β-Donor Interactions as Secondary Bonds in Dichlorobis(dimethylaminoxy)silane and -germane

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The compounds $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ were prepared by the reaction of the appropriate tetrachlorides with *N*,*N*-dimethylhydroxylamine in the presence of 2,6-lutidine as an auxiliary base. The compounds were obtained as crystalline solids and characterised by elemental analysis, IR and NMR spectroscopy (nuclei ^1H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si). Their molecular structures were determined by single-crystal X-ray diffraction. The compounds are isostructural and both show the presence of weak secondary bonds between the nitrogen and silicon centres (β-donor bonds), as is indicated by the small angles SiON [102.8(1) and 103.7(1)°] and GeON [102.0(1)°], and the distances Si···N (2.438 and 2.450 Å) and Ge···N (2.519 and 2.520 Å). The conformation is anti-gauche in both compounds (one O–Si–O–N torsion angle being about 180°, the other 60°), but the strength of the β-donor interaction is not significantly affected by the different *anti*-substituents at the nitrogen centres, although such behaviour was expected from earlier studies carried out on $ClH_2SiONMe_2$. The β-donor interactions are also weaker than those found in $ClH_2SiONMe_2$.

β-Donor interactions, i.e. donor-acceptor interactions between atoms in a geminal position to one another, are now well established in p-block chemistry. In a number of reports we have shown them to contribute significantly to the molecular structures of compounds containing Si−O−N[1] and Si−N−N units[2]. Examples are the (4 + 4)-coordinate $Si(ONMe_2)_4$,[3] and the (4 + 2)-coordinate $H_2Si(ONMe_2)_2$, which has an Si−O−N angle of only 95.2°,[4] and some silyl oximes.[5] The strongest β-donor bond found so far in Si−O−N systems occurs in $ClH_2SiONMe_2$, which has a Si−O−N angle of only 79.7° in the crystal, corresponding to a Si···N distance of 2.028 Å, which comes close to the sum of covalent radii of silicon and nitrogen atoms (1.87 Å).[6] According to a gas-phase structural analysis of $ClH_2SiONMe_2$ the vapour consists of two conformers. The *anti*-conformer (torsion angle Cl−Si−O−N 180°) has a substantially stronger β-donor interaction (smaller Si−O−N angle 87.1°) than the *gauche*-conformer (104.7°). It is obvious that the *anti*-positioned silicon substituent predominantly determines the strength of the β-donor interaction. In the *gauche* conformation, a H atom is in an *anti* position relative to the nitrogen donor centre, as is the case in $H_3SiONMe_2$, and the *gauche*-conformers of $ClH_2SiONMe_2$ and $H_3SiONMe_2$ have very similar Si−O−N angles. The β-donor interaction cannot be described as a simple electrostatic attraction between unevenly charged geminal centres, but negative hyperconjugation between the lone pair of electrons at the donor centre and empty σ^*-orbitals at the acceptor centre can be used as a rationale.[6] Another possible explanation involves intramolecular dipole interactions, but these models have not been explored in detail.

Other examples for β-donor interactions are found in the crystal structure of $Me_2AlONMe_2$[7] and the aminomethyl lithium compound Me_2NCH_2Li, as was shown very recently by Steinborn et al.[8] The interest in aminoxysilanes also arises from their use as cold curing catalysts in silicone polymer synthesis,[9] and the catalytic activity of hydroxylamines in the alcoholysis of Si−H functions.[10]

Our current aim was the synthesis of the compound $Cl_2Si(ONMe_2)_2$ and its germanium analogue, in order to answer the following questions: Does the strength of a β-donor interaction increase with an increasing number of electronegative substituents at the acceptor atom, or will effects like “back-bonding” reduce the acceptor ability? Which of the *anti*-substituents is preferred, O or Cl? Is the structure of $Cl_2Si(ONMe_2)_2$ more comparable to that of $H_2Si(ONMe_2)_2$ (∠SiON 95.2°) or to that of $ClH_2SiONMe_2$ (∠SiON 79.7°), or comparable to neither? The following study will show that finding the answers to these questions is actually more difficult than expected and that the nature of β-donor interactions is not yet sufficiently understood.

