ordination complex can be concluded to be *gauche*. The fact that the C≡N frequency of ethylene thiocyanate is not appreciably changed in the complex indicates that coördination takes place through the sulfur atom; furthermore the complex shows the usual color and chemical properties characteristic of Pt–S coördination compounds.

A similar conclusion was drawn from our infrared measurements for the configuration of ethylenediamine when this molecule is present as a chelating group in coördination complexes. The bond lengths in coördination complexes can best be explained on the basis of the *gauche* configuration of this chelating group and this configuration is in agreement with the results of the X-ray investigations.[2,3] The *cis* configuration has so far been tacitly assumed for the ethylenediamine ligand in these coördination compounds.

The conclusion of the *gauche* configurations is of interest to the stereochemistry of these complexes, for the *gauche* configuration has a mirror image non-superposable. Thus more optical isomers are theoretically possible if the chelating group present in these complexes has the *gauche* rather than the *cis* configuration.[4] For example, in *cis*-[Co(H_2NH_2C–$CH_2NH_2)_2Cl_2$]Cl there are more optical isomers than would be expected from the classical viewpoint. In the case of the corresponding *trans* isomer, however, only one configuration is present since our infrared analysis as well as the X-ray investigation[3] have shown that the two ethylenediammine ligands in the coördination complex are present as two configurations which are the mirror images of each other.

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RECEIVED SEPTEMBER 3, 1953

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(2) T. Watanabe and M. Atoji, *Kagaku* (*Science*), **21**, 301 (1951).

(3) A. Nakahara, Y. Saito and H. Kuroya, *Bull. Chem. Soc. Japan*, **25**, 331 (1952).

(4) M. Kobayashi, *J. Chem. Soc. Japan*, **64**, 648 (1943).

(5) Member, Radiation Project operated by the University of Notre Dame and supported in part under AEC Contract AT(11-1)-38.

THE PARTIAL AMMONOLYSIS OF SILICON TETRACHLORIDE

Sir:

It has been pointed out in earlier work[1] that the partial hydrolysis of silicon halides, carried out under conditions such that complete conversion into silica and hydrochloric acid is not effected, leads to the formation of mixtures containing oxyhalides of silicon, homologous series of which have been isolated by careful fractionation of the reaction products.

It seemed of interest to determine whether partial ammonolysis of such halides might be accomplished, leading, for example, to imino-halides, such as $Si_2(NH)Cl_6$, from the partial ammonolysis of $SiCl_4$.

Preliminary experiments in which ammonia gas, diluted with nitrogen, was passed into an ethereal solution of silicon tetrachloride at −75°, or over the surface of an ethereal solution of silicon tetrachloride at 0°, or over the surface of pure silicon tetrachloride at −70°, yielded only solid, highly polymerized materials of undetermined composition. Similar unsatisfactory results were obtained when an ether solution of silicon tetrachloride was allowed to react with silver chloride triamine, $AgCl{\cdot}3NH_3$, as the ammoniating agent.

However, when the vapors of silicon tetrachloride were allowed to react with ammonia, diluted with dry nitrogen, at 825° for thirty-five hours, there were isolated besides solid polymerized materials, two compounds of the silazane type. The first of these, a colorless liquid boiling at 34° under 3 mm. pressure, and freezing about −50°, was identified by analysis and molecular weight determinations as the iminochloride, $Si_2(NH)Cl_6$. The second substance, a colorless, crystalline solid at room temperature, boiling at 103° at 2 mm. pressure and melting at about 50°, corresponded similarly to the formula $Si_8N_4Cl_{20}$, a cyclic tetramer, or possibly to $Si_9N_5H_2Cl_{23}$, an open-chain structure. The alkyl analogs of the first compound, hexamethyldisilazane and hexaethyldisilazane, Me_6Si_2NH and Et_6Si_2NH, were reported by Sauer, *et al.*[2]

It is reasonable to suppose that hexachlorodisilazane represents the first member of a homologous series of straight-chain compounds of the general formula, $Sn_n(NH)_{n-1}Cl_{2n-2}$.

