

Notiz / Note

Bis[2,3-naphthalenediolato(2-)](pyrrolidiniomethyl)germanate—Tetartoacetonitrile, the First Zwitterionic λ^5 -Germanate: Synthesis and Crystal Structure Analysis

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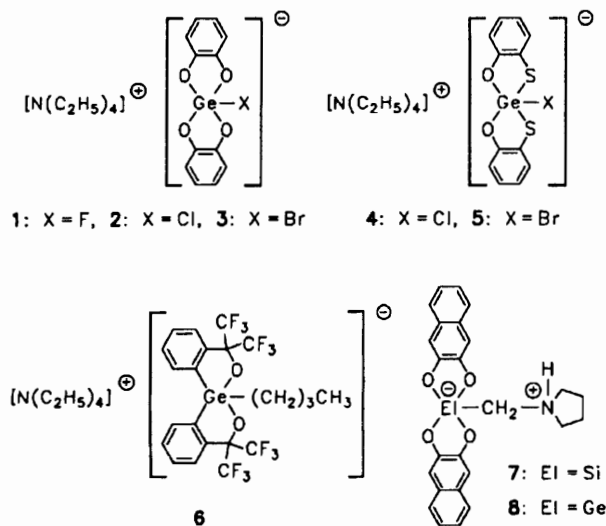
Received October 11, 1993

Key Words: λ^5 -Germanate, zwitterionic / Germanium, pentacoordinate

The zwitterionic spirocyclic λ^5 -germanate bis[2,3-naphthalenediolato(2-)](pyrrolidiniomethyl)germanate (**8**) was synthesized and the crystal structure of its tetartoacetonitrile solvate $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ studied by single-crystal X-ray diffraction. Compound **8** was prepared by reaction of $(\text{MeO})_3\text{-GeCH}_2\text{NC}_4\text{H}_8$ (**11**; $\text{NC}_4\text{H}_8 = \text{pyrrolidino}$) with two equivalents of 2,3-naphthalenediol (isolated as $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$; yield 92%). The coordination polyhedron around the pentacoordi-

nate germanium atom of $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ can be described as a strongly distorted trigonal bipyramid (the structure is displaced by 38.9% from the ideal trigonal bipyramid towards the ideal square pyramid), the carbon atom occupying an equatorial position. In the crystal lattice of $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$, the zwitterions form intermolecular N—H...O hydrogen bonds leading to the formation of dimers. ^1H - and ^{13}C -NMR studies revealed that **8** also exists in solution ($[\text{D}_6]\text{DMSO}$).

In contrast to the well established chemistry of pentacoordinate silicon^[1], the chemistry of pentacoordinate germanium is rather unexplored. Up to now only a few crystal structure analyses of neutral^[2] and anionic^[3] λ^5 -germanium species have been reported. The spirocyclic λ^5 -germanates **1**^[3b], **2**^[3a], **3**^[3c], **4**^[3c], **5** · CH_3CN ^[3c], and **6**^[3d] are examples of the last-mentioned type of compounds.



Recently, we have reported on the synthesis and structure of a series of zwitterionic λ^5 -silicates^[1d,4]. The spirocyclic λ^5 -silicate $\mathbf{7} \cdot 1/4 \text{ CH}_3\text{CN}$ ^[4a,4e] is an example of this type of compounds. In this paper we describe the synthesis and crystal structure of the corresponding germanium analogue, bis[2,3-naphthalenediolato-

(2-)](pyrrolidiniomethyl)germanate—tetartoacetonitrile ($\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$). To the best of our knowledge, compound $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ is the first zwitterionic λ^5 -germanate and the first structurally characterized λ^5 -germanium species with a GeO_4C framework. The aim of this study was to contribute to the chemistry of pentacoordinate germanium, with a special emphasis on the comparison of the Si/Ge analogues $\mathbf{7} \cdot 1/4 \text{ CH}_3\text{CN}$ and $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$.

