such behavior would be in keeping with that of trisilylamine and would be in accordance with the amply-demonstrated $d\pi-p\pi$ bonding between silicon and nitrogen or oxygen.[4] In very simple terms, any involvement of the extra electron pair of nitrogen in the d orbitals of silicon decreases its availability for coördination and in proportion to the degree of involvement. The change from one silicon link to two, therefore, should carry with it a significant change of properties.

To put these ideas to test, relative rates of hydrolysis were determined in a homogeneous medium consisting of ethyl ether to which a known amount of water and acetic acid had been added.[5] Samples were withdrawn at 20-minute intervals, the reaction stopped by adding a large excess of methanol and the remaining water titrated with Karl Fisher re-

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(2) S. D. Brewer and C. P. Haber, THIS JOURNAL, **70**, 3888 (1948).

(3) After we had prepared this polymer and studied its coördination to several metals, an account of its independent preparation by F. A. Henglein and K. Lienhard appeared in *Makromol. Chem.*, **32**, 218 (1959). They did not report on its coördination.

(4) (a) D. P. Craig, A. Maccoll, R. S. Nyholm, L. E. Orgel and L. E. Sutton, *J. Chem. Soc.*, 332 (1954). (b) F. G. A. Stone and D. Seyforth, *J. Inorg. & Nuclear Chem.*, **1**, 112 (1955).

(5) Since the polymers are insoluble in water and not wet by it, dependable rate studies could only be made in a solvent which had some water tolerance. Contrary to the behavior of most compounds containing Si–N links,[2] the present substances were hydrolyzed very slowly by water alone, even in the homogeneous system. Acetic acid was added to speed up the reaction.

agent.[6] The amount of water consumed in the reaction, obtained by difference, was compared with the amount theoretically required for the polymer of known weight and composition, and the half-reaction time was determined. The relative rates of hydrolysis of the original linear polymer I and the cross-linked polymer II are shown in Fig. 1. From the half-reaction times, polymer I consumed water three times as fast as polymer II. The xylene-insoluble, copper-containing polymer III was not soluble in ether, so its comparable rate of hydrolysis could not be determined. However, it was observed during the wet oxidations for the determination of silicon that although both polymers I and II reacted violently with concentrated nitric acid, the solid polymer III hydrolyzed quietly.

Experimental

Reagents.—Eastman 95–100% ethylenediamine was dried over KOH and distilled from molten sodium. Merck reagent-grade xylene was distilled from calcium hydride. Dimethyldichlorosilane was used as supplied by General Electric Company. Anhydrous copper chloride was prepared by treating $CuCl_2 \cdot 2H_2O$ with thionyl chloride.[7] Analytical grade pyridine, absolute methanol and iodine were found to be satisfactory for the preparation of Karl Fisher reagent. Sulfur dioxide was bubbled through sulfuric acid scrubber before being liquefied.

Preparation of the Polymer I.—A 1-liter, 3-neck flask equipped with a dropping funnel, Tru-Bore stirrer, and reflux condenser was purged with dry nitrogen. Anhydrous ethylenediamine, 115 g. (1.88 moles), was placed in the flask and diluted with 400 ml. of xylene. Dimethyl dichlorosilane, 121.5 g. (0.94 mole), was diluted with 150 ml. of xylene and placed in the dropping funnel. The chlorosilane was added, with stirring, over a 45-minute period. An ice-bath was used to keep the temperature between 45–50°. After all the chlorosilane had been added, stirring was continued until the temperature started to drop. By means of a heating mantle the flask was warmed gradually to the reflux temperature of xylene. At about 85° the fine white suspension of amine hydrochloride began to congeal to a yellow mass. By the time the boiling point of xylene had been reached the supernatant liquid was a clear, pale yellow. Refluxing was continued for 30 minutes and the contents then allowed to cool under nitrogen.

