and is determined principally by the hydration of the cations. As the basicity of the exchange groups increases through $-P(OH)O_2^-$, $>PO_2^-$, $-CO_2^-$, and $-PO_3^{-2}$ the groups interact more and more strongly with the (smaller) ion, the distribution ratios come closer together, and finally the order inverts for the last group, where the interactions with the resin groups dominate the behavior. Since these results all take place from dilute solution, they all involve the fully hydrated cation in the external aqueous phase, and the inversion can best be interpreted as being due to the increasing ability of the exchange groups to compete with water in solvating the cation. The resin elution order can be influenced by changing the relative solvating ability of the resin group with respect to the water in the external phase by other means also. This has been demonstrated for a carboxylate resin in this paper, and for sulfonate resins in this and earlier papers,[3-6] by employing concentrated electrolyte solutions where there are fewer water molecules available for solvating the cations. As the concentration increases, the growing difficulty of solvating the increasing number of ions with the smaller number of water molecules makes ion hydration less important and anion interactions more important. If the cations interact more strongly with the macroanion than with the resin group, the smaller cations will prefer the aqueous phase and the order will remain that of the dilute solution case. If the resin anion interacts more strongly with the cations than does the external macroanion, the smaller cations will preferentially go into the resin phase in order to obtain as complete solvation as possible and the selectivity order will tend to invert. For a given type of macroanion, the greater the complexing ability of the resin group, the lower the external solution concentration at which inversion occurs. For a given resin, the more poorly complexing the macroanion and the lower the water activity, the lower the solution concentration at which the elution order reversal occurs.

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

# Mixed Cyclic and Linear Compounds with Siloxane and Silazane Linkages

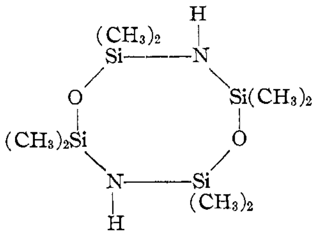
BY CARL KRÜGER AND E. G. ROCHOW

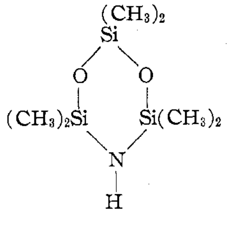
*Received February 16, 1963*

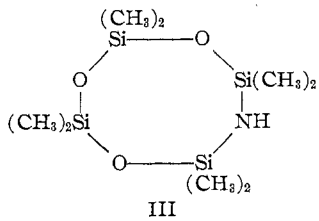
Dihalogenopolysiloxanes react with ammonia in ethereal solution to form ring compounds with mixed siloxane and silazane groups besides the corresponding polymers. Under similar conditions methylamine yields only monomeric linear compounds. The described new class of ring compounds is examined by infrared and n.m.r. spectroscopy.

## Introduction

Our investigation of catalytic polymerization of cyclic silicon–nitrogen compounds[1] has led to the preparation of some new substances in which siloxane groups alternate with silazane groups. In this context, we examined the physical and spectroscopic properties and the chemical behavior of some new mixed-ring compounds. Although pure cyclosiloxanes and pure cyclosilazanes are well known, only one mixed siloxane–silazane compound has been described.[2] We have found that such compounds can be prepared in reasonably good yields by treating the corresponding linear dihalogenopolysiloxanes in ethereal solution with gaseous ammonia


I


II


III

$$y\text{ClSi(CH}_3)_2[\text{OSi(CH}_3)_2]_x\text{Cl} + 3y\text{NH}_3 \xrightarrow{(\text{C}_2\text{H}_5)_2\text{O}} [\text{OSi(CH}_3)_2]_x[\text{NHSi(CH}_3)_2]_y + 2y\text{NH}_4\text{Cl}$$

In this way, we have prepared the new ring compounds I–III. In quite different fashion, methylamine reacts under the same conditions with dihalogenopolysiloxanes to give linear rather than cyclic compounds, *e.g.*

$$\text{CH}_3\text{NH—Si(CH}_3)_2\text{—O—Si(CH}_3)_2\text{—NHCH}_3$$

IV

$$\text{CH}_3\text{NH—Si(CH}_3)_2\text{—O—Si(CH}_3)_2\text{—O—Si(CH}_3)_2\text{—NHCH}_3$$

V

This reaction corresponds to the reaction of dialkyldihalogenosilanes with alkylamines, which also leads only to incompletely silylated alkylamines.[3] These

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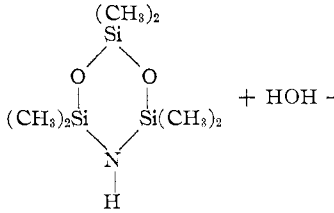
(1) C. Krüger and E. G. Rochow, *Angew. Chem.*, **74**, 588 (1962).

