DALTON
FULL PAPER

(4+4)-Coordinate germanium atoms in tetrakis(dialkylaminoxy)-germanes

Norbert W. Mitzel *† **and Krunoslav Vojinović**

Anorganisch-chemisches Institut, Technische Universität München, Lichtenbergstr. 4,
D-85747 Garching, Germany

Received 11th February 2002, Accepted 20th March 2002
First published as an Advance Article on the web 24th April 2002

The compounds $Ge(ONMe_2)_4$ and $Ge(ONEt_2)_4$ were prepared by the reaction of $LiONMe_2$ and $LiONEt_2$ with $GeCl_4$. They were characterized by ^1H and ^{13}C NMR and IR spectroscopy, by their decay patterns in the mass spectra, by high-resolution mass spectrometry and by elemental analyses. The crystal structure of $Ge(ONMe_2)_4$ was determined and shows the compound to have a (4+4) coordinate germanium atom as is evident from the Ge–O–N angles, which are in the range between 100.8(3) and 109.2(4)°, which is on average 15.2° smaller than the Ge–O–C angles in $Ge(ONCHMe_2)_4$. This compound was also prepared and examined by single crystal X-ray crystallography.

Following our studies on aminoxysilanes $R_3Si–O–NR'_2$,[1,2] which focused on their unique ability to form three-membered ring systems with Si ··· N donor–acceptor bonds and hypercoordinate silicon atoms, we have also started the investigation of analogous germanium compounds. The few germanium compounds with Ge–O–N linkages prepared so far include $Me_3GeONMe_2$,[3] $Cl_3GeONMe_2$,[4] $Cl_2Ge(ONMe_2)_2$,[5] the germole $Ph_4C_4Ge(ONMe_2)_2$[6] and most recently the simplest representative $H_3GeONMe_2$ has been prepared.[7] In all these cases the attractive interactions between the geminal Ge and N atoms are weaker than in the corresponding silicon compounds. The extreme examples from silicon chemistry with very pronounced Si ··· N interactions as in $H_2Si(ONMe_2)_2$,[1,2] $ClH_2SiONMe_2$[8] and $F_3SiONMe_2$[9] have so far not be realized in germanium chemistry.

An important step in the exploration of hypercoordinate silicon compounds was the finding of intramolecular hypercoordinate compounds with silicon in environments best described as (4+4)-coordinate. Salient examples of that type are the (4+4)-coordinated molecule, bis-1-[2,6-bis(dimethylaminomethyl)phenyl]silane,[10] whose Si coordination geometry was described as a SiC_2H_2 tetrahedron, tetra capped by four nitrogen donor centers (Si ··· N 2.895 and 3.117 Å) and the compound $[C_6H_2(CF_3)_3]_2SiF_2$,[11] which has a tetra capped tetrahedral geometry about the Si atom, with four Si ··· F contacts in the range between 2.715 and 3.056 Å. The first homoleptic (4+4)-coordinate Si compound was $Si(ONMe_2)_4$ with short Si ··· N contacts between 2.514(3) and 2.555(3) Å and narrow Si–O–N angles (109.1° on average).[12] This was compared to the isoelectronic $Si(OCHMe_2)_4$, which is not capable of forming attractive interactions between the Si atom and the geminal atoms and adopts an Si–O–C angle of 124.7(1)°.

Here we report the syntheses and properties of the analogous germanium compound $Ge(ONMe_2)_4$ and the ethyl homologue $Ge(ONEt_2)_4$ and the crystal structure of $Ge(ONMe_2)_4$. These compounds are related to the earlier reported $Ge(ON(CF_3)_2)_4$,[13–15] but as was shown in our investigations on $Me_3GeONMe_2$,[3] compounds with CF_3 groups at the nitrogen atoms behave quite differently in terms of molecular structure, as the reduced electron density at the N atoms does not permit a pronounced attractive interaction with the geminal group 14 element.

$Ge(ONMe_2)_4$ and $Ge(ONEt_2)_4$ were prepared by reacting $LiONMe_2$ or $LiONEt_2$ with germanium tetrachloride in diethyl ether. The compounds can be purified by crystallization and sublimation in the case of $Ge(ONMe_2)_4$ and distillation in the case of $Ge(ONEt_2)_4$.

$$GeCl_4 + 4\ LiONR_2 \longrightarrow Ge(ONR_2)_4 + 4\ LiCl$$

A few crystals of $Ge(ONMe_2)_4$ were also obtained in an attempt to prepare $F_3GeONMe_2$. We reacted GeF_4 with $LiONMe_2$, which resulted only in the formation of a non-volatile residue, which could not be dissolved in common solvents. Out of this residue, however, sublimed small amounts of $Ge(ONMe_2)_4$ as single crystals, one of which was used for structure determination. $Ge(ONEt_2)_4$ could not be obtained in crystalline form as it forms a glassy solid upon cooling.