The solid material was separated by suction filtration through a medium glass frit, and the flask was rinsed with two 75 ml. portions of fresh xylene which were poured over the solid material and added to the filtrate. About 250 ml. of xylene was removed from the filtrate at 35 mm. to remove any trace of excess reactants. The remaining solution was made up to 500.0 ml. with fresh xylene. A 15.00 ml. aliquot of this solution was freed of xylene at reduced pressure. This gave 2.517 g. of polymer (I) as an almost colorless heavy oil. The total yield of polymer was 76.5% of theoretical. The molecular weight in cyclohexane was found to be 1940.

Anal. Calcd. for $C_4H_{12}SiN_2$: C, 41.32; H, 10.41; Si, 24.40; N, 24.10; Si:N ratio = 2.00. Found: C, 41.38; H, 10.19; Si, 24.04; N, 24.26; Si:N ratio = 2.02.

The solid material recovered from the preparation weighed 146.9 g.; theory for amine hydrochloride was 125.1 g. A portion of the solid (54.5 g.) was placed in a Soxhlet extractor and extracted with a 50-50 mixture of benzene and methyl ethyl ketone. The loss in weight of the solid was 6.9 g. The remaining material was analyzed for chlorine.

Anal. Calcd. for $C_2H_8N_2Cl_2$ Cl,: 53.4. Found: Cl, 53.2.

Evidently some polymeric material of high molecular weight remained behind with the amine hydrochloride during the first filtration but was removed by extraction.

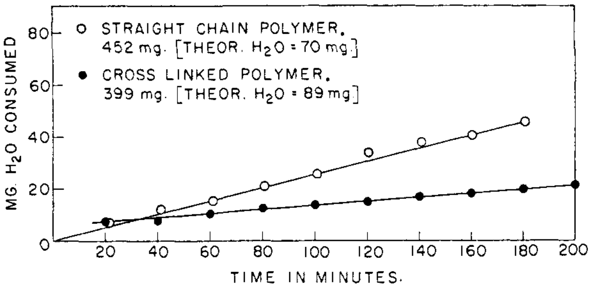

Fig. 1.

Reactions between Anhydrous Copper Chloride and the Straight-line Polymer.—One hundred and fifty ml. of the xylene solution (containing 22.65 g. of polymer) was transfered to a round-bottom flask containing 1.215 g. of anhydrous $CuCl_2$. The flask was fitted with a reflux condenser, the system purged with dry nitrogen, and refluxing continued for 5 hr. During this time the solution became a deeper yellow in color, and the $CuCl_2$ turned dark brown. After cooling, there were three distinct layers, an upper tan layer, an intermediate greenish layer and the brown $CuCl_2$ residue at the bottom.

The upper layers were decanted off the brown solid, which was then washed with xylene and petroleum ether and dried (weight, 2.20 g.). The upper layers were separated in a centrifuge, the green layer forming about 1 inch of blue gelatinous material in the bottom of the centrifuge bottle. The upper layer, yellow in color, was decanted off the gelatinous material, filtered through a medium glass frit, the volume measured and an aliquot freed of xylene to determine the yield of cross-linked polymer II (yield 15.10 g.).

Anal. Calcd. for C_3H_8SiN: C, 41.80; H, 9.36; Si, 32.59; N, 16.25; Si:N ratio = 1.00. Found: C, 42.5; H, 8.8; Si, 30.5; N, 15.8; Si:N ratio = 1.04.

The blue gelatinous material was washed with fresh xylene and petroleum ether. On adding the petroleum ether there was a considerable decrease in bulk. The solvents were evaporated under vacuum, yielding 1.05 g. of III. The combined yield of II and III was 16.15 g. (theory for ladder-type polymer 16.80 g.).

Anal. Calcd. for C_3H_8SiN: C, 41.80; H, 9.36; Si, 32.59; N, 16.25; Si:N ratio = 1.00. Found: C, 40.1; H, 9.0; Si, 31.5; N, 16.0; plus Cu 1.9 and Cl 1.1; Si:N ratio = 1.02.