(2) N. N. Skolow, *J. Gen. Chem. USSR*, **29**, 258 (1959).

(3) E. Larsson and B. Smith, *Acta Chem. Scand.*, **3**, 487 (1949).

compounds could not be converted to ring compounds by extensive heating. The interaction with catalysts is described below.

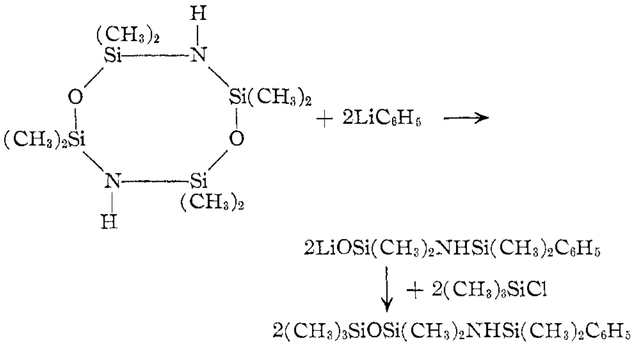
All these procedures involve side reactions which yield variable amounts of polymeric oils. These are thermally unstable and decompose upon heating to 250°, with formation of ammonia and cyclic siloxanes. On the other hand, the ring compounds are remarkably stable toward thermal decomposition. They are attacked by proton-active solvents with formation of cyclic siloxanes, *i.e.*, they react in a manner analogous to that of the pure cyclosilazanes.[4]



Compound II was found to be the most sensitive one. We believe that this effect is due to a considerable ring strain, as indicated in the Discussion.

Compounds I–III can be polymerized with ammonium halides as catalysts to rubbery or oily polymers and can be cross linked by trisubstituted nitrogen atoms, although up to 40% of volatile cyclic siloxanes also are formed in that reaction. Compounds IV and V undergo cleavage of methylamine to give analogous polymers.

Although it is well known that the cleavage of Si–O–Si bonds in organopolysiloxanes occurs when they are treated with certain organometallic reagents,[5] we tried to metalate compounds I–III to get reactive N–metal compounds. It was shown earlier that metalation of NH groups occurs quite readily,[6] so this reaction should be favored over the cleavage of Si–O–Si bonds. Compound I reacts exothermally in ethereal solution with lithium phenyl and after treating the reaction mixture with trimethylchlorosilane we could only isolate small amounts of compound VI. There was no evidence for metalation of NH groups.



VI

The reaction of I with sodamide in toluene solution proceeded the same way. In that particular case, no evolution of ammonia (a typical indicator of metalation of NH groups) was observed, although the sodamide was dissolved. The resulting silanolate was treated with dimethyldichlorosilane, producing viscous oils with Si–O–Si and Si–NH–Si linkages.

## Experimental

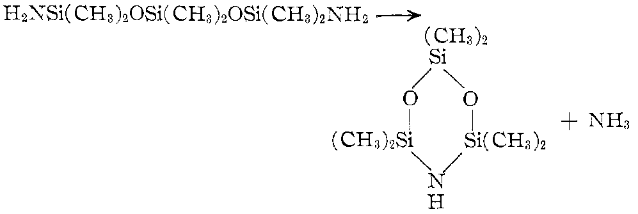
(a) **Starting Materials.**—Dihalogenopolysiloxanes were prepared either by partial hydrolysis of dimethyldichlorosilane[7] or by careful distillation of commercial crude material (General Electric SC 87) through an 80-cm. column packed with glass helices.

