The Crystal Structures of Chlorodimethyl(dimethylamino)silane and Dimethyl-bis-(dimethylamino)silane

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Single crystals of chlorodimethyl(dimethylamino)silane, Me₂NSiMe₂Cl, and dimethyl-bis-(dimethylamino)silane, (Me₂N)₂SiMe₂, have been grown in situ from the melt at low temperatures and their structures determined by X-ray diffraction. Important structural parameters (Å/°):

Me₂NSiMe₂Cl (C₂/m) Si-N 1.686(2), Si-C 1.851(1), Si-Cl 2.109(1), N-Si-Cl 111.7(1), C-Si-Cl 105.1(1), C-N-C 112.8(2), Si-N-C 123.4(1); (Me₂N)₂SiMe₂ (P2₁/c) Si-N(1) 1.725(1), Si-C(1) 1.868(1), N(1)-Si-N(2) 105.7(1), C(3)-N(1)-C(4) 111.6(1), Si-N(1)-C(3) 122.4(1), Si-N(1)-C(4) 120.0(1).

Key words: Silicon, Crystal Structure, Hypercoordination

The finding of a planar Si₃N skeleton in trisilylamine, (H₃Si)₃N, by Hedberg in 1955 [1] was followed by numerous investigations on the structure of Si/N compounds. In the course of these studies it became evident, that even a single silicon substituent at nitrogen is capable of flattening the nitrogen coordination sphere [2]. Only in a minority of cases, a significant deviation from a planar surrounding of the nitrogen substituents was found, including Me₂NSiH₃ [3], Me₃HNSiMe₂ [4] and Ph₃SiNH₂ [5].

The first examples of clearly pyramidal nitrogen atoms with silicon substituents were found in the hydroxylamine derivatives (p-TolSiH₂)₂NOMe [6], (H₃Si)₃NOMe [7] and (H₃Si)MeNOMe [8], which have deviations of the N-O vector from the NSi₂ and NSiC planes of 38.7(1), 31.3(2) (solid) and 33.2(25)° (gaseous), respectively.

Recently we have reported the crystal structure of Me₂NSiCl₃ [9], but there are still structurally unexplored silylamines bearing only the simple substituents Me₂N, H, Cl and Me. Here we report the structures of two of them: Me₂NSiMe₂Cl and (Me₂N)₂SiMe₂.

Dimethyl-bis-(dimethylamino)silane, (Me₂N)₂SiMe₂, was prepared from dimethylamine and dichlorodimethylsilane, and chlorodimethyl(dimethylamino)silane, Me₂NSiMe₂Cl, was obtained from the latter by equilibration with dichlorodimethylsilane. Both syntheses are established literature procedures [10]. The distilled compounds, sealed in thin-walled glass capillaries, were used for in situ crystallisation experiments, which afforded single crystals suitable for single crystal X-ray diffraction.

Chlorodimethyl(dimethylamino)silane, Me₂NSiMe₂Cl, crystallises in the monoclinic space group C₂/m. The molecular structure is shown in Fig. 1, selected bond lengths and angles (Å/°): Si-N 1.686(2), Si-C 1.851(1), Si-Cl 2.109(1), N-Si-Cl 111.7(1), C-Si-Cl 105.1(1), C-Si-C 112.8(2), Si-N-C 123.4(1). The Si-N bond length is 1.686(2) Å which is longer than in Me₂NSiCl₃ (1.665(3) Å) [9], but shorter than in Me₂NSiMe₃ (1.719(1) Å) [11]. This demonstrates its dependence on the number of electronegative substituents at the silicon atom. The Si-Cl and Si-C distances are of standard lengths. The coordination geometry about the silicon atom deviates slightly from a tetrahedral surrounding. Only the angles Cl-Si-C at 105.1(1)° are smaller than the tetra-
Dimethylbis(dimethylamino)silane, (Me₂N)₂SiMe₂, crystallises in the monoclinic space group P2₁/c. There are no intermolecular contacts of exceptional shortness. The molecular structure is shown in Fig. 3, selected bond lengths and angles are listed in the figure caption. The molecules of (Me₂N)₂SiMe₂ have approximate C₂ symmetry. The coordination sphere of the nitrogen atoms is not completely but almost planar with the sum of angles about these atoms being 354.0 and 355.8°. As in Me₂NSiMe₂Cl and many other dialkylaminosilanes, the Si-N-C angles [111.6(1) and 111.9(1)°] are larger than the CNC angles [111.6(1) and 111.9(1)°]. The Si-N bond lengths are 1.719(1) and 1.725(1) Å and thus longer than in Me₂NSiMe₂Cl, which bears a Cl substituent at the silicon atom. The Si-C distances [1.868(1) and 1.869(1) Å] are slightly longer than in Me₂NSiMe₂Cl at 1.851(1) Å. The silicon atom has a distorted tetrahedral coordination geometry with the smallest angle being N-Si-N at 105.7(1)°, a C-Si-C angle of 108.4(1)° and the N-Si-C angles falling over a range between 107.4(1) and 113.9(1)°.

Experimental Section

Crystal structure determination of Me₂NSiMe₂Cl and (Me₂N)₂SiMe₂

Single crystals of Me₂NSiMe₂Cl and (Me₂N)₂SiMe₂ were grown in situ on the diffractometer by slowly cooling the melt in a sealed capillary below the melting point after generation of a suitable seed crystal. Data collection was undertaken with a Nonius DIP2020 diffractometer. Crystal data for Me₂NSiMe₂Cl, C₄H₁₂NSiCl, Mr = 137.69, crystal system monoclinic, space group C₂/m, Z = 4, a = 11.8892(3), b = 10.6304(3), c = 6.3063(3) Å, β = 97.3629(17)°, V = 790.46(5) Å³ at 143(2) K, μ = 0.537 mm⁻¹, 2θ(max) = 63.46°, 16340 scattering intensities collected of which 1309 were unique (Rint = 0.030), 61 parameters, R₁ = 0.0449 for 1263 reflections with Fo > 4σ(Fo) and wR₂ = 0.1297 for all 1309 data. Crystal data for (Me₂N)₂SiMe₂, C₆H₁₈N₂Si, Mr = 146.31, crystal system monoclinic, space group P2₁/c, Z = 4, a = 9.5583(2), b = 7.7879(1), c = 13.4111(3) Å, β = 103.4749(8)°, V = 970.83(3) Å³ at 138(2) K, μ = 0.177 mm⁻¹, 2θ(max) = 63.96°, 44227 scattering intensities collected of which 3209 were unique (Rint = 0.037), 155 parameters, R₁ = 0.0445 for 2988 reflections with Fo > 4σ(Fo) and wR₂ = 0.1285 for all 3209 data. Structure solutions and refinements were undertaken with the program SHELXTL 5.01 [12]. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publica-
tion no. CCDC-206824 and CCDC-206825 (Me2NSiMe2Cl)
((Me2N)2SiMe2). Copies of the data can be obtained free of
charge on application to CCDC, 12 Union Road, Cambridge
CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk).

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P. P. Power, Angew. Chem. 105, 459 (1993); Angew.
[6] N. W. Mitzel, K. Angermaier, H. Schmidbaur,
Organometallics 13, 1762 (1994).
Robertson, D. E. Smitj, A. J. Welch, J. Chem. Soc. Dal-
ton Trans. 91 (1986).