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The First Zwitterionic Dinuclear Germanium(IV) Complex with Pentacoordinate Germanium Atoms: Synthesis and Crystal Structure Analysis

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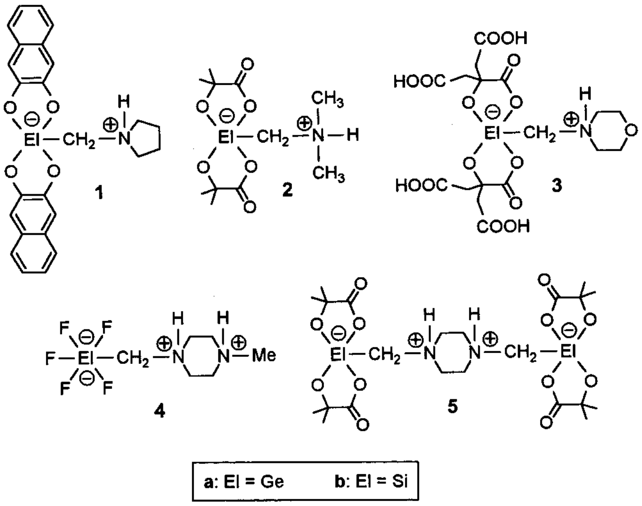
Introduction

In a series of recent papers we have reported on the synthesis and structural characterization of the zwitterionic (molecular) λ^5*Ge*-germanates **1a**·$^1/_4CH_3CN$,[1] **2a**·H_2O,[2] and **3a**·H_2O[3] as well as the zwitterionic λ^6*Ge*-germanate **4a**·H_2O.[4] The crystal structures of these compounds and those of their corresponding silicon analogues **1b**·$^1/_4CH_3CN$,[5] **2b**·H_2O,[2] **3b**·H_2O,[3] and **4b**·H_2O[6] were found to be isotypic. Here we report on the synthesis and structural characterization of compound **5a**·$8H_2O$, the first zwitterionic λ^5*Ge*,λ^5*Ge′*-digermanate. The synthesis and crystal structure of the corresponding silicon analogue **5b**·$8H_2O$ have recently been described.[7] Generally, compared to the well-established chemistry of pentacoordinate silicon, the chemistry of pentacoordinate germanium has been significantly less explored (Chart 1).[8−10]

Chart 1



Experimental Section

General Procedures. All syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Piperazine was purchased from Aldrich and purified by sublimation. Melting points were determined with a Leitz Biomed microscope equipped with a heater (Leitz, model M 350). The ^1H and ^{13}C NMR spectra were recorded at room temperature on a Bruker DRX-300 spectrometer (^1H, 300.1 MHz; ^{13}C, 75.5 MHz). $CDCl_3$ was used as solvent. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^1H, δ 7.24) and $CDCl_3$ (^{13}C, δ 77.0). Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments.

Preparation of *meso*-[1,4-Piperaziniumdiylbis(methylene)]bis{bis-[2-methyllactato(2−)-O^1,O^2]germanate} Octahydrate (5a·8H$_2$O). A solution of **7** (500 mg, 1.13 mmol) in acetone (10 mL) was added over 30 min at room temperature to a stirred solution of 2-methyllactic acid (469 mg, 4.51 mmol) in water (60 mL). After the mixture was stirred for a further 2 h at room temperature, a part of the solvent mixture (ca. 50 mL) was removed under reduced pressure (60 °C/40 Torr) and the reaction mixture then kept undisturbed for ca. 10 days at room temperature (slow evaporation of the solvent; the first crystals formed after about 3 days). The precipitate was filtered off, washed with acetone (3 × 5 mL), and then dried in a nitrogen stream to give **5a**·$8H_2O$ in 79% yield as a colorless crystalline product (723 mg, 891 μmol). For analytical purposes, the water of crystallization was removed by heating in vacuo (100 °C, 0.01 Torr, 8 h), mp 215−220 °C. Anal. Calcd for $C_{22}H_{38}Ge_2N_2O_{12}$: C, 39.57; H, 5.74; N 4.20. Found: C, 39.1; H, 5.9; N, 4.2.