Both compounds, $Ge(ONMe_2)_4$ and $Ge(ONEt_2)_4$, were characterized by ^1H and ^{13}C NMR spectroscopy, which showed the expected patterns. Attempts to record ^{17}O spectra failed, despite very concentrated samples being used in the experiments and prolonged accumulation times being allowed for. IR spectra of the solid $Ge(ONMe_2)_4$ and the liquid $Ge(ONEt)_4$ were measured and the data are listed in the experimental section.

The decay of the molecular ions was studied by mass spectra recorded in the EI mode and showed in both compounds the subsequent loss of the ONR_2 groups to be the preferred way of molecular ion degradation. There is some evidence from the nominal mass spectra for N–O bond cleavage and the formation of ions of the composition $(HO)_{4-x}Ge(ONR_2)_x$. High-resolution mass spectra were recorded and confirmed the identity of the compounds independently of the elemental analyses.

The crystal structure of $Ge(ONMe_2)_4$ (Fig. 1) was determined and shows the compound to possess a (4+4)-coordinate germanium atom, as is evident from the Ge–O–N angles, which are in the range between 100.8(3) and 109.2(4)° and 104.4° on average (Table 1). This corresponds to Ge ··· N distances, which fall over a range of 2.505 to 2.637 Å. This is about the same range as the Si ··· N distances (2.514(3) and 2.555(3) Å) in the homologous $Si(ONMe_2)_4$, but the Ge ··· N distances could be expected to be slightly longer due to the slightly larger radius of the germanium atom. The comparison of the average Ge–O–N angle in $Ge(ONMe_2)_4$ with the average Si–O–N angle in

---

† Present address: Institut für Anorganische und Analytische Chemie, Westfälische Wilhelms-Universität Münster, Wilhelm-Klemm-Str. 8, D-48149 Münster, Germany.

DOI: 10.1039/b201472f

This journal is © The Royal Society of Chemistry 2002

Table 1 Selected bond lengths and angles for $Ge(ONMe_2)_4$ [Å, °] listed for the four crystallographically different $ONMe_2$ groups

	$n = 1$	$n = 2$	$n = 3$	$n = 4$
Ge–O(*n*)	1.759(5)	1.757(5)	1.768(5)	1.767(4)
O(*n*)–N(*n*)	1.471(7)	1.481(7)	1.459(8)	1.476(7)
Ge–O(*n*)–N(*n*)	105.7(3)	102.0(3)	109.2(4)	100.8(3)
O(*n*)–N(*n*)–C(2*n* − 1)	105.8(5)	105.2(5)	105.1(6)	105.5(5)
O(*n*)–N(*n*)–C(2*n*)	105.4(5)	104.5(5)	104.5(6)	105.3(5)
C–N(*n*)–C	109.7(6)	110.3(6)	109.2(6)	111.2(6)
O(1)–Ge–O(*n*)	—	108.1(2)	115.2(2)	108.6(2)
O(2)–Ge–O(*n*)	—	—	111.4(2)	109.1(2)
O(3)–Ge–O(*n*)	—	—	—	104.2(2)

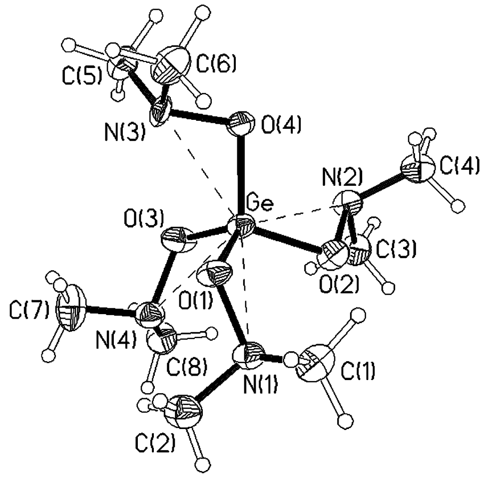

Fig. 1 Molecular structure of $Ge(ONMe_2)_4$ in the crystal.