(b) **Compound I.**—In a 1-l. three-necked flask, equipped with gas inlet tube, sealed stirrer, reflux condenser, and drying tubes, 40.6 g. (0.2 mole) of α,β-dichlorotetramethyldisiloxane was dissolved in 500 ml. of anhydrous ether. Under vigorous stirring, purified and absolutely dry ammonia was passed through the solution. After the exothermic reaction had slowed down, the suspension was stirred for an additional 3 hr. and filtered through a glass frit, yielding 21.2 g. of $NH_4Cl$, 99.5%, and a clear solution of I (besides some polymeric material). After removing the solvent, the liquid residue was distilled several times through a 30-cm. Vigreux column, yielding 19.6 g. (71.8%) of compound I (b.p. 206–208° at 760 mm. and 82–83° at 9 mm.; m.p. 37° besides 1 g. of oligomeric oils (b.p. 88–180° (12 mm.), $n^{20}_{D}$ 1.4331) and 5.5 g. (20%) of viscous polymeric residues ($n^{20}_{D}$ 1.4355). Repeating the trial with other amounts of starting material gave similar results.

*Anal.* Calcd. for $C_8H_{26}N_2O_2Si_4$: C, 32.62; H, 8.90; N, 9.51; Si, 38.11; mol. wt., 294.5. Found: C, 32.34, 32.32; H, 8.75, 8.74; N, 9.46, 9.48; Si, 37.88; mol. wt., 302. Analyses of the polymeric material: C, 30.45, 30.62; H, 7.92, 7.90; N, 9.64, 9.63.

The molecular weight of the polymeric material was 2700, corresponding to 18 units of the type $-O-Si(CH_3)_2-NH-Si(CH_3)_2$. The stability of the polymeric material resembles the stability of the ring compound.

**Compound II.**—The calculated amount of anhydrous ammonia was dissolved at −70° in 700 ml. of anhydrous ether contained in a 1-l. three-necked flask, equipped with sealed stirrer, reflux condenser, and cooled with Dry Ice–acetone, and thereafter 50 g. of 1,5-dichlorohexamethyltrisiloxane, dissolved in 100 ml. of anhydrous ether, was added slowly. The resulting suspension was stirred for 1 hr. at −70° and filtered at room temperature, yielding 18.7 g. of $NH_4Cl$, 98.5%. The filtered ammonium chloride was washed twice with absolute benzene, and then the solvent was removed from the combined solutions by distillation. The first distillation of the residue was accompanied by strong ammonia evolution, probably due to the reaction



After several fractionations (30-cm. Vigreux column) the yield of II was 22 g. (55%) (b.p. 151–151.5°, m.p. 9.5–10.5°, $n^{20}_{D}$ 1.4068, $d^{25}$ 0.9895) besides some polymeric residue.

*Anal.* Calcd. for $C_6H_{19}NO_2Si_3$: C, 32.54; H, 8.65; N, 6.33; Si, 38.02; mol. wt., 221.4. Found: C, 32.09, 32.52; H, 8.68, 8.43; N, 5.81, 5.97; Si, 37.40, 37.19; mol. wt., 228.

**Compound III.**—Compound III was prepared according to the procedure given for I: 70.5 g. of 1,7-dichlorooctamethyltetrasiloxane (0.2 mole) yielded 19.5 g. (33%) of III (b.p. 190–191°,

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[4] K. A. Andrianov and G. Y. Rumba, *J. Gen. Chem. USSR*, **31**, 4038 (1961).

[5] H. Gilman, H. N. Benedict, and H. Hartzfeld, *J. Org. Chem.*, **19**, 419 (1954); J. F. Hyde, O. K. Johannson, W. H. Daudt, R. F. Fleming, H. B. Laudenslager, and M. P. Roche, *J. Am. Chem. Soc.*, **75**, 5615 (1953).

[6] N. Wannagat and H. Niederprüm, *Chem. Ber.*, **94**, 1540 (1961).

[7] W. I. Patnode and D. F. Wilcock, *J. Am. Chem. Soc.*, **68**, 358 (1946).

m.p. 20–20.5°, $n^{20}_{D}$ 1.4151, $d^{26}$ 0.9921) besides 20.3 g. of $NH_4Cl$ (95.5%) and 22.3 g. of polymeric material.

*Anal.* Calcd. for $C_8H_{25}NO_3Si_4$: C, 32.52; H, 8.63; N, 4.53; Si, 37.99; mol. wt., 295.6. Found: C, 32.29, 32.12; H, 8.66, 8.54; N, 4.63, 4.56; Si, 37.31; mol. wt., 308. The polymeric residues probably contain rings of higher order: Found: C, 31.40; H, 7.85; Si, 36.88; mol. wt., 460.

