Trigermylamine

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SINCE the preparation of trisilylamine,[1] a number of unsuccessful attempts have been made to prepare the analogous germyl compound.[2] The heavy atoms in trisilylamine are coplanar;[3] this is said to indicate the existence of π-bonding between the nitrogen lone-pair electrons and the silicon *d*-orbitals. The possibility of similar π-bonding to germanium has increased the interest in trigermylamine, which has now been prepared (*ca.* 40%) by the gas-phase reaction of germyl chloride and ammonia, followed by immediate removal of the

$$4\ NH_3 + 3\ GeH_3Cl \rightarrow 3\ NH_4Cl + (GeH_3)_3N$$

product from the reaction vessel. If the gases are not mixed in the correct proportions, the trigermylamine produced is contaminated with one of the starting materials, but otherwise it is pure. The compound is also formed in the exchange reaction of germyl fluoride and trisilylamine, but it has not been isolated from the products.

The new compound was identified by its molecular weight, analysis (cleavage with HCl) and ^1H n.m.r. and i.r. spectroscopy: n.m.r. (100 MHz, Me_4Si, room temp.) τ 5·09s. Exchange with $(SiH_3)_3{}^{15}N$ gave $J(^{15}NGeH)$ 5 Hz.

In the i.r. spectrum of solid trigermylamine at −196° (Table), the band at 639 cm.$^{-1}$ is rather stronger than in the spectra of other similar molecules.[4] It is possible that the Ge_3N asymmetric stretch is coincident with one of the GeH_3 rocking modes. The presence of a band at 367 cm.$^{-1}$ is of great interest, since it is in the region where the Ge_3N symmetric stretching mode is expected. As this mode is i.r.-inactive in molecules with a planar heavy-atom skeleton, it seems that trigermylamine, unlike trisilylamine, is pyramidal. However, this does not necessarily rule out the possibility of $(p \rightarrow d)\ \pi$-bonding.[5] The absence of this band in the i.r. spectra of similar molecules has caused confusion in the past,[6] but its presence invariably implies non-planarity.

Trigermylamine is very unstable, as evidenced by the rapid thermal decomposition of the solid (the gas phase decomposes less rapidly) to give ammonia and GeH_2 polymer with a little monogermane. It is rapidly hydrolysed by water to give digermoxane.

Infrared spectrum of solid trigermylamine

Frequency, cm.$^{-1}$	Tentative assignment	
2074s, sh 2047s	Ge–H stretch	
871mw 851m 780vs	GeH_3 deformation	
639ms	Ge_3N asymm. stretch	GeH_3 rocking
581w, br		GeH_3 rocking
367m, v br	Ge_3N symm. stretch	

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