# **21.** *Co-ordination of Trimethylamine by Halides of Silicon, Germanium, and Tin.*

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Trimethylamine reacts with halides of silicon and germanium to give 1 : 1 adducts for which trends in dissociation pressures and heats of formation can be correlated with polar and steric influences. When these are sufficiently favourable, 2 : 1 complexes are also formed. Properties of the 1 : 1 compounds suggest a hexaco-ordinated halogen-bridged structure.

Tetra-*N*-methylethylenediamine forms hexaco-ordinated complexes with silicon and germanium tetrachlorides. Its complex with dichlorodifluorosilane differs from the trimethylamine–chlorofluorosilane adducts in showing no detectable disproportionation.

Trimethylamine and stannic chloride, reacting in the gas phase, give a product of typical composition (amine : halide) 1·35—1·5 : 1. This contains the stable compound $2Me_3N,SnCl_4$ together with a metastable component, probably the 1 : 1 adduct. Residues of composition close to $Me_3N,SnX_4,MeNO_2$ (X = Cl or Br) are obtainable from nitromethane solution.

Trimethylamine interacts with halides of Group IV elements [1-6] to form mono- or di-amine adducts, or occasionally both. However, because individual investigations have sometimes related only to specific halides or to restricted reaction conditions the trends in the co-ordination behaviour of the halides have not been clearly established. The present experiments extend to methyltrifluorosilane and the chlorofluorosilanes and include a closer study of the behaviour of germanium and tin halides (Table 1). Reaction of trimethylamine with excess of silicon or germanium halide invariably gives the mono-amine complex. Only when bond polarity and atomic sizes are particularly favourable is a second amine molecule co-ordinated. The same factors would account for trends in dissociation pressures and heats of sublimation of the mono-amine complexes formed by silicon and germanium halides. Pure mono-amine complexes from stannic chloride and bromide could not be isolated. Nevertheless in nitromethane solutions from which residues of composition $Me_3N,SnX_4,MeNO_2$ were obtainable, heats of reaction of the halides with 1 mol. of amine lay in the same order.

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[1] Burg, " Fluorine Chemistry," Vol. I, Ed. J. H. Simons, Academic Press Inc., New York, 1950, p. 109.

[2] Burg, *J. Amer. Chem. Soc.*, 1954, **76**, 2674.

[3] Wilkins and Grant, *J.*, 1953, 927.

[4] Barnard, Thesis, Cornell, 1954.

[5] Laubengayer and Smith, *J. Amer. Chem. Soc.*, 1954, **76**, 5935.

[6] Böhme and Boll, *Z. anorg. Chem.*, 1957, **292**, 61.

The separate effects of polarity and atomic size are illustrated by the varying silane substituents. Thus a predominant steric influence, previously recognised in the chlorosilane series,[2] explains the increasing dissociation pressures on passing from a trihalogenosilane to a methyltrihalogenosilane derivative. Atomic size and bond polarity co-operate in the chlorofluorosilane series, but the former is probably the more important again since the polarity of the silicon–fluorine bond is much reduced through π-bonding.[7] On the other hand polarity must determine the relative behaviour of silcon tetrachloride and methyltrichlorosilane since the substituents are now of closely similar size.[8] The absence of interaction between monosilane and trimethylamine [2] or between certain substituted silanes and pyridine or *p*-toluidine [9] is consistent with the sensitivity of the co-ordination behaviour of a silicon centre to these influences.

TABLE 1. *Stabilities of mono-amine complexes.*

| Compound | Dissn. pres. (mm.) | Heat of subln. (kcal./mole) | Heat of formn. of ion in soln. (kcal./mole) | Compound | Dissn. pres. (mm.) | Heat of subln. (kcal./mole) |
|---|---|---|---|---|---|---|
| $Me_3N,SiF_4$ (a) ...... | 6·5/0° [3] | 27·4 | — | $Me_3N,SiHF_3$ ...... | 24/0° [1] | 25·1 |
| $Me_3N,SiCl_4$ | 3·87/ −56·2° [2] | 24·0 | — | $Me_3N,SiMeF_3$ (c) ... | 11·7/ −70·5° | 21·2 |
| $Me_3N,GeF_4$ (a) ... | <0·01/0° | 38·4 ± 4 | — | $Me_3N,SiHCl_3$ (c) ... | 18—23/0° [2] | — |
| $Me_3N,GeCl_4$ (a) ... | 6·4/0° | 27·4 | 18·7 ± 0·6 | $Me_3N,SiCl_3F$ (d) ... | *ca.* 260/0° | — |
| " $Me_3N,SnCl_4$ " (a) | v. small/0° | — | 27·6 ± 0·7 (b) | $Me_3N,SiCl_2F_2$ (a, d) | 40—70/0° | — |
| " $Me_3N,SnBr_4$ " (a) | v. small/0° | — | 25·7 ± 0·7 (b) | $Me_3N,SiClF_3$ (a, d) | *ca.* 23/0° | — |

