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TRANSITION METAL COMPLEXES WITH
ORGANOSILYLAMINES.

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TRANSITION METAL COMPLEXES

WITH ORGANOSILYLAMINES

A thesis presented

by

Chang Hwan Kim

to

The Department of Chemistry

in partial fulfillment of the requirements

for the degree of

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in the subject of

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PLEASE NOTE:

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print. Filmed as received.

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To My Parents and

My Wife

Acknowledgements

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INTRODUCTION

Since silicon lies in the second short period, it has empty 3$\underline{d}$ orbitals of low energy. Silicon utilizes some of its five 3$\underline{d}$ orbitals to allow its valence shell to expand. This valence shell expansion is well recognized in the formation of compounds and reaction intermediates containing silicon of covalency higher than four. If some or all of the groups bound to silicon have filled lone-pair orbitals that are of π-symmetry relative to the σ-bonds, the 3$\underline{d}$ orbitals also can interact with the lone pair-orbitals to form dπ-pπ dative bonds.

Earlier evidence for the participation of 3$\underline{d}$ orbitals in the chemistry of silicon has been reviewed by Stone and Seyferth.[1] The hexacovalency of silicon is attained with elements of high nuclear charge and small atomic volume, like fluorine and oxygen. A well-known example of this is found in the hexafluosilicate ion, $SiF_6^=$. X-ray diffraction analysis shows that $SiF_6^=$ ion has an octahedral arrangement of fluorine atoms around silicon.[2] Hexacovalent complexes containing Si-O bonds have also been known for some time, particularly

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1. F.G.A. Stone and D. Seyferth, J. Inorg. Nucl. Chem., 1, 112 (1955).

2. J.A.A. Ketelaar, Z. Kristallogr., 92, 155 (1935); Chem. Abstr., 30, 2821^2 (1936).

salts of the cation A_3Si^+ (A = acetylacetonyl group) such as $A_3Si^+AuCl_4^-$.
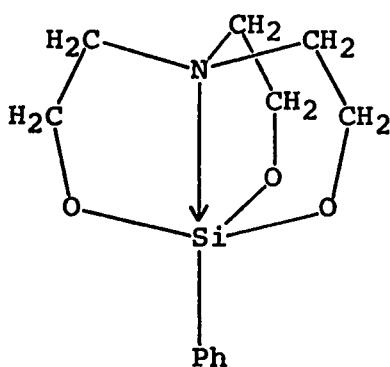
Besides the unstable complexes of trimethylamine with chlorosilanes and silicon tetrafluoride, ($SiCl_4 \cdot NMe_3$, $SiF_4 \cdot NMe_3$), the pentavalency of silicon has recently been demonstrated in a few stable compounds. Low-temperature X-ray diffraction analysis of dimethylsilylamine pentamer, $(H_3SiNMe_2)_5$, reveals that planar SiH_3 units are bridged by axial dimethylamino groups in a near planar ten-membered ring.[3] The pentacoordinated cage structure of organosilatranes*, (1-organo-2,8,9-trioxa-5-aza-1-silatricyclo 3,3,3,0-undecanes), and organoxy-silatranes

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* This nomenclature was suggested by Voronkov in ref. 5.

3. R. Rudman, W.C. Hamilton, S. Novick, and T.D. Goldfarb, J. Am. Chem. Soc., _89_, 5157 (1967).

was proposed on the bases of infra-red studies[4] and dipole
moment measurements.[5] Turley and Boer have shown by X-ray
diffraction methods that phenyl silatrane, $(C_6H_5)Si(OCH_2CH_2)_3N$,
has the distorted trigonal bipyramidal arrangement of atoms
about silicon with a transannular dative bond between nitrogen
and silicon.[6] In these silicon compounds with coordination

number greater than four, it is usually supposed that 3d
orbitals of silicon are substantially involved in the bonding
through $3sp^3d^2$ and $3sp^3d$ hybridizations.

Mechanisms involving the rapid initial formation of a
pentacovalent silicon complex have been commonly assumed in
discussions of displacement at a silicon atom in organosilicon

4. C.L. Frye, G.E. Vogel, and J.A. Hall, ibid., 83, 996 (1961).

5. M.G. Voronkov, Organosilicon Chemistry, Butterworths, London,
    1966, pp 35-59.

6. J.W. Turley and F.P. Boer, J. Am. Chem. Soc., 90, 4026
    (1968).

compounds. Sommer's work with optically active silicon compounds[7] is consistent with the postulated 3$\underline{d}$ orbital participation for lowering the energy of transition states.

The presence of multiple dπ-pπ bonding between silicon and electronegative atoms such as nitrogen, oxygen or halogens has been inferred in a variety of compounds by structural studies, by various spectroscopic studies, by chemical evidence and by other physical measurements. Hedberg[8] has shown by electron diffraction measurements that trisilylamine, $N(SiH_3)_3$, has a planar NSi_3 structure as contrasted with the normal pyramidal NC_3 skeleton of trimethylamine. This finding has also been supported by infra-red and Raman spectra measurements.[9,10] In the planar three-coordinated nitrogen, the electron pair which is not involved in σ-bonding to silicon may be regarded as occupying a $\underline{p}$ orbital that can overlap with vacant 3$\underline{d}$ orbitals on the silicon atoms. This results in a delocalization of the nitrogen lone-pair electrons over the three silicon atoms. This hypothesis of electron delocalization or dπ-pπ partial double bond is supported by the fact

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7. L.H. Sommer, Stereochemistry, Mechanism and Silicon, McGraw-Hill, New York, 1965.

8. K. Hedberg, J. Am. Chem. Soc., 77, 6491 (1955).

9. E.A.V. Ebsworth, J.R. Hall, M.J. Mackillop, D.C. Mckean, N. Sheppard, and L.A. Woodward, Spectrochim. Acta, 13, 202 (1958).

10. D.W. Robinson, J. Am. Chem. Soc., 80, 5924 (1958).

that Si-N bond length is much shorter than the one expected for a pure single bond,[8] and that it has very weak electron-donor power. In fact, it does not form complexes with diborane nor trimethylboron at temperatures down to -78°C, and even the adduct with boron trifluoride is unstable enough to give appreciable decomposition at -55°C.[11]

Contrary to the bent skeletal structures of H_3CNCO and H_3CNCS, linear structures of heavy atoms are found for silyl isocyanate, H_3SiNCO,[12] and silyl isothiocyanate, H_3SiNCS,[13,14] and near linear structures for their methyl derivatives, Me_3SiNCO and Me_3SiNCS.[15] These are also taken as indicative of $d\pi$-$p\pi$ bonding between silicon and nitrogen atoms. The similar marked increase in the bond angle due to $d\pi$-$p\pi$ bonding is also observed in siloxanes[16,17] and silazanes.[18]

11. A.B. Burg and E.S. Kuljian, ibid., 72, 3103 (1950).

12. M.C.L. Gerry, J.C. Thompson, and T.H. Sugden, Nature, 211 846 (1966).

13. E.V.A. Ebsworth, R. Mould, R. Taylor, G.R. Wilkinson, and L.A. Woodward, Trans. Faraday Soc., 58, 1069 (1962).

14. D.R. Jenkins, R. Kewley, and T.M. Sugden, ibid., 58, 1284 (1962).

15. K. Kimura, S. Katada, and S.H. Bauer, J. Am. Chem. Soc., 88, 416, (1966).

16. A. Almenningen, O. Bastiansen, V. Ewing, K. Hedberg, and M. Traetteberg, Acta Chem. Scand., 17, 2455 (1963).

17. M. Yokoi, Bull. Chem. Japan, 30, 100 (1957).

18. H. Kriegsmann, Z. Electrochem., 61, 1088 (1957).

-6-

The bond shortening is also observed in many silicon compounds of halogens, oxygen or nitrogen. Gordey et al[19] have found by microwave studies that silicon-halogen bond distances in a large number of halosilanes are shorter than those predicted by the additive rule, even allowing for corrections for ionic character of the bonds made by using the Schomaker-Stevens equation.[20] Further examples of bond shortening due to $d\pi$-$p\pi$ bond are also found in siloxanes.[16,17]

The dipole moments of chlorosilanes would be expected to be greater than those of chloromethanes, because silicon is larger and more electropositive than carbon. But the result observed by Brockway and Coop[21] indicates contrary to this expectation. This is believed to arise because the polarity of the Si-Cl bond is reduced by $d\pi$-$p\pi$ dative bonding. The dipole moments of compounds with bonds between oxygen or sulfur atoms and the group IV B elements have been measured in benzene solution by Cumper et al.[22] They deduced the Me_3MO- and Me_3MS- (where M = group IV B elements) group moments and attributed the small group moment of Me_3SiO- to the $d\pi$-$p\pi$ interaction in Si-O bond.

19. W. Gordy, W.V. Smith, and R.F. Trambarulo, "Microwave Spectroscopy", John Wiley and Sons, New York, N.Y., 1953, Chapter 8.

20. V. Schomaker and D.P. Stevenson, J. Am. Chem. Soc., 63, 37 (1941).

21. L.O. Brockway and I.E. Coop, Trans. Faraday Soc., 34, 1429 (1938).

22. C.W.N. Cumper, A. Melnikoff, and A.I. Vogel, J. Chem. Soc., A, 246 (1966).

A trimethylsilyl group on a benzene ring exerts two effects. Relative to the hydrogen atom it releases electrons toward the ring by inductive effect (+I) and at the same time withdraws π-electrons from the ring through dπ-pπ bonding between d orbitals of silicon and π-electrons of the ring (-T). The effect of m- and p-Me_3Si substitution on the ionization constants of aniline, dimethylaniline, phenol and benzoic acid has been studied, and their Hammett σ-values have been determined by Benkeser et al.[23] The σ-values show that a m-Me_3Si group exerts only an inductive effect, while a p-Me_3Si group enters into resonance with the aromatic ring (-T effect), resulting in reduction of the inductive effect of the group.

Eaborn et al. studied the rates of hydrogen exchange of substituted tritiated acetylenes, $X-C\equiv C-^3H$, in an aquous buffered methanolic solution, in which X = Me_3Si, Et_3Si and Me_3C.[24] Since the steric effect is practically absent in this reaction, the greater reactivity observed for trimethylsilyl and triethylsilyl derivatives as compared with the tertiary butyl compound is attributed to dπ-pπ interaction between silicon atom and the alkynyl group resulting in a stabilization of the negatively charged transition state.

West et al. studied the Lewis acidity and basicity of Ph_3MOH (where M = group IV B elements) by measuring the OH

23. R.A. Benkeser and H.R. Krysiak, J. Am. Chem. Soc., <u>75</u>, 2421 (1953).

24. C. Eaborn, G.A. Skinner, and D.R.M. Walton, J. Organomet. Chem., <u>6</u>, 438 (1966).

frequency shift upon hydrogen bonding when these compounds are mixed with a base (ethyl ether) or an acid (phenol).[25] The trends in acidity and basicity in these compounds indicate that dative π-bonding from oxygen to M is in the following order: Si>Ge>Sn≃Pb≃C. Abel et al. also obtained the similar results from the relative donor properties of some organo-metallic bases by measuring the C-D frequency shift of deuteriochloroform in solution of the bases.[26]

As dπ-pπ bonding in silicon compounds would significantly influence the screening of the nuclei and the polarity of the bonds, this effect can be studied using the nuclear magnetic resonance technique. Chemical shifts and coupling constants of organosilicon compounds such as organohalosilanes, silanols, siloxanes, phenylsilanes and silyl and disilanyl compounds have been measured, and the results were interpreted on the basis of dπ-pπ dative bonding.[27-32]

25. R. West, R.H. Baney, and D.L. Powell, J. Am. Chem. Soc., 82, 6269 (1960).

26. E.W. Abel, D.A. Armitage, and G.R. Willey, Trans. Faraday Soc., 60, 1257 (1964); E.W. Abel, D.A. Armitage, and D.B. Brady, ibid., 62, 3459 (1966).

27. E. Schnell and E.G. Rochow, J. Inorg. & Nucl. Chem., 6, 303 (1958).

28. A.L. Allred, E.G. Rochow, and F.G.A. Stone, ibid., 2, 416 (1956).

29. H. Schmidbaur, J. Am. Chem. Soc., 85, 2336 (1963).

30. G.M. Whitesides, J.G. Selgestad, S.P. Thomas, D.W. Andrews, B.A. Morrison, E.J. Panek and J. San Fillipo, Jr., J. Organomet. Chem., 22, 365 (1970).

31. C.H. Van Dyde and A.G. MacDiarmid, Inorg. Chem. 3, 1071 (1964); J. Mack and C.H. Yoder, ibid., 8, 278 (1969).

32. E.A.V. Ebsworth and J.J. Turner, J. Phys. Chem., 67, 805 (1963).

Curtis and Allred studied the electron spin resonance spectra of uninegative anion radicals of the biphenyl compounds, $Me_3M-C_6H_4-C_6H_5$ and $Me_3M-C_6H_4-C_6H_4-MMe_3$, (where M = Si, Ge and Sn), and by LCAO-MO calculation they estimate the π-bond orders of $Si-C_{ar}$ and $Ge-C_{ar}$ to be 0.18 and 0.13 respectively.[33] The most direct evidence of electron delocalization through d-orbitals of silicon has been revealed in the electron spin resonance study of anion radical of dodecamethylcyclohexasilane, $[Si(CH_3)_2]_6$.[34] Recently Nagy and Reffy have performed quantum chemical calculations for vinyl and phenyl derivatives of silicon and estimated the π-bond order of Si-C to be 0.11 in each compound,[35] which is somewhat smaller than the value of 0.18 by Curtis and Allred, in the case of negatively charged radical ion.[33]

It can therefore be concluded from the above evidence that the participation of 3d orbitals in silicon chemistry, particularly in the dative π-bonding, is at present well established, both by chemical evidence and physical measurements. It is the purpose of this work to contribute to the knowledge of such $d\pi$-$p\pi$ interaction in the Si-N bond, by investigating the donor property of silylamines in transition metal complexes. In order to pursue this purpose, several

33. M.D. Curtis and A.L. Allred, J. Am. Chem. Soc., 87, 2554 (1965).

34. G.R. Husk and R. West, ibid., 87, 3993 (1965).

35. J. Nagy and J. Reffy, J. Organomet. Chem., 22, 573 (1970), ibid., 23, 71 (1970).

new polydentate organosilylamines have been synthesized and transition metal complexes prepared with these new organosilylamines as well as with those that had been previously synthesized by others.

PART I.   SYNTHESIS OF ORGANOSILYL POLYAMINES
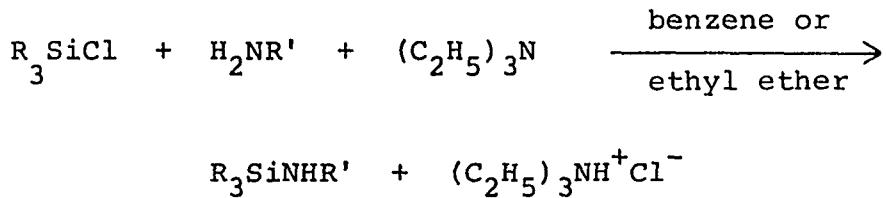
A.   Methods of Preparation

1.   General Methods

The N-organosilyl polyamines under study in this work have been prepared by one of the three methods described below:

a.   Direct Aminolysis

Triorganohalosilanes react with primary and secondary amines to form N-triorganosilyl amine and amine hydrochloride in a solvent such as ethyl ether or benzene.[36,37]   Because of its high basicity, triethylamine was used in excess to promote aminolysis by accepting HCl produced in all direct reactions.

$$R_3SiCl \; + \; H_2NR' \; + \; (C_2H_5)_3N \; \xrightarrow[\text{ethyl ether}]{\text{benzene or}}$$

$$R_3SiNHR' \; + \; (C_2H_5)_3NH^+Cl^-$$
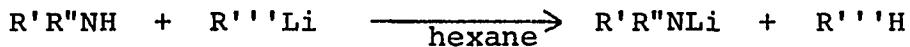
b.   Reaction with Lithium Amides

This involves the preparation of the lithium derivative of an amine, R'R"NLi, followed by its treatment with organohalosilanes. Lithium derivatives of amines can be prepared

36.   F.A. Henglein and K. Lienhard, Makromol. Chem., 32, 218 (1959).

37.   E. Larsson and O.M. Mjorne, Svensk. Kem. Tid., 61, 59 (1949); Chem. Abstr., 43, 5739 (1949).

by the addition of an organo-lithium reagent to the amines in a solvent such as pentane or hexane.

$$R'R''NH + R'''Li \xrightarrow[\text{hexane}]{} R'R''NLi + R'''H$$

$$R'R''NLi + R_3SiCl \xrightarrow[\text{hexane}]{} R'R''NSiR_3 + LiCl$$

Kummer and Rochow used lithium derivatives of N,N'-bis(trimethylsilyl)ethylenediamine, $(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$, and organohalosilanes to prepare tri- and tetra-substituted ethylenediamine compounds with good yields.[38]

c. Transamination

This method employs the reaction of a primary or secondary amine with a triorganosilylamine.

$$R_3SiNR_2' + HNR''R''' \rightleftharpoons R_3SiNR''R''' + HNR_2'$$

In view of the fact that the above reaction is reversible this technique can be used only if the amine formed is the most volatile component of the reaction mixture and the equilibrium of the reaction can be shifted to the right by distillation of the amine produced.[39] Trimethylsilyldiethylamine, $(CH_3)_3SiN(C_2H_5)_2$, was prepared in large quantities by direct aminolysis of $(CH_3)_3SiCl$ with $(C_2H_5)_2NH$ in ether solution.[40]

38. D. Kummer and E.G. Rochow, Zeit. Anorg. Allgem. Chem., 321, 21 (1963).

39. H.H. Anderson, J. Am. Chem. Soc., 73, 5803 (1951).
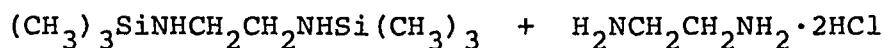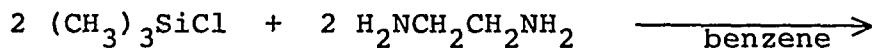
40. R.O. Sauer and R.H. Hasek, ibid., 68, 241 (1946).

A slightly excessive amount of trimethylsilyldiethylamine was refluxed with a desired amine, and the newly produced silylamine was recovered after distilling off diethylamine. This method of transamination is particularly valuable when a trialkylsilyl derivative of a less available amine is required, since it does not require any procedures other than distillation. Thus the method provides a high yield relative to the amount of amine used.

2. Methods for Synthesis of Specific Compounds

a. N,N'-bis(triorganosilyl)ethylenediamines
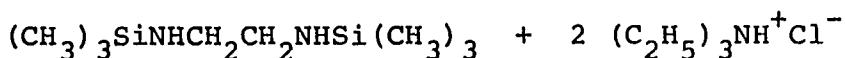
In preparing N,N'-bis(trimethylsilyl)ethylenediamine, $(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$, the direct aminolysis method as used by Henglein and Lienhard[36] was followed. In an initial preparation, trimethylchlorosilane was allowed to react with equimolar quantity of ethylenediamine in benzene solution. At the end of the reaction, ethylenediamine hydrochloride was removed by filtration from the reaction mixture. After removing benzene by distillation at atmospheric pressure

$$2 \ (CH_3)_3SiCl \ + \ 2 \ H_2NCH_2CH_2NH_2 \ \xrightarrow{\text{benzene}}$$

$$(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3 \ + \ H_2NCH_2CH_2NH_2 \cdot 2HCl$$

the product was fractionally distilled under reduced pressure.

Since large amounts of N,N'-bis(trimethylsilyl)ethylenediamine were needed for repeated reactions with the selected

metal halides to be described later, this silylamine had to

be prepared many times. In repeating the preparatory pro-

cedure, a slight modification of the original procedure was

adapted. Two moles of trimethylchlorosilane were allowed

to react with one mole of ethylenediamine in benzene solution,

with an excess of triethylamine as hydrogen chloride acceptor:

$$2 \ (CH_3)_3SiCl \ + \ H_2NCH_2CH_2NH_2 \ + \ 2 \ N(C_2H_5)_3 \ \xrightarrow{benzene}$$

$$(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3 \ + \ 2 \ (C_2H_5)_3NH^+Cl^-$$

Follwoing the completion of the reaction, triethylamine

hydrochloride was filtered off and the filtrate was worked

up as described previously.

The preparation of N,N'-bis(dimethylphenylsilyl)ethylene-

diamine, $(C_6H_5)(CH_3)_2SiNHCH_2CH_2NHSi(CH_3)_2(C_6H_5)$, was achieved

by the same modified aminolysis procedure as described above,

using dimethylphenylchlorosilane, $(C_6H_5)(CH_3)_2SiCl$. Because

of the high cost of this compound and also because of large

quantities of dimethyldichlorosilane, $(CH_3)_2SiCl_2$, available

in this laboratory (kindly supplied by General Electric

Company), dimethylphenylchlorosilane was prepared by the

standard Grignard reaction between dimethyldichlorosilane

and bromobenzene Grignard reagent.[41] The identity of
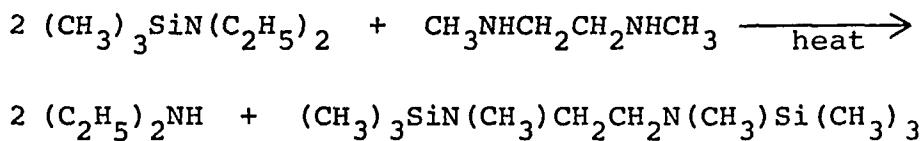
41. M. Maienthal, M. Hellmann, C.P. Haber, L.A. Hymo, S. Carpenter and A.J. Carr, J. Am. Chem. Soc., 76, 6392 (1954).

dimethylphenylchlorosilane was established by comparing the physical properties and infrared spectra with previous data reported by Grenoble and Launer.[42]

The result of this direct aminolysis reaction produced the desired di-substituted ethylenediamines described above. Additionally an appreciable amount of high boiling tri-substituted ethylenediamines, $(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$ and $(C_6H_5)(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2(C_6H_5)]_2$, was obtained as by-products.

b. N,N'-bis(triorganosilyl)dimethylethylenediamines

To prepare N,N'-bis(trimethylsilyl)dimethylethylene-diamine, $(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$, both the trans-amination and direct aminolysis methods were employed. For use in the transamination procedure, trimethylsilyldiethyl-amine, $(CH_3)_3SiN(C_2H_5)_2$, was prepared by using the direct aminolysis in ether.[40] Trimethylsilyldiethylamine was re-fluxed with a slight excess of N,N'dimethylethylenediamine, $CH_3NHCH_2CH_2NHCH_3$, for several hours.

$$2\ (CH_3)_3SiN(C_2H_5)_2\ +\ CH_3NHCH_2CH_2NHCH_3\ \xrightarrow[heat]{}$$

$$2\ (C_2H_5)_2NH\ +\ (CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$$

Diethylamine which had been formed during the transamination
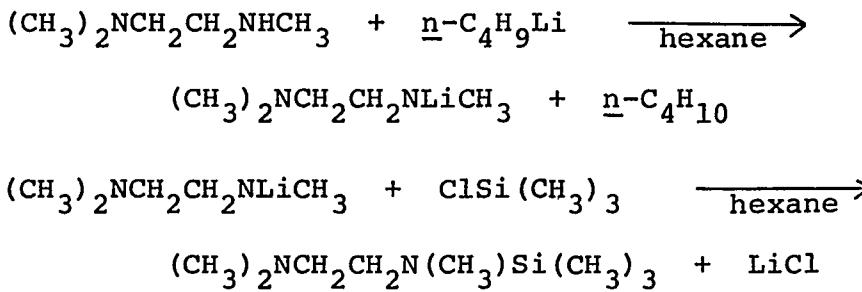
42. M.E. Grenoble and P.J. Launer, Appl. Spectrosc., 14, 85 (1960).

reaction was distilled away first. After removal of diethyl-
amine the mixture was heated additionally for several hours.
The resulting mixture contained low-boiling unreacted reactants
and possibly mono-substituted dimethylethylenediamine, which
was subsequently removed by further distillation. Following
this, the final product, N,N'-bis(trimethylsilyl)dimethyl-
ethylenediamine, was fractionally distilled.

Alternatively, the same product was also obtained by
the direct aminolysis technique mentioned previously. The
production of N,N'-bis(dimethylphenylsilyl)dimethylethylene-
diamine, $(C_6H_5)(CH_3)_2SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_2(C_6H_5)$, was
also achieved by the direct aminolysis reaction.

c. Triorganosilyltrimethylethylenediamines

In preparing trimethylsilyltrimethylethylenediamine,
$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$, a commercially available n-
butyllithium in hexane (22% by weight, Alfa Inorganics) was
reacted with trimethylethylenediamine, $(CH_3)_2NCH_2CH_2NH(CH_3)$.
About 25% excess of trimethylchlorosilane diluted in hexane
was allowed to drip into the lithium amide solution prepared
as above. When the exothermic reaction had subsided, the
reaction mixture was heated to its reflux temperature for
several hours. At the end of the reaction, the mixture was
allowed to cool and lithium chloride was removed subsequently
by filtration from the reaction product.

$$(CH_3)_2NCH_2CH_2NHCH_3 \ + \ \underline{n}\text{-}C_4H_9Li \ \xrightarrow[\text{hexane}]{}$$

$$(CH_3)_2NCH_2CH_2NLiCH_3 \ + \ \underline{n}\text{-}C_4H_{10}$$

$$(CH_3)_2NCH_2CH_2NLiCH_3 \ + \ ClSi(CH_3)_3 \ \xrightarrow[\text{hexane}]{}$$

$$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3 \ + \ LiCl$$
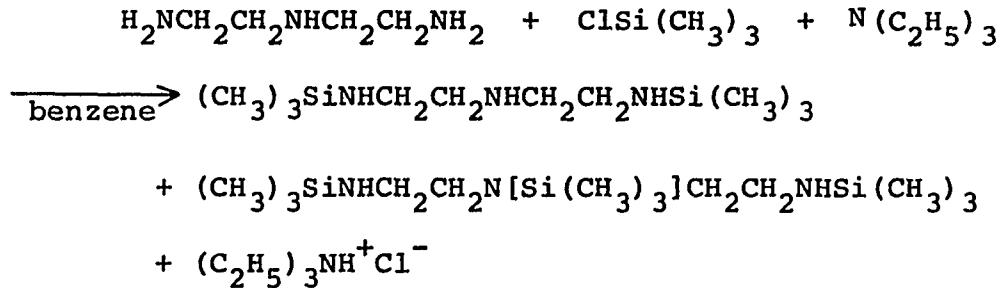
After removing hexane by distillation at atmospheric pressure, the product was fractionally distilled under reduced pressure. About 60% yield of trimethylsilyltrimethylethylenediamine was obtained, together with a small amount of $\underline{n}$-butyltrimethylsilane.

Alternatively, the same compound was prepared by the direct aminolysis technique mentioned previously. Dimethylphenylsilyltrimethylethylenediamine, $(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_2$-$(C_6H_5)$, was prepared by the direct aminolysis of dimethylphenylchlorosilane with trimethylethylenediamine in the presence of triethylamine.

d. N,N"-Bis(trimethylsilyl)- and N,N',N"-tris(trimethylsilyl)-
   diethylenetriamines

Bis- and tris(trimethylsilyl)diethylenetriamines were prepared by the direct aminolysis of diethylenetriamine and trimethylchlorosilane in benzene solution with an excess of triethylamine acting as HCl acceptor.

$$H_2NCH_2CH_2NHCH_2CH_2NH_2 \ + \ ClSi(CH_3)_3 \ + \ N(C_2H_5)_3$$

$$\xrightarrow[benzene]{} (CH_3)_3SiNHCH_2CH_2NHCH_2CH_2NHSi(CH_3)_3$$

$$+ \ (CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]CH_2CH_2NHSi(CH_3)_3$$

$$+ \ (C_2H_5)_3NH^+Cl^-$$

After removing amine hydrochloride and solvent in the standard manner, the product mixture was separated by fractional distillation under reduced pressure.

B. Results and Characterization of the Products

1. Trimethylsilyl and dimethylphenylsilyl derivatives of ethylenediamine, N,N'-dimethyl- and trimethylethylenediamine.

Even though some of these compounds were synthesized by earlier investigators,[43,44,45] and NMR studies of some have been reported by Kummer and Baldeschwieler,[46] infrared characteristics of these compounds had not been described before this work began. Since the structure of the compounds can be identified by characteristic bands in the IR and NMR spectra, the results of IR and NMR observations are summarized below. Individual recordings of these spectra can be found in the Appendix.

The assignments of general organic IR group frequencies discussed in this dissertation have been arrived at by comparing the results with those described by Bellamy,[47] Colthup,

43. H. Pfleger, "Contribution to the Chemistry of Silylamines and Silazanes", Technical report, NONR 1866 (13), September, 1961.

44. J.F. Klebe, J. Polym. Sci., Part A, 2, 2673 (1964).

45. W. Fink, Chem. Ber., 99, 2267 (1966).

46. D. Kummer and J.D. Baldeschwieler, J. Phys. Chem., 67, 98 (1963).

47. L.J. Bellamy, "The Infra-red Spectra of Complex Molecules", 2nd ed., John Wiley and Sons, New York, 1958, pp 13-33, 64-84, 248-262.