Preparation of (Chloromethyl)trimethoxygermane (6). This compound was synthesized according to ref 1.

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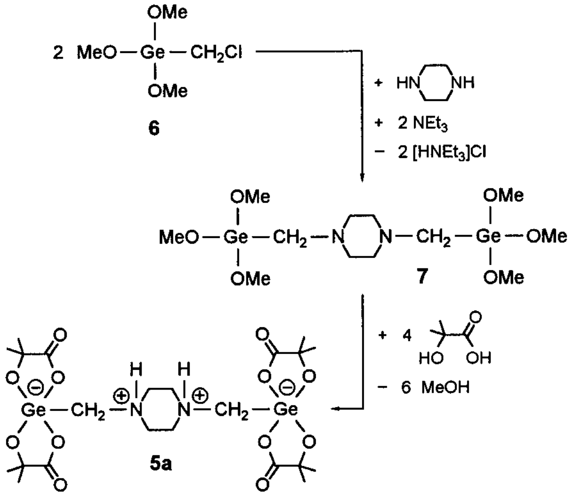
Scheme 1



Preparation of 1,4-Bis[(trimethoxygermyl)methyl]piperazine (7). A solution of **6** (16.0 g, 74.4 mmol), piperazine (3.20 g, 37.2 mmol), and triethylamine (11.3 g, 111 mmol) in toluene (150 mL) was heated under reflux for 18 h, and the mixture was then stirred for a further 48 h at room temperature. After the solvent and excess triethylamine were removed under reduced pressure, *n*-pentane (300 mL) was added and the mixture was kept at room temperature for 2 h. The precipitate was filtered off, the filtrate was concentrated under reduced pressure, and the oily residue was distilled in vacuo (Kugelrohr distillation; oven temperature 250 °C, 0.01 Torr) to give **7** in 60% yield as a colorless liquid (9.89 g, 22.3 mmol). ^{1}H NMR ($CDCl_3$): δ 2.4−2.5 (m, 8 H, CCH_2N), 2.68 (s, 4 H, $GeCH_2N$), 3.61 (s, 18 H, OCH_3). ^{13}C NMR ($CDCl_3$): δ 47.0 ($GeCH_2N$), 52.4 (OCH_3), 55.3 (CCH_2N). Anal. Calcd for $C_{12}H_{30}Ge_2N_2O_6$: C, 32.49; H, 6.82; N, 6.32. Found: C, 32.4; H, 7.0; N, 6.2.

Crystal Structure Analysis of 5a·8H$_2$O. A suitable single crystal of **5a**·8H$_2$O was obtained by crystallization of **5a** from water at room temperature (slow evaporation of the solvent). The crystal was mounted in inert oil (RS 3000, Riedel-de Haën) on a glass fiber and then transferred to the cold gas stream of the diffractometer (Enraf-Nonius four-circle diffractometer; graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); for the low-temperature attachment, see ref 11). Cell parameters were obtained from least-squares fits to the settings of 25 reflections in the range of $20 \leq 2\theta \leq 25°$. No significant deviations in intensity were registered for two monitor reflections recorded at regular intervals. Semiempirical absorption correction was applied. The structure was solved by direct methods.[12] All non-hydrogen atoms were refined anisotropically.[13] A riding model was employed in the refinement of the CH hydrogen atom positions. The positions of the NH and OH hydrogen atoms were localized in difference Fourier syntheses and refined freely.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analysis of **5a**·8H$_2$O