(*a*) A 2 : 1 complex is formed through uptake of further amine. (*b*) The residues from these solutions were of composition $Me_3N,SnX_4,MeNO_2$, but the heats of mixing of the stannic halides and nitromethane are less than 1 kcal./mole. (*c*) No complex is formed by methyltrichlorosilane down to −95°. (*d*) Disproportionation of these complexes made accurate measurement of physical properties impossible.

The wide occurrence of the mono-amine complexes and the regular trends in their dissociation pressures suggest that the crystalline compounds conform to a common structural type within which lattice energies and entropies of formation do not vary greatly. The suggestion of a covalency of five for the central (silicon) atom [10] is questionable. The (almost) complete dissociation in the vapour state of the complexes formed by silicon tetrafluoride,[3] germanium tetrachloride,[4] and dichlorosilane [2] suggests that the crystalline compounds are not unimolecular; no other examples of five-fold co-ordination around silicon and germanium are known. Four-fold co-ordination arising from ionisation [11] or six-fold co-ordination through halogen-bridging [12] are both alternatives which would account for the conspicuous effect on amine co-ordination of the first halogen atom introduced into the silane molecule. Other lines of evidence, though not individually decisive, are most readily interpreted in terms of the latter constitution. Stannic chloride and bromide, for which ionisation should occur readily, are exceptional in not forming pure stable mono-amine adducts. The specific conductivity of molten $Me_3N,SiF_4$ is only $1\cdot4 \times 10^{-3}$ ohm$^{-1}$ cm.$^{-1}$ and for $Me_3N,GeCl_4$ in acetonitrile $\Lambda_{0\cdot0075} = 31$ as compared with $\Lambda_{0\cdot018} \simeq 390$ for the ionic compound $Me_3N,SiH_3I$.[11] In its low volatility the iodosilane adduct differs so sharply from comparable members of the self-consistent series of tetrahalide and chlorosilane complexes as to suggest a different constitution. It is significant that of the silicon–halogen bonds that with iodine is the most readily ionised.[13]

Formation of hexaco-ordinated complexes from silicon and germanium tetrachlorides

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[7] Curran, Witucki, and McCusker, *J. Amer. Chem. Soc.*, 1950, **72**, 4471.

[8] Hückel, " Structural Chemistry of Inorganic Compounds," Vol. I, Elsevier Publishing Co., 1950, p. 170.

[9] Eaborn, *J.*, 1955, 2047.

[10] Stone and Seyferth, *J. Inorg. Nuclear Chem.*, 1956, **2**, 325.

[11] Aylett, Emeléus, and Maddock, *ibid.*, 1955, **1**, 187.

[12] As, *e.g.*, the structure of the ion $AlF_5^{2-}$; Brossett, *Z. anorg. Chem.*, 1937, **235**, 139.

[13] Eaborn, *J.*, 1950, 3077.

occurs with tetra-*N*-methylethylenediamine. That this ligand occupies two co-ordination positions is shown by the low dissociation pressures of its (1 : 1) adducts compared with those from trimethylamine, to which its individual amino-groups would have similar basic and steric properties. The conductivity of the silicon compound (which alone is soluble) in benzene is negligible. The compound * from tetra-*N*-methylethylenediamine and dichlorodifluorosilane differs from the trimethylamine–chlorofluorosilane adducts in showing no evidence from drifting dissociation pressure of spontaneous rearrangement of halogen atoms. This may be significant because a bridged structure, which is possible only in complexes from the unidentate amine, would provide a reaction path of low activation energy.

The steric requirement of trimethylamine lies between those of pyridine and of triethylamine which have (along with tributylamine) been reported by Trost [14] to form 4 : 1 complexes with tetrachlorides. The ready formation of dipyridine adducts by silicon tetrahalides [15,16] is consistent with the low steric demand of this base, but any predominantly steric interpretation of amine behaviour would be incompatible with Trost's results. However, re-examination of the interaction of silicon tetrachloride and triethylamine failed to substantiate the formation of a complex. The very small amount of solid obtained gave an *X*-ray powder photograph identical with that from triethylamine hydrochloride. The formation of tetrapyridinesilicon tetrachloride has also been discounted [16] and the existence of other such silicon tetrachloride adducts must be questioned.