Daly and Wiberley,[48] and Silverstein and Bassler.[49]

A significant and most obvious change in the infrared spectra of the amines upon silylation is the alteration in the N-H stretching range. The asymmetric and symmetric stretching bands of the NH_2 groups of ethylenediamine at 3360 and 3280 cm^{-1} (Fig. 1.1) disappear, and a single band corresponding to N-H stretching vibration appears in the same region (3400-3350 cm^{-1}) upon silylation (Fig. 1.5 and Fig. 1.6). The secondary amines, N,N'-dimethyl- and trimethyl-ethylenediamine, show an N-H stretching band at 3290 and 3320 cm^{-1} respectively (Fig. 1.2 and Fig. 1.3). Upon total silylation this band disappears completely (Fig. 1.7, Fig. 1.9, Fig. 1.17 and Fig. 1.18).

For the trimethylsilyl derivatives, the most characteristic band is the symmetric deformation band of the methyl group on silicon, at 1250 cm^{-1}. This band is intense and sharp, and therefore readily identified. When there are three methyl groups attached to one silicon atom, this band sometimes splits into two components of unequal intensity. This symmetric deformation band at 1250 cm^{-1} is usually

48. N.B. Colthup, L.H. Daly and S.E. Wilberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964, pp 191-199, 220-233, 278-282.

49. R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compounds", 2nd ed., John Wiley and Sons, New York, 1967, pp 64-109.

accompanied by one or more equally strong bands at 840 cm^{-1} and 750 cm^{-1}, arising from the methyl rocking and Si-C stretching vibrations, respectively.[50] The characteristic bands of trimethylsilyl groups of the compounds are tabulated in Table 1.

With respect to the dimethylphenylsilyl derivatives, the characteristic bands include the same symmetric deformation band of a methyl group on silicon at 1250 cm^{-1} and the methyl rocking band at 830 cm^{-1} which are observed in trimethylsilyl derivatives. However, the Si-C stretching mode shows a slight difference, registering two bands at 790 and 640 cm^{-1} due to asymmetric and symmetric stretching vibrations, respectively.

Several other prominent and invariant bands characteristic of diemthylphenylsilyl derivatives are due to vibrations of the silicon-phenyl grouping. These characteristic silicon-phenyl bands are as follows:

i   Several weak bands in the range of 3000-3055 cm^{-1}, representing aromatic carbon-hydrogen stretching vibration.

ii   Four weak bands between 2000-1650 cm^{-1} for overtones and combination bands. These indicate the presence of a monosubstituted benzene ring.

iii   Three bands at 1425, 1486 and 1590 cm^{-1}, related to C=C ring-stretching modes.

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50. A.L. Smith, Spectrochim. Acta, <u>16</u>, 87 (1960).

Table 1. <u>The Characteristic IR Absorption Bands of the Trimethylsilyl Group</u>

Compounds	$\delta_s CH_3(Si)$	ρCH_3	$\nu_{asy} Si-C$
$(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$	1260, 1251	835	740
$(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$	1260, 1252	836	750
$(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$	1260, 1250	830	758, 742
$(CH_3)_3SiN(CH_3)CH_2CH_2NH(CH_3)$	1252	834	754, 742
$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$	1262, 1255	834	756, 742
$(CH_3CH_2)_2NSi(CH_3)_3$	1263, 1250	838	752, 743

iv An intense and sharp band at 1120 cm^{-1}, due to a
planar ring vibration with some Si-C stretching
character.[51]

v Strong bands at 740 and 700 cm^{-1}, representing the
out-of-plane hydrogen bending and ring bending modes,
respectively.

vi Three additional weak but invariant bands at 997,
620 and 470 cm^{-1}, which have not been identified.

The characteristic bands of dimethylphenyl groups of the
compounds are recorded in Table 2. (Carbon-Hydrogen stretch-
ing bands and the bands due to overtones and combination bands
are not included.) There is very good agreement between
these band positions and those reported by previous workers
for other compounds containing silicon-phenyl groups.[52,53,54]

Next to the strong methyl rocking band at 835 cm^{-1}, there
appears a medium-strength peak or shoulder on the higher fre-
quency side at about 830-900 cm^{-1}, which might be attributed
to N-Si stretching vibration. In terms of band position this

51. R.N. Kniseley, V.A. Fassel and E.E. Conrad, Spectrochim.
Acta, 15, 651 (1959).

52. M.E. Grenoble and P.J. Launer, Appl. Spectrosc., 14, 85
(1960).

53. H. Kriegsmann and K.H. Schowtka, Z. Phys. Chem. (Leipzig),
209, 261 (1958).

54. H. Kriegsmann and G. Engelhardt, Z. Anorg. Allgo. Chem.,
310, 320 (1961).
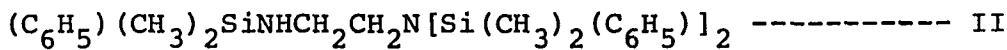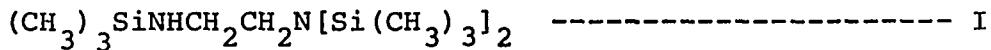
Table 2. The Characteristic IR Absorption Bands of the Dimethylphenylsilyl Group

Compounds	$-Si(CH_3)_2-$ group*				$-Si(C_6H_5)-$ group*				
$PhSi(CH_3)_2Cl$	1256	839 810	788	658	1590 1487 1429	1118	998	733	695
$Ph(CH_3)_2SiOSi(CH_3)_2Ph$	1255	830	787	648	1590 1487 1428	1118	996	726	696
$Ph(CH_3)_2SiNHCH_2CH_2NHSi(CH_3)_2Ph$	1248	824	779	638	1588 1485 1425	1112	996	729	697
$Ph(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2Ph]_2$	1249	825	780	643	1588 1485 1426	1112	997	727	697
$\underset{CH_3}{\overset{CH_3}{PhSiN(CH_3)CH_2CH_2N(CH_3)SiPh}}$	1250	825	775	639	1589 1486 1426	1111	994	725	698
$(CH_3)_2NCH_2CH_2N(CH_3)\underset{CH_3}{SiPh}$	1251	828 816	776	628	1586 1485 1425	1113	997	725	698

* The assignment of each individual vibrational mode is discussed on pages 20 and 22.

-24-

assignment is in agreement with previously published data (Table 3). However, this is not an **unequivocal** assignment for N-Si stretching vibration, since the characteristically high intensity of N-Si vibration is not observed.

On the other hand, the asymmetric and symmetric Si-N-Si stretching vibrations can be assigned unambiguously for the compounds with a silazane moiety, i.e. tris(trimethylsilyl)-ethylenediamine(I) and tris(dimethylphenylsilyl)ethylene-diamine(II).

$(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$ ---------------------- I

$(C_6H_5)(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2(C_6H_5)]_2$ ----------- II

These Si-N-Si stretching modes are located at 913 and 560 cm^{-1} in I and 911 and 580 cm^{-1} in II. This assignment is in clear agreement with the data reported previously for silazanes both with regards to the band positions and their intensity (Table 4).

NMR spectra of N,N'-bis(trimethylsilyl)ethylenediamine and N,N,N'-tris(trimethylsilyl)ethylenediamine show trimethyl-silyl proton resonance at 9.92-10.00 τ, a complex multiplet centered at 7.38-7.40 τ for the bridging methylene protons, and a very broad peak centered at about 9.4 τ for NH protons. The integration of the three resonance peaks agrees well with the expected ratio of the protons from the structural con-sideration. N,N'-bis(trimethylsilyl)dimethylethylenediamine

Table 3. <u>N-Si Stretching Vibrations in N-Si Compounds</u>

Compounds	ν_{N-Si}	Reference
$(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$	865	
$(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$	865, 913, 560	
$(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$	855	
$CH_3NHCH_2CH_2N(CH_3)Si(CH_3)_3$	850	
$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$	850, 865	
$Ph(CH_3)_2SiNHCH_2CH_2NHSi(CH_3)_2Ph$	870	
$Ph(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2Ph]_2$	850, 911, 580	
$Ph(CH_3)_2SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_2Ph$	830	
$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_2Ph$	860	
$R-CONHSi(CH_3)_3$	841-850	55
$CH_3NHSi(CH_3)_3$	866	56
$(CH_3)_2NSi(CH_3)_3$	851	56
$PhNSi(CH_3)_3$	899	57

55. J. Pump and U. Wannagat, Monatsh. Chem., <u>93</u>, 352 (1962).

56. J. Goubeau and J. Jiménez-Barbera, Z. Anorg. Allg. Chem., <u>303</u>, 217 (1960).

57. E.W. Randall, J.J. Ellner and J.J. Zuckerman, Inorg. Nucl. Chem. Lett., <u>1</u>, 109 (1966).

Table 4. <u>Asymmetric and Symmetric Stretching
Vibrations of Si-N-Si in Organosilazanes</u>

Compounds	$\nu_{as}N\text{-}Si_2$	$\nu_s N\text{-}Si_2$	References
I	913	560	
II	911	580	
$HN[Si(CH_3)_3]_2$	929	564	56
$CH_3N[Si(CH_3)_3]_2$	909	504	56
$[(CH_3)NSi(CH_3)_2]_3$	915	570	58
$[(C_2H_5)NSi(CH_3)_2]_3$	922	579	58
$HN[Si(CH_3)_2(C_6H_5)]_2$	935	598	54

58. E.W. Abel and R.P. Bush, J. Inorg. Nucl. Chem., <u>26</u>, 1685 (1964).

also shows a strong peak at 9.99 τ for trimethylsilyl protons, a sharp single peak at 7.34 τ for bridging methylene protons, and a peak at 7.55 τ for N-CH$_3$ protons with a correct integration. All these observations are in good agreement with previously published results by Kummer and Baldeschwieler.[46]

NMR spectra of trimethylsilyl-N,N'-dimethylethylene-diamine, shown in Fig. 2.2, exhibits clear resonance peaks. Their spectral characteristics are summarized in Table 5.

Table 5. Proton Chemical Shifts in Trimethylsilyl-N,N'-dimethylethylenediamine

Proton Type	Chemical Shift (τ)	Integration Observed	Theoretical
-Si(CH$_3$)$_3$	9.95	9.0	9.0
-NH-	∿9.0(broad)	∿1	1.0
-CH$_2$-	∿7.5(complex)	⎤	4.0
-N(CH$_3$)-	7.56	⎦ 9.9	6.0

These assignments of the proton resonance peaks are achieved on the basis of the proton chemical shifts in trimethylsilyl derivatives of ethylenediamine mentioned in the previous reference.[46] The intense resonance peak at 9.95 τ is due to the trimethylsilyl protons. Although its intensity of absorption is extremely low, a broad N-H resonance approximately centered at 9.0 τ is readily detected by integration. This

broad N-H proton resonance results from the slow exchange rate of an N-H proton, and from the spin number of 1(I=1) and electrical quadrupole moment of the ^{14}N nucleus.[59] A sharp peak at 7.56 τ is due to N(CH$_3$) protons. A group of small complex peaks centered approximately at 7.5 τ is assigned to the bridging methylene protons. This complex resonance results from the mutual coupling of the methylene protons with the NH proton. Since the sharp N-CH$_3$ proton resonance peak is located in the middle of the wide complex methylene proton resonance, the separate integration can not be achieved easily. However, the combined effect is readily measured. From the integration, the trimethylsilyl protons, N-H protons and those of methylene and N(CH$_3$) are found to be in the ratio of 9.0 : ∿1 : 9.9, which is in excellent agreement with the theoretical value of 9.0 : 1.0 : 10.0(4.0+6.0).

The NMR spectrum of trimethylsilyltrimethylethylenediamine is shown in Fig. 2.3, and the observations are summarized in Table 6. It is clear that the 9.96 τ resonance line is due to the trimethylsilyl protons. The other somewhat smaller lines at 7.75 τ and 7.51 τ are readily assigned to N-methyl protons of -N(CH$_3$)$_2$ and of -SiN(CH$_3$), respectively. This assignment is based on the relative intensity of the peaks, which is approximately 2 : 1, and on the consideration of

59.   R.M. Silverstein and G.C. Bassler, "Spectrometric Identification of Organic Compounds", 2nd ed., John Wiley and Sons, New York, 1967, p 123.

Table 6. <u>Proton Chemical Shifts in Trimethylsilyltrimethyl-ethylenediamine</u>

Proton Type	Chemical Shift (τ)	Integration Observed	Theoretical
$-Si(CH_3)_3$	9.96	9.0	9.0
$-CH_2-$	7~8(complex)		4.0
$-N(CH_3)_2$	7.75	13.0	6.0
$-SiN(CH_3)$	7.51		3.0

electron-withdrawing characteristics of the trimethylsilyl group. The trimethylsilyl group will withdraw electron density away from a nitrogen atom by $d\pi$-$p\pi$ interaction. In turn, this electron withdrawal apparently results in slight deshielding of the methyl protons on the nitrogen atom. Therefore, the proton resonance line produced by the methyl group of $-SiNCH_3-$ lies at a lower field strength than the resonance of methyl protons of a $-N(CH_3)_2$ group. Likewise, the complex multiplet centered at 7.2 τ is assignable to the bridging methylene protons next to a $-N(CH_3)Si(CH_3)_3$ group, while the other multiplet centered approximately at 7.6 τ can be assigned to the bridging methylene protons next to a $-N(CH_3)_2$ group.

Since the two methyl proton peaks are so closely located, their integration does not separate one kind of protons from

the other. However, results of the integration indicate the ratio of trimethylsilyl protons to the sum of all the other protons to be 9.0 to 13.0, which is in exact agreement with the theoretical value.

NMR spectra of dimethylphenylsilyl derivatives of ethylenediamine, N,N'-dimethylethylenediamine and trimethyl-ethylenediamine are shown in Figs. 2.5 through 2.10, and their results are summarized in Tables 7, 8, 9, and 10.

The resonances of dimethylphenylsilyl derivatives are readily assigned to the corresponding protons indicated in the above tables. These assignments are based on the integra-tion of peaks and on the comparison of analogous chemical shifts observed in trimethylsilyl derivatives of the diamines described earlier. The general spectral features of the di-methylphenylsilyl derivatives resemble those of trimethylsilyl derivatives, except for the appearance of a complex phenyl proton resonance at 2.7 τ and a slight down-field shift of the absorption for silylmethyl group protons.

2. Trimethylsilyl derivatives of diethylenetriamine

As indicated under General Methods of Preparation, a low-boiling fraction of the trimethylsilyl derivative of diethyl-enetriamine, with a boiling range of 116-118°C at 7 mm Hg, was obtained by fractional vacuum distillation of the reaction product of aminolysis of $(CH_3)_3SiCl$ by the triamine. Addition-ally, a high-boiling fraction of the trimethylsilyl derivative

Table 7. Proton Chemical Shifts in N,N'-Bis(di-
methylphenylsilyl)ethylenediamine

Proton Type	Chemical Shifts (τ)	Integration Observed	Theoretical
$=Si(CH_3)_2$	9.77	12.0	12.0
$-NH-$	9.3(broad)	$\sim$2	2.0
$-CH_2-$	7.37(complex)	3.9	4.0
$\equiv Si(C_6H_5)$	2.75(complex)	10.0	10.0

Table 8. Proton Chemical Shifts in Tris(dimethyl-
phenylsilyl)ethylenediamine

Proton Type	Chemical Shifts (τ)	Integration Observed	Theoretical
$=Si(CH_3)_2$	9.88	1⎤ 18.0	18.0
$N[Si(CH_3)_2-]_2$	9.76	2⎦	
$-CH_2-$	7.35(complex)	4.0	4.0
$\equiv Si(C_6H_5)$	2.78	14.8	15.0

Table 9. <u>Proton Chemical Shifts in N,N'-Bis(dimethyl-</u>

<u>phenylsilyl)dimethylethylenediamine</u>
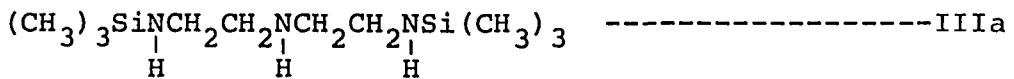
Proton Type	Chemical Shifts (τ)	Integration Observed	Theoretical
$=Si(CH_3)_2$	9.75	11.9	12.0
$=N(CH_3)$	7.57	6.0	6.0
$-CH_2-$	7.24	4.0	4.0
$\equiv Si(C_6H_5)$	2.75(complex)	10.2	10.0

Table 10. <u>Proton Chemical Shifts in Dimethylphenyl-</u>

<u>silyltrimethylethylenediamine</u>

Proton Type	Chemical Shifts (τ)	Integration Observed	Theoretical
$=Si(CH_3)_2$	9.72	6.0	6.0
$-CH_2-$	7∿8(complex)		
$-N(CH_3)_2$	7.66	13.2	13.0
$=N(CH_3)$	7.47		
$\equiv Si(C_6H_5)$	2.70	5.0	5.0

/

of the amine, with a boiling range of 133-134°C at 7 mm Hg,
also was obtained from further distillation. From elemental
analysis, molecular weight determination, and NMR spectra,
the low-boiling fraction was found to be bis(trimethylsilyl)-
diethylenetriamine, $C_{10}H_{29}N_3Si_2$, whereas the high-boiling
fraction was determined to be tris(trimethylsilyl)diethyl-
enetriamine, $C_{13}H_{37}N_3Si_3$. In the following section the
possible structures of each compound are discussed, and the
correct structure of each compound is determined by the chemi-
cal evidence and from IR and NMR spectra.

From the aminolysis reaction, two structures, IIIa and
IIIb, can reasonably be proposed for bis(trimethylsilyl)-
diethylenetriamine, called III:

$$(CH_3)_3Si\underset{\overset{|}{H}}{N}CH_2CH_2\underset{\overset{|}{H}}{N}CH_2CH_2\underset{\overset{|}{H}}{N}Si(CH_3)_3 \quad \text{------------------IIIa}$$

$$(CH_3)_3Si\underset{\overset{|}{H}}{N}CH_2CH_2\underset{\overset{|}{Si(CH_3)_3}}{N}CH_2CH_2NH_2 \quad \text{------------------IIIb}$$

Both structures, IIIa and IIIb satisfy all characteristic IR
bands related to the trimethylsilyl group which are observed
in Fig. 1.11 a, b and c. However, the following points permit
the differentiation of the two structures from each other.
For the structure IIIb, distinct characteristic IR bands
would result from the presence of the primary amine group,
$-NH_2$, at one end of the molecule. Such characteristic bands

would include strong asymmetric and symmetric stretching bands at 3550-3250 cm^{-1}, an intense NH_2 deformation band at 1650-1590 cm^{-1}, and broad, strong multiple absorption bands at 850-750 cm^{-1} due to the NH_2 wagging and twisting vibrations.[60] The IR spectra of the compound III, Figs. 1.11 a, b, and c, show two weak bands at 3385 cm^{-1} and 3315 cm^{-1}. Based on the appearance and intensity of these bands, it is reasonable to consider these two bands are not due to asymmetric and symmetric N-H stretching vibrations of IIIb, but rather due to the two different kinds of secondary amine N-H stretching vibrations present in the structure IIIa. Additionally there is no strong band at 1650-1590 cm^{-1} assignable to an NH_2 deformation vibration. An intense band at 838 cm^{-1} and a shoulder at 865 cm^{-1} are observed in the general range of NH_2 wagging and twisting vibrations. However, they are not pertinent in characterizing structures under consideration, as they can be clearly assigned to $Si(CH_3)_3$ methyl rocking and $N-Si(CH_3)_3$ stretching vibrations.[50] Thus, all the IR information discussed above favors the structure IIIa for the compound.

NMR spectra of the compound III are shown in Fig. 2.12, and are summarized in Table 11. From the chemical shifts

60. N.B. Colthup, L.H. Daly and S.E. Wilberley, "Introduction to Infrared and Raman Spectroscopy", Academic Press, New York, 1964, p. 278.
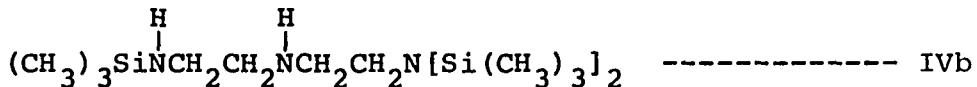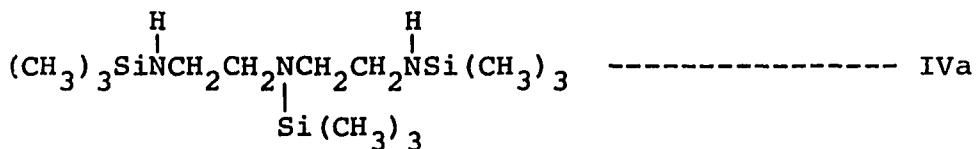
Table 11. Proton Chemical Shifts in N,N"-Bis(trimethyl-
silyl)diethylenetriamine

Proton Type	Chemical Shift (τ)	Integration Observed	Integration Theoretical
$-Si(CH_3)_3$	9.94	17.9	18
$-NH-$	8.84 (broad) 9.1 (very broad)] 3		3
$-CH_2-$	7.36 (broad complex)	8.0	8

and relative intensities of the peaks the resonances are easily

assigned. Trimethylsilyl proton resonance gives a sharp peak

at 9.94 τ, indicating the presence of an identical environ-

ment for the two trimethylsilyl groups. This is consistent

with the structure IIIa, but not with IIIb. Note also that

the absence of a sharp peak around 8.7 τ related to the

primary amine $-NH_2$ protons of diethylenetriamine (Fig. 2.11),

which would be expected for the structure IIIb, negates the

possibility that the compound III is in the form of IIIb.

Instead, there appear two wide bands centered at 8.84 τ and

at about 9.1 τ which can be attributed respectively to RSiN-H

and R_2N-H protons of the structure IIIa. Thus the NMR and

IR spectra both indicate that IIIa represents the probable

structure of bis(trimethylsilyl)diethylenetriamine. Further-

more a consideration of the activity of the N-H group toward

silylation suggests that the above assignment is correct, since the primary-amine hydrogen is more reactive in silylation than the secondary-amine hydrogen.

From the direct aminolysis reaction the following two alternative structures are possible for tris(trimethylsilyl)-diethylenetriamine, IV.

$$(CH_3)_3SiNCH_2CH_2NCH_2CH_2NSi(CH_3)_3 \quad\text{---------------- IVa}$$

with H on the first and last N, and Si(CH_3)_3 on the middle N.

$$(CH_3)_3SiNCH_2CH_2NCH_2CH_2N[Si(CH_3)_3]_2 \quad\text{------------- IVb}$$

with H on the first and middle N.

It is a well-established fact that silylation of a secondary amine can proceed under much milder conditions than the further silylation of the silylamines. For instance, N,N'-dimethyl-ethylenediamine reacts readily with trimethylchlorosilane to form N,N'-bis(trimethylsilyl)dimethylethylenediamine at room temperature (p 15). However, the preparation of tris(trimethyl-silyl)ethylenediamine was achieved only by reacting trimethyl-chlorosilane with N,N'-bis(trimethylsilyl)ethylenediamine at higher temperature, or with the aid of a mono-lithium deriva-tive of the latter compound at room temperature[38]. Thus the chemical reactivity characteristics of silylation favors the structural formula IVa over IVb.

As was the case for compound III, two closely-located N-H stretching vibrations are expected for the structural formula

IVb. This has not been observed (Figs. 1.12a, c). On the contrary, the IR spectra demonstrate only a single peak, which would be expected if the compound had a structural formula corresponding to IVa.

For structure IVb, a strong asymmetric and a weak symmetric stretching vibration of the $N-Si_2$ group should appear at about 910 cm^{-1} and 580-560 cm^{-1}, respectively, which is a well-characterized feature in IR spectra of $(CH_3)_3SiNHCH_2CH_2-N[Si(CH_3)_3]_2$ and $(CH_3)_2(C_6H_5)SiNHCH_2CH_2N[Si(CH_3)_2(C_6H_5)]_2$ (p.25). But in the IR spectra of the compound IV, Fig. 1.12b, the band at 910 cm^{-1} is a weak one and cannot readily be assigned to an asymmetric $N-Si_2$ stretching vibration. Thus the IR spectra also favor the structure IVa over IVb for tris-(trimethylsilyl)diethylenetriamine.

NMR spectra of the compound IV are shown in Fig. 2.15 and summarized in Table 12.

Table 12. <u>Proton Chemical Shifts in N,N',N"-Tris(trimethyl silyl)diethylenetriamine</u>

Proton Type	Chemical Shift (τ)	Integration Observed	Theoretical
$Si(CH_3)_3$	9.94 9.90	$\left.\begin{array}{c}2\\1\end{array}\right]$ 26.6	27
-NH-	9.56	∿2	2
$-CH_2-$	7.32 (doublet)	8.0	8

From integration and chemical shifts of the resonances the assignment of peaks shown in Table 12 can be readily achieved. The peaks at 9.94 and 9.90 have a relative intensity of 2:1, and must be assigned to two $-Si(CH_3)_3$ groups of a kind and to one $-Si(CH_3)_3$ group of another kind. In both structures, IVa and IVb, there are two different kinds of $-Si(CH_3)_3$ groups with a ratio of 2:1. From the intensity consideration, the structural formula IVb requires that the peak at higher field represent $-N[Si(CH_3)_3]_2$ protons, while the peak at lower field results from $-HNSi(CH_3)_3$. A comparison of NMR spectra of the compound IV with those of $(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$ (Table 13), which has much the same $-Si(CH_3)_3$ environment as the compound IVb, show that such a requirement is not met.

Table 13. <u>Proton Chemical Shifts in Tris(trimethylsilyl)-</u>
<u>ethylenediamine</u>[46]

Proton Type	Chemical Shift (τ)	Integration
$=N-Si(CH_3)_3$	10.00	9
$-N[Si(CH_3)_3]_2$	9.92	18
$=N-H$	9.42	1
$-CH_2-$	7.40	4

An analogous comparison of NMR spectra of the compound IV with those of $(C_6H_5)(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2(C_6H_5)]_2$ (Table 8), reveals the same result and therefore renders support to the above conclusion. In terms of IVa, the two peaks are readily assigned to the methyl protons of $\overset{C}{\underset{H}{>}}N-Si(CH_3)_3$ groups at the both ends of the molecule and the other methyl protons of the $\overset{C}{\underset{C}{>}}N-Si(CH_3)_3$ group at the center of the molecule, respectively.

The broad N-H resonance at 9.56 τ is assignable to $\equiv Si-NH-$ hydrogen of the structure IVa. With respect to the structure IVb, a broad band at about same chemical shift due to $\equiv Si-NH-$ at one end and another slightly sharper peak at lower field due to the secondary $>NH$ proton are expected. Fig. 2.15 fails to show the latter sharp peak and therefore does not satisfy the requirement for the structure IVb. These considerations of the NMR spectra of tris(trimethylsilyl)diethylenetriamine clearly indicate that the structure IVa represents the compound.

C. EXPERIMENTAL

1. Spectroscopic Measurements

Infrared spectra were recorded on a Perkin Elmer IR Spectrophotometer (Models 237 or 337) using a liquid film between KBr discs. In a few cases a Cary White IR Spectrometer, Model 90, was used to improve resolution. All the pertinent IR spectra obtained throughout this work are included in Appendix 1.

Nuclear magnetic resonance spectra were measured on a Varian A-60 NMR Spectrometer or a Varian T-60 NMR Spectrometer. A solution of approximately 10% of the material by volume in carbon tetrachloride was used unless otherwise indicated. A small amount of tetramethylsilane was used internally as the calibration standard. Since the chemical shift of trimethylsilyl protons is too close to that of the TMS signal, the integration could not be achieved with TMS. Therefore, TMS was added only after the completion of integration. The chemical shifts of the resonance peaks were measured from the TMS peak. (Example: Figs. 2.3 and 2.4.)

2. Analysis

Elemental analyses of compounds were carried out at the Schwarzkopf Microanalytical Laboratory, N.Y., or at the laboratory of the Institut für Anorganische Chemie der Technischen Hochschule, Graz, Austria.

3. Molecular Weight Determinations

The Beckmann freezing-point depression method was employed for trimethylsilyl derivatives of ethylenediamine, with benzene as solvent. Molecular weights were calculated by using the following formula:[61]

$$\text{Molecular Weight} = 1000 \, \frac{g}{G} \cdot \frac{Kf}{\Delta Tf}$$

where g : weight of sample

G : weight of benzene

ΔTf: freezing-point depression

Kf: molar freezing-point depression constant
= 5.12 deg. molal^{-1}

Molecular weights also were obtained by measuring the neutralization equivalent weight of the silylamines. The neutralization equivalent weight was calculated by hydrolysis of the sample in 50.0 ml. of 0.100 N HCl and back titration of excess acid with 0.100 N NaOH solution, using a pH meter. Since this method was simple and found to be satisfactory with diethylenetriamine and bis(trimethylsilyl)ethylenediamine, molecular weights of all compounds (with the exception of trimethylsilyl derivatives of ethylenediamine) were determined by using the second method.