Results and Discussion

Synthesis: The compounds $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ have been prepared by the reaction of *N*,*N*-dimethylhydroxylamine with the corresponding tetrachloride of silicon and germanium in the presence of the auxiliary base 2,6-lutidine with pentane as a solvent. The formation of these compounds seems to be favoured under these conditions, as attempts to prepare the triply substituted compounds $ClSi(ONMe_2)_3$ and $ClGe(ONMe_2)_3$ also

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resulted in the formation of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$, despite the application of an excess of *N*,*N*-dimethylhydroxylamine. A suitable temp. to perform the reactions is −60°C. The overall yields achieved in this way are typically >60%.

$$2\ Me_2NOH + SiCl_4 + 2\ C_7H_9N \rightarrow Cl_2Si(ONMe_2)_2 + 2\ C_7H_9N\cdot HCl$$

$$2\ Me_2NOH + GeCl_4 + 2\ C_7H_9N \rightarrow Cl_2Ge(ONMe_2)_2 + 2\ C_7H_9N\cdot HCl$$

Both compounds are crystalline solids soluble in organic solvents. They are air-sensitive, and the solutions fume in moist air. The compounds can be stored at ambient temp. under an inert atmosphere.

Spectroscopy: The identity of the compounds $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ was proved by gas-phase IR spectroscopy, by NMR spectroscopy of the nuclei ^1H, ^{13}C, ^{15}N, ^{17}O, and ^{29}Si and by mass spectrometry.

The solution-NMR spectra recorded at 21°C do not show any preference for certain conformations. Both Me_2NO groups are magnetically equivalent. The proton and proton-decoupled carbon spectra show one singlet each. The occurrence of a quartet of quartets in the proton-coupled carbon spectra verify the presence of a Me_2N group.

The ^{15}N-NMR chemical shifts of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ are $\delta = -228.5$ and $\delta = -231.8$, which is a shift of about 20 ppm to higher frequencies as compared to the shifts of $ClH_2SiONMe_2$ ($\delta = -249.5$) and the compounds $H_{4-n}Si(ONMe_2)_n$ ($n = 1-4$, $\delta = -248.1$ to -249.2. The ^{17}O-chemical shift of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ are $\delta = 188$ and $\delta = 193$. This corresponds to a shift to higher frequencies relative to the shifts of the compounds $H_{4-n}Si(ONMe_2)_n$ ($n = 1-4$, $\delta = 135-141$) and ClH_2SiOMe_2 ($\delta = 137$). The NMR data do not indicate the existence of inter- or intramolecular donor-acceptor interactions, but rather show such interactions to be efficiently broken by the solvent (C_6D_6), which has also been observed in comparable compounds.

Crystal Structure Determination of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$: Single crystals of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ were grown by crystallisation from pentane and ether, respectively. Both compounds crystallise in the monoclinic space group $P2_1/c$ with $Z = 4$ formula units in the unit cell. They are isostructural, with only slightly different cell parameters.

In the crystals of both compounds the molecules are present as monomers. Intermolecular contacts, which would normally be regarded as significant, are absent.

Both compounds adopt the same conformation, which is *anti-gauche*, i.e. one torsion angle OSiON is close to 180° [$Cl_2Si(ONMe_2)_2$: −177.5(1), $Cl_2Ge(ONMe_2)_2$: −178.1(1)°], whereas the other is close to 60° [$Cl_2Si(ONMe_2)_2$: −64.8(1), $Cl_2Ge(ONMe_2)_2$: −64.5(1)°]. The nitrogen atoms of *gauche*-substituents have chlorine atoms in an *anti*-position in almost perfect orientation [torsion Cl(Si/Ge)ON $Cl_2Si(ONMe_2)_2$: 176.1(1), $Cl_2Ge(ONMe_2)_2$: 176.4(1)°].