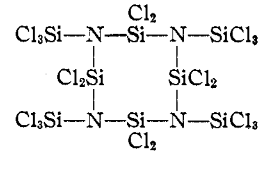
Anal. Si: calcd., 19.77; found, 19.90, 19.48, 19.60; av., 19.66. Cl: calcd., 74.94; found, 76.04, 75.60, 75.94; av., 75.86. N: calcd., 4.94; found, 4.85, 4.91, 5.05; av., 4.94. Mol. wt., for $Si_2(NH)Cl_6$: calcd., 283.9; found, 293, 275; av., 284.

Analysis of the second, crystalline compound gave the following results:

	Calcd. for $Si_8N_4Cl_{20}$	Calcd. for $Si_9N_5Cl_{23}$	Found	Av.
Si:	22.68	22.15	22.60, 22.47	22.53
Cl:	71.66	71.53	71.66, 71.86, 71.69	71.74
N:	5.66	6.14	5.90, 6.18, 6.24	6.11

Mol. wt., calcd. for $Si_8N_4Cl_{20}$, 990; for $Si_9N_5H_2Cl_{23}$, 1140; found, 1178, 1060; av., 1119.

This crystalline solid substance could be considered as derived from hexachlorodisilazane by the elimination of HCl and the formation of a cyclic tetramer



The analytical data and observed molecular weight are in agreement with this formulation, as indicated above.

Alternatively, if condensation of three moles of $Si_2(NH)Cl_6$ with one of the second member of the series, $Si_3(NH)_2Cl_8$, occurred, with splitting out of

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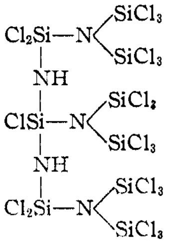
(1) W. C. Schumb and A. J. Stevens, THIS JOURNAL, **69**, 726 (1947); **72**, 3178 (1950); W. C. Schumb and R. A. Lefever, *ibid.*, **75**, 1513 (1953).

(2) R. O. Sauer, THIS JOURNAL, **66**, 1707 (1944); R. O. Sauer and R. H. Hasek, *ibid.*, **68**, 241 (1946).

HCl, the following chain structure, corresponding with $Si_9N_5H_2Cl_3$, would result



The agreement here with the analytical results is substantially as good as that given by the first structure, and the molecular weight found is somewhat closer to the calculated value in this case.

The analysis of the solid polymeric residue left after heating the solid reaction products under reduced pressure, to sublime away any ammonium chloride, while not as conclusive as that presented for the silazanes, led to results approaching the requirements of the simple empirical formula, $(Cl{-}Si{\equiv}N)_x$. One such sample, for example, gave the following data:

Si: 36.5, 35.9; av. 36.3; g.-atoms, 1.1
Cl: 40.9, 40.5; av. 40.7; g.-atoms, 1.0
N: 18.6, 19.4; av. 19.0; g.-atoms, 1.2

Under the conditions of sublimation *in vacuo* any entrapped ammonium chloride would be expected to have been removed; nevertheless, X-ray film of samples thus treated invariably showed lines due to ammonium chloride, which is believed to have resulted from hydrolysis of the sample due to contact with moisture of the air. It is thought, therefore, that the solid is not merely a mixture of either $Si(NH)_2$ or $Si(NH_2)_2NH$, reported by Stock,[3] with ammonium chloride, but rather that it consists essentially of the polymerized chloronitride, $(ClSiN)_x$.

Further studies on the ammonolytic and hydrolytic characteristics of the halides and oxyhalides of silicon, which have been in progress for the past few years, will be presented shortly in a definitive paper.

[3] A. Stock and F. Zeidler, *Ber.*, **56**, 986 (1923).