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61. D.P. Shoemaker and C.W. Garland, "Experiments in Physical Chemistry" 2nd ed., McGraw-Hill Book Co., New York, pp. 135-136.

4. Preparation of the Chemicals Used

The solvents used in the preparations (benzene, diethyl ether and n-hexane) were dried in the original container with sodium wire for several days.

All amines used were refluxed with potassium hydroxide pellets for several hours and distilled immediately prior to use.

Trimethylchlorosilane and dimethyldichlorosilane (both kindly supplied by General Electric Company) were purified by one-plate distillation.

Dimethylphenylchlorosilane was prepared by standard Grignard reaction between dimethyldichlorosilane and bromobenzene Grignard reagnet.[41]

Trimethylsilyldiethylamine was prepared by direct aminolysis of trimethylchlorosilane by diethylamine in ether solution at room temperature.[40]

n-Butyllithium was used as purchased from Alfa Inorganics, Inc. without further purification.

5. Preparation of Organosilylamines

a. N,N'-Bis(trimethylsilyl)ethylenediamine[36]

A three-liter, three-neck flask was fitted with a dropping funnel, a reflux condenser and a Teflon paddle stirrer. The dropping funnel was equipped with a nitrogen inlet tube. A drying tube filled with Drierite was attached to the reflux condenser. All glassware had been dried in an electric oven

at 130°C for at least overnight prior to assembly of the
apparatus. While the system was cooling, it was purged with
prepurified nitrogen, dried by passage through a three feet-
long drying tube containing Drierite and phosphorus pentoxide.
Exactly 60.1 g (1.0 mole) of ethylenediamine dissolved in 1200
ml of benzene was placed in the flask, and cooled with ice-
water bath. Then 108.6 g (1.0 mole) of trimethylchlorosilane
in 300 ml of benzene was added dropwise into the ice-cooled
amine solution over a period of two hours. The formation of
white amine hydrochloride was observed immediately from the
beginning of addition. The reaction mixture was stirred at
the ice-water temperature for another hour. After removing
the ice bath, the stirring was continued for an additional
period of six hours at room temperature. The system was
swept with nitrogen throughout the entire reaction period.
When the white amine hydrochloride settled down, the super-
natant solution showed a slight yellow tinge. The amine
hydrochloride was removed by filtration with an oven-dried
inert-atmosphere filtering apparatus under nitrogen. Three
portions of 100 ml benzene were used for washing the reaction
flask and filtered solid, and were combined with the filtrate.
When benzene was removed by distillation at atmospheric pressure,
a small amount of amine hydrochloride again was precipitated.
To eliminate this the solution was filtered with a small
inert-atmosphere filtering device, and collected in a 250 ml
round bottom flask with a thermometer well. Fractional

distillation under reduced pressure with a 40 cm heated column, filled with glass helices, gave 39.0 g (38.1% yield) of the colorless product, b.p. 80-82°C/16 mm Hg, n_D^{20} 1.4280. Afterward, 5.0 g of tris(trimethylsilyl)ethylenediamine was obtained as by-product, b.p. 117-118°C/16 mm Hg, n_D^{20} 1.4445.

Chemical Analysis

Bis(trimethylsilyl)ethylenediamine, $C_8H_{24}N_2Si_2$

	% C	% H	% N	% Si	Mol. Wt.
Found	47.31	11.83	13.72	27.51	201[a] 202[b]
Calc'd	46.99	11.83	13.70	27.48	204.5

a. obtained by freezing-point depression method.

b. obtained by measuring the neutralization equivalent weight.

Tris(trimethylsilyl)ethylenediamine, $C_{11}H_{32}N_2Si_3$

	% C	% H	% N	% Si	Mol. Wt.
Found	47.94	11.76	10.62	30.20	270[a]
Clac'd	47.76	11.66	10.13	30.46	276.7

For repeated preparations of the same compound a slight modification of the original procedure was adapted. Here, 108.6 g (1.0 mole) of trimethylchlorosilane in 300 ml of benzene was added to a solution of 30.1 g (0.5 mole) of ethylenediamine and 121 g (1.2 mole) of triethylamine in 1300 ml of sodium-dried benzene. The apparatus used was the same as that used in the first experiment described above. After six to

eight hours of stirring at room temperature, triethylamine hydrochloride was filtered off and the filtrate was worked up as in the first procedure. This modified procedure gave 45 to 50 grams (45 to 50% yield) of the same product. The yield of the product is improved slightly over that of the original procedure.

b. Trimethylsilyldiethylamine[40]

Using the same apparatus used in the preparation of N,N'-bis(trimethylsilyl)ethylenediamine described above, 108.6 g (1.0 mole) of trimethylchlorosilane in 300 ml of sodium-dried diethyl ether was added dropwise to 161 g (2.2 moles) of diethylamine dissolved in 1800 ml of ether. After removing diethylamine hydrochloride, ether was distilled from the reaction mixture, and it was then transferred into a 250 ml round-bottom flask. Fractional distillation gave 53 g (36.5% yield) of trimethylsilyldiethylamine, b.p. 126-128°C, n_D^{20} 1.4105. Some 18.8 g of hexamethyldisiloxane was also obtained as by-product, b.p. 97-99°C, n_D^{20} 1.3779.

c. N,N'-Bis(trimethylsilyl)dimethylethylenediamine[43]

A mixture of 17.6 g (0.2 mole) of N,N'-dimethylethylene-diamine and 64.0 g (0.44 mole) of trimethylsilyldiethylamine was refluxed in a 250 ml round-bottom flask over an oil bath. After 5 hours of refluxing, the reflux condenser was replaced by a distillation head and condenser, and diethylamine pro-duced by the transamination was distilled off (18.5 g, 63%

of expected amount). Once again the reflux condenser was attached and the remaining reaction mixture was heated for an additional 10 hours. The mixture was then fractionally distilled at atmospheric pressure. In addition to about 10 g of unreacted trimethylsilyldiethylamine which came off at 127°C, 2.5 g of trimethylsilyl-N,N'-dimethylethylenediamine distilled at 161-165°C, n_D^{20} 1.4123, and 15.5 g (33.3% yield) of N,N'-bis(trimethylsilyl)dimethylethylenediamine was collected at 210-212°C, n_D^{20} 1.4350.

Chemical Analysis

Trimethylsilyl-N,N'-dimethylethylenediamine, $C_7H_{20}N_2Si$

	% C	% H	% N	% Si	Mol. Wt.
Found	52.40	12.31	17.03	18.15	164[b]
Calc'd	52.44	12.57	17.47	17.52	160.3

N,N'-bis(trimethylsilyl)dimethylethylenediamine, $C_{10}H_{28}N_2Si_2$

	% C	% H	% N	% Si	Mol. Wt.
Found	51.59	12.30	12.46	23.85	230.8[b]
Calc'd	51.66	12.14	12.05	24.16	232.5

d. Trimethylsilyltrimethylethylenediamine

About 64 grams of 22% solution (by weight) of n-butyl-lithium in n-hexane (0.22 moles) was weighed out on a tribeam balance in a glove bag and diluted with 200 ml of n-hexane in a one-liter three-neck flask. Then, 20.4 g (0.2 moles) of trimethylethylenediamine in 100 ml of n-hexane was added

dropwise from a dropping funnel to the ice-cooled reaction
flask over a period of one hour. The n-butane which resulted
from this reaction was conducted to a hood through rubber
tubing connected to the reflux condenser. When the dropping
funnel became empty, it was replaced with a second dropping
funnel containing 27.2 g (0.25 moles) of trimethylchlorosilane
in about 100 ml of n-hexane. The silane solution was allowed
to drip into the lithium amide solution over a period of one
hour, whereupon lithium chloride precipitated out. After the
exothermic reaction had subsided, the reaction mixture was
refluxed for three hours with constant stirring. Subsequently,
the reaction mixture was stirred overnight at room temperature.
The lithium chloride was removed from the reaction mixture
by filtration, and n-hexane was distilled off from the fil-
trate at atmospheric pressure. The remaining solution was
fractionally distilled under reduced pressure to give 2.3 g
of n-butyltrimethylsilane, b.p. 56-57°C/90 mm Hg, n_D^{20} 1.4032,
and 20.5 g (59% yield) of trimethylsilyltrimethylethylene-
diamine, b.p. 65-66°C/18 mm Hg, n_D^{20} 1.4286.

Chemical Analysis

Trimethylsilyltrimethylethylenediamine, $C_8H_{22}N_2Si$

	% C	% H	% N	% Si	Mol. Wt.
Found	55.16	12.96	16.20	15.93	173.8[b]
Calc'd	55.11	12.71	16.07	16.11	174.4

e. Dimethylphenylchlorosilane[41]

Phenylmagnesium bromide prepared from 26.6 g (1.1 moles) of magnesium and 181 g (1.1 moles) of bromobenzene in 400 ml of ether was placed in a dropping funnel. A solution of 129 g (1 mole) of dimethyldichlorosilane and 1000 ml of ether was placed in a three-liter three-neck flask of the same apparatus set-up used in the preparation of N,N'-bis(tri-methylsilyl)ethylenediamine described previously. The Grignard reagent was added dropwise to the flask with constant stirring over a period of two hours.

Throughout this addition, the reaction flask was cooled in an ice bath. Following this, the reaction mixture was stirred at room temperature for six hours. After filtration of magnesium halide and removal of ether, fractional distillation gave 65 g of dimethylphenylchlorosilane boiling at 192 to 194°C, n_D^{20} 1.5087.

f. N,N'-Bis(dimethylphenylsilyl)ethylenediamine

This compound, along with compounds described in subsections g through i, was prepared in a manner similar to that employed for the synthesis of N,N'-bis(trimethylsilyl)ethyl-enediamine. Using 9.0 g (0.15 moles) of ethylenediamine, 51.2 g (0.30 moles) of dimethylphenylchlorosilane and 40.5 g (0.40 moles) of triethylamine in benzene, the final fractional distillation under reduced pressure gave 21.5 g (43.6% yield)

of the product, b.p. 140-141°C/0.02 mm Hg, n_D^{20} 1.5345, and

6.2 g of tris(dimethylphenylsilyl)ethylenediamine, b.p.

167-168/0.03 mm Hg, n_D^{20} 1.5500.

Chemical Analysis

N,N'-bis(dimethylphenylsilyl)ethylenediamine, $C_{18}H_{28}N_2Si_2$

	% C	% H	% N	% Si	Mol. Wt.
Found	65.81	8.35	8.78	17.18	315[b]
Calc'd	65.79	8.59	8.52	17.09	328.6

Tris(dimethylphenylsilyl)ethylenediamine, $C_{26}H_{38}N_2Si_3$

	% C	% H	% N	% Si	Mol. Wt.
Found	67.30	8.20	6.24	18.01	448[b]
Calc'd	67.47	8.28	6.05	18.20	462.9

g. **N,N'-Bis(dimethylphenylsilyl)dimethylethylenediamine**

By using 17.6 g (0.20 moles) of N,N'-dimethylethylene-

diamine, 68.3 g (0.40 moles) of dimethylphenylchlorosilane

and 50.6 g (0.50 moles) of triethylamine in dry ether, the

final fractional distillation under reduced pressure gave

6.5 g of 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane, b.p.

85-87/1.5 mm Hg, n_D^{20} 1.5179, and 33.2 g (46.5% yield) of

the desired compound, b.p. 116-119°C/0.08 mm Hg, n_D^{20} 1.5289.

Chemical Analysis

N,N'-bis(dimethylphenylsilyl)dimethylethylenediamine,

$C_{20}H_{32}N_2Si_2$

	% C	% H	% N	% Si	Mol. Wt.
Found	67.05	9.04	7.66	16.00	340[b]
Calc'd	67.35	9.04	7.85	15.75	356.7

h. <u>Dimethylphenylsilyltrimethylethylenediamine</u>

Using 20.4 g (0.20 moles) of trimethylethylenediamine, 34.1 g (0.20 moles) of dimethylphenylchlorosilane and 25.3 g (0.25 moles) of triethylamine in dry ether, the fractional distillation under reduced pressure gave 21.4 g (45.3% yield) of the colorless liquid product, b.p. 63-64°C/0.05 mm Hg, n_D^{20} 1.4970. Also 4.5 g of 1,1,3,3-tetramethyl-1,3-diphenyl-disiloxane was collected as a by-product.

<u>Chemical Analysis</u>

Dimethylphenylsilyltrimethylethylenediamine, $C_{13}H_{24}N_2Si$

	% C	% H	% N	% Si	Mol. Wt.
Found	66.07	10.15	11.50	12.10	226[b]
Calc'd	66.04	10.23	11.85	11.88	236.4

i. <u>N,N"-Bis(trimethylsilyl)- and N,N',N"-tris(trimethylsilyl)-diethylenetriamine</u>

Again the direct aminolysis reaction was carried out using the same procedure adopted in the preparation of N,N'-bis(trimethylsilyl)ethylenediamine. A mixture of 217.5 g (2.0 moles) of trimethylchlorosilane in 500 ml of benzene, and 103.2 g (7.0 mole) of diethylenetriamine and 243 g

(2.4 moles) of triethylamine in 1300 ml of the same solvent, was allowed to react. The filtrate was then distilled under reduced pressure and 182 g of a colorless liquid boiling over a range from 100° to 150°C at 7 to 8 mm Hg was collected. This distillate was fractionally distilled through a 40 cm glass helix-filled heated column under reduced pressure to give 65 g (26.3% yield) of N,N"-bis(trimethylsilyl)diethylenetriamine, b.p. 116-118°C/7 mm Hg, n_D^{20} 1.4459, and also 32 g of N,N',N"-tris(trimethylsilyl)diethylenetriamine as by-product, b.p. 133-134°C/7 mm Hg, n_D^{20} 1.4615.

Chemical Analysis

N,N"-bis(trimethylsilyl)diethylenetriamine, $C_{10}H_{29}N_3Si_2$

	% C	% H	% N	% Si	Mol. Wt.
Found	48.65	11.97	17.33	22.14	246[c], 235[b]
Calc'd	48.52	11.81	16.98	22.69	247.5

N,N',N"-tris(trimethylsilyl)diethylenetriamine, $C_{13}H_{37}N_3Si_3$

	% C	% H	% N	% Si	Mol. Wt.
Found	49.08	11.74	13.30	26.07	316[c], 312[b]
Calc'd	48.84	11.67	13.14	26.35	319.7

c. Obtained by ebullioscopic method in ether at the laboratory of the Institut für Anorganische Chemie der Technischen Hoshschule, Graz, Austria.

PART II.   SYNTHESIS OF TRANSITION METAL COMPLEXES WITH

ORGANOSILYLAMINES

A.   Methods and Materials

a.   General

As discussed in the Introduction, the lone-pair elec-
trons on nitrogen atom in organosilylamines are believed
to be delocalized through partial $p\pi$-$d\pi$ bonding between
nitrogen and silicon atoms. If a transition metal coordina-
tion compound of organosilylamines, $M \leftarrow NR_2SiR'_3$, can be
prepared, the lone-pair electrons of silylamines will be
used for the coordination toward the metal atom, with con-
sequent reduction of the partial double-bond character of
the N-Si bond in the organosilylamine. On the other hand
if the energy gained by forming an $M \leftarrow NR_2SiR'_3$ coordination
bond were not quite sufficient to compensate for the loss
of the delocalization energy of the lone-pair electrons, then
the assumed coordination compound would not be stable under
normal conditions.

In the study of polymeric silylamine compounds, Minné
and Rochow[62] had succeeded in obtaining polymeric coordina-
tion compounds from silylamines as well as from silazanes.
They refluxed the polymer obtained from ethylenediamine and

62.   R.N. Minné and E.G. Rochow, J. Am. Chem. Soc., 82 (1960),
      5625, 5628.

dimethyldichlorosilane with anhydrous metal chlorides in dry xylene under dry nitrogen atmosphere. However, they obtained coordination polymers in which only part of the nitrogen in the polymers was coordinated with the metal. Preliminary work on the coordination chemistry of silicon-nitrogen compounds was carried out by Weiss,[63] who has reported the isolation of N,N'-bis(trimethylsilyl)ethylene-diamine complexes of anhydrous $CuCl_2$ and $CoCl_2$ without complete analytical or any spectroscopic data. While work described in this thesis was in progress, Willey[64] reported on donor properties of hexamethylcyclotrisilazane (HMT). Although the trimeric ring is a potential pseudoaromatic system, his attempts to prepare half-sandwich complexes of group VI metals, (π-HMT) $Cr(CO)_3$ and (π-HMT)$Mo(CO)_3$ had failed. However, Willey succeeded in isolating $TiCl_3 \cdot HMT$ and $VCl_3 \cdot HMT$ from the reaction of hexamethylcyclotrisilazane with anhydrous metal trichlorides in tetrahydrofuran. In these compounds hexamethylcyclotrisilazane acts as a tridentate nitrogen donor.

b. <u>Selection of ligands</u>

There are three kinds of Si-N compounds which could be

63. R. Weiss and E.G. Rochow, Coordination of Silicon Nitrogen Compounds, Technical Report NONR-1866(13), 1961.

64. G.R. Willey, J. Am. Chem. Soc., <u>90</u>, 3362 (1968).

considered as ligands, according to the number of silyl

groups on the nitrogen atoms:

    i Organosilylamines, $R_3Si-NR'R''$,

      containing one organosilyl group on the nitrogen atom

    ii Organosilizanes, $R_3Si-\underset{\underset{R'}{|}}{N}-SiR_3$,

      containing two organosilyl groups on the nitrogen atom

    iii Trisorganosilylamines, $R_3Si-\underset{\underset{SiR_3}{|}}{N}-SiR_3$,

      containing three organosilyl groups on the nitrogen

      atom

where SiR_3 is $Si(CH_3)_3$, or $Si(CH_3)_2(C_6H_5)$

and R' and R" are hydrogen or alkyl groups.

From simple steric considerations of the organosilyl

groups, it could readily be assumed that the silylamines

would be the best donors among the above three kinds of Si-N

compounds. In fact, Brown and Taylor[65] have shown that this

kind of steric effect is related to the dissociation constants

for the trimethylboron compounds of ethylated amines. Their

data clearly demonstrate that the stability of the ethylated

amine-trimethylboron adduct is decreased by increasing the

number of ethyl groups on nitrogen.

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65. H.C. Brown and M.D. Taylor, J. Am. Chem. Soc., 69, 1332
    (1947).

Since the simple ethyl group has such a pronounced steric effect, it is naturally expected that the more bulky tri-organosilyl groups would show a much higher degree of steric effect.

In addition to the steric effect, it is recognized that the use of d-orbitals on silicon to delocalize the nitrogen lone-pair electrons results in the absence of any donor property in trisilylamine.[8] In silazanes (ii) two silicon atoms compete with the metal for the lone-pair electrons on the nitrogen atom, whereas in organosilylamine only one silicon atom does the same, therefore the latter should be a much better donor than the former.

Accordingly, organosilylamines with a relatively small organosilyl groups, i.e. trimethylsilyl or dimethylphenyl-silyl, were selected as the most promising ligand system in the synthesis.

The most characteristic feature of chelation is the enhanced stability for metal chelates when these are compared with simple metal complexes containing monodentate ligands with nearly identical donor groups. For instance, the following data taken from Jones[66] clearly illustrate the point in question.

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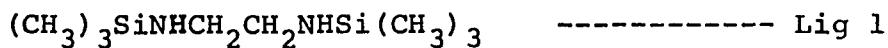
66. M.M. Jones, Elementary Coordination Chemistry, Prentice-Hall Inc., Englewood Cliffs, N.J. 1964, p. 336.

Stability Constants for Amines and Ethylenediamine
Complexes.[66]
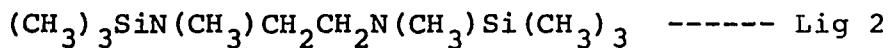
	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}
$\log \overline{K}_{M(NH_3)_2}$	3.68	4.99	7.68	4.69	4.69
$\log K_{M(en)}$	5.99	7.77	10.73	5.92	5.63

Thus instead of using simple organosilylamines as mono-
dentate ligands, various organosilyl derivatives of ethylene-
diamine and diethylenetriamine have been used in this work as
polydentate chelating agents. Consequently, the following
seven organosilyl polyamines, whose synthesis were discussed
in Part I were selected as possible ligands for the synthesis
of transition metal complexes.
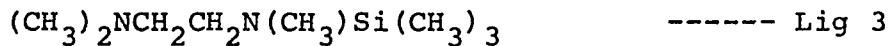
i   N,N'-bis(trimethylsilyl)ethylenediamine
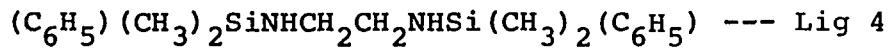
$(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$ ------------ Lig 1

ii N,N'-bis(trimethylsilyl)dimethylethylenediamine

$(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$ ------ Lig 2

iii N-trimethylsilyltrimethylethylenediamine

$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$ ------ Lig 3

iv N,N'-bis(dimethylphenylsilyl)ethylenediamine

$(C_6H_5)(CH_3)_2SiNHCH_2CH_2NHSi(CH_3)_2(C_6H_5)$ --- Lig 4

v   N,N'-bis(dimethylphenylsilyl)dimethylethylenediamine

$(C_6H_5)(CH_3)_2SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_2-$
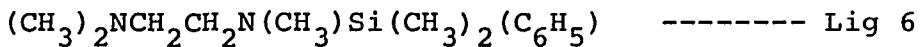
(C_6H_5) -------- Lig 5

vi   N-dimethylphenylsilyltrimethylethylenediamine

$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_2(C_6H_5)$ -------- Lig 6

vii   N,N"-bis(trimethylsilyl)diethylenetriamine

$(CH_3)_3SiNHCH_2CH_2NHCH_2CH_2NHSi(CH_3)_3$ -------- Lig 7

c.   Selection of Solvents

In preliminary experiments, anhydrous copper (II) chloride
and cobalt (II) chloride in benzene or petroleum ether under-
went a heterogeneous reaction to form 1:1 adduct with N,N'-
bis(trimethylsilyl)ethylenediamine. However the analysis
of the products showed higher values for metal and chloride
than those expected for 1:1 adducts, implying either one or
both of the following possibilities: some of the product
might have undergone hydrolysis to some extent, or the pro-
duct might contain unreacted metal halide, probably covered
with the coordination compound. In subsequent experiments
extreme precautions were taken in order to achieve better
solubility, and to exclude moisture from the solvent and the
apparatus. These efforts, together with a longer period of
reaction time with vigorous stirring, resulted in the synthesis
of high purity products using benzene as solvent.

In the meantime Küpper from this laboratory suggested

the use of a more polar solvent to achieve a homogeneous reaction condition. In earlier work Küpper had used tetrahydrofuran in the synthesis of a coordination compound between anhydrous iron (II) chloride and an aryl-alkyl substituted ethylenediamine.[67] Similarly, the same solvent was used in the synthesis of titanium and vanadium complexes with hexamethylcyclotrisilazane.[64] In light of the above, the author employed tetrahydrofuran as the solvent in some later experiments.

d. Methods for Synthesis of Transition Metal Complexes

i) With Metal Halides

A slight excess (about 5%) of silylamine in benzene was allowed to drop slowly into an anhydrous metal chloride suspended in benzene, stirring constantly with a magnetic stirrer. After the addition was completed, the mixture was allowed to complete the reaction for a period of 12 to 14 hours with continuous stirring.

With $CuCl_2$ the brown solid became light green during this reaction period, whereas the light blue $CoCl_2$ turned into deep blue. The solid was then collected in an inert-atmosphere filtering apparatus using dry argon. The filtered solid product in both cases was washed and dried under reduced pressure at room temperature for at least 4 hours.

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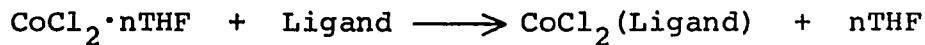
67. F.W. Küpper, J. Organometal. Chem., 13, 219 (1968).

Similar experiments were also performed using tetra-hydrofuran in place of benzene. A slight excess (about 10%) of metal halide suspended in tetrahydrofuran was placed in the reaction flask, and was stirred for 3 to 4 hours to achieve complete solvation, as judged by respective changes in color of the solution. With cobalt (II) chloride a deep blue color of the supernatant and copious blue solid at the bottom of the flask were obtained. After this was completed,

$$CoCl_2 + nTHF \longrightarrow CoCl_2 \cdot nTHF$$

light blue   deep blue

silylamine solution in tetrahydrofuran was added slowly and dropwise. The mixture was allowed to complete the replacement reaction for a minimum of 12 hours at room temperature.

$$CoCl_2 \cdot nTHF + Ligand \longrightarrow CoCl_2(Ligand) + nTHF$$

deep blue   deep blue
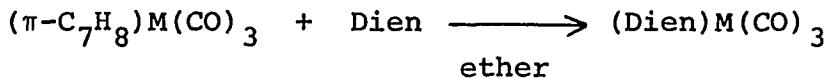
The solid, probably a mixture in part of solvated metal halide and of reaction product, was filtered off, and the solvent was evaporated from the filtrate under reduced pressure at temperatures lower than 40°C to avoid possible thermal de-composition. The residue was dried for at least 4 to 5 hours at reduced pressure using an oil pump.

Identical steps were followed in preparing the products

using copper (II) chloride and iron (II) chloride. With CuCl$_2$ a light green product resulted from evaporation of the deep green reaction mixture. The final products obtained from FeCl$_2$ were brown.

ii) With Group VI Metal Carbonyls

Two sixth group metal carbonyls, Cr(CO)$_6$ and Mo(CO)$_6$, were refluxed with Lig. 7 in dry hexane to prepare N,N"-bis(trimethylsilyl)diethylenetriamine-metal tricarbonyls. After several hours of refluxing, a small amount of yellow solid was noticed. The solid was filtered and washed with hexane. Following this, unreacted metal hexacarbonyl was sublimed away. Infrared spectra of the yellow solid indicated a complete loss of trimethylsilyl groups and showed that the product was diethylenetriamine-metal tricarbonyl. The same product, diethylenetriamine-metal tricarbonyl, could easily be synthesized by reacting cycloheptatriene-metal tricarbonyl with the tridentate ligand under much milder conditions by the ligand exchange reaction.[68] This type of ligand exchange

$$(\pi\text{-}C_7H_8)M(CO)_3 \ + \ Dien \ \xrightarrow[ether]{} \ (Dien)M(CO)_3$$

where M is Cr or Mo and Dien stands for diethylenetriamine

reaction of cycloheptatriene-metal tricarbonyls had been proven

68. E.W. Abel, M.A. Bennett, and G. Wilkinson, J. Chem. Soc., 2323 (1959).

to be a useful method even for a number of monodentate ligands with donor atoms such as nitrogen, phosphorus, arsenic, and antimony.[68] Adopting the same ligand exchange procedure, the synthesis of N,N"-bis(trimethylsilyl)diethyl-enetriamine-chromium tricarbonyl and molybdenum tricarbonyl were attempted.

Cycloheptatriene tricarbonyls of chromium and molybdenum were prepared by reacting cycloheptatriene with the respect-ive metal hexacarbonyl in petroleum ether.[69] The hydrocarbon metal tricarbonyls were purified by sublimation just before use. An equimolar amount of N,N"-bis(trimethylsilyl)diethyl-enetriamine in dry tetrahydrofuran was added dropwise to the red tetrahydrofuran solution of cycloheptatriene-metal tri-carbonyl, and the reaction mixture was allowed to stand for one hour. This resulted in the formation of a fine yellow precipitate. The product was filtered from the red solution, washed twice with tetrahydrofuran, and dried under high vacuum.

B. <u>Results and Characterization of the Products</u>

a. <u>Copper Complexes</u>

During the early stages of this work benzene was used as solvent. Drying of benzene was achieved simply be keeping

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69. E.W. Abel, M.A. Bennett, R. Burton and G. Wilkinson, J. Chem. Soc., 4559 (1958).

sodium wire in the original container. The reaction mixture
of anhydrous $CuCl_2$ and N,N'-bis(trimethylsilyl)ethylenediamine
turned green. However, the product became blue during the
subsequent stirring, which lasted for several hours.

Infrared spectra of the blue solid product indicated
the almost complete disappearance of trimethylsilyl groups
from the coordination compound, as evidenced by the lack of
the two characteristic absorption peaks at 1250 cm^{-1} and 840
cm^{-1} attributable to symmetric deformation of the $Si(CH_3)_3$
group and to the methyl rocking mode, respectively[50]. The
elemental analysis also indicated very low content of silicon,
and higher values for copper and chlorine compared to those
values expected for N,N'-bis(trimethylsilyl)ethylenediamine
copper chloride. These observed facts could readily be ex-
plained by assuming that the presence of a small amount of
water in the system had facilitated hydrolysis of the reaction
product, resulting in the formation of an ethylenediamine com-
plex of copper chloride.

In later experiments extreme caution was taken in order
to remove moisture from the reaction system by using more
carefully dried solvent and specially dried silicone treated
glassware. The isolation of a light green colored product
then was achieved from the reaction of $CuCl_2$ with N,N'-
bis(trimethylsilyl)ethylenediamine.

