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Bis[2,3-naphthalenediolato(2−)](pyrrolidiniomethyl)germanate–Tetartoacetonitrile, the First Zwitterionic λ⁵-Germanate: Synthesis and Crystal Structure Analysis

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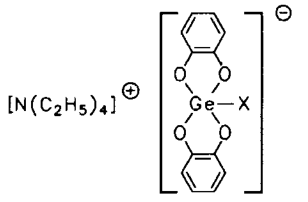
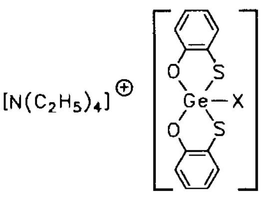
The zwitterionic spirocyclic λ^5-germanate bis[2,3-naphthalenediolato(2−)](pyrrolidiniomethyl)germanate (**8**) was synthesized and the crystal structure of its tetartoacetonitrile solvate **8** · 1/4 CH_3CN studied by single-crystal X-ray diffraction. Compound **8** was prepared by reaction of $(MeO)_3GeCH_2NC_4H_8$ (**11**; NC_4H_8 = pyrrolidino) with two equivalents of 2,3-naphthalenediol (isolated as **8** · 1/4 CH_3CN; yield 92%). The coordination polyhedron around the pentacoordinate germanium atom of **8** · 1/4 CH_3CN 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 **8** · 1/4 CH_3CN, 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 ($[D_6]DMSO$).

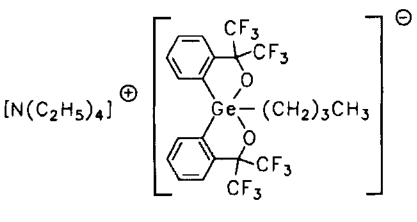
In contrast to the well established chemistry of pentacoordinate silicon[1], the chemistry of pentacoordinate germanium is rather unexplored. Up to now only a few crystal structure analyses of neutral[2] and anionic[3] λ^5-germanium species have been reported. The spirocyclic λ^5-germanates **1**[3b],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



1: X = F, **2**: X = Cl, **3**: X = Br



4: X = Cl, **5**: X = Br



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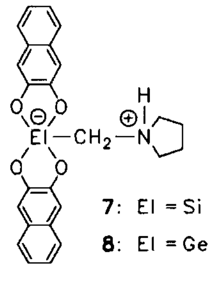

Recently, we have reported on the synthesis and structure of a series of zwitterionic λ^5-silicates[1d,4]. The spirocyclic λ^5-silicate **7** · 1/4 CH_3CN[4a,4e] is an example of this type of compounds. In this paper we describe the synthesis and crystal structure of the corresponding germanium analogue, bis[2,3-naphthalenediolato(2−)](pyrrolidiniomethyl)germanate–tetartoacetonitrile (**8** · 1/4 CH_3CN). To the best of our knowledge, compound **8** · 1/4 CH_3CN is the first zwitterionic λ^5-germanate and the first structurally characterized λ^5-germanium species with a $\mathit{Ge}O_4C$ 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 **7** · 1/4 CH_3CN and **8** · 1/4 CH_3CN.

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 **8** · 1/4 CH_3CN (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 **8** · 1/4 CH_3CN).

The germanes **10** and **11** were obtained as hydrolytically sensitive, colorless liquids, whereas the λ^5-germanate **8** · 1/4 CH_3CN 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, **8** · 1/4 CH_3CN was characterized by single-crystal X-ray diffraction.

Single crystals of **8** · 1/4 CH_3CN 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 **7** · 1/4 CH_3CN, the λ^5-germanate **8** · 1/4 CH_3CN crystallizes in the space group $I\bar{4}2d$. The molecular

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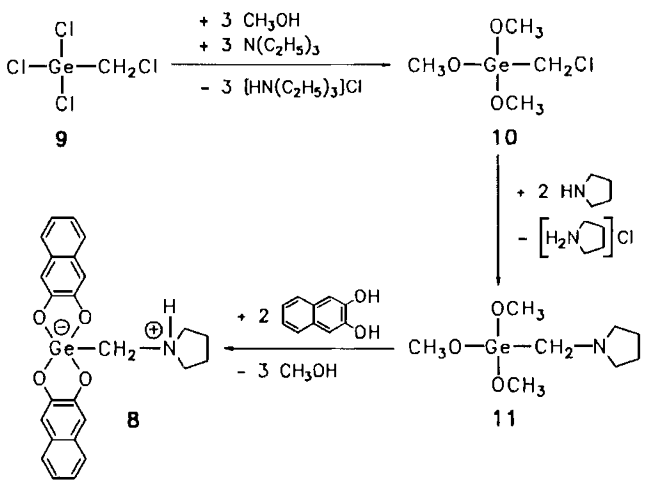
Scheme 1



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 CH_3CN 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 CH_3CN are within the range of the respective values reported for the ionic λ^5-germanates **1**–**6**. The geometries of the coordination polyhedra of the latter compounds range from a distorted trigonal bipyramid (**5** · CH_3CN: degree of distortion[9] 23.6/26.2%; two crystallographically independent species) to a slightly distorted square pyramid (**2**: degree of distortion[9] 91%).