## EXPERIMENTAL

Procedures were based on vacuum technique. Compound formation was examined at temperatures to −78° by determining pressure–composition isotherms and by quantitative synthesis (Table 2). The purity of all reactants was checked tensimetrically. Germanium tetrafluoride from barium fluorogermanate [17] was difficult to purify but vapour pressures of the final sample agreed closely with those given by Fischer and Weidemann.[18]

Calorimetric measurements were made as described by Brown and Horowitz,[19] excepting that, to avoid use of mercury, the solutions were brought together by rupturing a glass membrane across the lower end of the calorimeter partition. Rigorous precautions were taken against access of moisture. Standard solutions of trimethylamine in nitromethane were made by breaking a weighed ampoule beneath the solvent and were checked by titration.

TABLE 2. *Characterisation of addition complexes.*

| Compound | Combining ratio (obs.) | M.p.; thermal stability | Dissn. pres., $\log_{10} p$ |
|---|---|---|---|
| $Me_3N,SiMeF_3$ .............. | 0·99 : 1 | −51·5° [b] | 12·745 − 2319/$T$ |
| $Me_3N,GeF_4$ .................. | 1·03 : 1 | 129—131 (decomp.) [d] | 12·188 − 4315/$T$ [d] |
| $2Me_3N,GeF_4$ .............. | 2·00 : 1 [a] | Decomp. at 120° | — |
| $Me_3N,GeCl_4$ .............. | 0·98 : 1 | 75—76° | 11·764 − 2995/$T$ |
| $2Me_3N,GeCl_4$ .............. | 2·01 : 1 | Not formed at −60° [c] | — |
| $2Me_3N,SnCl_4$ .............. | 1·99 : 1 | 174—175° (decomp.) | — |

(*a*) Deduced from isotherm at 0°. (*b*) The dissociation pressure reaches twice the vapour pressure of trimethylamine at −53°. (*c*) Sublimes incongruently at −78°. (*d*) Near 100° there is slight formation of uncondensable gas. Dissociation pressures were: 64°, 0·25 mm.; 74·1°, 0·60; 84·3°, 1·25; 94·0°, 2·74; 96·5°, 3·07.

*Behaviour of Chlorofluorosilanes towards Trimethylamine.*—Mono-amine adducts were obtained in each case by passing the mixed vapours through a trap at −78° irrespective of the component in excess,[3] but on allowing $Me_3N,SiCl_2F_2$ and $Me_3N,SiClF_3$ to remain in contact with

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* The desirability of examining this compound was suggested by a Referee.

[14] Trost, *Canad. J. Chem.*, 1951, **29**, 1075; 1952, **30**, 835.

[15] Schwarz and Wannagat, *Z. anorg. Chem.*, 1954, **277**, 73.

[16] Wannagat and Vielberg, *ibid.*, 1957, **291**, 310.

[17] Dennis and Laubengayer, *Z. phys. Chem.*, 1927, **130**, 520.

[18] Fischer and Weidemann, *Z. anorg. Chem.*, 1933, **213**, 106.

[19] Brown and Horowitz, *J. Amer. Chem. Soc.*, 1955, **77**, 1730.

excess of amine at this temperature conversion into the di-amine complexes occurred during 8—24 hr. Table 3 gives typical compositions. Isotherms having sharp breaks could not be obtained for trichloroflurosilane and dichlorodifluorosilane owing to disproportionation, which likewise caused the divergence of the compositions of the dichlorodifluorosilane adducts from the stoicheiometric ratios.

TABLE 3.

| Silane | $SiCl_3F$ | $SiCl_2F_2$ | $SiClF_3$ |
|---|---|---|---|
| Amine : silane in solid condensed from gaseous reactants at −78° | 1·02 | 0·95—1·05 | 0·995 |
| Amine : silane after standing with excess of liquid amine at −78° | 1·02 | 1·92 | 1·96 |

At 0° the initial dissociation pressure of $Me_3N,SiCl_3F$ fell and that of $Me_3N,SiCl_2F_2$ rose too quickly to permit reproducible measurements. Disproportionation of the former was almost quantitative after 4 months at ordinary temperature. From 39·5 ml. of trichlorofluorosilane and 19·7 ml. of amine in a sealed tube there were recovered 28·4 ml. of silicon tetrachloride (calc., 29·6 ml.) and crystalline $2Me_3N,SiF_4$ (vap. pres. 6 mm./0°) which released 8·3 ml. of amine (calc., 9·85 ml.) upon distillation through a trap at −78°.[3]