The elemental analyses of this compound and the other
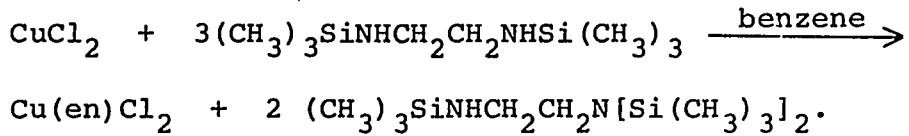
copper chloride complexes with other silylamines, as shown in Table 14, indicate that all of the compounds are 1:1 adducts. The infrared spectra of the complexes obtained as nujol mulls between KBr discs, are included in the Appendix.

Table 14. Elemental Analyses of $CuCl_2$ Complexes with Organosilylamines

		% C	% H	% N	% Si	% Cu	% Cl
$CuCl_2 \cdot Lig\ 1$	Found	27.95	7.06	8.45	16.33	18.68	21.10
$(CuCl_2C_8H_{24}N_2-Si_2)$	Calc'd	28.35	7.14	8.27	16.57	18.75	20.92
$CuCl_2 \cdot Lig\ 2$	Found	32.50	7.51	7.58	14.97	17.53	19.62
$(CuCl_2C_{10}H_{28}N_2-Si_2)$	Calc'd	32.73	7.69	7.63	15.31	17.31	19.32
$CuCl_2 \cdot Lig\ 3$	Found	30.96	6.89	8.76	9.12	20.83	23.05
$(CuCl_2C_8H_{22}N_2-Si\ )$	Calc'd	31.12	7.18	9.07	9.10	20.58	22 96
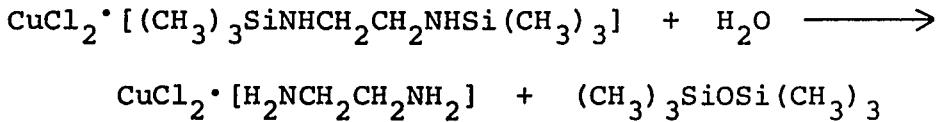
To prepare a fully coordinated copper complex (1:2 adduct), $CuCl_2$ was refluxed with an excess amount of Lig 1 in benzene for a period of 20 hours. The infrared spectra of the bluish purple solid product showed that the trimethylsilyl group disappeared and that it was simple copper(II) monoethylene-diamine chloride, $Cu(en)Cl_2$. The filtrate contained some

unreacted N,N'-bis(trimethylsilyl)ethylenediamine and a
fair amount of N,N,N'-tris(trimethylsilyl)ethylenediamine,
which resulted from a rearrangement reaction according to
the equation

$$CuCl_2 + 3(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3 \xrightarrow{\text{benzene}}$$

$$Cu(en)Cl_2 + 2(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2.$$
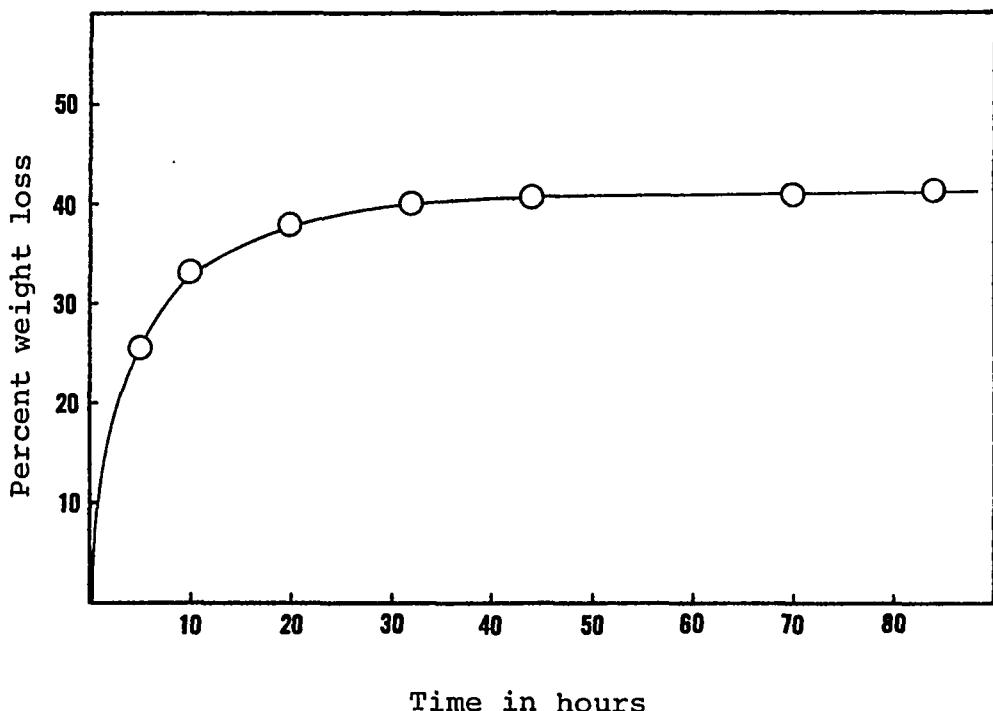
The mechanism of this rearrangement is similar to that postu-
lated by Minné and Rochow for the rearrangement of silylamine
polymers in the presence of metal chloride,[62] and explained
by Weiss[63] elsewhere. This being the case, further attempts
to isolate stable fully coordinated complexes was discontinued.

When finely powdered $CuCl_2$ Lig 1 was exposed to atmos-
pheric moisture, it lost its trimethylsilyl group by hydroly-
sis and the compound turned light blue in color:

$$CuCl_2 \cdot [(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3] + H_2O \longrightarrow$$

$$CuCl_2 \cdot [H_2NCH_2CH_2NH_2] + (CH_3)_3SiOSi(CH_3)_3$$

The above process of hydrolysis was followed by measuring the
weight loss of the compound exposed in the laboratory atmos-
phere. After 10 hours of exposure, 33.1% of the original
weight was lost, corresponding to about 78% of the expected
weight loss of the above process. As shown in Figure 1, a
weight loss of 41.5% was observed after 70 hours. In order
to establish its identity, the hydrolyzed product was analyzed

Figure 1

Hydrolysis of $CuCl_2 \cdot [(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3]$

In this experiment 523.0 milligrams of the complex was used. The expected percent weight loss due to complete loss of trimethylsilyl groups is 42.5%.

for copper and chlorine contents. The results (Cu, 32.1; Cl, 35.8%) were in good agreement with calculated values for the mono-ethylenediamine complex of copper (II) chloride (Cu, 32.66%, Cl, 36.45%). The latter was prepared by reacting equimolar amounts of anhydrous $CuCl_2$ and ethylenediamine[70] in tetrahydrofuran. The infrared spectrum of this compound was found to be identical to that of the decomposed coordination compound (Figs. 1.21 and 1.22).

As part of an effort to assign the infrared absorption of $CuCl_2 \cdot Lig\ 1$, prominent peaks of the relatively simple infrared spectra of $Cu(en)Cl_2$ were assigned as in Table 15 by comparing the spectra with previous results obtained for other ethylenediamine metal complexes.[71]

Due to incomplete assignments of infrared absorption bands of the silylamine ligand, it is impossible to assign all of the absorption peaks in the $CuCl_2$ complex of this ligand. However, the following partial assignments were derived from comparing the spectra of this complex with those of the ligand molecule and the result obtained for $Cu(en)Cl_2$ described above. The infrared spectra of $CuCl_2 \cdot Lig\ 1$, (Fig. 1.19) contain all

70. The same compound had been prepared from aqueous solution by F.W. Chattaway and H.D.K. Drew, J. Chem. Soc., 947 (1937) and from alcoholic solution by V. Caglioti, C. Furlan; G. Dessy, and C. Ibarra, Gazz. Chim. Ital, 92 1276 (1962); Chem. Abstr. 59, 212^C (1963).

71. D.B. Powell and N. Sheppard, Spectrochim. Acta, 17, 68 (1961).

Table 15. <u>Partial Assignments of Infrared Absorption</u>

<u>Bands of Copper(II) Monoethylenediamine Chloride</u>

Fundamental Modes	Frequencies (cm^{-1})
N-H stretching	3290, 3222, 3112(weak)
NH_2 Scissoring	1566
CH_2 twisting	1271
Skeletal vibration involving C-C and C-N	1047
NH_2 rocking	679
Cu-N stretching	528

of the strong characteristic absorption bands of the ligand

molecule (Fig. 1.5) with slight modifications. The partial

assignments (and certain pertinent observations) are:

i   The N-H stretching vibration appearing at 3400 cm^{-1}

for the ligand molecule has shifted to 3185 and 3135

cm^{-1}, with a sharp increase in its intensity. This

shift to lower energy with increased intensity is

typical for amine coordination.[72]

ii The symmetric deformation band of Si(CH$_3$)$_3$ at 1251

cm^{-1} and methyl rocking band at 835 cm^{-1} also showed

a small shift, and recorded at 1256 and 844 cm^{-1}.

iii A sharp medium intensity band at 1180 cm^{-1} was ob-

served in the spectra of this complex, and was

assigned to N-H deformation band. In the ligand

spectra one of the two weak bands at 1200 and 1178

cm^{-1} could correspond to N-H deformation band. The

increase of this band intensity can also be related

to the metal coordination.

iv The copper-nitrogen stretching mode in this complex

might be assigned to a weak band at 470 cm^{-1}, or it

72. G.F. Svatos, C. Curran and J.V. Quagliano, J. Am. Chem.
     Soc., 77, 6159 (1955).

might possibly be located in a region lower than
the potassium bromide range. As described earlier,
this mode of vibration in $Cu(en)Cl_2$ was assigned to
a medium-strength band at 528 cm^{-1}. This shift to
lower frequency can be assumed to result partly from
the lower stability of this chelate complex compared
to that of $Cu(en)Cl_2$[73] and/or partly from the addition-
al mass on nitrogen by the replacement of a hydrogen
atom with a heavy trimethylsilyl group.

v   A medium strength band at 1061 cm^{-1} in the complex
is probably due to one of the three[71] expected
skeletal stretching vibrations involving C-C and
C-N. This mode of vibration in $Cu(en)Cl_2$ is assigned
to a strong band at 1047 cm^{-1}.

The infrared spectra of the slightly hydrolyzed $CuCl_2 \cdot Lig$
1 (Fig. 1.20) produced by a brief exposure to atmospheric mois-
ture contained all of the bands for the pure complex and for
the completely hydrolyzed product, $Cu(en)Cl_2$. As the degree
of hydrolysis increased the peaks corresponding to the pure
complex became progressively weaker while those related to

73. The stability of metal-ethylenediamine complexes is
    correlated with the decreasing order of metal-nitrogen
    stretching frequencies of the complex by D.B. Powell
    and N. Sheppard, J. Chem. Soc., 1112 (1961).

$Cu(en)Cl_2$ gradually gained intensity.

From the chemical behavior and the spectroscopic evidence it is tempting to conclude that the adduct compound is a chelate complex which has a planar molecular structure like that of $Cu(en)Cl_2$.[74]

b. Cobalt Complexes

Preparation and isolation of the blue cobalt chloride adducts with Ligands 1, 2 and 3 were carried out in the same way as described previously for the copper complexes, from benzene or tetrahydrofuran solution. With Ligands 4, 5 and 6 only tetrahydrofuran was used as the solvent to obtain cobalt chloride adducts. The characteristics of the cobalt chloride adducts were similar to those of the copper complexes. The elemental analysis of the complexes, as listed in Table 16, indicated that they were 1:1 adducts.

When it hydrolyzed in air, $CoCl_2 \cdot Lig$ 1 also lost weight and turned to light, pinkish-blue color. The analysis of the completely hydrolyzed compound for cobalt and chlorine indicated it was the mono-ethylenediamine complex of cobalt chloride. (Found: Co 31.4%, Cl 37.5%, Calculated: Co 31.03%, Cl 37.33%). A hydrolysis experiment similar to that

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74. G. Giuseppetti and F. Mazzi, Rend. Soc. Mineralog. Ital., 11 202 (1955); Chem. Abstr., 50, 13552a (1956).

Table 16.   Elemental Analyses of $CoCl_2$ Complexes with

Organosilylamines
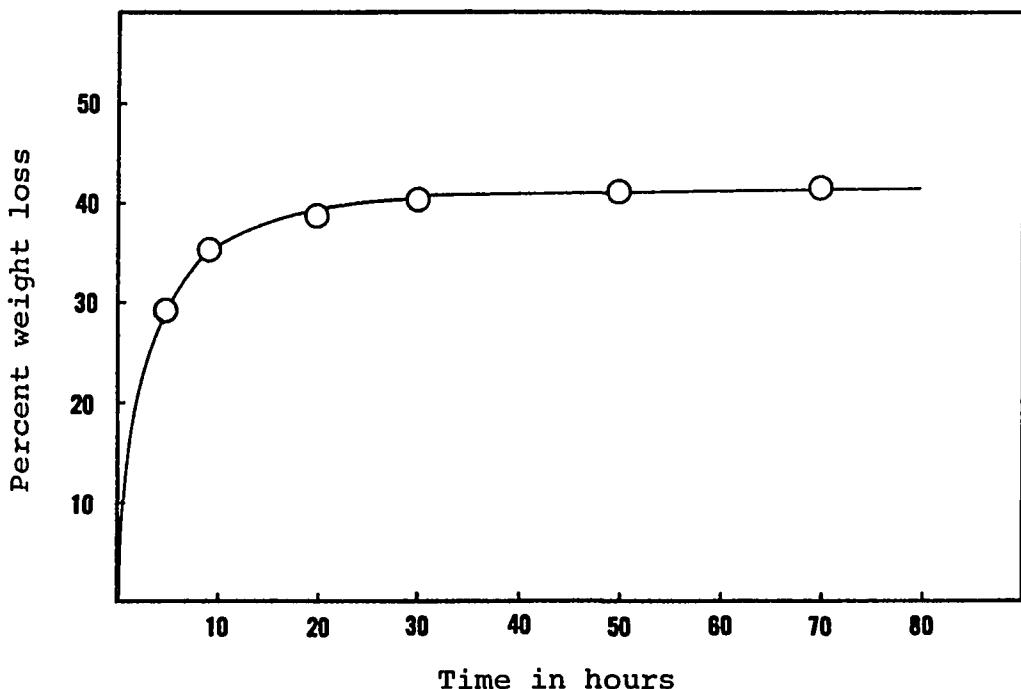
		% C	% H	% N	% Si	% Co	% Cl
$CoCl_2 \cdot Lig\ 1$	Found	27.82	6.89	8.26	17.20	17.47	20.93
$(CoCl_2C_8H_{24}N_2-Si_2)$	Calc'd	28.74	7.24	8.38	16.80	17.63	21.21
$CoCl_2 \cdot Lig\ 2$	Found	32.75	7.51	7.96	15.23	16.13	19.89
$(CoCl_2C_{10}H_{28}N_2-Si_2)$	Calc'd	33.15	7.79	7.73	15.50	16.26	19.57
$CoCl_2 \cdot Lig\ 3$	Found	31.23	7.05	9.63	9.01	19.61	23.91
$(CoCl_2C_8H_{22}N_2-Si\ )$	Calc'd	31.59	7.29	9.21	9.23	19.37	23.31
$CoCl_2 \cdot Lig\ 4$	Found	48.06	6.25	6.54	11.81	11.98	15.18
$(CoCl_2C_{18}H_{28}N_2-Si_2)$	Calc'd	47.16	6.16	6.11	12.25	12.85	15.47
$CoCl_2 \cdot Lig\ 5$	Found	49.07	6.37	6.03	11.13	12.01	14.80
$(CoCl_2C_{20}H_{32}N_2-Si_2)$	Calc'd	49.38	6.63	5.76	11.55	12.11	14.57
$CoCl_2 \cdot Lig\ 6$	Found	42.31	6.30	7.90	7.38	15.87	19.01
$(CoCl_2C_{13}H_{24}N_2-Si\ )$	Calc'd	42.63	6.60	7.65	7.67	16.09	19.36

described earlier showed that after 10 hours of exposure 35.5% of the original weight was lost, corresponding to 82% of the expected weight loss. As shown in Figure 2, the characteristics of hydrolysis closely resembled those of $CuCl_2$·Lig 1. With $CoCl_2$·Lig 1, however, the rate of hydrolysis seemed to be slightly faster, although a reliable comparison was not possible to make. This was due to the fact that the texture of the solid powder was different, and that its weight loss was not measured in a controlled environment (at constant temperature and constant water vapor press re).

Further evidence for the similarity of this complex with $CuCl_2$·Lig 1 is its infrared spectrum, which was nearly identical to those of $CuCl_2$·Lig 1, as shown in Figs. 1.19 and 1.25.

With dimethylphenylsilyl derivatives of diamines, only the reaction with anhydrous $CoCl_2$ in tetrahydrofuran solution was successful, and that only partially. Similarly, all attempts to prepare pure chelate complexes with $CuCl_2$ or $FeCl_2$ have failed. Even with $CoCl_2$ the isolation of chelate complexes was difficult to achieve. As shown in Table 16, their analytical results were acceptable but the quality of their infrared spectra was less than satisfactory. While making nujol mulls in a glove bag filled with argon, the compounds tended to decompose and became sticky. Their infrared spectra indicated that hydrolysis took place to some

Figure 2

Hydrolysis of $CoCl_2 \cdot [(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3]$.

In this experiment 630.2 milligrams of the complex was used. The expected percent weight loss due to the complete loss of trimethylsilyl groups is 43.2%.

extent as evidenced by the appearance of a broad and strong absorption band at 1060 cm^{-1}, which could be attributed to th asymmetric Si-O-Si stretching vibration mode. Even though the infrared spectra showed characteristic absorptions of the dimethylphenylsilyl group, it was questionable whether they originated from the coordinated dimethylphenylsilyl diamines or from the decomposed product such as 1,1,3,3-tetramethyl-1,3-diphenyldisiloxane. The instability of these complexes of Ligands 4, 5 and 6 was also demonstrated while sealing the compounds in thick-walled tubes under vacuum. When a constricted part of the tube with sample was closed with a flame torch, the compound which was at the other end of the tube at least 15 cm away from the point of heating became slightly wet. When the sealed tube was put in an oil bath at 60°C, the compound decomposed slowly and became quite wet. A small amount of colorless clear liquid condensed out at the cooling end, where dry ice was applied.

c. Iron Complexes

From the deep brown reaction mixture in tetrahydrofuran, iron (II) chloride adducts of Ligands 1, 2 and 3 were obtained. The results of the elemental analyses of the brown solid products are listed in Table 17. They indicate that they are all 1:1 adducts. The infrared spectra of these compounds are

included in the Appendix.

Table 17. Elemental Analyses of $FeCl_2$ Complexes with

Organosilylamines

		% C	% H	% N	% Si	% Fe	% Cl
$FeCl_2 \cdot Lig\ 1$	Found	28.51	7.05	8.12	16.62	17.06	21.11
$(FeCl_2C_8H_{24}N_2-Si_2)$	Calc'd	29.01	7.30	8.46	16.96	16.86	21.41
$FeCl_2 \cdot Lig\ 2$	Found	32.92	7.30	8.17	15.22	15.27	19.83
$(FeCl_2C_{10}H_{28}N_2-Si_2)$	Calc'd	33.43	7.86	7.80	15.63	15.54	19.74
$FeCl_2 \cdot Lig\ 3$	Found	31.62	7.21	9.06	9.17	19.18	23.71
$(FeCl_2C_8H_{22}N_2-Si\ )$	Calc'd	31 91	7.36	9.30	9.33	18.55	23.55

They seemed to decompose more readily than the $CuCl_2$
and $CoCl_2$ adducts. The brown solid immediately turned wet
and became a very dark brown in color upon exposure to
laboratory atmosphere. The identity of this decomposed pro-
duct was not pursued any further.

d. With other Metal Chlorides

Because of the stability of numerous amine complexes of Ni (II) ions, efforts were made to synthesize silylamine complexes of nickel halides. In benzene and petroleum ether anhydrous $NiCl_2$ and Lig 1 were stirred for a period of two days. The residue showed that it was practically unchanged $NiCl_2$. Even with the more soluble $NiBr_2$, no appreciable reaction occurred. Likewise, attempts to synthesize the adduct using tetrahydrofuran as solvent were not successful.

e. Chromium and Molybdenum Complexes

As discussed previously, the reaction of hexacarbonyls of Group VI metals (Cr and Mo) with N,N"-bis(trimethylsilyl)-diethylenetriamine in dry hexane was not successful. However, by reacting the above tridentate ligand with cyclo-heptatriene-metal tricarbonyls the desired complexes were obtained. The results of elemental analysis are shown in Table 18. The infrared spectra of the complexes as well as those of the hydrolyzed products, are included in the Appendix.

By exposure to atmospheric moisture, the complexes lost all their trimethylsilyl groups, as evidenced by complete disappearance of the characteristic bands at 1250 and 840 cm^{-1} (Figs. 1.35 and 1.37). Two strong bands (of which the lower-frequency one is very broad) in the C-O stretching region

Table 18. Elemental Analyses of Chromium and Molybdenum
Compounds with Organosilylamines

		% C	% H	% N	% Si	% Metal
$Cr(CO)_3 \cdot Lig\ 7$	Found	40.47	7.52	11.08	13 88	13.73
$(CrC_{13}H_{29}N_3O_3-$ $Si_2)$	Calc'd	40.71	7.62	10.96	14.64	13.56
$Mo(CO)_3 \cdot Lig\ 7$	Found	36.19	6.83	10.21	12.71	22.60
$(MoC_{13}H_{29}N_3O_3-$ $Si_2)$	Calc'd	36.52	6.84	9.83	13.13	22.44

are the same as those reported for diethylenetriamine-metal
tricarbonyls.[68] The reason for having only two C-O stretch-
ing modes in these compounds, despite the lower symmetry,
was given in the reference cited above.[68] A local symmetry
of $M(CO)_3$ in these compounds belongs to the point group C_{3v}
since the donor atoms(N) are the same.

However, in the complexes of Lig. 7, there are three
well-separated strong bands in the same carbonyl stretching
region. The presence of the bulky trimethylsilyl groups on
both end nitrogen atoms of the ligand molecule would destroy
the local symmetry of the C_{3v} point group. Thus the broad
band at the lower frequency side was resolved into separate

bands.

Table 19. <u>Carbonyl Stretching Bands of Chromium and</u>
        <u>Molybdenum Tricarbonyls Compounds</u>

Compounds	CO Stretching Frequencies in cm^{-1}		
$Cr(CO)_3 \cdot$ Lig 7	1880,	1750,	1704
$Mo(CO)_3 \cdot$ Lig 7	1892,	1774,	1718
(Dien)$Cr(CO)_3$	1881,	1737 (broad)	
(Dien)$Mo(CO)_3$	1883,	1735 (broad)	

From the intermediate reaction which involved cyclohepta-
triene metal carbonyls, and from the spectroscopic results
discussed above, it could be concluded that, in the tricar-
bonylmetal complexes of Lig 7 prepared in this work, the
tridentate ligand occupies a face of the coordinate octahedron
in such a way that the three nitrogen atoms form a triangle
(facial or 1,2,3 isomer). Therefore the molecular structure
of the complexes with Lig 7 resembles closely that for the
diethylenetriamine-metal tricarbonyls of chromium and molyb-
denum.[68]

From the difficulties confronted in the preparation of
transition-metal complexes with silylamines, it was concluded
that the lone-pair electrons on nitrogen atoms in silylamines
are less available toward coordination than those in alkylamines.

Presumably this is due to the pπ-dπ partial double bond character in the N-Si bond. Stable transition-metal complexes of chelating organosilyl polyamines were isolated only with considerable difficulty. In these situations the lone-pair electrons of the nitrogen atoms would be removed from N-Si partial double bond. If this is the case, then the N-Si bond would be weakened considerably. This probably is the main reason for the rearrangement in certain metal complexes, and for the easy hydrolysis and decomposition of other silylamine adducts.

C. EXPERIMENTAL

1. Analysis

All elements other than copper, cobalt, iron, and chlorine were determined commercially at the Schwarzkopf Microanalytical Laboratory, N.Y.

a. Copper and Cobalt

About 100 mg of the complex was weighed in a weighing ampule under argon atmosphere. This ampule was opened in about 25 ml of water-methanol mixture (1:1) in a 250 ml Erlenmeyer flask. After hydrolysis of the metal complex was completed, the solution was diluted with about 75 ml of distilled water. Copper was determined by adjusting the pH of the solution to 8 and titrating with standard EDTA solution,

using murexide as indicator.[75]

Cobalt was determined by adding an excess of standard EDTA solution, adjusting the pH to about 10 with ammonium hydroxide and back-titrating with standard zinc solution using Eriochrome Black T as indicator.[76]

b. Iron

Approximately 100 mg of iron complex was completely oxidized by the standard wet oxidation method, using 10 ml of concentrated H_2SO_4 and 10 ml of 30% H_2O_2. After neutralization with NaOH, this solution was diluted to 100 ml with distilled water. The pH of this solution was adjusted to 2.5 with 10% sodium acetate. The solution was then titrated with EDTA, using sulfosalicylic acid as indicator.[77]

c. Chlorine

A solution of about 100 mg of sample in a 250 ml beaker was prepared as in the case of the copper or cobalt determination. Standard silver nitrate solution was added in excess, and the resulting solution was back-titrated potentiometrically

75. O. Kinnunen and B. Merikanto, Chem. Anal. 43, 93 (1954).

76. W.F. Harris and T.R. Sweet, Anal. Chem., 26, 1649 (1954).

77. H.A. Flaschka, "EDTA Titrations" 2nd ed., Pergamon Press, Oxford, 1964, pp 85-86

with standard chloride solution.[78] A standard gravimetric method was also employed in chloride determination. Both methods were proven to be equally effective and satisfactory.

2. Preparation of Chemicals Used

The anhydrous metal chlorides used in this work, with the exception of anhydrous iron (II) chloride, were prepared by refluxing hydrated chlorides with thionyl chloride as described by Pray.[79] Anhydrous iron dichloride was obtained from Alfa Inorganics, Inc.

Chromium hexacarbonyl was purchased from Alfa Inorganics, Inc.

Molybdenum hexacarbonyl was kindly supplied by Climax Molybdenum Company. Both metal hexacarbonyls were purified by sublimation under reduced pressure before use.

3. Drying of the Solvents

Since an absolutely anhydrous condition of the reaction mixture was essential for success in the preparation of the metal complexes, a brief account of the drying procedure for the solvent is mentioned here.

78. D.A. Skoog and D.M. West, Fundamentals of Analytical Chemistry, Holt, Rinehart and Winston, New York, 1963, pp. 549-556.

79. A.R. Pray in "Inorganic Syntheses", Vol. V, T. Moeller, Ed., McGraw-Hill, New York, 1957.

Tetrahydrofuran was first refluxed with potassium hydroxide pellets for 12 hours, and then distilled into a two-liter flask. Sodium wire was pressed into this flask, and a solvent-drying and distillation apparatus[80] with a reflux condenser was attached. Tetrahydrofuran was refluxed with sodium wire for 12 to 24 hours before distilling into a pint-size brown bottle directly and without exposing to atmospheric moisture. Sodium wire was pressed into this bottle and kept at least for 24 hours. By this time hydrogen bubbles had ceased to form on the shiny surface of the sodium wire. For each experiment a new solvent bottle was opened. After a portion of the solvent was used for one experiment the rest of it was returned to the refluxing flask and redistilled later.

Dry benzene was prepared by simple distillation into a two-liter solvent distilling flask without refluxing with potassium hydroxide pellets. The subsequent steps were identical to those applied for tetrahydrofuran.

4. Preparation of Metal Complexes with Organosilylamines

Preparations were carried out using standard-taper glassware, size 14/20, which was dried with extreme caution. Clean glassware was filled with a 10% solution of dimethyldichlorosilane in benzene for 10 to 30 minutes. After draining the silane solution, the glassware was kept in an electric oven

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80. K.B. Wiberg, Laboratory Technique in Organic Chemistry, McGraw-Hill, New York, 1960, p. 243.

at 130°C for not less than 12 hours. The pieces were then
cooled in a large desiccator with Drierite. After assembly
of the apparatus the whole system was purged with argon gas
which was dried by passage through a three-foot long drying
tube filled with Drierite and phosphorus pentoxide.

a. With Metal Halides

About 10 mmoles of anhydrous metal chloride was suspended
in 100 ml of carefully dried benzene in 250 ml three neck
flask. This reaction flask was equipped with a dropping
funnel, a reflux condenser and an argon inlet tube. Approxi-
mately 10.5 mmoles (about 5% excess) of silylamine dissolved
in 30 ml of benzene was added over a period of one hour from
the dropping funnel. Following this, the reaction mixture
was kept at room temperature with constant stirring not less
than 12 hours. The solid product of this reaction was collect-
ed in an inert-atmosphere filtering apparatus. The product
was washed and dried under reduced pressure at room tempera-
ture for 4 hours or more. The dried product was then trans-
ferred with argon either into a Schlenk vessel or into a
thick-walled tube which was subsequently sealed under vacuum
for analysis.