Figure 1. Molecular structure of $Cl_2Si(ONMe_2)_2$. The non-hydrogen atoms are shown as thermal ellipsoids at the 50% probability level, hydrogen atoms are drawn as circles of arbitrary size

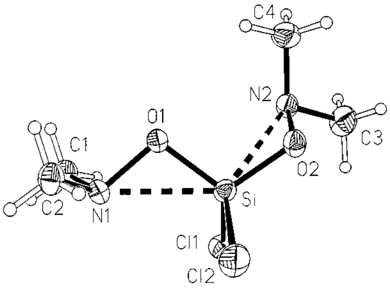

Figure 2. Molecular structure of $Cl_2Ge(ONMe_2)_2$. The non-hydrogen atoms are shown as thermal ellipsoids at the 50% probability level, hydrogen atoms are drawn as circles of arbitrary size

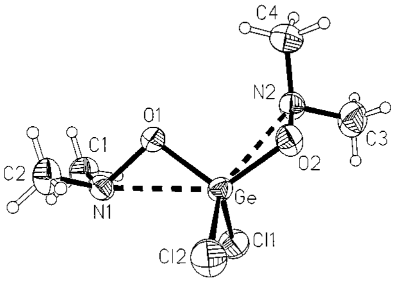

Table 1. Selected bond lengths and angles of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$

Parameter	$Cl_2Si(ONMe_2)_2$	$Cl_2Ge(ONMe_2)_2$
E−O(1)/E−O(2)	1.628(1)/1.626(1)	1.745(2)/1.753(2)
E−Cl(1)/E−Cl(2)	2.028(1)/2.033(1)	2.112(1)/2.118(1)
O(1)−N(1)/O(2)−N(2)	1.489(2)/1.486(2)	1.491(2)/1.482(3)
N(1)−C(1), N(1)−C(2)	1.461(2)/1.459(2)	1.463(3)/1.459(3)
N(2)−C(3), N(2)−C(4)	1.454(2)/1.453(3)	1.456(4)/1.455(4)
O(1)−E−O(2)	109.6(1)	109.5(1)
O(1)−E−Cl(1)/ O(1)−E−Cl(2)	112.2(1)/111.5(1)	111.5(1)/111.0(1)
O(2)−E−Cl(1)/ O(2)−E−Cl(2)	111.4(1)/103.7(1)	111.3(1)/104.6(1)
E−O(1)−N(1)/ E−O(2)−N(2)	102.8(1)/103.7(1)	102.0(1)/102.0(1)
O(1)−N(1)−C(1)/ O(1)−N(1)−C(2)	104.7(1)/105.0(1)	104.6(2)/105.2(2)
O(2)−N(2)−C(3)/ O(2)−N(2)−C(4)	105.3(1)/105.3(1)	105.2(2)/104.9(2)

Despite the different *anti*-substituents, the Si−O−N and Ge−O−N angles on either side of the molecule are almost the same. The angles GeON in $Cl_2Ge(ONMe_2)_2$ are only slightly smaller than the angles SiON in $Cl_2Si(ONMe_2)_2$. This is surprising with reference to the results of crystal structures of $ClH_2SiONMe_2$ (∠SiON 79.7°) and $H_2Si(ONMe_2)_2$ (∠SiON 95.2°): First of all the angles in $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ are much larger than in the compounds referred to above. Secondly, the influence of the *anti*-substituent on the magnitude of the SiON angle seems to be negligible in this case. At this stage it might be concluded that either the increased steric requirements at the acceptor atom, or its reduced acceptor character by backbonding from the lone pairs at the chlorine and oxygen substituents, is the reason for the weaker β-donor interactions in $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$. In fact the SiON angles in these compounds are similar to that of the parent compound $H_3SiONMe_2$, with no further electronegative substituents at the silicon atom apart from that of the single aminoxy substituent.

The bond lengths of both parts of the molecules are very similar. According to the negative hyperconjugation model for the description of β-donor interactions, one would have to expect the E−O and E−Cl bonds in an *anti*-position relative to a nitrogen donor centre to be slightly lengthened with respect to those in a *gauche* position. The conformations of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ provide us with one of each of these possibilities. In fact the *anti*-positioned chlorine atoms Cl(2) have slightly longer bonds to the central atom than the atoms Cl(1), and the same is the case for the Ge−O(2) bond in $Cl_2Ge(ONMe_2)_2$, which is slightly longer than the Ge−O(1) bond. However, the two Si−O bonds in $Cl_2Si(ONMe_2)_2$ are of the same length within experimental errors.