empirical formula	$C_{22}H_{54}Ge_2N_2O_{20}$
formula mass, g mol^{-1}	811.85
collection *T*, °C	−100(2)
λ(Mo Kα), Å	0.71073
cryst syst	monoclinic
space group (no.)	$P2_1/n$ (14)
a, Å	6.30(2)
b, Å	16.147(2)
c, Å	17.94(2)
β, deg	93.48(7)
V, Å^3	1823(5)
Z	2
D(calcd), g cm^{-3}	1.479
μ, cm^{-1}	17.26
F(000)	848
cryst dimens, mm	0.3 × 0.2 × 0.2
2θ range, deg	4.54−50.16
index ranges	$-7 \leq h \leq 2, -19 \leq k \leq 0, -21 \leq l \leq 21$
no. of collcd reflns	4385
no. of indep reflns	3208
R_{int}	0.0174
max/min transm	0.7241/0.6255
no. of reflns used	3208
no. of params	240
S^a	1.015
weight params *a*/*b*^{b}	0.0245/0.8814
$R1^c$ [$I > 2\sigma(I)$]	0.0258
$wR2^d$ (all data)	0.0563
extinction coeff	0.0050(4)
max/min res electron dens, e Å^{-3}	+0.335/−0.345

^{a} $S = \{\Sigma[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; n = no. of reflections; p = no. of parameters. ^{b} $w^{-1} = \sigma^2(F_o^2) + (aP)^2 + bP$, with $P = (F_o^2 + 2F_c^2)/3$. ^{c} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{d} $wR2 = \{\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]\}^{0.5}$.

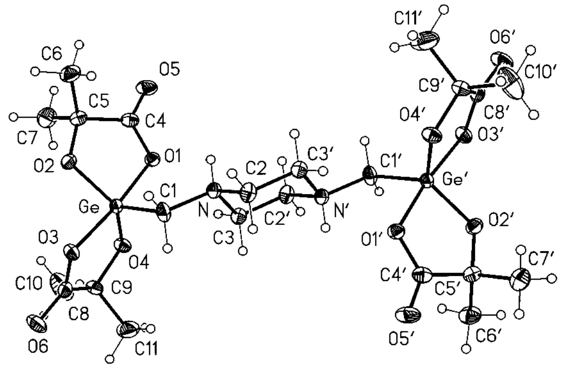


Figure 1. Molecular structure of **5a** in the crystal of **5a**·8H$_2$O (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

Results and Discussion

The zwitterionic dispirocyclic λ^5*Ge*,λ^5*Ge′*-digermanate **5a** was prepared by a two-step synthesis according to Scheme 1, following the strategy used for the synthesis of the analogous λ^5*Si*,λ^5*Si′*-disilicate **5b**.[7] In the first step, 1,4-bis[(trimethoxygermyl)methyl]piperazine (**7**) was synthesized by reaction of (chloromethyl)trimethoxygermane[1] (**6**) with piperazine (molar ratio 2:1) in boiling toluene in the presence of triethylamine as hydrogen chloride acceptor (yield 60%). Subsequent reaction of **7** with 2-methyllactic acid (molar ratio 1:4) in water/acetone at room temperature yielded the dinuclear germanium(IV) complex **5a** which was isolated as the crystalline octahydrate **5a**·8H$_2$O [yield 79%; overall yield 47% (related to **6**)]. Its identity was established by elemental analyses (C, H, N) and single-crystal X-ray diffraction.

The crystal data of **5a**·8H$_2$O and the experimental parameters used for the crystal structure analysis are given in Table 1 (for further details, see Experimental Section). The molecular structure of **5a** in the crystal of **5a**·8H$_2$O is depicted in Figure 1. Selected interatomic distances and angles are listed in Table 2.