The same apparatus was used when dry tetrahydrofuran was
adopted as reaction solvent. In this case a slight excess of
metal halide, about 10 mmoles, was suspended in about 100 ml

of tetrahydrofuran and stirred with a magnetic stirrer. When the solvation of metal halide was completed by stirring for 3 to 4 hours, 9 mmoles of the silylamine in 30 ml of tetrahydrofuran was allowed to drip slowly into the flask. This reaction mixture was stirred at room temperature for a minimum of 12 hours. Subsequently, the reaction mixture was filtered and the filtrate was collected in another dry 250 ml three-neck flask with a magnetic stirring bar in it. During a gradual evaporation of the solvent under reduced pressure at temperature lower than 40°C, the solution was stirred slowly with the magnetic stirrer to avoid a vigorous bumping. The residue was dried for 4 to 5 hours at reduced pressure using an oil pump. The solid product was powdered with the magnetic stirring bar and transferred as before.

b. With Group VI Metal Carbonyls

A 50 ml, three-neck flask equipped with a dropping funnel, a reflux condenser and a filtering apparatus was used in this experiment. To 5 mmoles of cycloheptatriene-metal tricarbonyl dissolved in 10 ml of tetrahydrofuran in the flask 5 mmoles of N,N"-bis(trimethylsilyl)diethylenetriamine in about 10 ml of the same solvent was added dropwise. Soon a yellow precipitate started to appear from the deep red colored solution. The stirring was continued for an hour to allow the replacement

reaction to be completed. The yellow solid was collected in the usual manner and dried under vacuum.

Appendix 1

Infrared Spectra
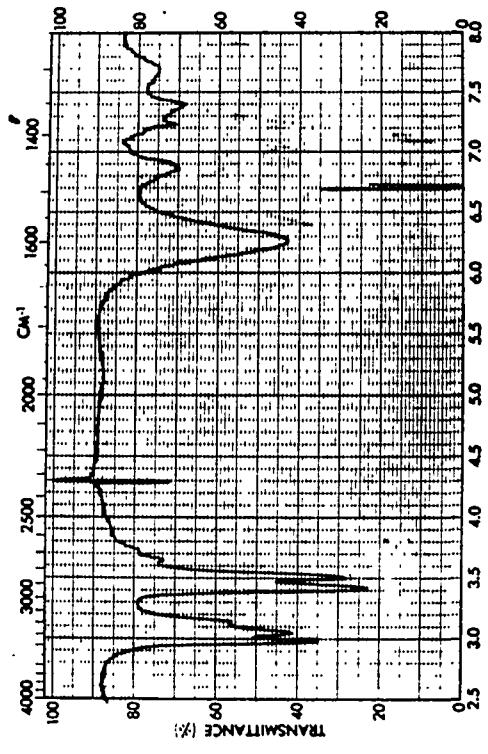
Fig. 1.1 a. $H_2NCH_2CH_2NH_2$
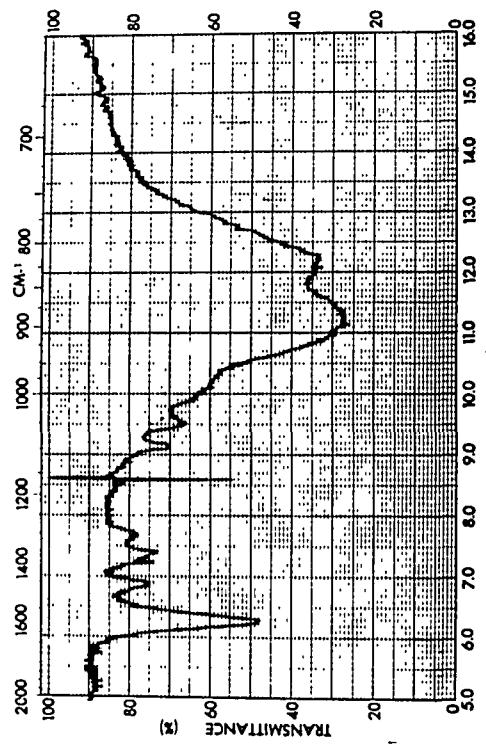
Fig. 1.1 b.
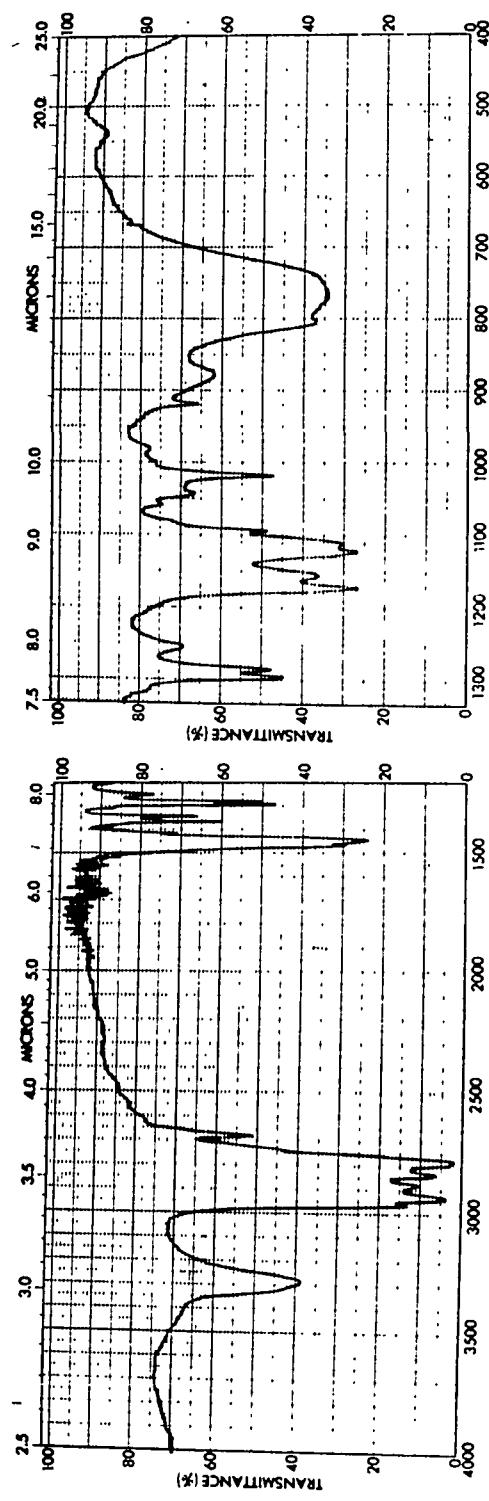
Fig. 1.2 a. $CH_3NHCH_2CH_2NHCH_3$

Fig. 1.2 b.
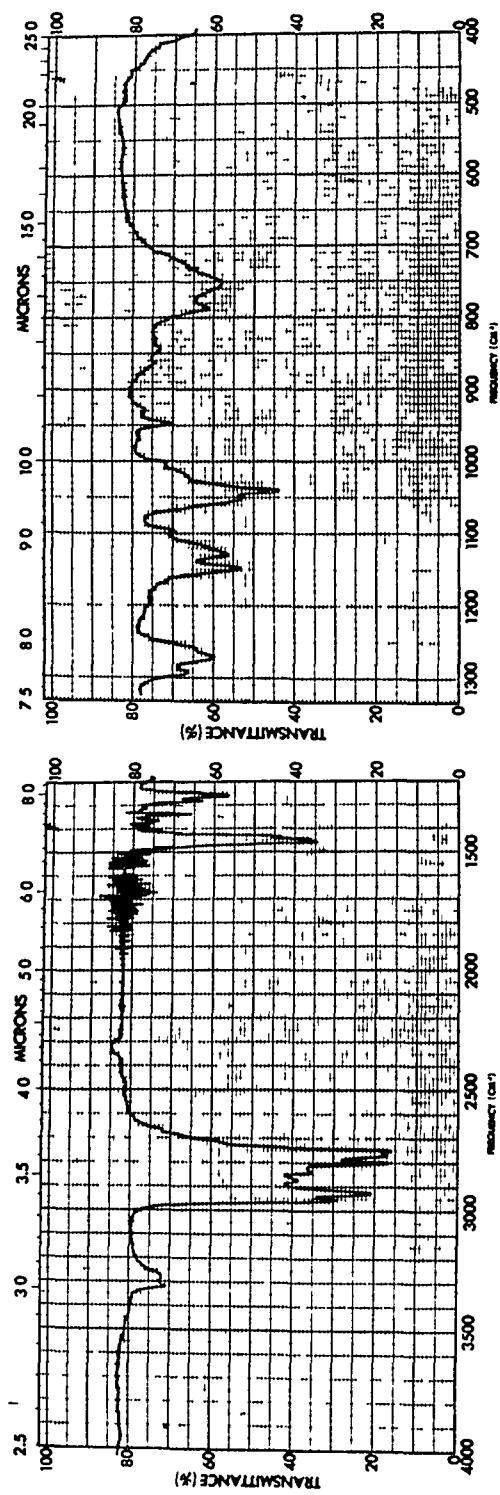
Fig. 1.3 b.

Fig. 1.4 b.

Fig. 1.3 a. $(CH_3)_2NCH_2CH_2NHCH_3$
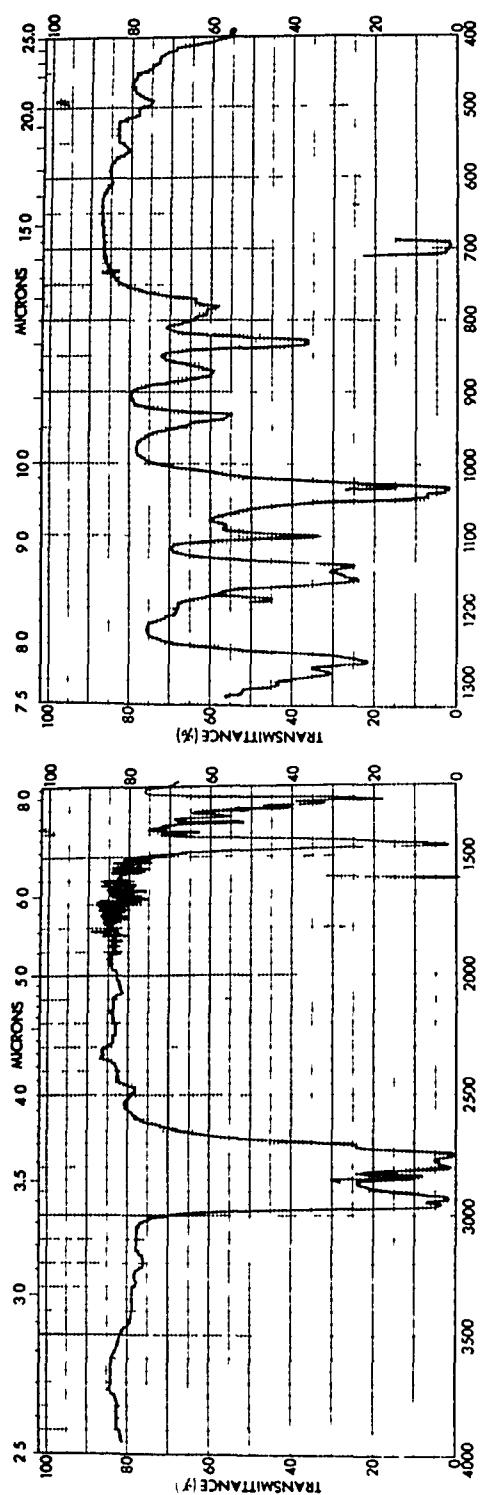
Fig. 1.4 a. $(CH_3)_2NCH_2CH_2N(CH_3)_2$
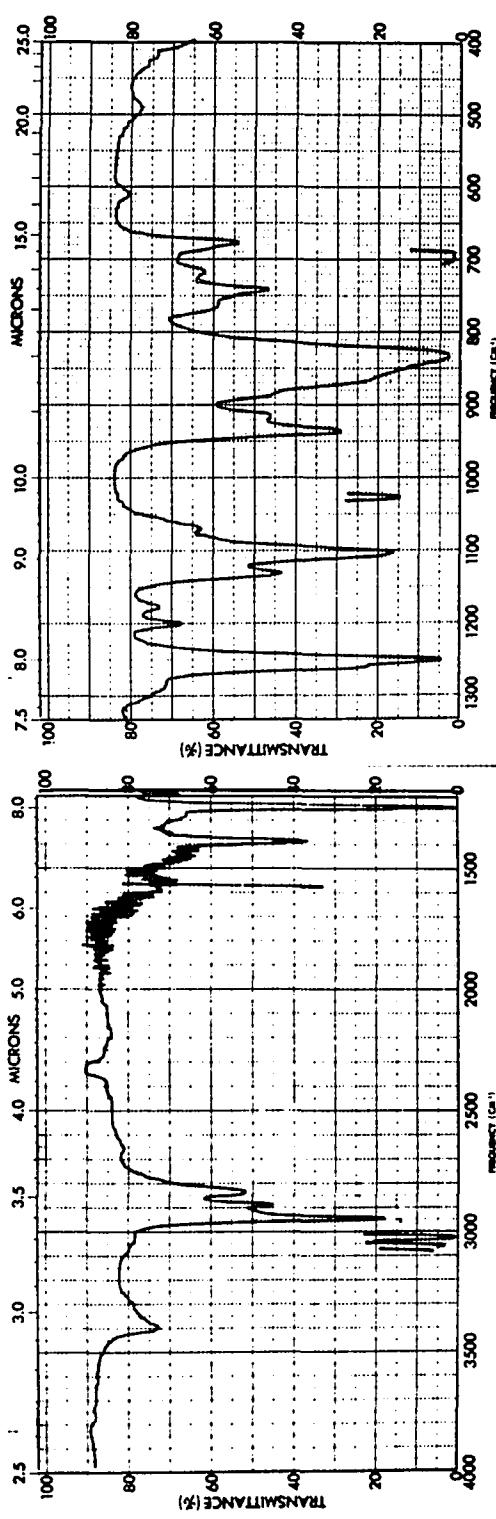
Fig. 1.5 a. $(CH_3)_3SiNHCH_2CH_2NHSi(CH_3)_3$

Fig. 1.5 b.
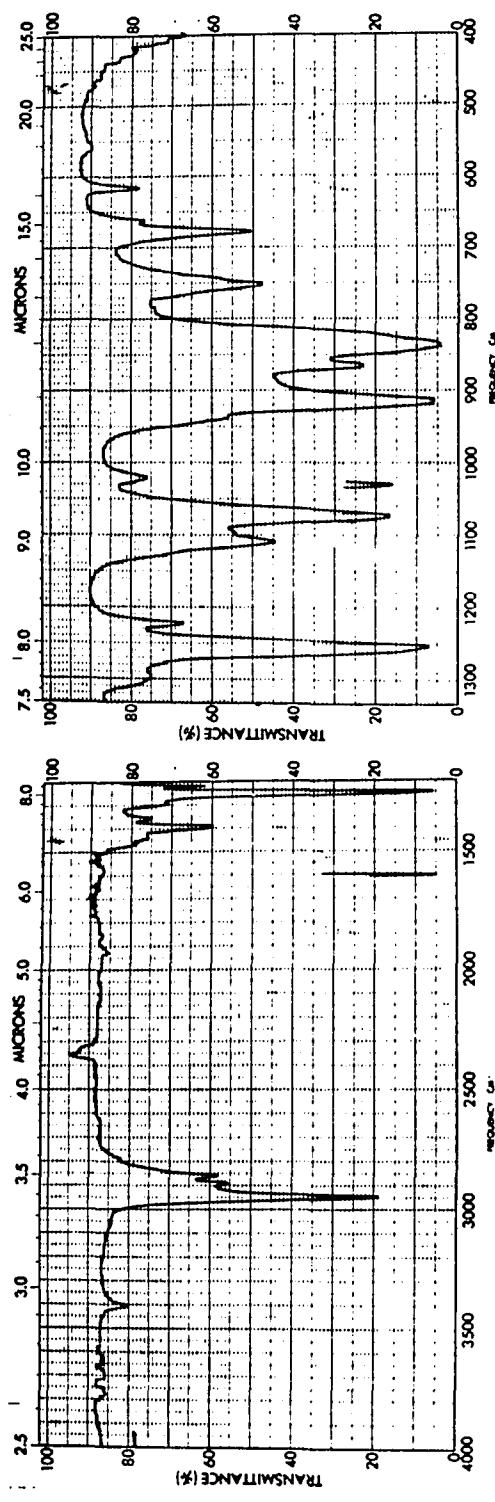
Fig. 1.6 a. $(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$

Fig. 1.6 b.
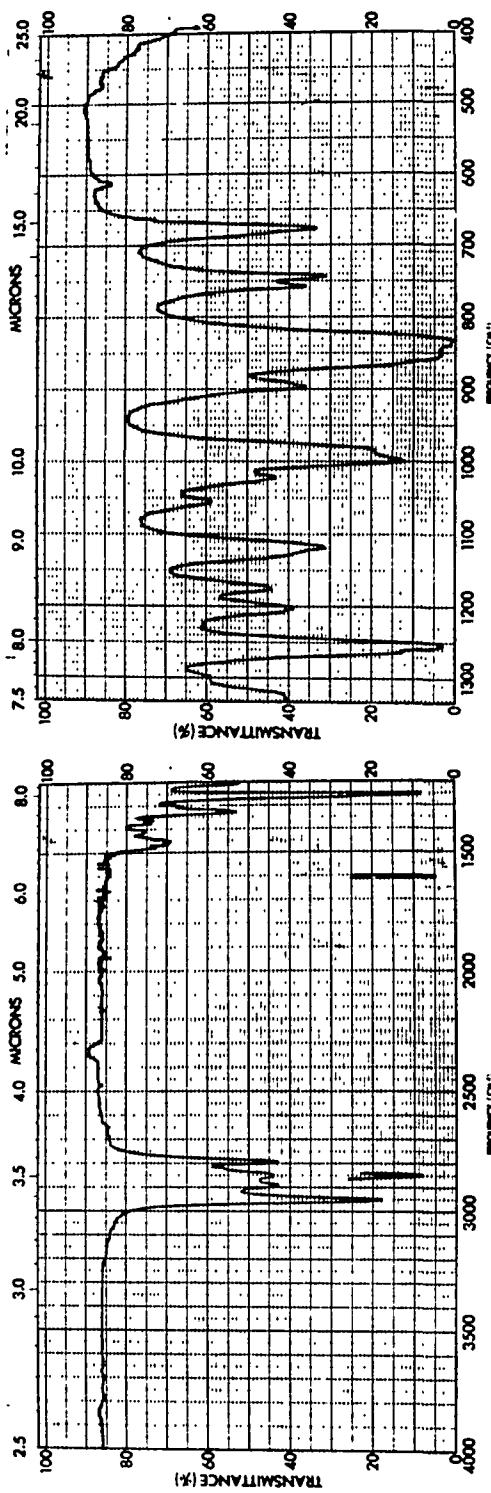
Fig. 1.7 b.

Fig. 1.7 a.
$(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3$
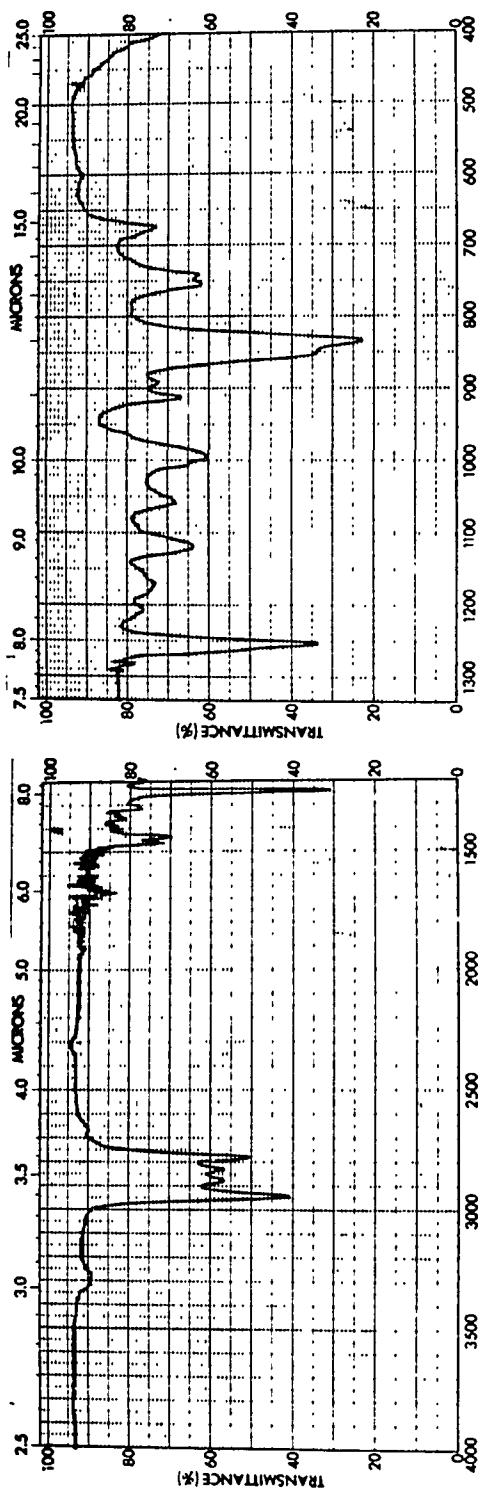
Fig. 1.8 b.

Fig. 1.8 a. $CH_3NHCH_2CH_2N(CH_3)Si(CH_3)_3$
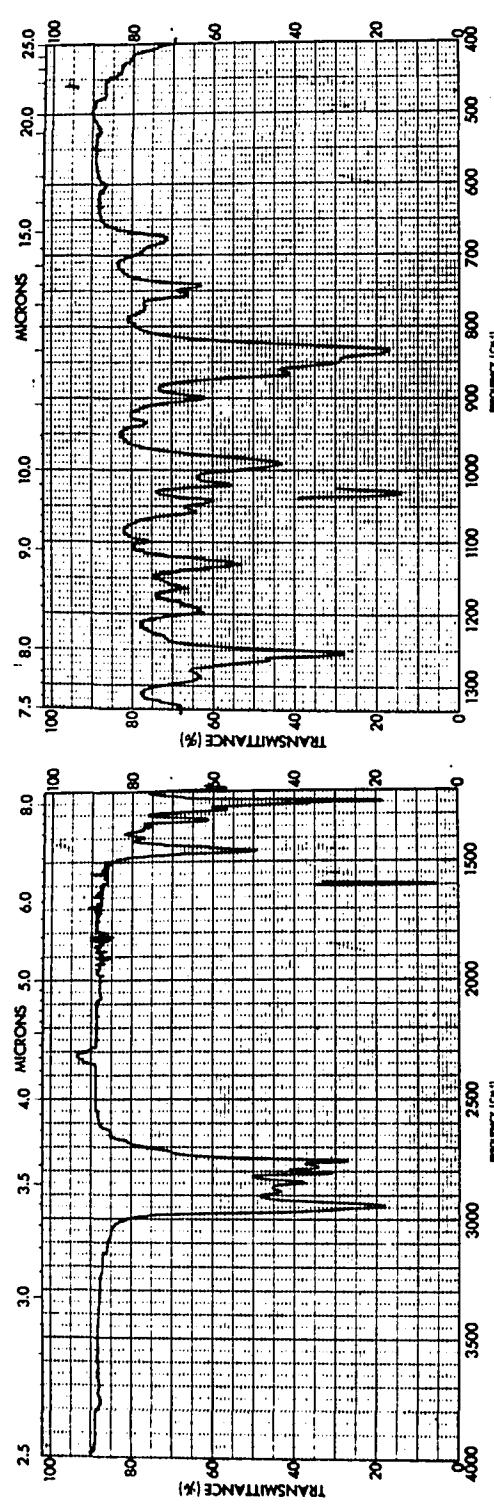
Fig. 1.9 b.

Fig. 1.9 a. $(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$
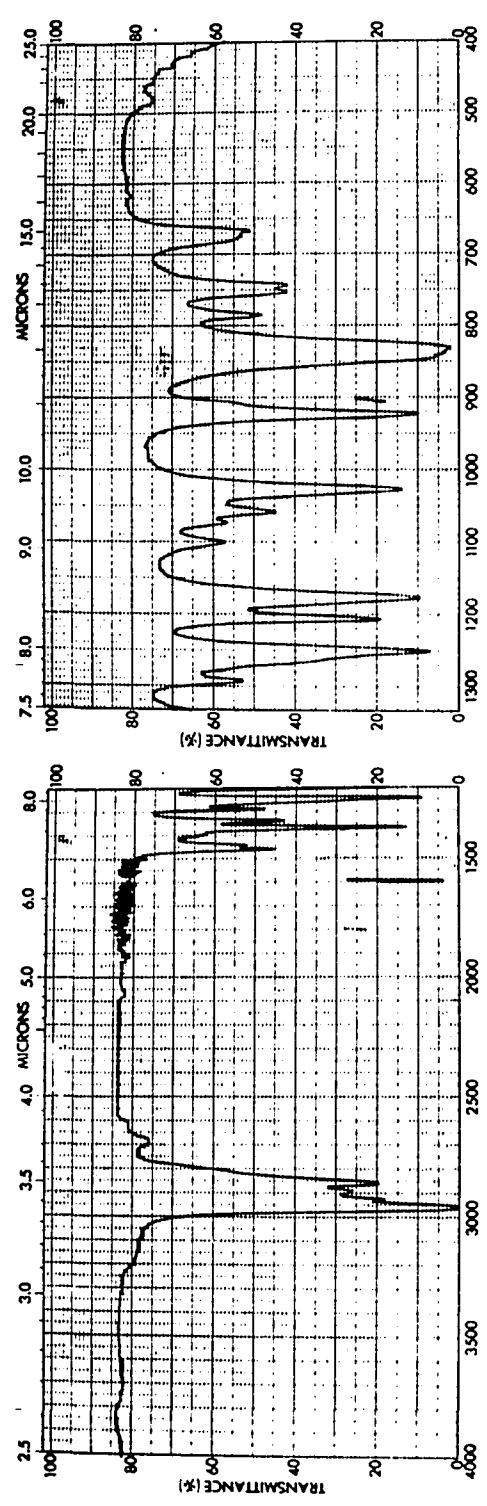
Fig. 1.10 b.

Fig. 1.10 a. $(CH_3CH_2)_2NSi(CH_3)_3$

Fig. 1.11 a.
(CH₃)₃SiNHCH₂CH₂NHCH₂CH₂NHSi(CH₃)₃
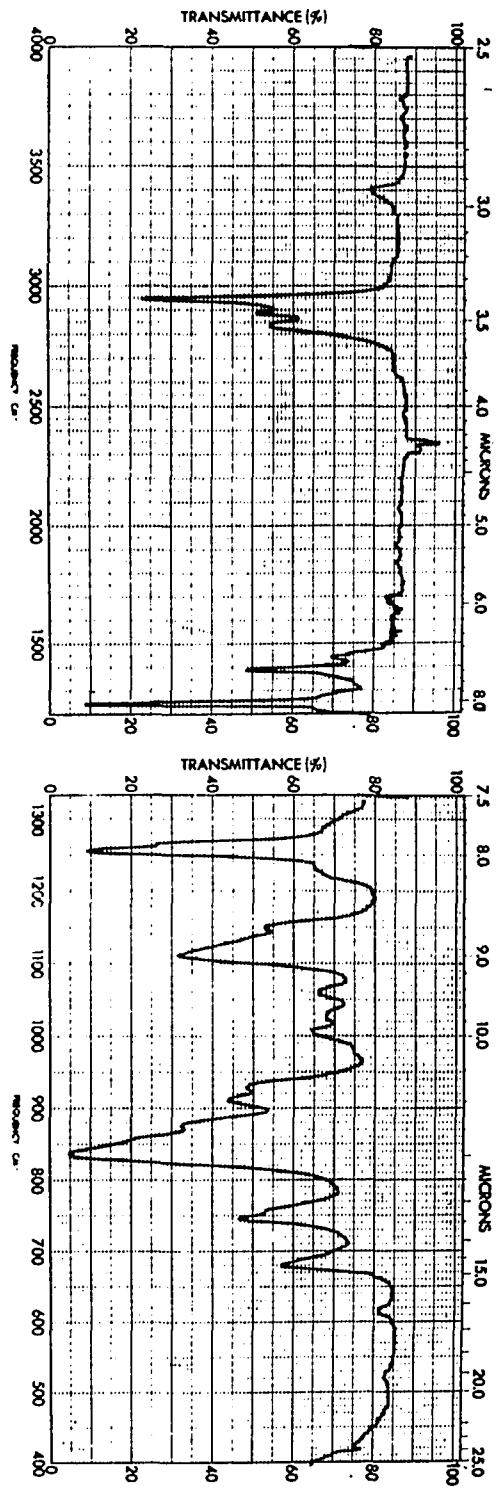
Fig. 1.11 b.