Conclusion

The present study shows that the occurrence of strong β-donor interactions in SiON systems, which is represented by small SiON angles, is not simple to predict. Although the silicon (and germanium) atom in $Cl_2Si(ONMe_2)_2$ bears more electronegative substituents than in $ClH_2SiONMe_2$ the SiON angle in the first case is much larger. This cannot be understood in terms of simple electrostatic interactions. However, it has already been shown for $ClH_2SiONMe_2$ that a simple electrostatic model cannot explain the very different Si−O−N angles in the *gauche* and *anti* conformers of this compound,[6] and that compounds with even higher positive charges at silicon, such as $Si(ONMe_2)_4$, have wider SiON angles.[4] Therefore the influence of electrostatics should not be overestimated. Clearly the steric requirements at the silicon centre in $Cl_2Si(ONMe_2)_2$ are very different from that in $ClH_2SiONMe_2$, which might account for the differences. A similar argument for the rationalisation of the angle at the oxygen atom can be based upon the low directionality of the Si−O bonds, which is predominantly ionic.[11] However, $Cl_2Si(ONMe_2)_2$ and $H_3SiONMe_2$ have similar SiON angles but the silyl groups are very different in size. Steric requirements and electrostatic interactions could be competing effects, but even a consideration of both could not fully account for the structures observed in SiON compounds.

We are presently investigating the intramolecular electronic effects concerning β-donor-acceptor systems, including dipole interactions and the distribution of electron density, in more detail. Studies on other compounds with geminal acceptor and donor centres in geminal positions should also improve our knowledge on those systems.

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Experimental Section

The experiments were carried out using a standard Schlenk line or a vacuum line with greaseless stopcocks (Young taps), directly attached to the gas cell in an FTIR spectrometer (Midac Prospect FTIR). *N,N*-Dimethylhydroxylamine was liberated from its hydrochloride in liquid ammonia.[12] − NMR: Jeol JNM-LA400 spectrometer; samples in sealed tubes with C_6D_6 as a solvent (21 °C) directly condensed onto the sample from K/Na alloy.

Bis(dimethylaminoxy)dichlorosilane: A solution of *N,N*-dimethylhydroxylamine (3.0 ml, 42 mmol) and 2,6-lutidine (4.9 ml, 42 mmol) in pentane (25 ml) was added dropwise to a cooled solution (−60 °C) of tetrachlorosilane (2.4 ml, 21 mmol) in pentane (50 ml). The mixture was slowly warmed to ambient temp. After filtration from the salt the solvent was removed in vacuo. The residue was dissolved in 5 ml of diethyl ether and kept at −18 °C for 1 d. Bis(dimethylaminoxy)dichlorosilane was isolated as large colourless crystals extremely sensitive to moist air (3.1 g, 67%). − ^{1}H NMR: δ = 2.43 (s, 12 H, H_3C). − ^{13}C NMR: δ = 49.8 (q q, $^1J_{CH}$ = 136.0 Hz, $^3J_{CNCH}$ = 5.4 Hz, CH_3). − ^{15}N{^{1}H} NMR: δ = −228.5 (s). − ^{17}O NMR: δ = 188 (s). − ^{29}Si NMR: δ = −51.9 (s). − MS(CI): *m/z* (%) = 174 (100) [M^+ − NMe_2]. − $C_4H_{12}N_2O_2Cl_2Si$ (171.1): calcd. C 22.0, H 5.5, N 12.8; found C 22.0, H 5.5, N 12.9.