Results and Discussion

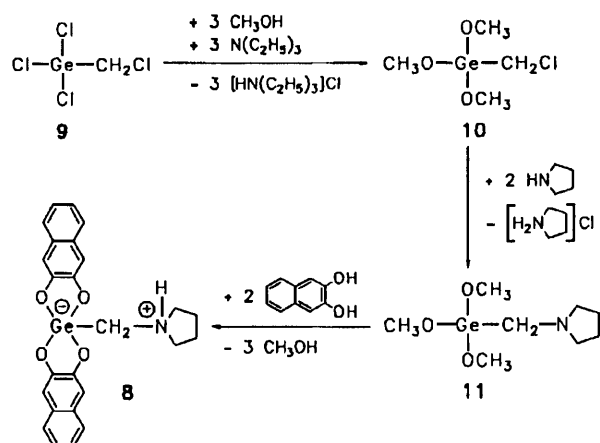
Starting from trichloro(chloromethyl)germane (**9**)^[5], we synthesized the zwitterionic λ^5 -germanate **8** by a three-step synthesis and isolated it as the tetartoacetonitrile solvate $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ (Scheme 1). In the first step, (chloromethyl)trimethoxygermane (**10**) was prepared by methanolysis of **9** in *n*-pentane in the presence of triethylamine (yield 90%). Reaction of **10** with an excess of pyrrolidine in boiling methanol gave trimethoxy(pyrrolidinomethyl)germane (**11**) (yield 51%), along with dipyrrolidinomethane^[6] as by-product. Compound **11** was then transformed into the λ^5 -germanate **8** by reaction with two equivalents of 2,3-naphthalenediol in acetonitrile at room temperature (yield 92%, related to $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$).

The germanes **10** and **11** were obtained as hydrolytically sensitive, colorless liquids, whereas the λ^5 -germanate $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ was isolated as a crystalline solid. The identity of the new germanium compounds was established by elemental analyses and by NMR-spectroscopic (^1H , ^{13}C) and mass-spectrometric studies (**10**, **11**: EI MS; **8**: FD MS). In addition, $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ was characterized by single-crystal X-ray diffraction.

Single crystals of $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ were obtained by recrystallization from acetonitrile. The results of the crystal structure analysis are summarized in Figure 1.

By analogy with the λ^5 -silicate $\mathbf{7} \cdot 1/4 \text{ CH}_3\text{CN}$, the λ^5 -germanate $\mathbf{8} \cdot 1/4 \text{ CH}_3\text{CN}$ crystallizes in the space group $I\bar{4}2d$. The molecular

Scheme 1



structures of these Si/Ge analogues in the crystal are quite similar. The coordination polyhedron around the germanium atom can be described as a strongly distorted trigonal bipyramid (Figure 1). The oxygen atoms O(2) and O(4) occupy the axial positions, the oxygen atoms O(1) and O(3) and the carbon atom C(21) the equatorial sites. In terms of the Berry pseudorotation coordinate, the dihedral angle method^[7-9] shows that the geometry of the coordination polyhedron is displaced by 38.9% from the ideal trigonal bipyramid towards the ideal square pyramid. For the silicon analogue **7** · 1/4 CH₃CN a distortion of only 21.0% was observed^[4e]. The axial Ge–O distances [Ge–O(2) 1.904(5), Ge–O(4) 1.865(5) Å] are significantly longer than the equatorial Ge–O bond distances [Ge–O(1) 1.820(5), Ge–O(3) 1.844(6) Å]. The Ge–O distances observed for **8** · 1/4 CH₃CN are within the range of the respective values reported for the ionic λ⁵-germanates 1–6. The geometries of the coordination polyhedra of the latter compounds range from a distorted trigonal bipyramid (**5** · CH₃CN: degree of distortion^[9] 23.6/26.2%; two crystallographically independent species) to a slightly distorted square pyramid (**2**: degree of distortion^[9] 91%).