Fig. 1.12 a.
(CH₃)₃SiNHC₂H₄N[Si(CH₃)₃]C₂H₄NHSi(CH₃)₃
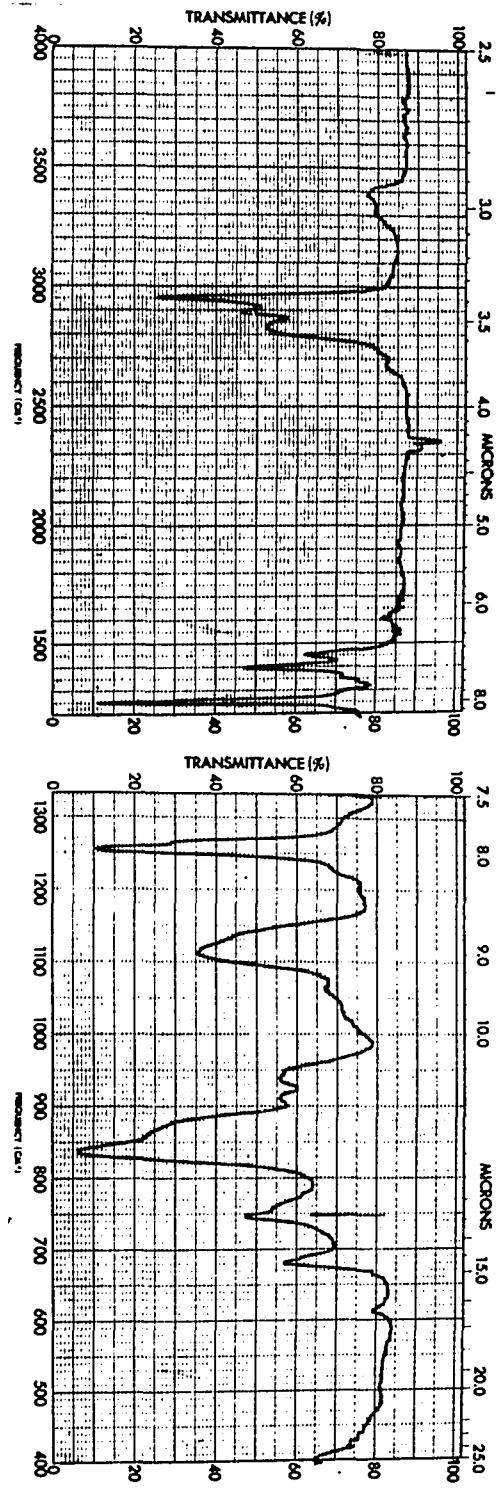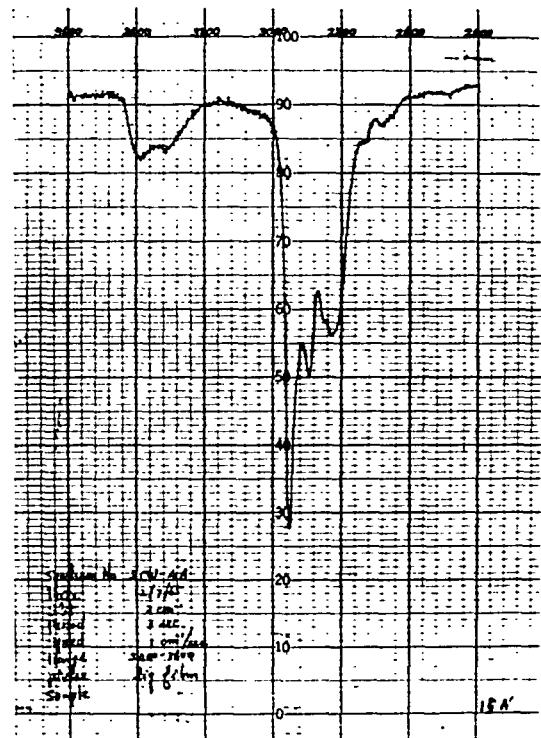
Fig. 1.12 b.

Fig. 1.11 c.

$(CH_3)_3SiNHCH_2CH_2NHCH_2CH_2NHSi(CH_3)_3$
Recorded on Cary White 90
between 3600 and 2400 cm^{-1}
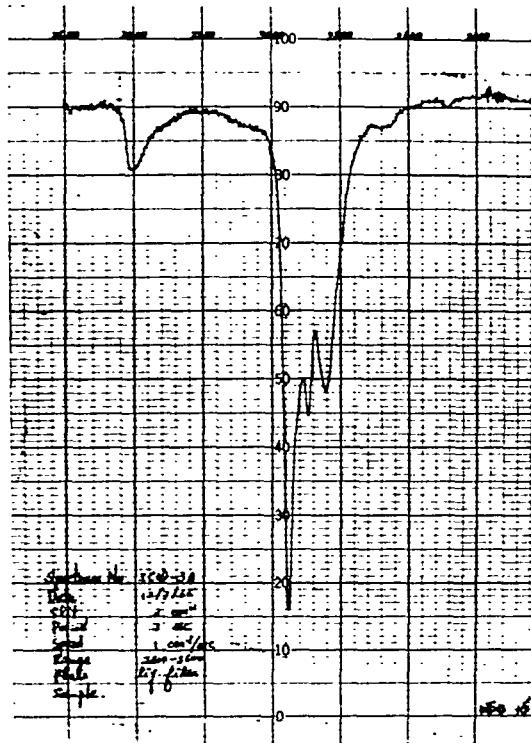
Fig. 1.12 c.

$(CH_3)_3SiNHC_2H_4N[Si(CH_3)_3]C_2H_4NHSi(CH_3)_3$
+ Recorded on Cary White 90
between 3600 and 2400 cm^{-1}
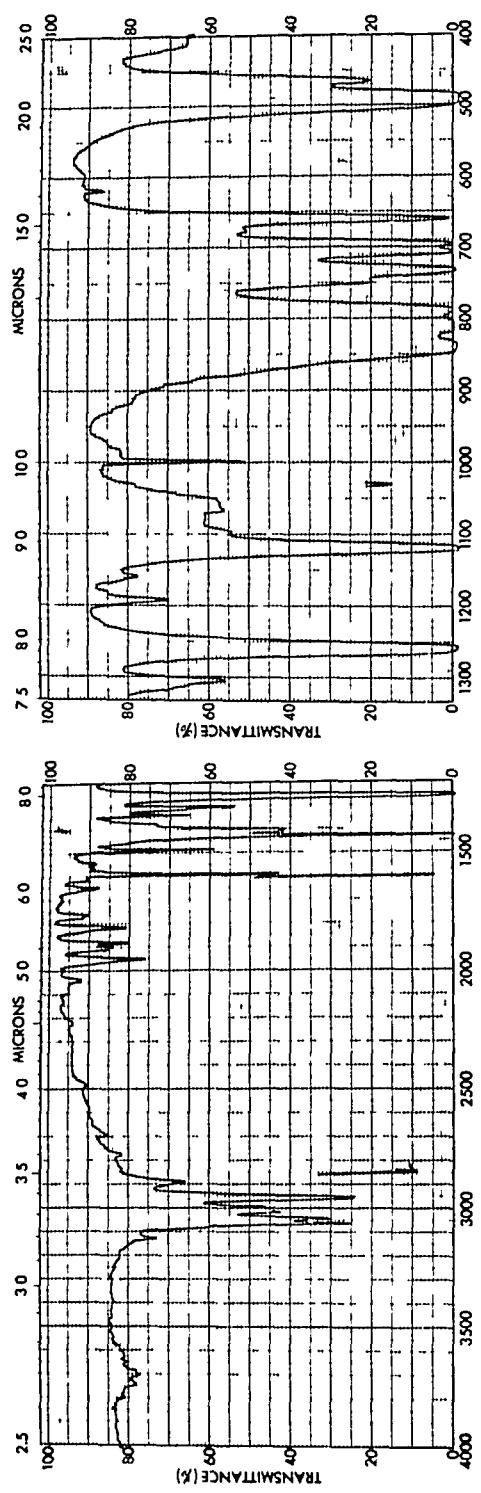
Fig. 1.13 b.

Fig. 1.13 a. $(C_6H_5)Si(CH_3)_2Cl$

Fig. 1.14 b.
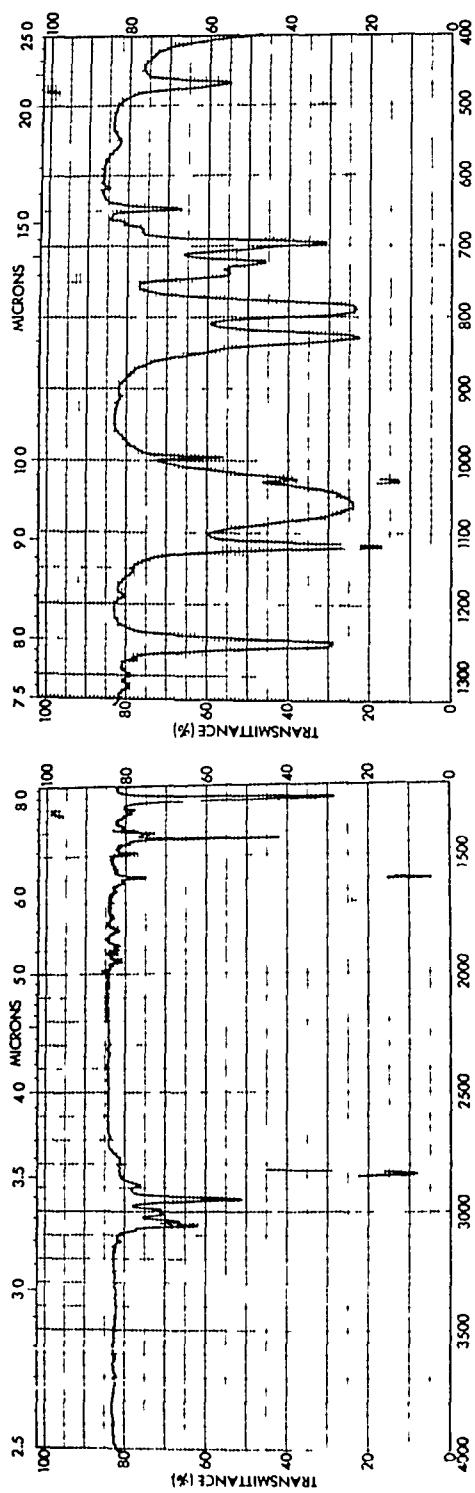
Fig. 1.14 a. $(C_6H_5)(CH_3)_2SiOSi(CH_3)_2(C_6H_5)$

Fig. 1.15 a.
(C$_6$H$_5$)(CH$_3$)$_2$SiNHCH$_2$CH$_2$NHSi(CH$_3$)$_2$(C$_6$H$_5$)
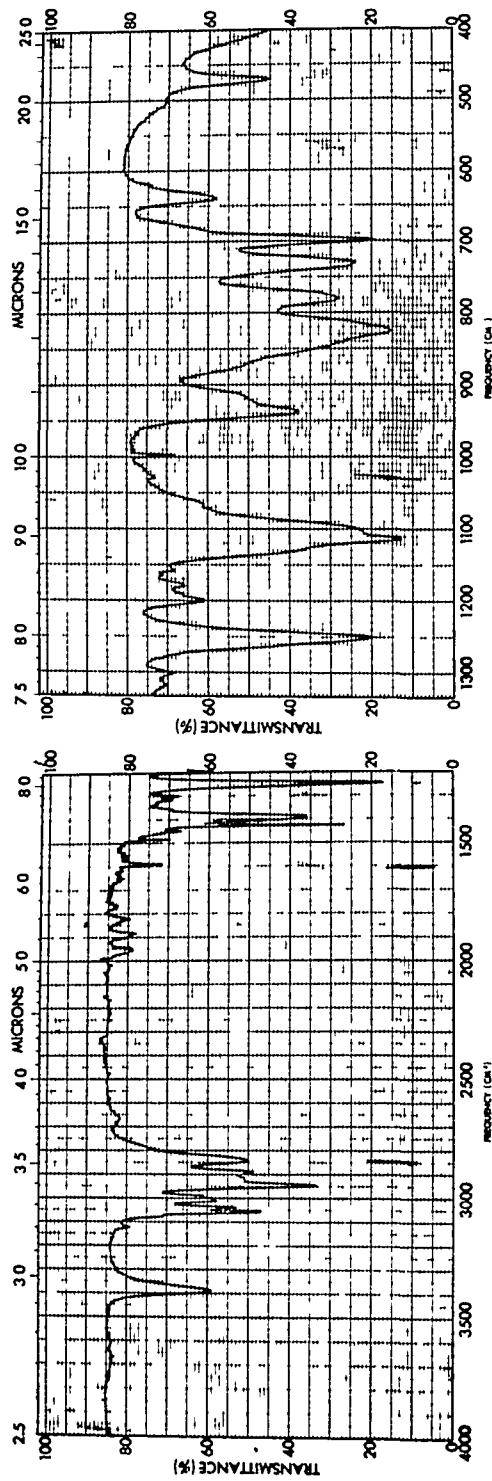
Fig. 1.15 b.
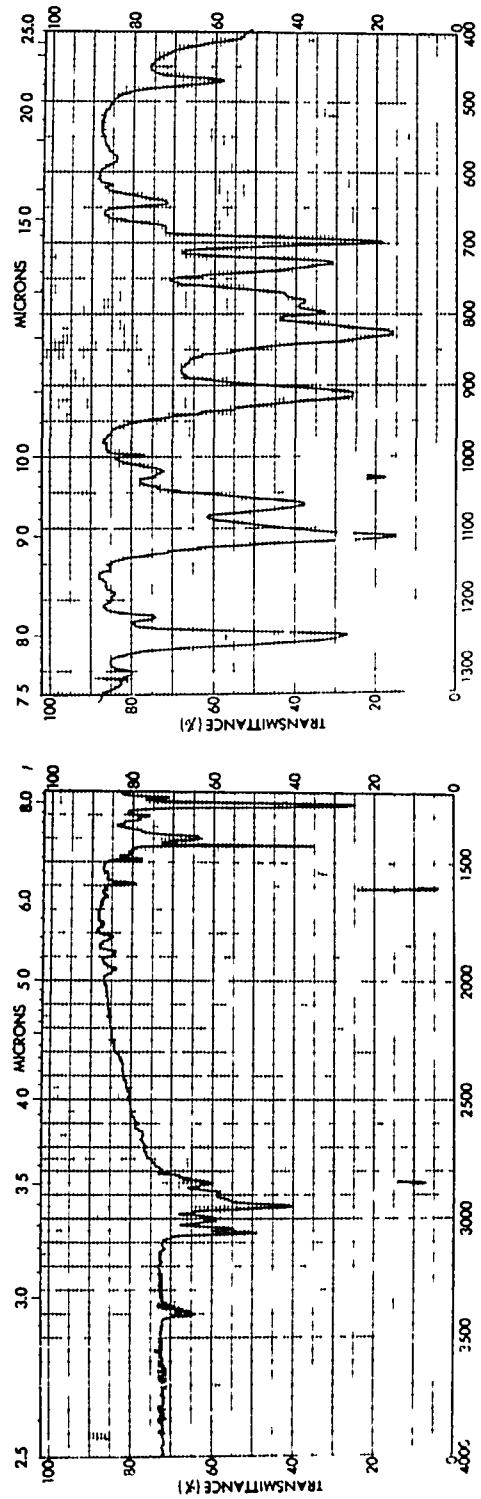
Fig. 1.16 a.
(C$_6$H$_5$)(CH$_3$)$_2$SiNHCH$_2$CH$_2$N[Si(CH$_3$)$_2$(C$_6$H$_5$)]$_2$

Fig. 1.16 b.
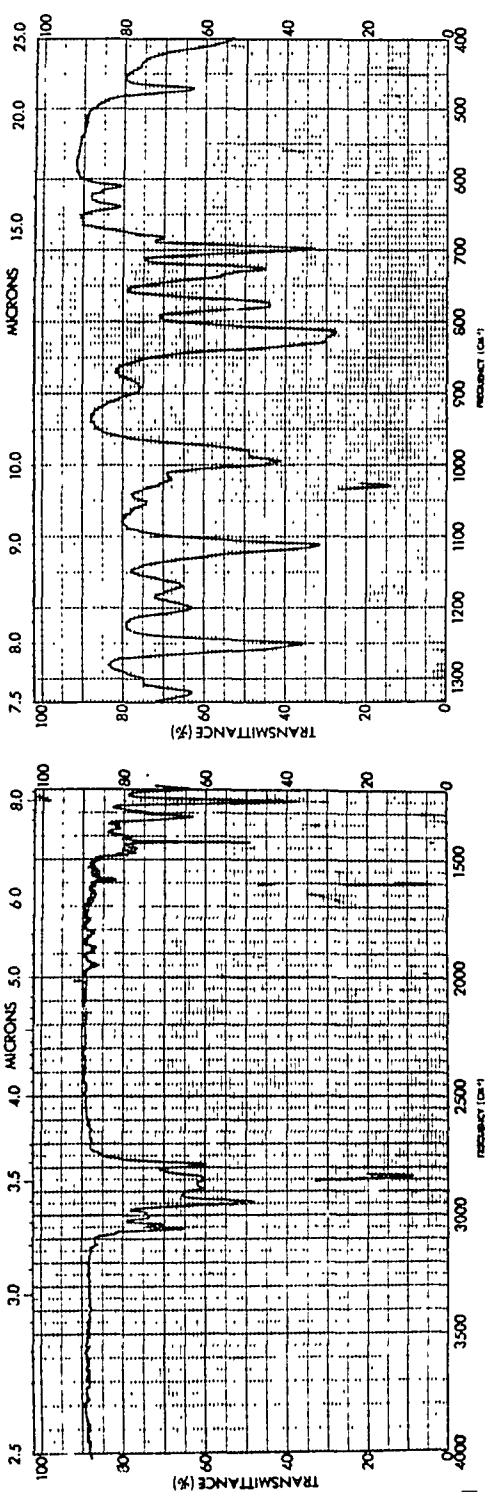
Fig. 1.17 a.
$(C_6H_5)(CH_3)_2SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_2(C_6H_5)$

Fig. 1.17 b.
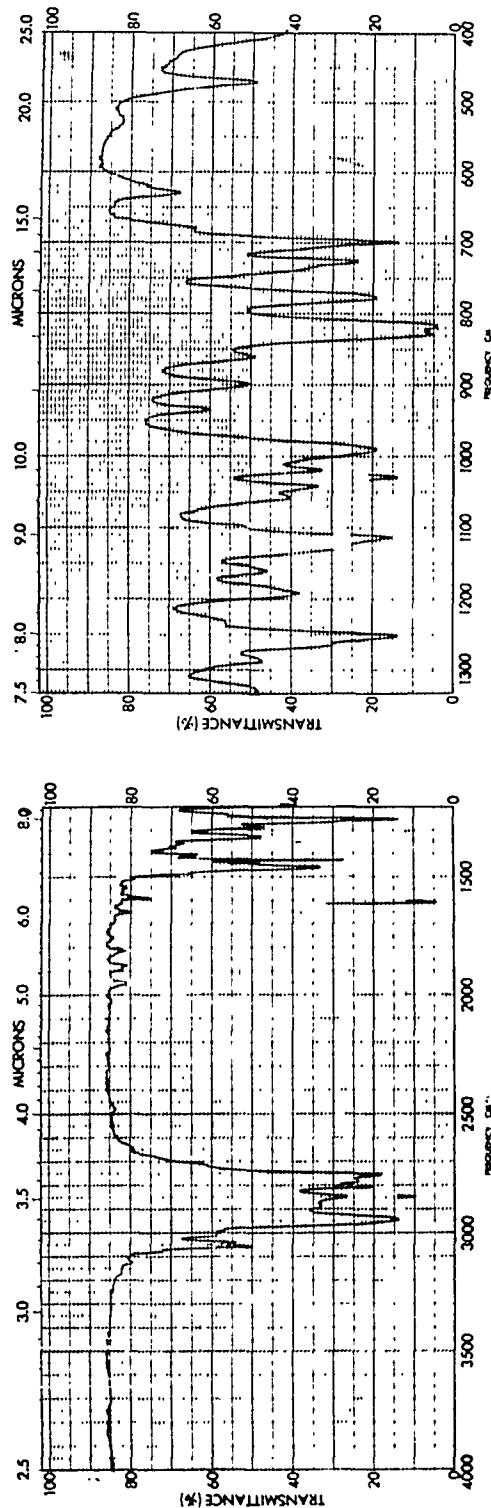
Fig. 1.18 a.
$(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_2(C_6H_5)$