Bis(dimethylaminoxy)dichlorogermane: A solution of *N,N*-dimethylhydroxylamine (2.0 ml, 28 mmol) and 2,6-lutidine (3.3 ml, 28 mmol) in pentane (25 ml) was added dropwise to a cooled solution (−60 °C) of tetrachlorogermane (1.6 ml, 14 mmol) in pentane (50 ml). The mixture was slowly warmed to ambient temp.. After filtration from the salt the solution was slowly fractionated through a series of cooled traps and bis(dimethylaminoxy)dichlorogermane remained as a small amount of colourless crystals, extremely sensitive to moist air. − ^{1}H NMR: δ = 2.41 (s, 12 H, H_3C). − ^{13}C NMR: δ = 50.3 (q q, $^1J_{CH}$ = 136.0 Hz, $^3J_{CCCH}$ = 5.4 Hz, CH_3). − ^{15}N{^{1}H} NMR: δ = −231.8 (s). − ^{17}O NMR: δ = 193 (s). −MS(CI): *m/z* (%) = 264 (85) [M^+ − H]. − $C_4H_{12}Cl_2GeN_2O_2$ (263.63): calcd. C 18.2, H 4.6, N 10.6; found C 18.7, H 4.6, N 10.4.

Crystal Structure Determinations: Single crystals of $Cl_2Si(ONMe_2)_2$ and $Cl_2Ge(ONMe_2)_2$ were selected under a polarisation microscope and mounted into a glass capillary under Ar [$Cl_2Si(ONMe_2)_2$] and under inert perfluoropolyether [Fomblin, $Cl_2Ge(ONMe_2)_2$], respectively. Diffractometer: Enraf-Nonius CAD4, Mo-K_α radiation, graphite monochromator (λ = 0.71073 Å). Solution: direct methods;[13] refinement: SHELXL93.[14] No absorption correction applied. Non-H atoms were refined with anisotropic thermal displacement parameters, hydrogen atoms were located in difference Fourier maps and refined isotropically.

$Cl_2Si(ONMe_2)_2$: $C_4H_{12}Cl_2N_2O_2Si$, M = 219.15, monoclinic; a = 7.935(1), b = 9.472(1), c = 13.583(2) Å, β = 96.47(1); V = 1014.4(2) Å^3 at 133(2) K; cell from 88 reflections (θ-range 19 − 24°); space group $P2(1)/c$; Z = 4; D_c = 1.435; $2\theta_{max.}$ = 53.96°; h = −10 → 10, k = 0 → 12, l = −9 → 17; ω-scan, 3215 reflections collected, 2197 indep. reflections [$R_{int.}$ = 0.0298]. 148 Parameters, R = 0.0349 [for 2028 refl. with $F_o > 4\,\sigma(F_o)$], wR_2 = 0.1227 for all 2182 reflections. Residual electron density: min. 0.39, max. 0.45

e$\mathrm{Å}^{-3}$. Weight = $1/[\sigma^2(F_o^2) + (0.0666\ \mathrm{P})^2 + 0.49 \cdot P]$ where $P = [\mathrm{Max}\ (F_o^2,0) + 2 \cdot F_c^2]/3$.

$Cl_2Ge(ONMe_2)_2$: $C_4H_{12}Cl_2N_2O_2Ge$, M = 263.65, monoclinic; a = 8.043(1), b = 9.631(1), c = 13.789(1) Å, β = 96.42(1); V = 1061.4(2) $\mathrm{Å}^3$ at 188(2) K; cell from 100 reflections (θ-range 19 − 23°); space group $P2(1)/c$; Z = 4; D_c = 1.650; $2\theta_{\mathrm{max.}}$ = 56.84°; $h = 0 \rightarrow 10$, $k = -12 \rightarrow 0$, $l = -18 \rightarrow 18$; ω-scan, 2715 reflections collected, 2541 indep. reflections [$R_{\mathrm{int.}}$ = 0.0205]. 148 Parameters, R = 0.0263 [for 2078 refl. with $F_o > 4\ \sigma(F_o)$], wR_2 = 0.0761 for all 2529 reflections. Residual electron density: min. 0.46, max. 0.28 e $\mathrm{Å}^{-3}$. Weight = $1/[\sigma^2(F_o^2) + (0.028\ P)^2 + 0.56 \cdot P]$ where $P = [\mathrm{Max}\ (F_o^2,0) + 2 \cdot F_c^2]/3$.

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