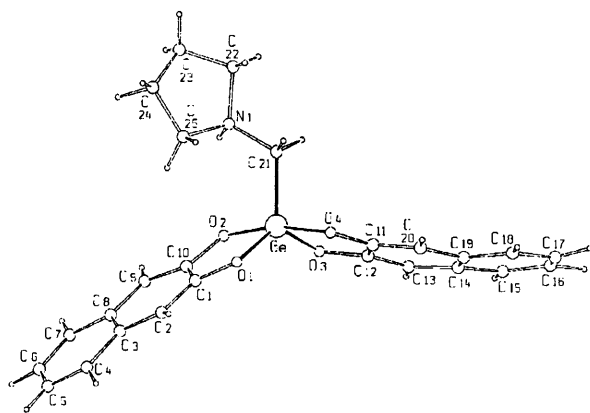


Figure 1. Molecular structure of **8** in the crystal of **8** · 1/4 CH₃CN showing the atomic numbering scheme [the acetonitrile molecule H₃C(26)–C(27)≡N(2) is not shown]. Selected bond distances [Å]: Ge–O(1) 1.820(5), Ge–O(2) 1.904(5), Ge–O(3) 1.844(6), Ge–O(4) 1.865(5), Ge–C(21) 1.96(1); selected bond angles [°]: O(1)–Ge–O(2) 86.4(2), O(1)–Ge–O(3) 128.0(3), O(1)–Ge–O(4) 89.2(2), O(1)–Ge–C(21) 119.2(3), O(2)–Ge–O(3) 86.2(2), O(2)–Ge–O(4) 167.2(3), O(2)–Ge–C(21) 98.4(3), O(3)–Ge–O(4) 87.1(2), O(3)–Ge–C(21) 112.8(3), O(4)–Ge–C(21) 94.2(3)

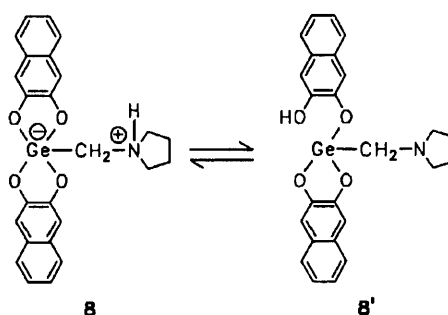
The Ge–C(21) distance in **8** · 1/4 CH₃CN [1.96(1) Å] is almost the same as observed for the Ge–C distance of the Ge–C₄H₉ group in the λ⁵-germanate **6** [1.947(9) Å]. Further details of the molecular structure of **8** in the crystal of **8** · 1/4 CH₃CN are given in the legend of Figure 1.

As observed for the silicon compound **7** · 1/4 CH₃CN, the zwitterions in the crystal of the germanium analogue **8** · 1/4 CH₃CN form intermolecular N(1)–H···O(2') hydrogen bonds leading to the formation of dimers [N(1)···O(2') 2.774(8), N(1)H···O(2') 1.786(63) Å, N(1)–H···O(2') 168.8(57)°]. This hydrogen bonding scheme is reflected by (i) the position of the N(1)H hydrogen atom (localized in the difference Fourier syntheses), (ii) by the binding geometries at the nitrogen atom N(1), and (iii) by the different Ge–O(2) and Ge–O(4) distances. Significant interactions between the acetonitrile molecules and the zwitterions in the crystal of **8** · 1/4 CH₃CN were not detected [shortest intermolecular distance between non-hydrogen atoms: N(2)···C(12) 2.986(13) Å].

¹H and ¹³C solution-state NMR studies (solvent [D₆]DMSO) revealed that the zwitterion **8** also exists in solution. The NMR data of **8** (see Experimental) are quite similar to those obtained for the silicon analogue **7**, whose pentacoordinate central atom could be established directly by ²⁹Si-NMR spectroscopy. As the ¹H- and ¹³C-NMR data for the ligands bound to the silicon (**7**) and germanium atom (**8**) are very similar, we conclude that the germanium atom is also pentacoordinated. Further evidence for the zwitterionic nature of **8** in solution comes from the characteristic resonance signal for the NH proton (δ = 9.6), indicating the presence of the ammonium group.

The existence of an equilibrium between **8** and the tautomeric species **8'** according to Scheme 2 (rapid N–H/O–H interchange) cannot be totally ruled out; but if the germane **8'** plays any role at all in solution, the zwitterion **8** must clearly dominate this equilibrium.

Scheme 2



We thank the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie* for financial support, and the *Bayer AG* (Leverkusen and Wuppertal-Elberfeld) for support with chemicals. In addition, we thank Mr. G. Mattern and Priv.-Doz. Dr. W. F. Kuhs (Institut für Kristallographie, Universität Karlsruhe) for collecting the X-ray diffraction data and for helpful discussions.