$Si(ONMe_2)_4$ shows that the latter is 4.7° wider, which suggests that the attractive Ge ··· N forces would be at least as pronounced in $Ge(ONMe_2)_4$ as the Si ··· N forces in $Si(ONMe_2)_4$.

For comparison of the geometry of $Ge(ONMe_2)_4$ with an isoelectronic molecule not capable of formation of attractive interactions between germanium and geminal donor atoms, we determined the crystal structure of $Ge(OCHMe_2)_4$ (Fig. 2). Solid $Ge(OCHMe_2)_4$ is isomorphous with its homologous compound $Si(OCHMe_2)_4$ and crystallizes in the tetragonal space group $I4_1/a$. All four isopropoxy groups are crystallographically equivalent. The conformation of the isopropoxy groups relative to the germanium center is such that both methyl groups are approximately in *gauche*-conformation relative to the GeON unit, as is evident from the torsion angles Ge–O–C–C which are −115.6(1)° and 121.8(1)°. This is in analogy to the isoelectronic $Ge(ONMe_2)_4$ with torsion angles Ge–O–N–C in the ranges −131.5(5) to −118.9(5)° and 112.3 to 124.9(4)°.

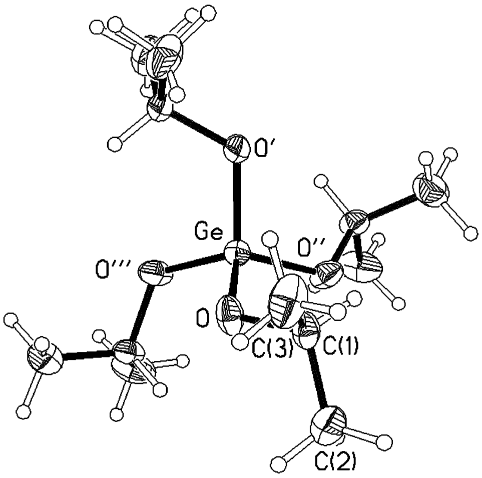

Fig. 2 Molecular structure of $Ge(OCHMe_2)_4$ in the crystal as determined by low-temperature X-ray crystallography of an *in-situ* grown crystal. Selected bond lengths and angles [Å, °]: Ge–O 1.745(1), O–C(1) 1.448(2), C(1)–C(2) 1.509(3), C(1)–C(3) 1.511(2), Ge–O–C(1) 119.6(1), O–Ge–O′ 106.8(1) (4 symmetry equivalent angles), O–Ge–O″ 114.9(1) (2 symmetry equivalent angles).

The Ge–O–C angle in $Ge(OCHMe_2)_4$ is 119.5(1)°, which seems typical for such an unit. This Ge–O–C angle is 15.2° wider than the average Ge–O–N angle in $Ge(ONMe_2)_4$. This parallels the pair of compounds $Si(ONMe_2)_4$ and $Si(OCHMe_2)_4$ in which the difference between the Si–O–N and Si–O–C angles is 15.6°. As in $Si(ONMe_2)_4$ we can therefore conclude that weak attractive interactions between the germanium atom and the four geminal nitrogen centers lead to a (4+4)-coordination at germanium in $Ge(ONMe_2)_4$.

Experimental

Syntheses

$Ge(ONMe_2)_4$. 5.3 g *N,N*-dimethylhydroxylamine (86 mmol) are dissolved in 100 mL hexane and cooled to 0 °C. 34 mL of a 2.5 M solution of *n*-butyllithium are added dropwise and the suspension is stirred for an hour. At 0 °C 2.45 mL germanium tetrachloride (21.5 mmol) are added, the suspension is stirred for 1/2 h and then refluxed for 1 h. The suspension is cooled to 0 °C, filtered and the filtrate concentrated by applying vacuum. Crystalline material is obtained, which is recrystallized from hexane. Yield 7.05 g (95%) $Ge(ONMe_2)_4$, mp 53 °C.