Fig. 1.18 b.
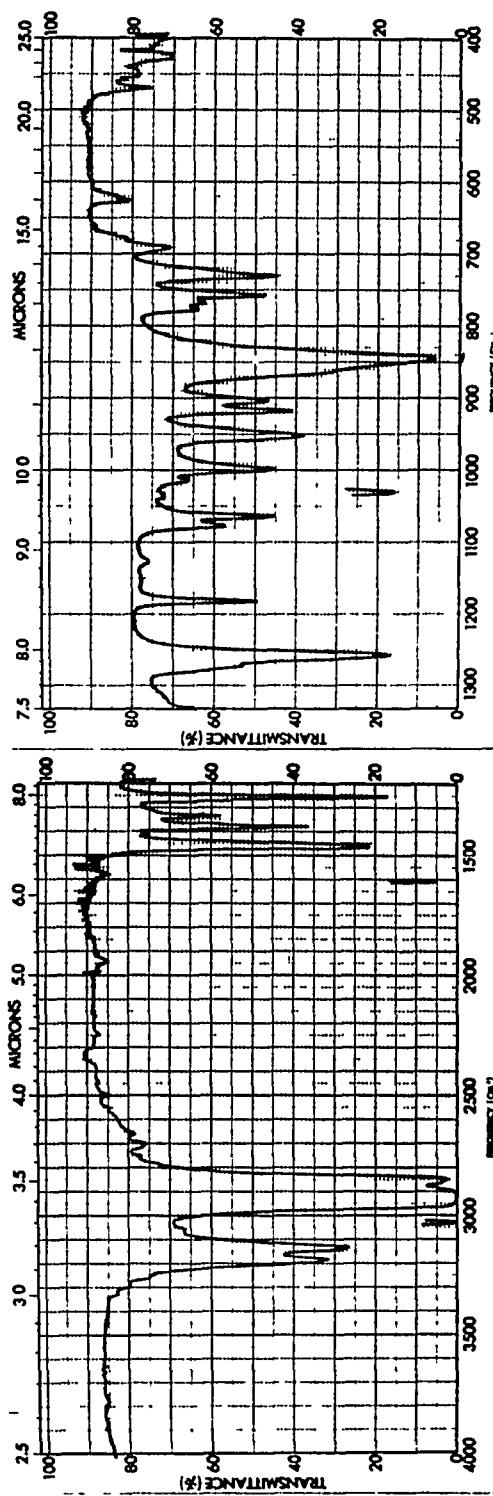
Fig. 1.19 CuCl$_2$·[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHSi(CH$_3$)$_3$]
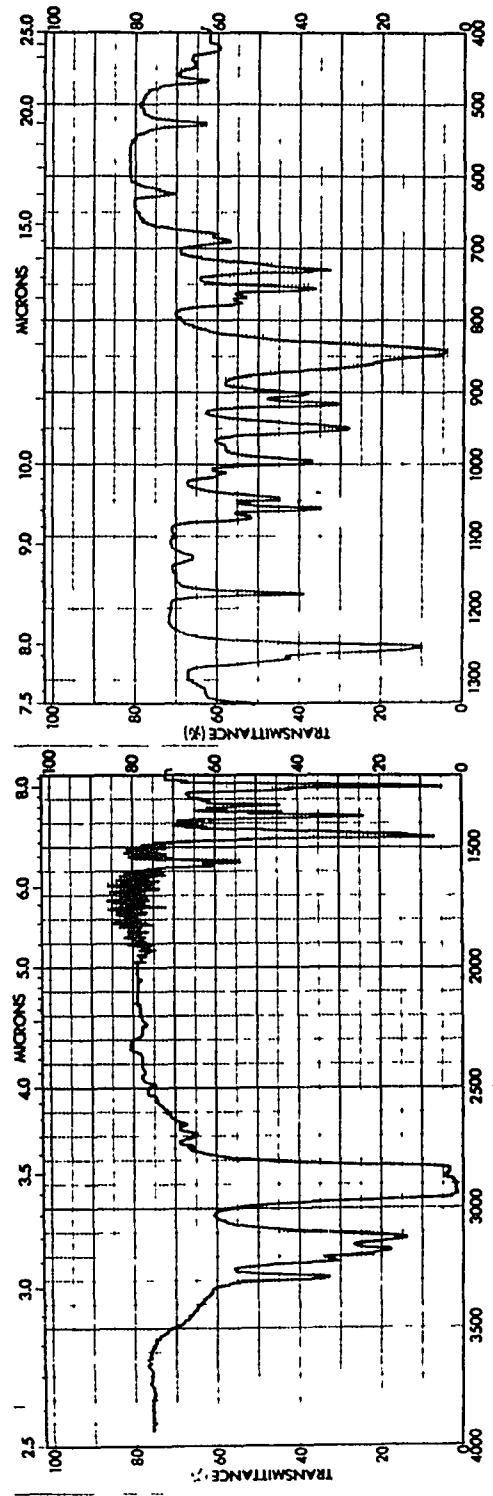
Fig. 1.20 CuCl$_2$·[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHSi(CH$_3$)$_3$],exposed briefly to atmospheric moisture
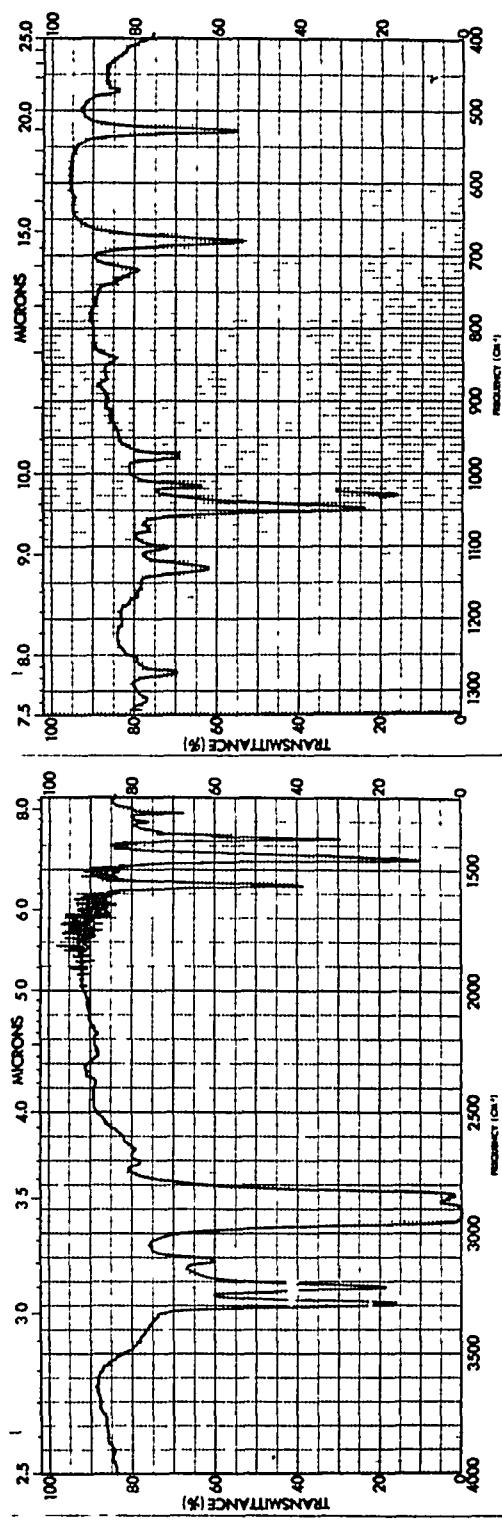
Fig. 1.21 CuCl$_2$·[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHSi(CH$_3$)$_3$], exposed to atmospheric moisture for 84 hours
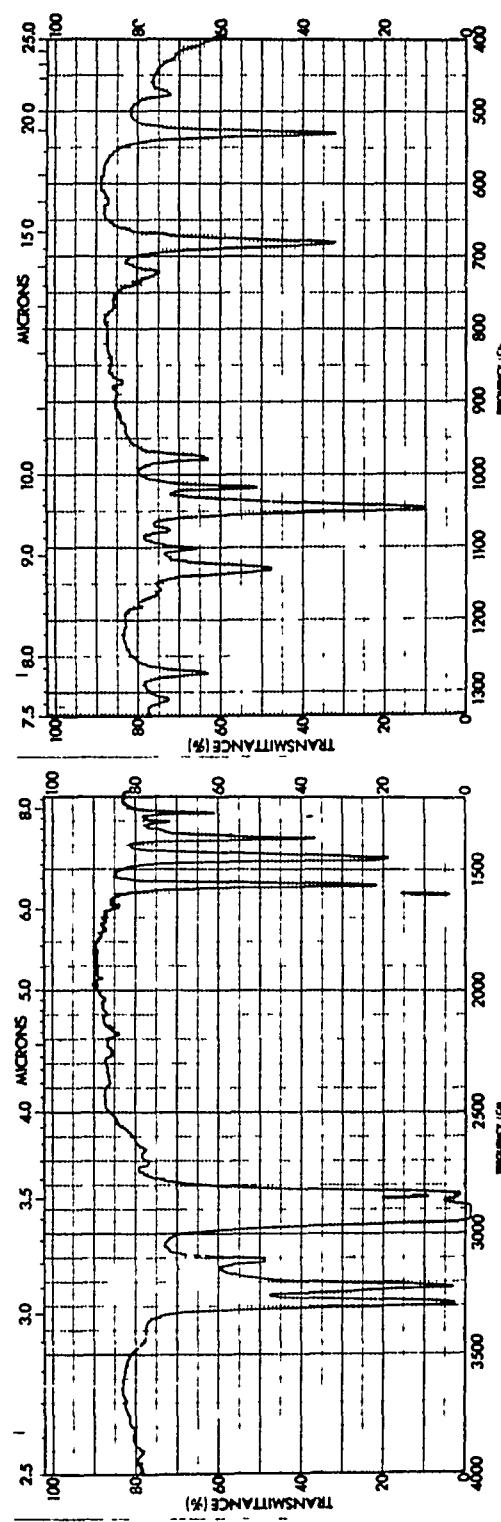
Fig. 1.22 CuCl$_2$·[H$_2$NCH$_2$CH$_2$NH$_2$]
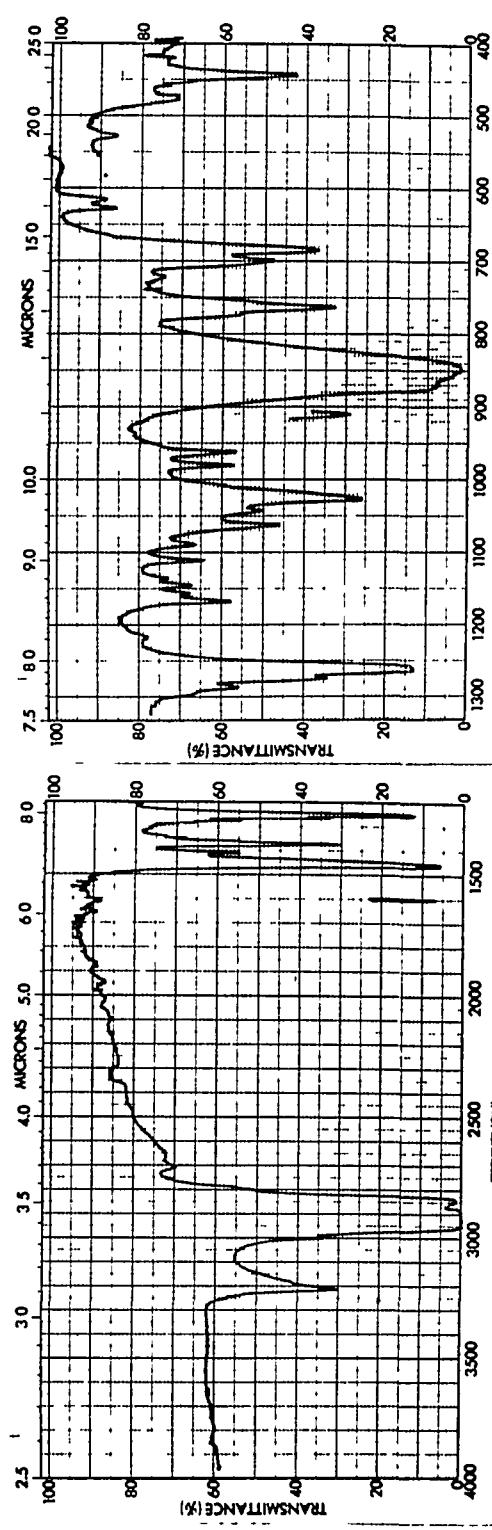
Fig. 1.23 CuCl₂·[(CH₃)₃SiN(CH₃)CH₂CH₂N(CH₃)Si(CH₃)₃], slightly hydrolyzed
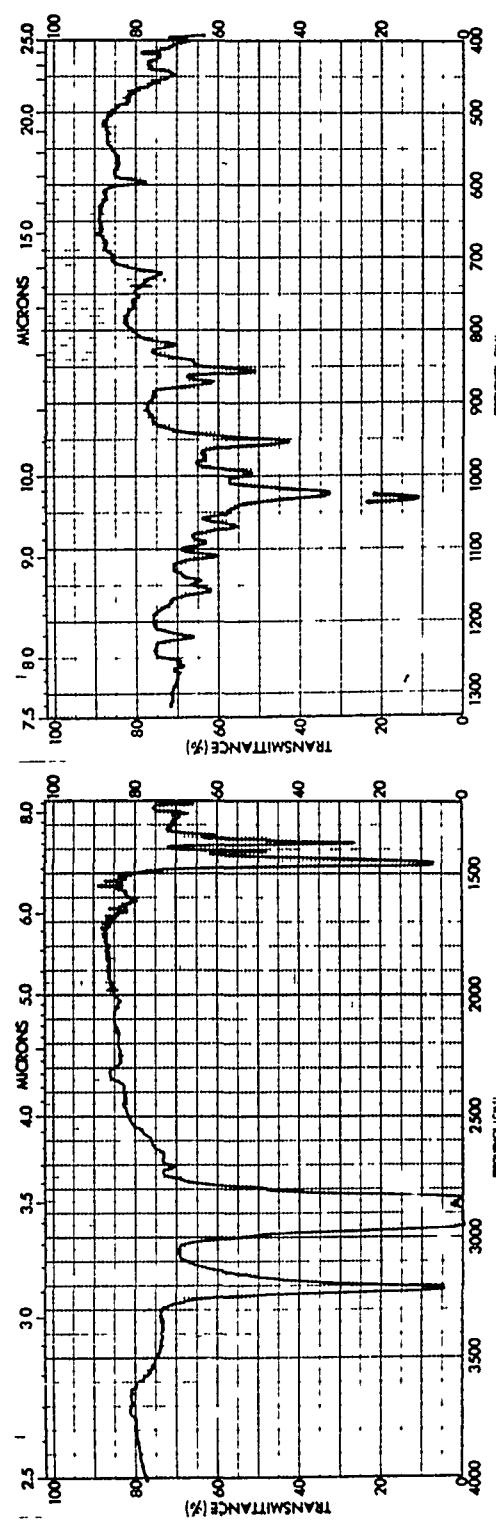
Fig. 1.24 CuCl₂·[(CH₃)₃SiN(CH₃)CH₂CH₂N(CH₃)Si(CH₃)₃], completely hydrolyzed
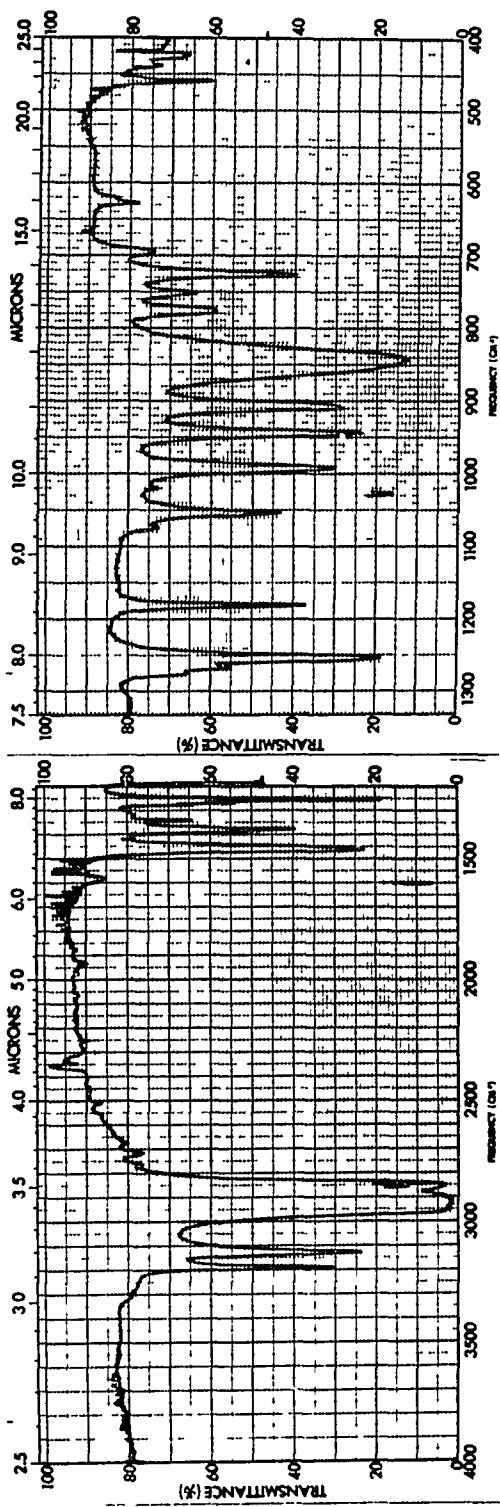
Fig. 1.25 CoCl$_2$·[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHSi(CH$_3$)$_3$]
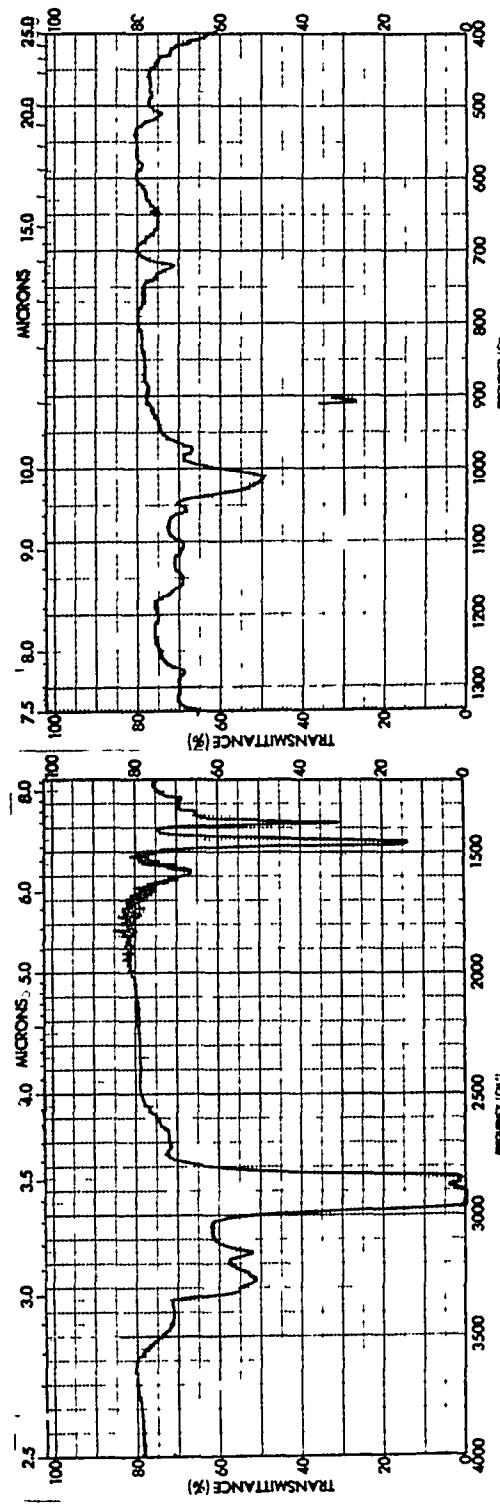
Fig. 1.26 CoCl$_2$·[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHSi(CH$_3$)$_3$], exposed to atmospheric moisture for 70 hours

Fig. 1.27 $CoCl_2 \cdot [(CH_3)_3SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_3]$
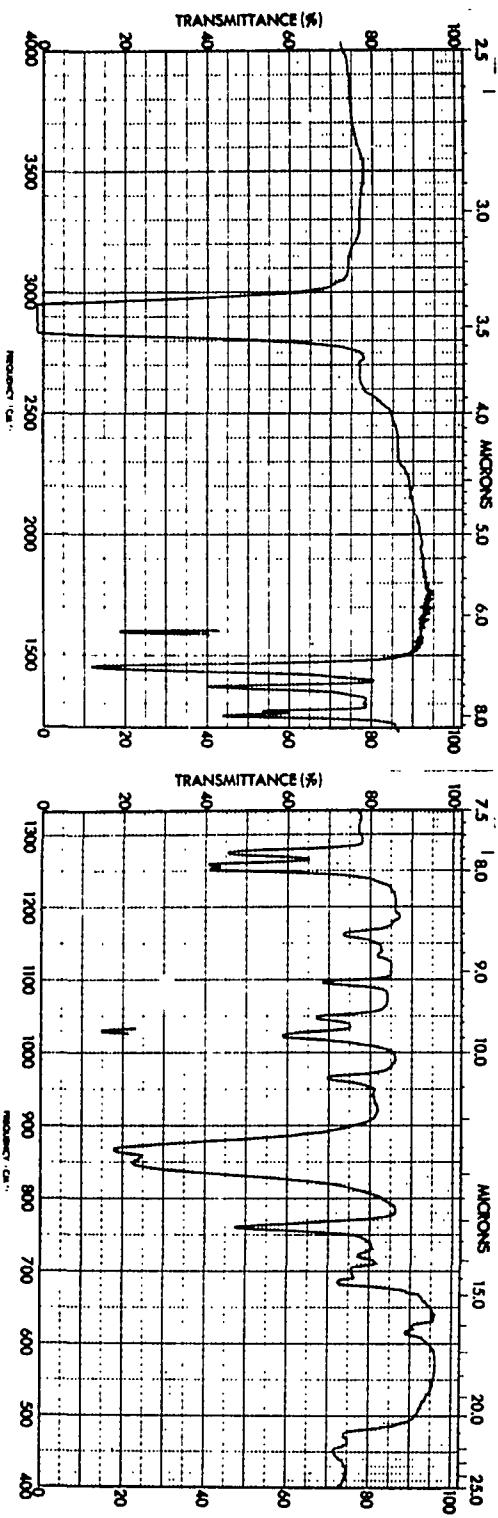
Fig. 1.28 $CoCl_2 \cdot [(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3]$
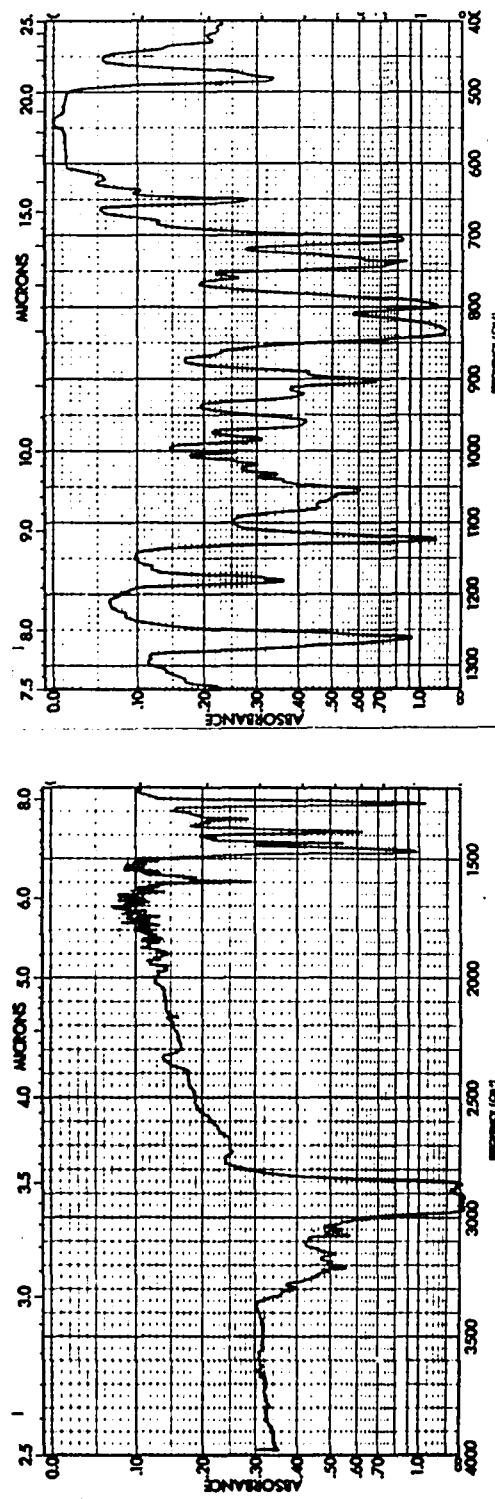
Fig. 1.29 CoCl$_2$·[(C$_6$H$_5$)(CH$_3$)$_2$SiN(CH$_3$)CH$_2$CH$_2$N(CH$_3$)Si(CH$_3$)$_2$(C$_6$H$_5$)]
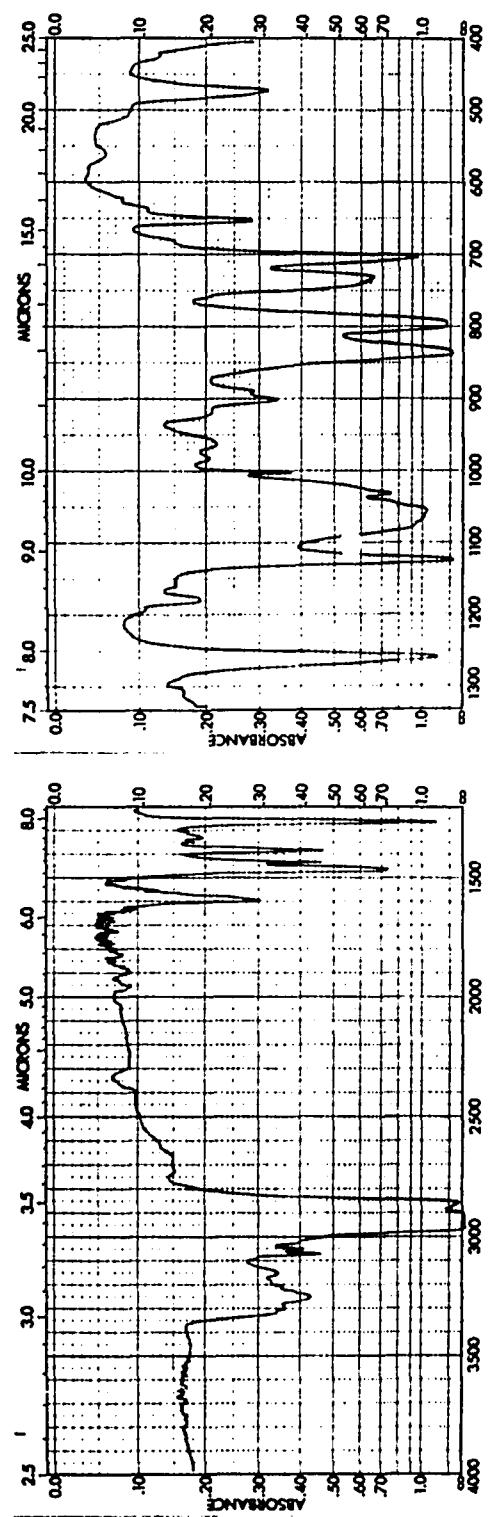
Fig. 1.30 CoCl$_2$·[(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)Si(CH$_3$)$_2$(C$_6$H$_5$)]

Fig. 1.33 FeCl$_2$·[(CH$_3$)$_2$NCH$_2$CH$_2$N(CH$_3$)Si(CH$_3$)$_3$]
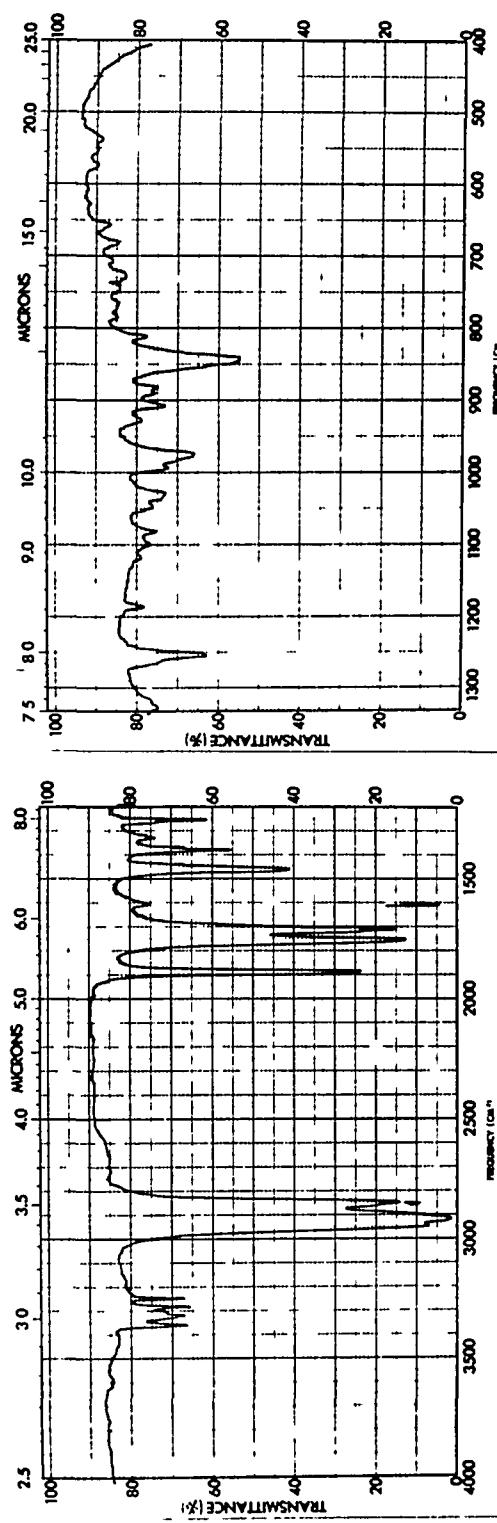
Fig. 1.34 (CO)$_3$Cr[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHCH$_2$CH$_2$NHSi(CH$_3$)$_3$]
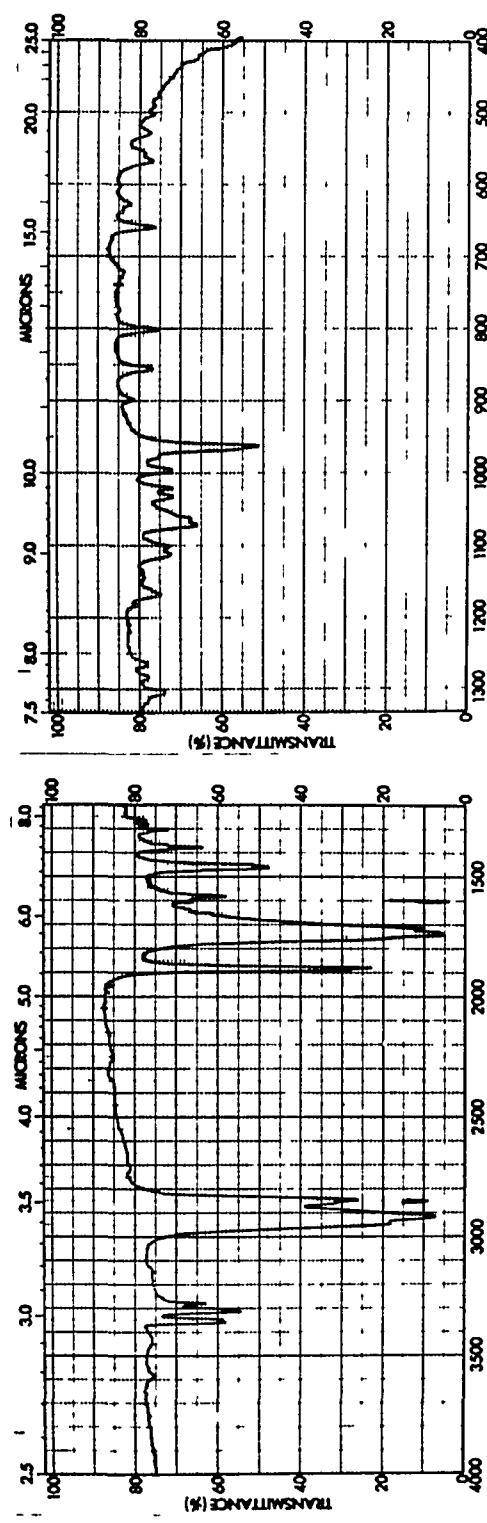
Fig. 1.35 (CO)$_3$Cr[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHCH$_2$CH$_2$NHSi(CH$_3$)$_3$], completely hydrolyzed
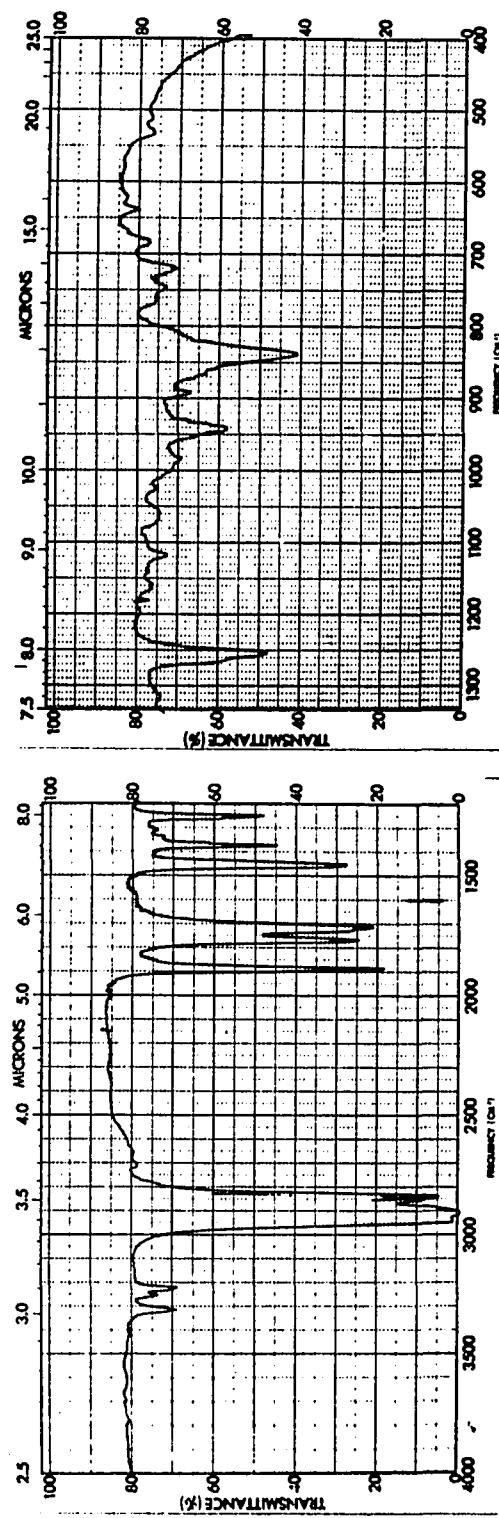
Fig. 1.36   (CO)$_3$Mo[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHCH$_2$CH$_2$NHSi(CH$_3$)$_3$]
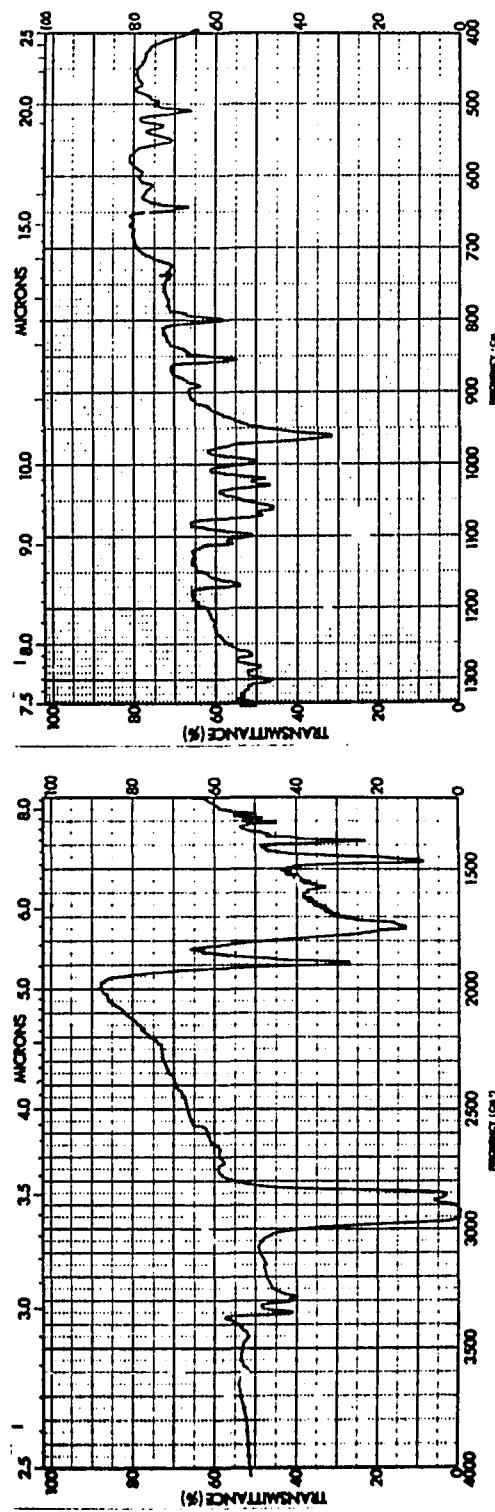
Fig. 1.37   (CO)$_3$Mo[(CH$_3$)$_3$SiNHCH$_2$CH$_2$NHCH$_2$CH$_2$NHSi(CH$_3$)$_3$], completely hydrolyzed