By analogy with the λ^5*Si*,λ^5*Si′*-disilicate **5b**·8H$_2$O,[7] the analogous λ^5*Ge*,λ^5*Ge′*-digermanate **5a**·8H$_2$O crystallizes in the space group $P2_1/n$. The crystal structures of the Ge/Si analogues

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Table 2. Selected Interatomic Distances (Å) and Angles (deg) for **5a**·$8H_2O$

Ge−O1	1.919(3)	Ge−O4	1.769(2)
Ge−O2	1.786(3)	Ge−C1	1.935(4)
Ge−O3	1.895(2)		
O1−Ge−O2	86.19(8)	O2−Ge−O4	122.71(11)
O1−Ge−O3	172.21(6)	O2−Ge−C1	119.72(10)
O1−Ge−O4	90.64(13)	O3−Ge−O4	87.60(12)
O1−Ge−C1	95.2(2)	O3−Ge−C1	92.3(2)
O2−Ge−O3	88.38(8)	O4−Ge−C1	117.53(13)

are isotypic. This result again emphasizes the distinct similarities in the structural chemistry of analogous zwitterionic λ^5*Ge*-germanates and λ^5*Si*-silicates (in this context, see also refs 1−3 and 5).

The molecular structure of **5a** is characterized by a crystallographic center of inversion, localized in the middle of the piperazinium ring system. This heterocycle displays a nearly ideal chair conformation (weighted average of the absolute ring torsion angles 58.3°; maximum deviation from this value 1.0°). The coordination polyhedra surrounding the germanium atoms of **5a** can be described as slightly distorted trigonal bipyramids, the axial positions being occupied by the carboxylate oxygen atoms O1(O1′) and O3(O3′). In terms of the Berry pseudorotation coordinate, the dihedral angle method[14] shows that the geometry of these coordination polyhedra is displaced by 13.9% from the ideal trigonal bipyramid (TBP) toward the ideal square pyramid (SP) [pivot atom C1(C1′)]. This distortion is quite similar to that observed for the silicon analogue **5b**·$8H_2O$ (TBP → SP: 11.5%).[7] Due to the center of inversion, the two chiral trigonal-bipyramidal germanate frameworks exhibit opposite absolute configurations. Thus, the molecular structure of **5a** represents the meso configuration. The axial Ge−O distances [1.919(3) Å, 1.895(2) Å] are significantly longer than the equatorial ones [1.786(3) Å, 1.769(2) Å]. These values as well as the Ge−C distance [1.935(4) Å] are similar to the Ge−O and Ge−C distances of related spirocyclic zwitterionic λ^5*Ge*-germanates with *Ge*O_4C frameworks containing ligands of the glycolato(2−)-O^1,O^2 type (typical values: Ge−O_{ax}, 1.88−1.96 Å; Ge−O_{eq}, 1.77−1.80 Å; Ge−C_{eq}, 1.95−1.96 Å).[2,3] For anionic and zwitterionic λ^5*Ge*-germanates with ligands of the benzene-1,2-diolato(2−) type distances of 1.82−1.92 Å (Ge−O) and 1.90−1.96 Å (Ge−C) have been reported.[1,15] These compounds contain *Ge*O_4C skeletons with strongly distorted trigonal-bipyramidal or square-pyramidal coordination polyhedra around the central germanium atoms.

As would be expected from the presence of 36 potential proton-donating groups (4 NH and 32 OH functions) and 40 potential acceptor atoms (oxygen atoms) in the unit cell, a complex three-dimensional hydrogen-bonding system in the crystal of **5a**·$8H_2O$ is observed. All NH and OH donor functions are involved in this hydrogen-bonding network.

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Supporting Information Available: Atomic coordinates and equivalent isotropic displacement parameters for the non-hydrogen atoms (Table S1), anisotropic displacement parameters (Table S2), atomic coordinates and equivalent isotropic displacement parameters for the hydrogen atoms (Table S3), and additional interatomic distances and angles (Table S4) for **5a**·$8H_2O$ (4 pages). Ordering information is given on any current masthead page.

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(15) For publications dealing with anionic λ^5*Ge*-germanates containing a *Ge*O_4C framework: see ref 9d,e.