^1H NMR (C_6D_6, 21 °C) δ 2.59 (s, $^1J_{CH}$ = 134.8 Hz). $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 50.9 (s). $^{15}N\{^1H\}$ NMR (C_6D_6, DEPT, 21 °C) δ −229.81 (s). IR 2995 w, 2958 m, 2891 m, 2855 m, 2812 m, 2766 m, 1468 m, 1443 m, 1414 w, 1209 m, 1091 w, 999 m, 946 m, 890 vw, 811 s, 795 vs, 713 m, 696 w, 668 s cm^{-1}. High-resolution MS: Found *m*/*z* = 314.10166, Calcd. *m*/*z* = 314.10259. MS (EI) *m*/*z* (%) = 314 (0.1, M^+), 272 (0.4), 254 (5.9, $Ge(ONMe_2)_3^+$), 227 (0.4), 211 (2.3, $HOGe(ONMe_2)_2^+$), 194 (41.7, $Ge(ONMe_2)_2^+$), 185 (4.5), 151 (11.8), 134 (65.8, $Ge(ONMe_2)^+$), 91 (15.0, $GeOH^+$), 60 (100, Me_2NO^+), 42 (81.9), 28 (77.6). Elemental analysis for $C_8H_{24}N_4O_4Ge$: found C 30.65 H 7.71 N 17.84; calcd. C 30.71, H 7.73, N 17.91%.

$Ge(ONEt_2)_4$. 10 mL *N,N*-diethylhydroxylamine (97.5 mmol) are dissolved in 100 mL hexane and cooled to 0 °C. 39 mL of a 2.5 M solution of *n*-butyllithium are added dropwise, the suspension is cooled to −10 °C and stirred for 1 h. At this temperature 2.78 mL germanium tetrachloride (24.4 mmol) are added, the suspension is stirred for 1/2 h and then refluxed for 1 h. The suspension is filtered and the solvents are slowly removed *in vacuo* from the filtrate. The residue is distilled to give 9.13 g (88%) $Ge(ONEt_2)_4$, bp 108–109 °C (10^{-2} mbar).

^1H NMR (C_6D_6, 21 °C) δ 1.03 (t, $^3J_{CH}$ = 7.2 Hz), 2.86 (q). $^{13}C\{^1H\}$ NMR (C_6D_6, 21 °C) δ 11.2 (s), 53.2 (s). IR 2973 s, 2938 s, 2874 m, 2841 m, 1463 m, 1378 m, 1344 w, 1303 w, 1272 w, 1182 m, 1159 w, 1132 m, 1108 vw, 1087 vw, 1072 w, 1050 m, 1009 w, 869 vs, 779 vs, 708.1 m cm^{-1}. High-resolution MS: Found *m*/*z* = 426.22624, Calcd. *m*/*z* = 426.22613. MS (EI) *m*/*z* (%) = 426 (0.1, M^+), 356 (1.4), 338 (4.9, $Ge(ONEt_2)_3^+$), 307 (10.9), 250 (73.6, $Ge(ONEt_2)_2^+$), 162 (64.2, $Ge(ONEt_2)^+$), 89 (85.5, Et_2NOH^+), 74 (100), 56 (50.8), 42 (64.1), 29 (95.0). Elemental analysis for $C_{16}H_{40}N_4O_4Ge$: found C 45.02, H 9.51, N 13.09; calcd. C 45.21, H 9.48, N 13.18%.

Crystal structure determinations

$Ge(ONMe_2)_4$. Single crystals of $Ge(ONMe_2)_4$ grew accidentally by sublimation out of the solid residue of a reaction aiming at the preparation of $F_3GeONMe_2$. This was attempted by reacting germanium tetrafluoride (45 mmol) in 15 mL dimethyl ether with 2.01 g $LiONMe_2$ (30 mmol) at −96 °C, and later at −50 °C where the mixture was stirred. The volatile components were removed and separated, but consisted only of GeF_4 and Me_2O. The solid residue appeared to be insoluble in all common aprotic solvents and was kept under argon. Out of this residue sublimed crystals of $Ge(ONMe_2)_4$ over a period of 6 weeks under an atmosphere of argon. A suitable crystal was selected under inert perfluoropolyether oil and mounted onto a Nonius DIP2020 diffractometer. Crystallographic data for $Ge(ONMe_2)_4$: $M_r = 312.89$ ($C_8H_{24}N_4O_4Ge$), triclinic, $P\bar{1}$ (No. 2), $Z = 2$, $a = 8.9412(4)$ Å, $b = 9.1281(4)$ Å, $c = 9.2285(4)$ Å, $\alpha = 96.516(3)°$, $\beta = 96.585(3)°$, $\gamma = 91.3672(16)°$, $V = 742.87(4)$ Å^3, $T = 143(2)$ K, $\lambda = 0.71073$ Å, $D_{calc} = 1.399$ g cm^{-3}, $\mu = 2.562$ mm^{-1}, $R_1(F_o^2) = 0.0779$ ($F_o > 4\sigma(F_o)$), $wR_2(F_o^2) = 0.1838$.