Appendix 2

Nuclear Magnetic Resonance Spectra
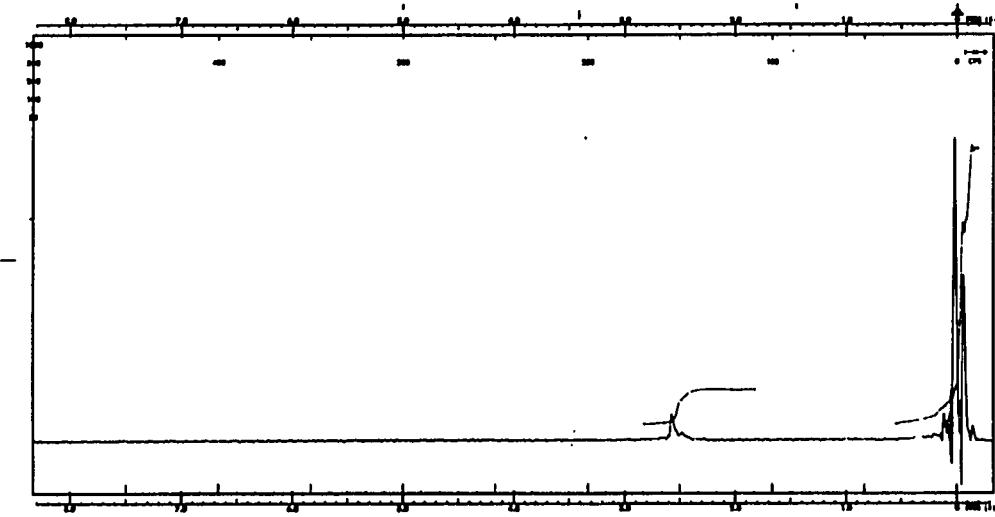
Fig. 2.1 $(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]_2$,
TMS external standard
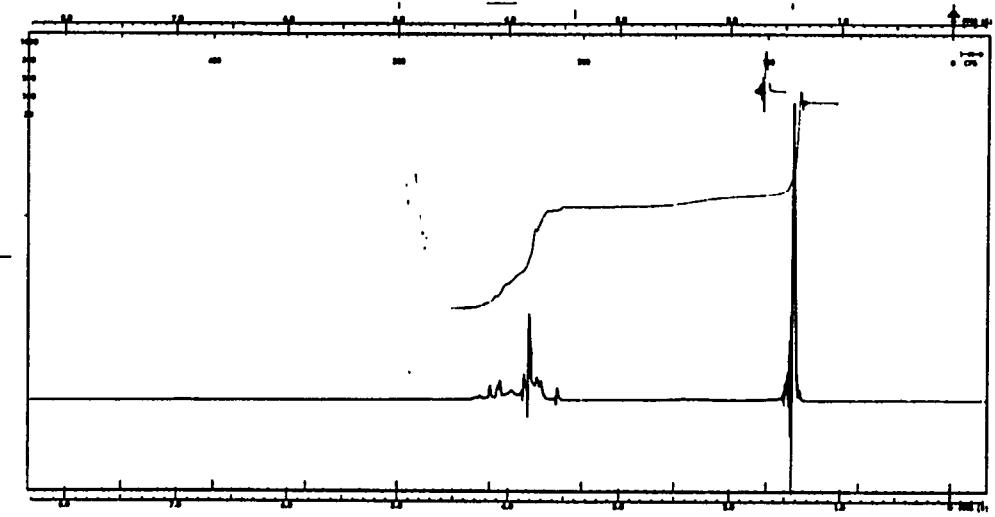
Fig. 2.2 $(CH_3)NHCH_2CH_2N(CH_3)Si(CH_3)_3$, 100 cps
offset, TMS external standard
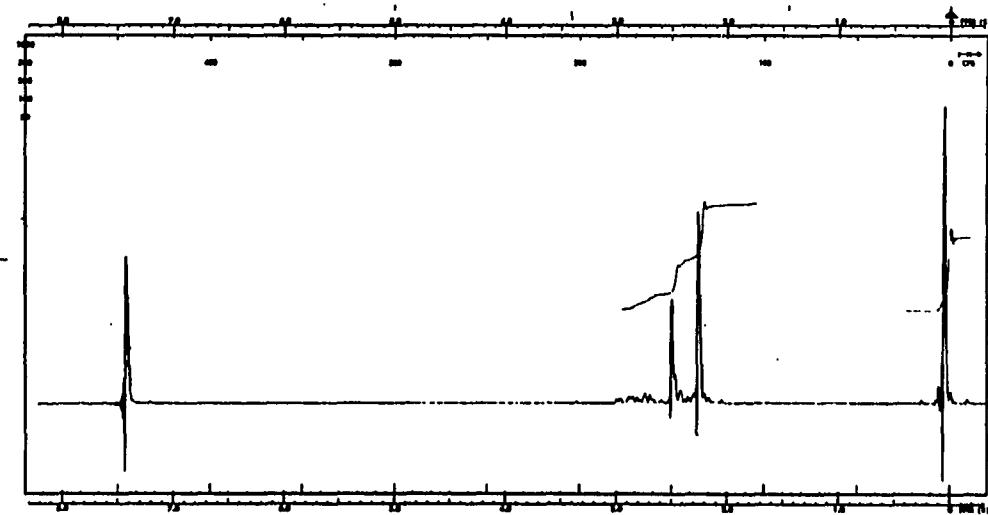
Fig. 2.3 $(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$, in $CHCl_3$,
TMS external standard
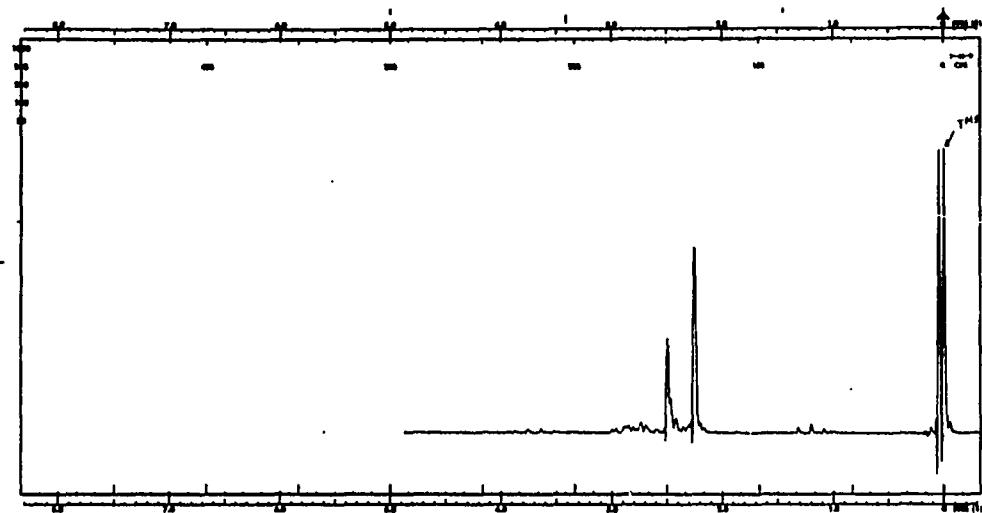
Fig. 2.4 $(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_3$, in $CHCl_3$,
TMS internal standard
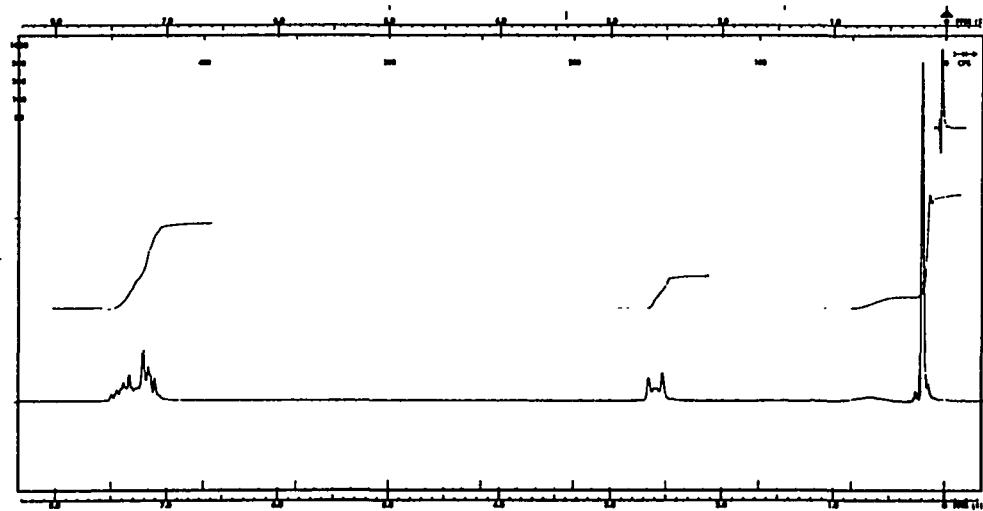
Fig. 2.5 $(C_6H_5)(CH_3)_2SiNHCH_2CH_2NHSi(CH_3)_2(C_6H_5)$, TMS external standard
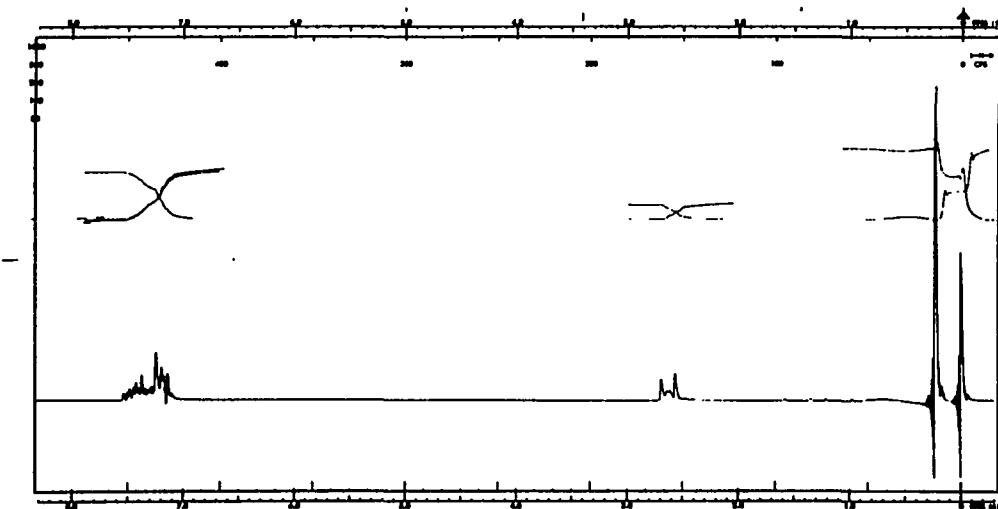
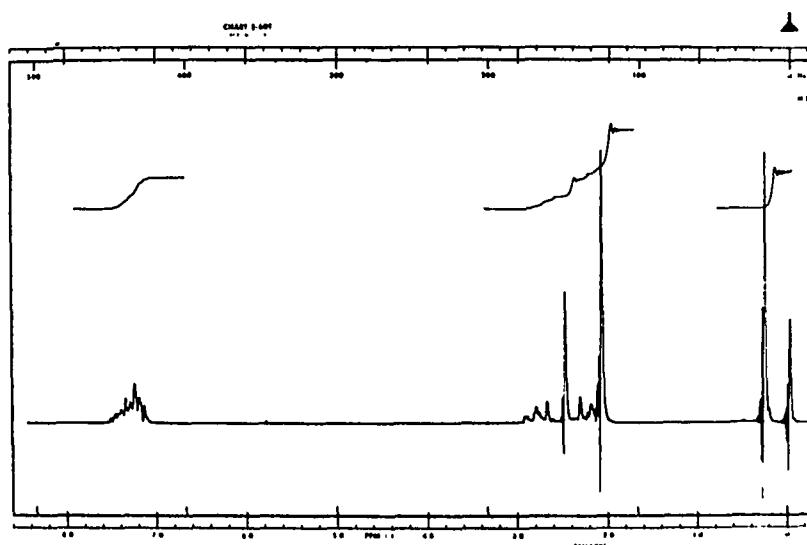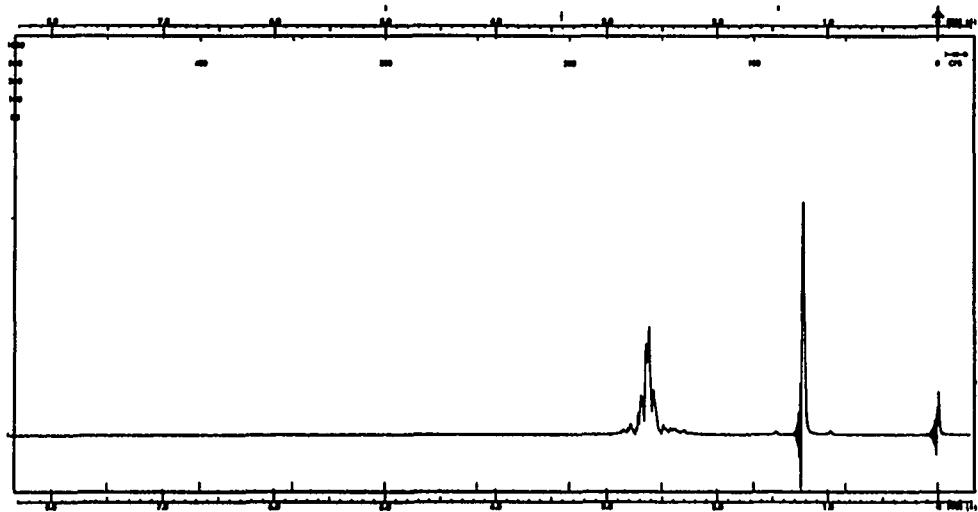Fig. 2.6 $(C_6H_5)(CH_3)_2SiNHCH_2CH_2NHSi(CH_3)_2(C_6H_5)$, TMS internal standard
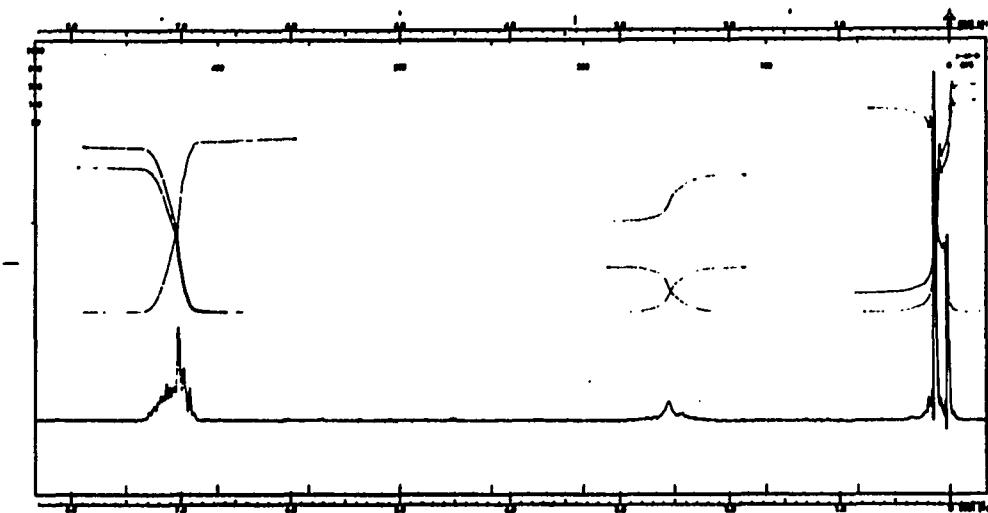
Fig. 2.7 $(C_6H_5)(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2(C_6H_5)]_2$, TMS external standard
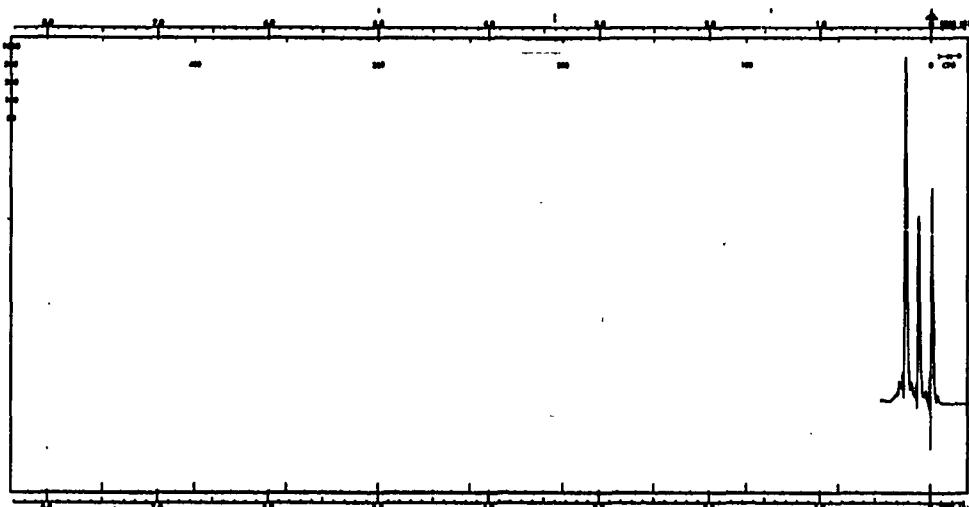
Fig. 2.8 $(C_6H_5)(CH_3)_2SiNHCH_2CH_2N[Si(CH_3)_2(C_6H_5)]_2$, TMS internal standard
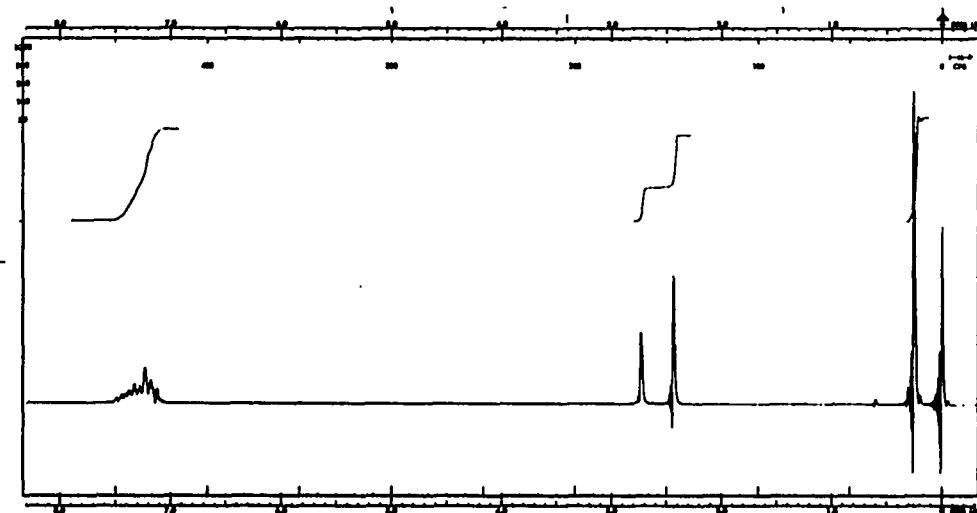
Fig. 2.9 $(C_6H_5)(CH_3)_2SiN(CH_3)CH_2CH_2N(CH_3)Si(CH_3)_2(C_6H_5)$,
TMS internal standard

Fig. 2.10 $(CH_3)_2NCH_2CH_2N(CH_3)Si(CH_3)_2(C_6H_5)$,
TMS internal standard

Fig. 2.11 $H_2NCH_2CH_2NHCH_2CH_2NH_2$, TMS internal
standard
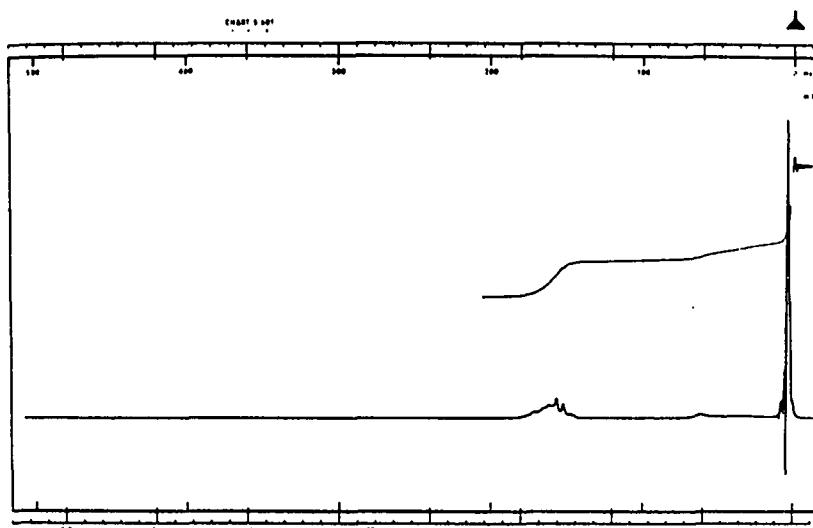
Fig. 2.12 $(CH_3)_3SiNHCH_2CH_2NHCH_2CH_2NHSi(CH_3)_3$,
TMS external standard
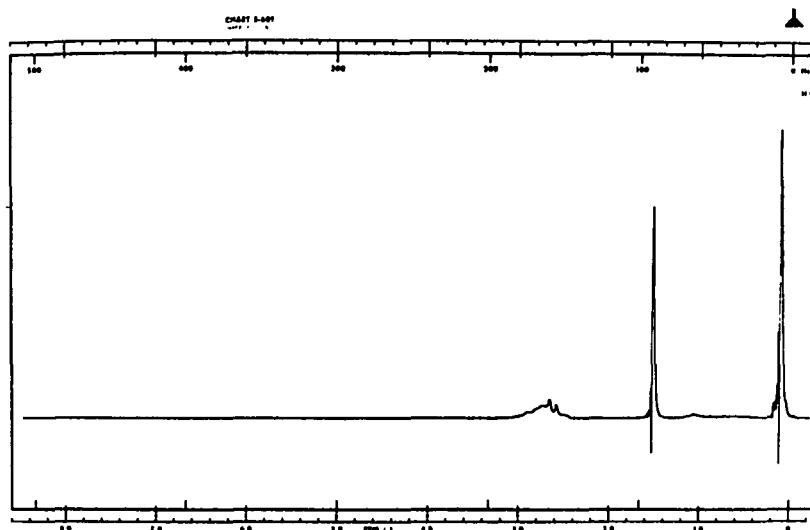
Fig. 2.13 $(CH_3)_3SiNHCH_2CH_2NHCH_2CH_2NHSi(CH_3)_3$,
cyclohexane internal standard
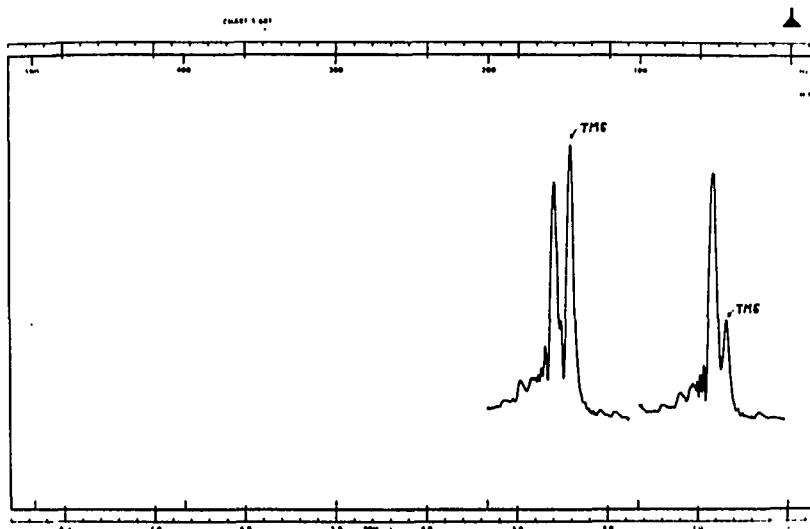
Fig. 2.14 $(CH_3)_3SiNHCH_2CH_2NHCH_2CH_2NHSi(CH_3)_3$,
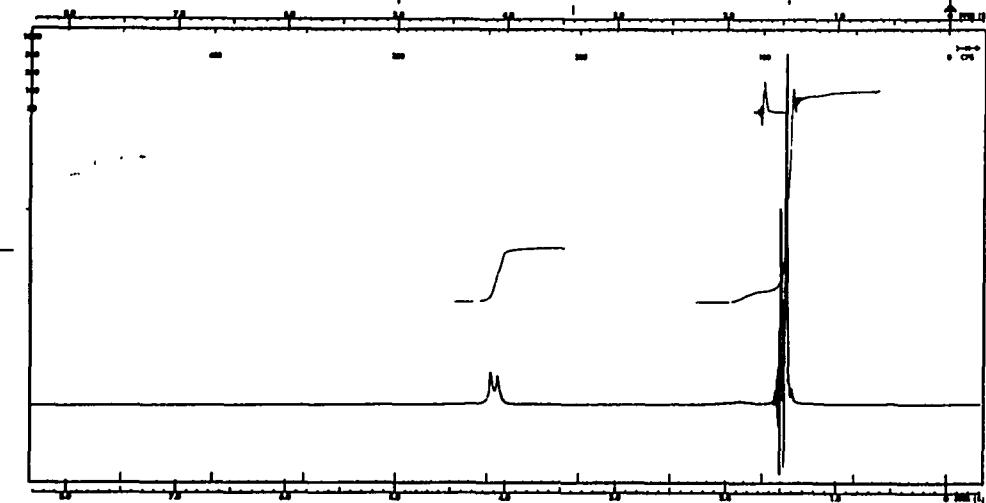sweep width 50 cps, TMS was added
stepwise

Fig. 2.15 $(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]CH_2CH_2NHSi(CH_3)_3$,
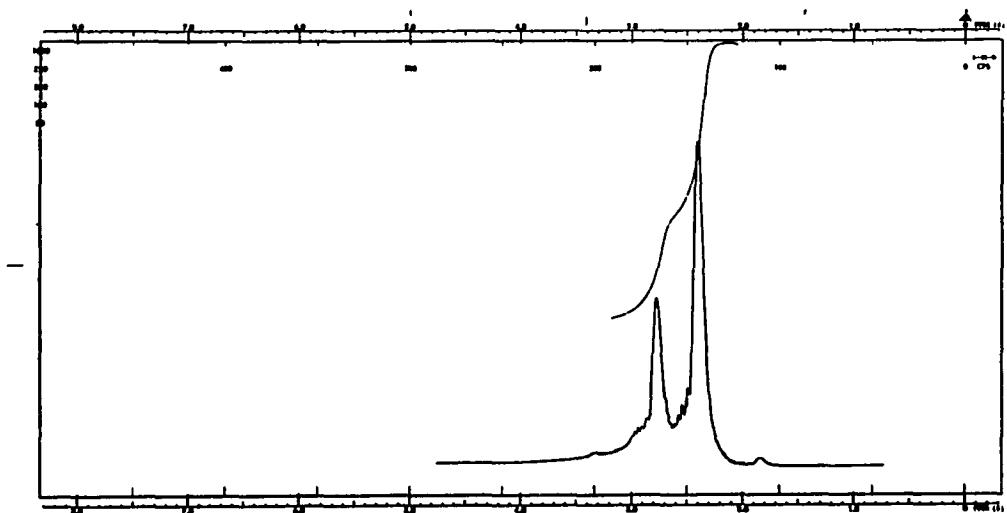100 cps offset, TMS external standard

Fig. 2.16 $(CH_3)_3SiNHCH_2CH_2N[Si(CH_3)_3]CH_2CH_2NHSi(CH_3)_3$,
sweep width 50 cps

SYNTHESIS OF TRANSITION METAL COMPLEXES
WITH ORGANOSILYLAMINES

A SUMMARY

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Twelve complexes of $CuCl_2$, $CoCl_2$ and $FeCl_2$ with bidentate
organosilylamines, and chromium and molybdenum tricarbonyl
compounds with tridentate organosilylamines were prepared.
From the difficulties confronted in the preparation of the
compounds, it was concluded that the lone-pair electrons on
nitrogen atoms in organosilylamines are less available toward
coordination than those in alkylamines. Presumably this is
due to $p\pi$-$d\pi$ partial double bond character in the N-Si bond.
In the stable transition metal complexes, which were obtained
with considerable difficulties, the lone-pair electrons on
the nitrogen atom would be removed from N-Si partial double
bond. This probably is the main reason for the rearrangement
in certain metal complexes, and for the easy hydrolysis and
decomposition of other organosilylamine adducts.

To synthesize the above metal complexes a few new organo-
silylamines were used as well as those that had been previously
prepared by others. In the process of preparation of ligands,
six new organosilyl polyamines were synthesized. Three methods
were used to prepare these compounds: the reaction of triorgano-
chlorosilanes with amines, the reaction of triorganosilyldi-
ethylamine with amines, and the reaction of the lithium deriva-
tives of amine with triorganochlorosilanes.

From the considerations of infrared and NMR spectra, the
structure of N,N"-bis(trimethylsilyl)diethylenetriamine and
N,N',N"-tris(trimethylsilyl)diethylenetriamine were assigned
to the two trimethylsilyl derivatives of diethylenetriamine.