*Stannic Chloride and Trimethylamine.*—After 171·6 ml. of amine and 41·0 ml. of stannic chloride were allowed to react for 24 hr. at −10°, 90·8 ml. of amine were recovered, corresponding to a residue of composition 1·97 : 1. Absorption of amine occurred rapidly up to the equimolecular ratio and thereafter more slowly, indicating intermediate formation of a phase of this composition. The *X*-ray powder photograph was identical with that from a product of composition 1·96 : 1 obtained from excess of stannic chloride at room temperature, θ values for Cu-$K_\alpha$ radiation being: 6·6°(s), 7·0°(s), 7·3°(m), 8·0°(s), 8·3°(s), 9·1°(w), 10·9°(m), 11·6°(w), 12·4°(m), 13·4°(m), 14·3°(w), 14·7°(w), 16·4°(m), 16·9°(m), 18·0°(m), 18·4°(m), 18·8°(w), 19·4°(m), 19·9°(m), 21·2°(s), 22·3°(m), 22·8°(m), 23·9°(s), 24·9°(m).

Contact with either liquid component was necessary to promote formation of the stable 2 : 1 phase, presumably because the initial crystalline phase is metastable and disproportionates in contact with solvent. Contrary to Laubengayer and Smith [5] who report the 2 : 1 compound from gaseous reactants, combination of the vapours carried in nitrogen repeatedly gave products of typical composition 1·35—1·5 : 1 irrespective of the component in excess. These samples gave the stronger *X*-ray powder lines of the 2 : 1 phase together with lines, probably corresponding to a 1 : 1 phase, at 6·2°(s), 10·3°(m), 12·1°(m), 14·6°(m), 15·1°(w), 19·2°(m).

When 145·4 ml. of stannic chloride and 146·3 ml. of amine were distilled into nitromethane and the volatile material pumped off at room temperature, 4·0 ml. of halide were removed with the solvent so that the combining ratio amine : halide was 1·035 : 1. Traces of solvent free from halide continued to distil during 16 hr. leaving 2·34 g. of white solid (Found: C, 12·4; H, 3·4; N, 6·6; Cl, 38·2. Calc. for $Me_3N,SnCl_4,MeNO_2$: C, 12·6; H, 3·15; N, 7·4; Cl, 37·3. Calc. for $Me_3N,SnCl_4$: C, 11·3; H, 2·8; N, 4·4; Cl, 44·4%). The *X*-ray powder photograph was distinctive but included weak lines corresponding to several of the stronger lines of $2Me_3N,SnCl_4$. It is concluded that 3—4% of this phase was present.

Stannic bromide (1·008 g.) and trimethylamine in equimolecular proportion in nitromethane gave a *residue* (1·271 g.) (Found: C, 9·2; H, 2·4; N, 4·4; Br, 57·3. $Me_3N,SnBr_4,MeNO_2$ requires C, 8·6; H, 2·2; N, 5·0; Br, 57·2%).

*Co-ordination of Tetra*-N-*methylethylenediamine.*—Addition of amine [20] (b. p. 121—122°) to silicon tetrachloride or germanium tetrachloride at room temperature caused a sharp fall in pressure at the equimolecular ratio. No other breaks in the isotherms were detected. The adducts were also prepared by using light petroleum (low-boiling) as diluent. Compositions of samples of silicon derivative always corresponded to an amine : halide ratio of 1·03—1·06 : 1, probably because incongruent sublimation led to preferential loss of silicon tetrachloride under vacuum. The *germanium derivative* had C, 22·5; H, 4·55; N, 8·5; Cl, 42·2 ($C_6H_{16}N_2GeCl_4$ requires C, 21·8; H, 4·9; N, 8·5; Cl, 42·9%). Dissociation pressures of the former are 2 mm. at 0°, 6 mm. at 18°, and of the latter $<$0·1 mm. at 0°. The silicon derivative immediately hydrolyses in air. Both are insoluble in acetonitrile, dimethylformamide, nitromethane, and triethylamine.

During 14 days the dissociation pressure ($<$0·1 mm. at 20°) of the dichlorodifluorosilane adduct (combining ratio 1·01 : 1) did not increase as would have been expected if rearrangement to yield the silicon tetrachloride adduct had occurred. However, treatment with hydrogen

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[20] Hanhart and Ingold, *J.*, 1927, 997.

chloride seemingly caused rearrangement because the silane which was slowly released contained a full range of disproportionation products, as judged from rough examination of vapour pressures of fractions.

*Triethylamine and Silicon Tetrachloride.*—In a typical experiment made in the vacuum system 5·5 g. of chloride and 23·1 g. of amine (redistilled and dried over sodium) gave 0·31 g. of triethylamine hydrochloride. This was identified from its *X*-ray powder photograph since $4Et_3N,SiCl_4$ would be close in composition. It was not possible to eliminate formation of this product through repurification of the reactants.

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