$Ge(OCHMe_2)_4$. $Ge(OCHMe_2)_4$ was obtained by a literature procedure.[16] The liquid was sealed in a thin-walled Duran® glass capillary and a solid–liquid equilibrium was established in the cryostream of a Nonius DIP2020 diffractometer. By slowly cooling the melt after carefully melting all but one seed crystals a single crystal filling the whole capillary was grown. Crystallographic data for $Ge(OCHMe_2)_4$: $M_r = 308.93$ ($C_{12}H_{28}O_4Ge$), tetragonal, $I4_1/a$ (No. 88), $a = 8.0693(6)$ Å, $b = 8.0693(6)$ Å, $c = 24.7868(13)$ Å, $V = 1613.69(19)$ Å^3, $Z = 4$, $T = 133(2)$ K, $\lambda = 0.71073$ Å, $D_{calc} = 1.271$ g cm^{-3}, $\mu = 1.90$ mm^{-1}, $R_1(F_o^2) = 0.0355$ ($F_o > 4\sigma(F_o)$), $wR_2(F_o^2) = 0.0860$.

Intensity corrections were applied by the program SCALEPACK.[17] Structure solutions and refinements were undertaken with the program SHELXTL 5.01.[18]

CCDC reference numbers 177890 and 177891.

See http://www.rsc.org/suppdata/dt/b2/b201472f/ for crystallographic data in CIF or other electronic format.

Acknowledgements

This work was supported by Deutsche Forschungsgemeinschaft, Fonds der Chemischen Industrie and the Leonhard-Lorenz-Stiftung. Generous support from Professor H. Schmidbaur (Garching) is gratefully acknowledged.

References

1 N. W. Mitzel and U. Losehand, *Angew. Chem., Int. Ed. Engl.*, 1997, **24**, 2807.
2 U. Losehand and N. W. Mitzel, *Inorg. Chem.*, 1998, **37**, 3175.
3 N. W. Mitzel, U. Losehand and A. D. Richardson, *Inorg. Chem.*, 1999, **38**, 5323.
4 U. Losehand, N. W. Mitzel and D. W. H. Rankin, *J. Chem. Soc., Dalton Trans.*, 1999, 4291.
5 N. W. Mitzel and U. Losehand, *Eur. J. Inorg. Chem.*, 1998, 2023.
6 U. Losehand and N. W. Mitzel, *J. Chem. Soc., Dalton Trans.*, 2000, 1049.
7 N. W. Mitzel, U. Losehand, S. Hinchley and D. W. H. Rankin, *Inorg. Chem.*, 2001, **40**, 661.
8 N. W. Mitzel and U. Losehand, *J. Am. Chem. Soc.*, 1998, **120**, 7320.
9 N. W. Mitzel, U. Losehand, A. Wu, D. Cremer and D. W. H. Rankin, *J. Am. Chem. Soc.*, 2000, **122**, 4471.
10 F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi and C. Reyé, *Angew. Chem.*, 1994, **106**, 1152; F. Carré, C. Chuit, R. J. P. Corriu, A. Mehdi and C. Reyé, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 1097.
11 J. Braddock-Wilking, M. Schieser, L. Brammer, J. Huhmann and R. Shaltout, *J. Organomet. Chem.*, 1996, **499**, 89.
12 N. W. Mitzel, A. J. Blake and D. W. H. Rankin, *J. Am. Chem. Soc.*, 1997, **119**, 4143.
13 H. J. Emeléus, J. M. Shreeve and P. M. Spaziante, *Chem. Commun.*, 1968, 1252.
14 H. J. Emeléus, J. M. Shreeve and P. M. Spaziante, *J. Chem. Soc. (A)*, 1969, 431.
15 H. J. Emeléus, P. M. Spaziante and S. M. Williamson, *J. Inorg. Nucl. Chem. (A)*, 1970, **32**, 3219.
16 D. Sukhani, V. D. Gupta and R. C. Mehrotra, *Aust. J. Chem.*, 1968, **21**, 1175.
17 Z. Otwinowski and W. Minor, *Methods Enzymol.*, 1976, **276**, 307.
18 SHELXTL 5.01, Siemens Analytical X-Ray Instrumentation Inc., Madison, WI, 1995.