(c) **Bis-(dimethylamino)-tetramethyldisiloxane.**—Anhydrous ether (500 ml.) was saturated at 0° with anhydrous methylamine in a three-necked flask equipped with stirrer, reflux condenser, and drying tubes. Then a solution of 40.6 g. (0.2 mole) of 1,3-dichlorotetramethyldisiloxane in 50 ml. of absolute ether was added while stirring, keeping the suspension at 0°. After a 2-hr. period, the suspension was filtered with suction through a glass frit, yielding 26.9 g. of methylammonium chloride (99.5%). After removing the solvent, the remaining residue was fractionated several times through a 30-cm. Vigreux column, yielding at last 24.4 g. of 1,3-bis-(methylamino)-tetramethyldisiloxane (63.5%), b.p. 50–52° (11 mm.), $n^{20}_{D}$ 1.4105.

*Anal.* Calcd. for $C_6H_{20}N_2OSi_2$: C, 37.46; H, 10.48; N, 14.57. Found: C, 36.49, 36.37; H, 9.89, 9.79; N, 14.20, 14.24.

Starting with 27.8 g. of 1,3-dichlorohexamethyltrisiloxane, an analogous procedure yielded 1,5-dimethylaminohexamethyltrisiloxane (57%, 15.2 g.), b.p. 78–79° (11 mm.), $n^{20}_{D}$ 1.4089. *Anal.* Calcd. for $C_8H_{26}N_2O_2Si_3$: C, 36.06; H, 9.84; N, 10.51. Found: C, 35.84, 35.64; H, 9.70, 9.44; N, 9.98, 9.99.

(d) **Reaction of Compound I with Sodamide and Dimethyldichlorosilane.**—I (14.5 g., 0.05 mole) was dissolved in 150 ml. of anhydrous toluene (500-ml. three-necked flask, equipped with sealed stirrer, nitrogen inlet tube, reflux condenser, drying tube, and dropping funnel) and 4 g. of powdered sodamide was added under nitrogen atmosphere. The suspension was refluxed until complete solution of the sodamide occurred (6 hr.). After cooling to room temperature, 4.5 g. of dimethyldichlorosilane in 50 ml. of toluene was added. The reaction mixture warmed up slightly during this procedure and became gelatinous. After addition of 100 ml. more of toluene the mixture was refluxed for 3 hr., filtered through a glass frit (yielding 7.4 g. of NaCl), and the solvent was evaporated. Distillation of the remaining residue yielded 4 g. of oligomeric oils (b.p. 95–180° (4 mm.)) and 11.2 g. of viscous, oily polymeric residue with the approximate composition $[-Si(CH_3)_2-O-Si(CH_3)_2-NH-]_x$.

*Anal.* Calcd. for $C_4H_{13}NOSi_2$: C, 32.62; H, 8.90; N, 9.51; Si, 38.11. Found: C, 32.86; H, 8.61; N, 9.23; Si, 37.26; mol. wt., 1340.

## Discussion

**Spectra of the Substances Prepared.**—The investigation of the infrared and n.m.r. spectra of the compounds which were prepared provided information on the Si–O and Si–N bonds. The frequency of vibration of the $Si(CH_3)_2$ group in our substances, compared with that of the corresponding known compounds,[8] shows that coupling effects with the vibrations of the cyclic framework are almost missing. Supposing that the force constants of the asymmetric Si–X–Si vibrations are applicable to our compounds, although they are of lower symmetry and have different neighboring groups, it should be possible to calculate the Si–X–Si bond angles by methods for calculating the angles of three-mass models.[9] Similar calculations have been carried out earlier by Kriegsmann for cyclosiloxanes, as well as by Simmler, *et al.*, for disilamorpholines.[10] Whereas Kriegsmann uses for his calculations an apparent vibrating mass of the $Si(CH_3)_2$ group, Simmler, *et al.*, use only the atomic masses of the Si atoms. We preferred for our calculations the vibration-effective mass of the dimethylsilyl group (38), as it gave better results when used for calculating the already known bond angles of cyclosiloxanes and cyclosilazanes. As force constant for Si–N we used 3.84 mdynes/Å. and Si–O 4.97 mdynes/Å.