Experimental

All syntheses were carried out under dry nitrogen. The solvents used were dried according to standard procedures and stored under nitrogen. – Melting points: Leitz Laborlux S microscope, equipped with a heater (Leitz, model M 350). – ¹H NMR: solvent CDCl₃ or [D₆]DMSO; internal standard CHCl₃ (δ = 7.25) or [D₂]DMSO (δ = 2.49); Bruker AC-250 spectrometer (250.1 MHz). – ¹³C NMR: solvent CDCl₃ or [D₆]DMSO; internal standard CDCl₃

($\delta = 77.05$) or $[D_6]DMSO$ ($\delta = 39.9$); Bruker AC-250 spectrometer (62.9 MHz). Assignment was supported by DEPT experiments. – EI MS (70 eV) and FD MS (11 kV; CH_3CN as liquid matrix): Finnigan MAT 711 spectrometer (Varian). The selected m/z values given refer to the isotopes 1H , ^{12}C , ^{14}N , ^{16}O , ^{35}Cl , and ^{74}Ge .

Bis[2,3-naphthalenediolato(2-)](pyrrolidinomethyl)germanate–Tetraoacetonitrile (8 · 1/4 CH_3CN): 2,3-Naphthalenediol (3.20 g, 20.0 mmol) was dissolved in acetonitrile (50 ml). After addition of **11** (2.50 g, 10.0 mmol) at room temp. (formation of crystals), the reaction mixture was stirred for 1 min and then kept at room temp. for 72 h. The precipitate was filtered off, washed with acetonitrile (20 ml), and then dried in vacuo (0.01 Torr, 20°C, 3 h); yield 4.45 g (92%) of a white, finegrained solid. For analytical purposes, the product was recrystallized from acetonitrile and again dried in vacuo (0.01 Torr, 20°C, 3 h); decomposition at 248°C. – 1H NMR ($[D_6]DMSO$): $\delta = 1.8–1.9$ (m, 4H; CCH_2C), 2.07 (s, 0.75H; CH_3CN), 2.8–2.9 and 3.4–3.5 (m, 4H; NCH_2C), 3.32 (s, 2H; $GeCH_2N$), 7.02 (s, 4H; 1-, 4-H, $C_{10}H_6O_2$), 7.1–7.2 and 7.5–7.6 (m, 8H; remaining protons of $C_{10}H_6O_2$), 9.6 (broad s, 1H; NH). – ^{13}C NMR ($[D_6]DMSO$): $\delta = 23.4$ (CCH_2C), 47.5 ($GeCH_2N$), 57.0 (NCH_2C), 105.7, 122.5 and 126.0 (C-1/C-4, C-5/C-8, and C-6/C-7, $C_{10}H_6O_2$); the sequence of these atoms does not imply a direct assignment to the aforementioned chemical shifts), 129.2 (C-9/C-10, $C_{10}H_6O_2$), 150.6 (C-2/C-3, $C_{10}H_6O_2$), CH_3CN resonances not localized. – FD MS, m/z (%): 475 (100) [M_z^{+}]. – The elemental analysis was carried out with solvent-free crystals (after additional drying; 0.01 Torr, 20°C, 3 h). – $C_{25}H_{23}GeNO_4$ (474.1): calcd. C 63.34, H 4.89, N 2.95; found C 61.3, H 5.0, N 2.9.

Trichloro(chloromethyl)germane (9): Synthesis as described in ref.^[5]

(Chloromethyl)trimethoxygermane (10): Methanol (16.0 g, 499 mmol) was added dropwise at 0°C during 10 min to a stirred solution of **9** (36.5 g, 160 mmol) and triethylamine (50.6 g, 500 ml) in *n*-pentane (1 l). After heating under reflux for 6 h and stirring for 16 h at room temp., the precipitate was filtered off and the solvent removed by distillation from the filtrate under reduced pressure. The residue was distilled in vacuo (Vigreux column); yield 30.9 g (90%) of a colorless liquid, b.p. 88°C/65 Torr. – 1H NMR ($CDCl_3$): $\delta = 3.28$ (s, 2H; $GeCH_2Cl$), 3.70 (s, 9H; OCH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 24.4$ ($GeCH_2Cl$), 53.2 (OCH_3). – EI MS, m/z (%): 215 (<1) [$M^+ - H$], 185 (17) [$M^+ - OCH_3$], 167 (100) [$M^+ - CH_2Cl$]. – $C_4H_{11}ClGeO_3$ (215.2): calcd. C 22.23, H 5.15; found C 22.2, H 5.0.