The brown solid residue from the $CuCl_2$ reaction contained 19.9% C, 5.6% H, 17.7% N, 29.3% Cl and 27.0% Cu. The Cu:Cl ratio was 1:1.94 and the Cu:N ratio was 1:3.02.

Analyses for C, H and N were done commercially by combustion. Silicon was determined by wet oxidation with fuming nitric and sulfuric acids, followed by ignition of the SiO_2. The reagents alone gave no residue. Copper was determined by titration of the hydrolyzed sample with EDTA, using PAN indicator. Chlorine was determined by titration with $Hg(NO_3)_2$, using diphenyl carbazide as indicator.

To determine whether or not the linear polymer rearranged in the absence of copper(II) chloride, a sample of the xylene solution of I was refluxed for 6 hr. under an atmosphere of nitrogen. The xylene was removed at reduced pressure, leaving a polymeric oil that had the same physical appearance as the original linear silylamine polymer.

Anal. Calcd. for silylamine polymer $C_4H_{12}SiN_2$: C, 41.32; H, 10.41; Si, 24.40; N, 24.10; Si:N ratio = 2.00. Found: C, 43.00; H, 10.28; Si, 24.20; N, 21.92; Si:N ratio = 1:1.82.

The high values for carbon probably are due to unremoved xylene. The silicon-to-nitrogen ratio shows that some rearrangement does take place at the temperature of refluxing xylene (*ca.* 140°) but that it is far less in extent than that brought about by the agency of copper(II) chloride. Using the copper compound, complete rearrangement results in the same length of time.

Hydrolysis Reactions.—Karl Fischer reagent was prepared and standardized against methanol–water solution.[8] The

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(6) Karl Fischer reagent will titrate silanol hydrogen as water; see H. Gilman and L. S. Miller, THIS JOURNAL, **73**, 2367 (1951).

(7) "Inorganic Syntheses," Vol. V, McGraw-Hill Book Co., New York, N. Y., 1957, p. 153.

(8) I. M. Kolthoff and R. Belchev, "Volumetric Analysis," Vol. III, Interscience Publishers Inc., New York, N. Y., 1957.

reactions were carried out in glass-stoppered 250 ml. Erlenmeyer flasks which had been dried at 140° and cooled in a desiccator. 10.00 ml. of ethyl ether saturated with water, and 10.00 ml. of ethyl ether containing 4.2 mg. per ml. of glacial acetic acid were placed in each flask. 3.00 ml. of the xylene solution of polymer were added, and zero time taken when the last drop of solution left the pipet. A blank with no polymer was titrated to determine original H_2O content. The hydrolysis reaction was stopped by adding a large excess of methanol and glacial acetic acid (25 and 5 ml.) which had been pretitrated to a red end-point with Karl Fischer reagent. During the titration a yellow solid formed in the flask, but this did not obscure the end-point. The end-point was taken when a definite red color persisted for 1 minute. Successive titrations of samples "killed" at the same time agreed within 1–1.5 mg. of H_2O.

In a typical experiment, a volume of solution equivalent to 452 mg. of polymer I was added to each of ten flasks and left at 26°. At successive intervals of 20 minutes a flask was removed and titrated as described. Theoretical consumption of water was calculated to be 70 mg., which, at the observed rate, would give a half-reaction time of 138 minutes. Similar calculation of half-reaction time for the ladder-type polymer II was 420 minutes, or 3.04 times as long.

Reaction of the Ladder-type Polymer II with Excess Copper(II) Chloride.—A sample of the xylene-soluble ladder-type polymer II was hydrolyzed with 1 *N* nitric acid. The hydrolyzed material gave a negative test for copper with cuproin.[9] To determine whether the polymer II could coordinate with copper, a 1.86 g. sample of the polymer was dissolved in xylene. 0.55 g. of copper (II) chloride was added and the suspension refluxed for 6 hr. After cooling, the supernatant liquid was green in color. The suspension was filtered through a medium glass frit to give a clear, green filtrate. This was freed of xylene under reduced pressure, and a sample of the residue was hydrolyzed in nitric acid and analyzed for copper using EDTA. Found: 1.7% copper.