Table I shows values calculated in this way for Si–X–Si angles which are compared with values ascertained in different ways for hexamethylcyclotrisiloxane and hexamethyltrisilazane. It was shown by Frevel and Hunter and as well by Aggarwal and Bauer[11] by X-ray analyses and electron diffraction that the bond angle Si–O–Si of the planar hexamethylcyclotrisiloxane is 125 ± 5°, whereas for the puckered tetrasiloxane 142.5 ± 5° was obtained.[12] The Si–N–Si angles in hexamethylcyclotrisilazane and octamethylcyclotetrasilazane were determined by the same methods to be 117 ± 5° and 123 ± 5°,[13] respectively.

The extremely good agreement of these values with the values calculated from infrared valence vibrations encourages us to make statements on the bonding character of the new compounds I–III. We conclude that compound II has the same Si–O–Si angle as the related cyclotrisiloxane, but an Si–N–Si angle enlarged from 117 to 133° compared with cyclotrisilazane. Assuming the planarity of the ring as well as the constancy of the angle O–Si–O (the difference between the O–Si–O angle, 115 ± 5°, and the N–Si–N angle, 111 ± 5°, and by this also the N–Si–O angle, is within the range of error of the applied method), the insertion of an Si–N–Si group into the cyclotrisiloxane framework causes an observed enlargement of the Si–N–Si angle and therefore considerable ring strain. These increased ring tensions probably are responsible for the extraordinary sensitivity of ring II toward solvolysis. Addition of the calculated and assumed angles leads to ~720°; the theoretical sum for a planar six-membered ring is 720°.

The assumed nonplanarity of the rings with eight members prepared in this study prohibits analogous considerations. It only can be stated that the Si–O–Si angle in compound I, compared with the corresponding angle in octamethylcyclotetrasiloxane, is reduced, whereas the Si–N–Si angle is as large as it is in the corresponding octamethylcyclotetrasilazane. The Si–N–Si angle in compound III, by comparison, shrinks from the value in the corresponding octamethylcyclotetrasilazane to that of the cyclotrisilazane. Furthermore, compound III shows an interesting splitting of the Si–O–Si vibration. We explain this phenomenon as due to two different Si–O–Si angles in the ring, depending on whether the Si–O–Si group is isolated or is in the neighborhood of an Si–N–Si group. Splitting of Si–O–Si frequencies is also observed in the spectra of the

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(8) H. Kriegsmann, *Z. anorg. allgem. Chem.*, **298**, 223 (1959).

(9) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," D. Van Nostrand Co., Inc., Princeton, N. J., 1959, p. 168.

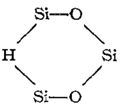
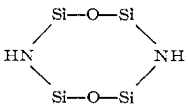
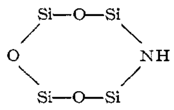
(10) W. Simmler, W. Meise, and H. Malz, *Z. anorg. allgem. Chem.*, **314**, 245 (1962).

(11) L. K. Frevel and M. J. Hunter, *J. Am. Chem. Soc.*, **67**, 2275 (1945); E. H. Aggarwal and S. H. Bauer, *J. Chem. Phys.*, **18**, 42 (1950).

(12) H. Steinfink, B. Post, and I. Fankuchen, *Acta Cryst.*, 420 (1955).

(13) M. Yokoi and M. Yamasaki, *J. Am. Chem. Soc.*, **75**, 4139 (1953).

TABLE I

| | $[Si(CH_3)_2NH]_3$ |  | $[Si(CH_3)_2]_3$ | $[Si(CH_3)_2NH]_4$ |  |  | $[Si(CH_3)_2O]_4$ |
|---|---|---|---|---|---|---|---|
| $\nu_{as}$ Si—O—Si, cm.$^{-1}$ | ... | 1022 | 1022 | ... | 1050 | 1065<br>1025 | 1078 |
| Calcd. bond angle | ... | 124° | 124° | ... | 132° | 137°<br>125° | 141.5° |
| Found bond angle | ... | ... | 125 ± 5° | ... | ... | ... | 142.5 ± 5° |
| $\nu_{as}$ Si—N—Si, cm.$^{-1}$ | 928 | 978 | ... | 938 | 938 | 928 | ... |
| Calcd. bond angle | 118.5° | 133.3° | ... | 121.3° | 121.3° | 118.8° | ... |
| Found bond angle | 117 ± 4° | ... | ... | 123 ± 4° | ... | ... | ... |

larger cyclosiloxane rings, but has not been explained up to now.