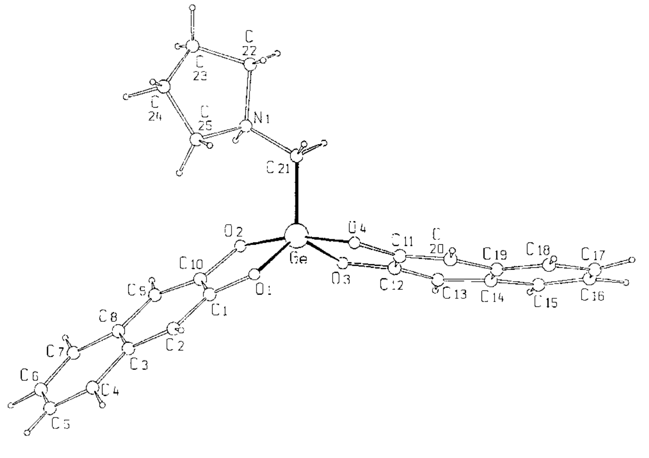


Figure 1. Molecular structure of **8** in the crystal of **8** · 1/4 CH_3CN showing the atomic numbering scheme [the acetonitrile molecule $H_3C(26)-C(27){\equiv}N(2)$ is not shown]. Selected bond distances [Å]: Ge–O(1) 1.820(5), Ge–O(2) 1.904(5), Ge–O(3) 1.844(6), Ge–O(4) 1.865(5), Ge–C(21) 1.96(1); 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)

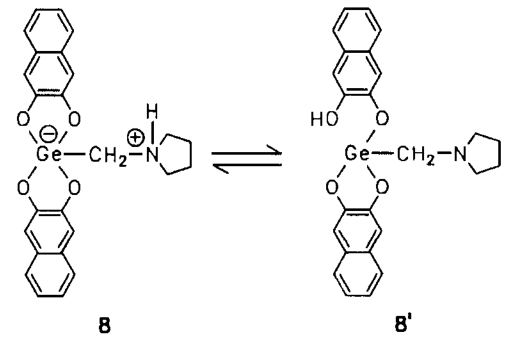
The Ge–C(21) distance in **8** · 1/4 CH_3CN [1.96(1) Å] is almost the same as observed for the Ge–C distance of the Ge–C_4H_9 group in the λ^5-germanate **6** [1.947(9) Å]. Further details of the molecular structure of **8** in the crystal of **8** · 1/4 CH_3CN are given in the legend of Figure 1.

As observed for the silicon compound **7** · 1/4 CH_3CN, the zwitterions in the crystal of the germanium analogue **8** · 1/4 CH_3CN 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 CH_3CN were not detected [shortest intermolecular distance between non-hydrogen atoms: N(2)···C(12) 2.986(13) Å].

^1H and ^{13}C solution-state NMR studies (solvent [D_6]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 ^{29}Si-NMR spectroscopy. As the ^1H- and ^{13}C-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



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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 $CDCl_3$ or [D_6]DMSO; internal standard $CHCl_3$ (δ = 7.25) or [D_5]DMSO (δ = 2.49); Bruker AC-250 spectrometer (250.1 MHz). – ^{13}C NMR: solvent $CDCl_3$ or [D_6]DMSO; internal standard $CDCl_3$

(δ = 77.05) or [D_6]DMSO (δ = 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−)](pyrrolidiniomethyl)germanate − Tetartoacetonitrile (**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): δ = 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): δ = 23.4 ($C\mathit{C}H_2C$), 47.5 ($GeCH_2N$), 57.0 ($N\mathit{C}H_2C$), 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, $C_{10}H_6O_2$), $\mathit{C}H_3\mathit{C}N$ resonances not localized. − FD MS, *m/z* (%): 475 (100) [$M^+_{\text{zwitterion}}$]. − 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 ($CDCl_3$): δ = 3.28 (s, 2H; $GeCH_2Cl$), 3.70 (s, 9H; OCH_3). − ^{13}C NMR ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 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 ($CDCl_3$): δ = 24.2 ($C\mathit{C}H_2C$), 43.3 ($GeCH_2N$), 52.4 (OCH_3), 56.8 ($N\mathit{C}H_2C$). − 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** · 1/4 CH_3CN[10]: Crystal data: $C_{25.5}H_{23.75}GeN_{1.25}O_4$, M = 484.3 g · mol^{-1}, tetragonal space group $I\bar{4}2d$ (No. 122), a = 19.087(5), c = 23.569(7) Å, V = 8586.5 $Å^3$, Z = 16, ρ_{calc} = 1.498 g · cm^{-3}, μ(Mo-K_α) = 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_α radiation (graphite monochromator) for $2\Theta \leqslant 50°$. 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 [$H_3C(26){-}C(27){\equiv}N(2)$] 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 $\{R = \Sigma(||F_o| - |F_c||)/\Sigma|F_o|$; $R_w = [\Sigma w^{1/2} \cdot (||F_o| - |F_c||)]/[\Sigma w^{1/2} \cdot |F_o|]\}$; 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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[6] The identity of dipyrrolidinomethane was proven by NMR and EI MS studies {^{1}H NMR ($CDCl_3$): δ = 1.7−1.8 (m, 8H; CCH_2C), 2.5−2.6 (m, 8H; NCH_2C), 2.84 (s, 2H; NCH_2N). − ^{13}C NMR ($CDCl_3$): δ = 24.3 ($C\mathit{C}H_2C$), 52.9 ($N\mathit{C}H_2C$), 77.6 (NCH_2N). − EI MS, *m/z* (%): 154 (1) [M^+], 84 (100) [$H_2C{=}NC_4H_8^+$]}: *Beilsteins Handbuch der Organischen Chemie*, E III/IV, Vol. 27, Part 1, 4th Ed., Springer-Verlag, Berlin/Heidelberg/New York, **1977**, Syst.-Nr. 3037/H5, S. 166. − The mode of formation of the by-product dipyrrolidinomethane has not been studied.

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[10] Further details of the crystal structure investigation are available on request from the Fachinformationszentrum Karlsruhe, Gesellschaft für wissenschaftlich-technische Information mbH, D-76344 Eggenstein-Leopoldshafen, on quoting the depository number CSD-57936, the names of the authors, and the journal citation.

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