Reaction of Cross-linked Copper-containing Polymer III with Ethylenediamine in Xylene.—A 48 mg. sample of the polymer was placed in 25 ml. of xylene, and the xylene brought to reflux temperature. The sample did not dissolve but swelled to give a blue gelatinous material. After cooling, 1.00 ml. (900 mg.) of ethylenediamine was added, and the temperature brought up to 100°. After 2.5 hr. the cooled solution was filtered to give a very small amount of purple solid and a yellow filtrate. The filtrate was freed of xylene, and a hydrolyzed sample gave a faint positive test for copper with cuproin, but there was not enough copper present to obtain a significant analysis with 0.002 *N* EDTA. The original sample contained 3.5% copper.

Conclusion

The nitrogen atoms of the dimethylsilylamine polymer I are capable of coördination with Cu^{++} ions, but the polymer is stretched thereby into a new configuration, the ladder-type silazane polymer II. Nitrogen atoms of the latter are poorer donors than those of I, probably because of $d\pi$–$p\pi$ bonding to two silicon atoms instead of one. The silazane polymer II coördinates reversibly to copper ion (if in excess) but loses the copper to free ethylenediamine, which is a stronger donor. Copper-containing silazane polymer III is swelled by xylene but is insoluble in it and in mixtures of xylene with ketones and ethers. It very probably is further cross-linked by the coördination of its chains to copper. Other ions with different coördination requirements might be expected to react differently with I and with related polymeric organosilylamines; results on several such reactions will be reported separately.

Acknowledgment.—The authors are grateful to the Office of Naval Research for funds to defray the cost of reagents and combustion analyses.

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[9] F. Feigl, "Spot Tests in Inorganic Analysis," Elsevier Publishing Co., Houston, Texas, 1958, p. 92.

[CONTRIBUTION FROM THE MALLINCKRODT LABORATORY OF CHEMISTRY AT HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS]

Coördination of Polymeric Organosilyl Amines. II. Reactions with Anhydrous Beryllium Chloride[1]

BY RONN MINNÉ AND EUGENE G. ROCHOW

RECEIVED APRIL 1, 1960

Anhydrous $BeCl_2$ reacts with a polymeric silylamine, $[Me_2SiNHCH_2CH_2NH]_n$, in xylene solution to form a coördination polymer in which about one-third of the nitrogen is coördinated to beryllium. The coördinated polymer is more stable towards hydrolysis than the original polymeric silylamine and has very different physical properties. It also differs markedly from the corresponding reaction product of $CuCl_2$ with the same silylamine.

In the previous paper in this series, the preparation of a linear polymeric silylamine by the reaction of anhydrous ethylene diamine with dimethyldichlorosilane was reported, together with a discussion of the rearrangement of this polymer under the influence of copper(II) ions to form a cross-linked silazane. It was postulated that the role of the copper ion was to form a square-planar intermediate in which two polymer chains were coördinated to the copper ion and that the resulting distortion of structure led to the splitting out of ethylene diamine, resulting in a polymeric silazane.

This paper deals with the reaction of anhydrous beryllium chloride with the same polymeric silylamine. Beryllium ion was chosen for the second study of organosilicon coördination polymers because it is known to have very strong coördinating properties and because its tetrahedral coördination would provide a means of testing the theory that a square-planar complex brings about rearrangement of the polymeric silylamine.[2] Also, if an appreciable amount of beryllium were to be taken up by the polymer and remain coördinated to the amine or silazane nitrogen atoms, the rate of hydrolysis of the polymer should be affected. Normally, beryllium–amine links would be expected to hydrolyze, but the complex $Been_2Cl_2$ is reported to be fairly stable to hydrolysis.[2] If the beryllium ions were strongly held in the polymer, there should

[1] For Part I in this series see THIS JOURNAL, **82**, 5625 (1960).

[2] R. Fricke and L. Havestadt, *Z. Anorg. Chem.*, **152**, 357 (1926).