The n.m.r. spectra of the substances prepared in this study are without any peculiarity. As is to be expected, I shows only one sharp signal at 4 c.p.s. ($\delta$ = 0.067) because of the identical surrounding of the methyl groups, whereas compound III shows two equal signals at 3 c.p.s. ($\delta$ = 0.05) and 5.1 c.p.s. ($\delta$ = 0.085).

Comparison with the chemical shifts of compounds which contain only one kind of Si–X–Si bond allows an assignment. Hexamethylcyclotrisilazane absorbs at 3.2 c.p.s. (60 Mc.) ($\delta$ = 0.053), whereas the corresponding tetramer shows absorption at 2.8 c.p.s. ($\delta$ = 0.047). Hexamethylcyclotrisiloxane shows a shift of 7 c.p.s. ($\delta$ = 0.117). The more downfield absorption of compound III is therefore due to the methyl groups in a pure siloxane neighborhood, whereas the higher frequency is due to the methyl groups near adjacent siloxane and silazane groups. Compound II surprisingly shows no splitting of its one signal at 6.2 c.p.s. ($\delta$ = 0.104), but this signal is extraordinarily broadened. Probably this band should show splitting at higher resolution. Compounds I–III show an interesting behavior in broadline n.m.r. at different temperatures which will be reported elsewhere.

Infrared spectra were taken with a Perkin-Elmer Model 221 spectrograph, using either capillaries or $CCl_4$ solutions; n.m.r. spectra were taken in $CCl_4$ solution using tetramethylsilane as internal standard, with a Varian A-60 high resolution spectrometer.

**Acknowledgment.**—Financial support of this work by the Advanced Research Projects Administration by contract with Harvard University is gratefully acknowledged.

# Notes

JOINT CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND MATERIALS RESEARCH CENTER, NORTHWESTERN UNIVERSITY, EVANSTON, ILLINOIS, AND THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF MICHIGAN, ANN ARBOR, MICHIGAN

## The Crystal Structure of Trimethylamine Gallane, $(CH_3)_3NGaH_3$

BY D. F. SHRIVER AND C. E. NORDMAN

*Received February 28, 1963*

Recently trimethylamine gallane was independently prepared in two different laboratories by the reaction of lithium gallium hydride with trimethylammonium chloride.[1,2]

$$LiGaH_4 + (CH_3)_3NHCl = LiCl + H_2 + (CH_3)_3NGaH_3$$

Raman spectra of the solid[3] and infrared spectra of the gas[4] were interpretable in terms of a *monomer* with $C_{3v}$ symmetry analogous to the well known $(CH_3)_3NBH_3$. By contrast aluminum, the element between boron and gallium in the periodic table, is thought to form hydrogen-bridged dimers in benzene solutions of the compound $(CH_3)_3NAlH_3$.[5–8]

The present study was undertaken to confirm positively the monomeric nature of $(CH_3)_3NGaH_3$ and to obtain the molecular parameters which are of interest in the interpretation of Lewis salt formation.

### Experimental

Crystals were prepared by sublimation of the compound into thin-walled Pyrex capillaries which subsequently were sealed under vacuum. The resulting multicrystalline mass was suitable for obtaining a Debye–Sherrer X-ray pattern, which has been reported elsewhere.[1] Single crystals were grown in the sealed capillary by slow sublimation in a small thermal gradient at room temperature. The resulting crystals were globular and usually imperfect. Out of a large number of such crystals only two

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[1] D. F. Shriver and R. W. Parry, *Inorg. Chem.*, **2**, 1039 (1963).

[2] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *ibid.*, **2**, 1036 (1963).

[3] D. F. Shriver, R. L. Amster, and R. C. Taylor, *J. Am. Chem. Soc.*, **84**, 1321 (1962).

[4] N. N. Greenwood, A. Storr, and M. G. H. Wallbridge, *Proc. Chem. Soc.*, 249 (1962).

[5] E. Wiberg, H. Graf, and R. Uson, *Z. anorg. allgem. Chem.*, **272**, 221 (1953).

[6] J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, **82**, 2141 (1960).

[7] E. Wiberg, H. Graf, M. Schmidt, and R. Uson, *Z. Naturforsch.*, **7b**, 278 (1952).

[8] G. Schomburg and E. G. Hoffmann, *Z. Elektrochem.*, **61**, 1101, 1110 (1957). These authors believe dimerization occurs through dipole-dipole interaction.