Trimethoxy(pyrrolidinomethyl)germane (11): A solution of **10** (10.7 g, 49.7 mmol) and pyrrolidine (10.7 g, 150 mmol) in methanol (50 ml) was stirred under reflux for 20 h. After cooling to room temp., the solvent and the excess pyrrolidine were removed by distillation under reduced pressure, and *n*-pentane (100 ml) was added to the residue. The resulting precipitate was filtered off and the solvent evaporated from the filtrate under reduced pressure. The residue was distilled in vacuo (Vigreux column) to yield 7.68 g of a colorless liquid (b.p. 61–68°C/0.01 Torr) consisting of **11** (83 weight %) and dipyrrolidinomethane^[6] (17 weight %) (1H NMR). Redistillation of this mixture with a spinning column gave pure (1H and ^{13}C NMR) **10**; yield 6.37 g (51%) of a colorless liquid, b.p. 58°C/0.001 Torr. – 1H NMR ($CDCl_3$): $\delta = 1.7–1.8$ (m, 4H; CCH_2C), 2.5–2.6 (m, 4H; NCH_2C), 2.84 (s, 2H; $GeCH_2N$), 3.64 (s, 9H; OCH_3). – ^{13}C NMR ($CDCl_3$): $\delta = 24.2$ (CCH_2C), 43.3 ($GeCH_2N$), 52.4 (OCH_3), 56.8 (NCH_2C). – EI MS, m/z (%): 251 (2) [M^+], 167 (1) [$M^+ - CH_2NC_4H_8$], 84 (100) [$H_2C=NC_4H_8^+$]. – $C_8H_{19}GeNO_3$ (249.8): calcd. C 38.46, H 7.67, N 5.61; found C 38.7, H 7.8, N 5.7.

Crystal Structure Determination of $8 \cdot 1/4 CH_3CN$ ^[10]: Crystal data: $C_{25}H_{23.75}GeN_{1.25}O_4$, $M = 484.3$ g · mol⁻¹, tetragonal space group $I42d$ (No. 122), $a = 19.087(5)$, $c = 23.569(7)$ Å, $V = 8586.5$ Å³, $Z = 16$, $\rho_{calc} = 1.498$ g · cm⁻³, $\mu(Mo-K\alpha) = 13.9$ cm⁻¹. – Data collection and calculations: Intensities for a colorless crystal (0.13 × 0.20 × 0.32 mm) were collected on a four-circle diffractometer (Syntex R3) at 203 K by using $Mo-K\alpha$ radiation (graphite monochromator) for $2\theta \leq 50^\circ$. 15836 reflections were measured (opt. ω scan, 3793 unique reflections, $R_{Merge} = 0.040$) and 3019 used for subsequent refinement with $I > 2\sigma(I)$ [hkl range: $-22/0, -22/+22, -28/+28$]. The data were corrected for absorption effects (empiric). – Structure solution and refinement: The structure was solved by direct methods. Calculations were performed by using the programs SHELXS-86^[11] (structure solution) and SHELX-76^[12] (structure refinement) on a Micro-VAX station 3400. The non-hydrogen atoms of the zwitterion were refined with anisotropic displacement parameters; all hydrogen atoms were included in the refinement with idealized geometry and isotropic displacement parameters. The acetonitrile molecule [$H_3C(26)-C(27)=N(2)$] is disordered. As no distinction between the non-hydrogen atoms of the acetonitrile molecule could be made, these three atoms were refined with the atomic scattering factor of a carbon atom. The carbon atom C(27) and the nitrogen atom N(2) [Wyckoff position 8(c)] were refined with an occupation factor of 0.5 and isotropic displacement parameters. The carbon atom C(26) [Wyckoff position 4(b)] was refined with an occupation factor of 1.0 and with an isotropic displacement parameter. Weighting factor $w = [\sigma^2(F_o) + 0.0005 \cdot |F|^2]^{-1} \cdot R = 0.071$, $R_w = 0.058$ for 293 refined parameters [$R = \sum(|F_o| - |F_c|)/\sum|F_o|$; $R_w = [\sum w^{1/2} \cdot (|F_o| - |F_c|)]/[\sum w^{1/2} \cdot |F_o|]$]; residual electron density $+1.44/-1.20$ e · Å⁻³, located near the germanium atom. Selected bond distances and angles are listed in the legend of Figure 1. The atomic numbering scheme is given in Figure 1.

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