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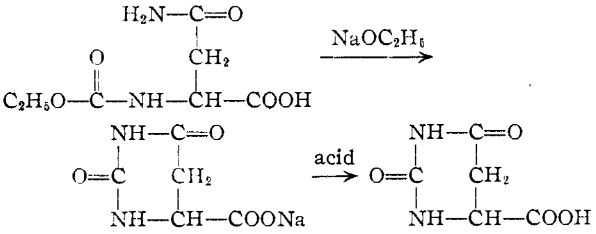
DIHYDROÖROTIC ACID

Sir:

Bachtez and Cavallini[1] have reported a synthesis of "dihydroörotic acid" by fusion of maleic acid and urea. Workers in this laboratory[2] have reported that "dihydroörotic acid" prepared by this method was not active in supporting growth of *Lactobacillus bulgaricus 09* which responds to either ureidosuccinic acid or orotic acid. Recently, Kornberg and co-workers[3] discovered an enzyme system which reversibly converts orotic acid to dihydroörotic acid but which would not utilize "dihydroörotic acid" prepared by the method of Bachtez and Cavallini.

While seeking an answer to this discrepancy, a new synthesis of dihydroörotic acid was devised. D- L- or DL-N$^\alpha$-carbethoxyasparagine was heated under reflux for four hours in an ethanol solution containing 2 molar equivalents of sodium ethoxide to give the corresponding D-, L- or DL-dihydroörotic acid in yields up to 70%. The use of sodium methoxide in methanol gave erratic results.



Heating of dihydroörotic acid with strong mineral acid converts it into 5-hydantoinacetic acid. This reaction apparently goes via ureidosuccinic acid since use of too much acid in the isolation of DL-dihydroörotic acid results in a product contaminated with DL-ureidosuccinic acid.

L-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-L-asparagine had the properties: decomposed at 266°; $[\alpha]^{25.3}\mathrm{D}$ +33.23° (*c* 1.992)[4] in 1% $NaHCO_3$. *Anal.* Calcd. for $C_5H_6O_4N_2$: C, 37.98; H, 3.83; N, 17.72. Found: C, 38.18; H, 3.97; N, 17.69.[5]

D-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-D-asparagine had the properties: decomposed at 266°; $[\alpha]^{25.3}\mathrm{D}$ −31.54° (*c* 2.01) in 1% $NaHCO_3$. *Anal.* Found: C, 37.69; H, 4.03; N, 17.71. A sample of this material was converted to the brucine salt which was recrystallized to constant decomposition point (268°) and constant optical rotation [$[\alpha]^{25}\mathrm{D}$ −32.15° (*c* 1.039) in water]. The brucine salt was decomposed with acid and the dihydroörotic acid obtained freed from brucine by repeated recrystallization from water. Its properties were $[\alpha]^{26.5}\mathrm{D}$ −34.29° (*c* 2.488) in 2.5% $NaHCO_3$ and decomposition at 267–268°.

DL-Dihydroörotic acid obtained from N$^\alpha$-carbethoxy-DL-asparagine decomposed at 259° and was optically inactive. *Anal.* Found: C, 38.23; H, 3.85; N, 17.67.

DL-Dihydroörotic acid prepared from N$^\alpha$-carbethoxy-DL-asparagine has been found to differ in melting point, infrared spectrum and solubility with material prepared by the method of Bachtez and Cavallini. An attempt to resolve the material prepared by the method of Bachtez and Cavallini into D and L isomers by recrystallization of its brucine salt was unsuccessful.

Microbiological tests carried out in these labora-

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[1] M. Bachtez and G. Cavallini, *Ber.*, **66B**, 681 (1933).

[2] D. S. Spicer, K. V. Liebert, L. D. Wright and J. W. Huff, *Proc. Soc. Exptl. Biol. Med.*, **79**, 587 (1952).

[3] J. Lieberman and A. Kornberg, *Federation Proc.*, **12**, 239 (1953).

[4] We are indebted to H. C. Zell for the optical measurements.

[5] We are indebted to Joyce Pyett, Arthur Fadenrecht and Kermit B. Streeter for the microanalyses.