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Zwitterionic Bis[citrato(2−)-O^3,O^4](morpholiniomethyl)germanate Hydrate and Its Silicon Analogue: Syntheses and Crystal Structure Analyses[†]

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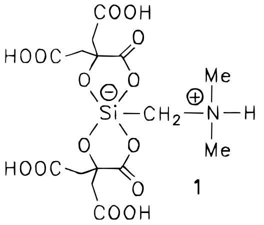
The zwitterionic spirocyclic λ^5Ge-germanate bis[citrato(2−)-O^3,O^4](morpholiniomethyl)germanate (**2**) and its silicon analogue bis[citrato(2−)-O^3,O^4](morpholiniomethyl)silicate (**3**) were synthesized by reaction of citric acid with trimethoxy(morpholinomethyl)germane (**4**) and trimethoxy(morpholinomethyl)silane (**5**), respectively. Both reactions were carried out at room temperature in acetonitrile and the products isolated, after crystallization from water, as the hydrates **2**·H_2O and **3**·H_2O. In addition to NMR spectroscopic (solution-state ^{1}H, ^{13}C, and ^{29}Si NMR; solid-state ^{29}Si CP/MAS NMR) and mass spectrometric (FAB MS) characterization of **2**, **2**·H_2O, **3**, and **3**·H_2O, the hydrates were structurally characterized by single-crystal X-ray diffraction. The zwitterions **2** and **3** contain a pentacoordinate (formally negatively charged) germanium and silicon atom, respectively, and a tetracoordinate (formally positively charged) nitrogen atom. The central atom of **2** (Ge) and **3** (Si) is surrounded by four oxygen atoms and one carbon atom. In the crystal of **2**·H_2O and **3**·H_2O, the coordination polyhedra around the germanium and silicon atom can be best described as distorted trigonal bipyramids, the carboxylate oxygen atoms occupying the axial sites. In terms of the Berry pseudorotation coordinate, the geometries are displaced by 14.0% (**2**·H_2O) and 13.4% (**3**·H_2O) from the ideal trigonal bipyramid toward the ideal square pyramid. According to NMR spectroscopic studies, the zwitterions **2** and **3** also exist in solution ([D_6]DMSO).

Introduction

In the course of our studies on zwitterionic (molecular) spirocyclic λ^5Si-silicates,[1] we have recently reported on the synthesis and structural characterization of the first pentacoordinate silicon compound containing bidentate citrato(2−)-O^3,O^4 ligands (**1**·H_2O).[1j] Here we describe the synthesis and crystal structure of the related zwitterionic λ^5Ge-germanate **2**·H_2O, the first pentacoordinate germanium compound containing citrato(2−)-O^3,O^4 ligands. In addition, we report on the synthesis and crystal structure analysis of the corresponding silicon analogue **3**·H_2O. This study was carried out with a special emphasis on the structural comparison of the analogous λ^5Ge-germanate and λ^5Si-silicate. Compared to the well-established chemistry of pentacoordinate silicon,[2] the chemistry of pentacoordinate germanium has been significantly less explored.[3−5]



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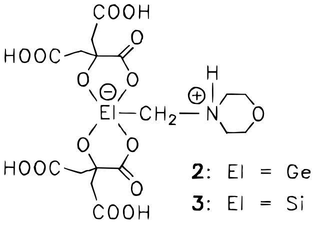

2: El = Ge
3: El = Si

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[†] Dedicated to Professor Manfred Weidenbruch on the occasion of his 60th birthday.

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(1) (a) Strohmann, C.; Tacke, R.; Mattern, G.; Kuhs, W. F. *J. Organomet. Chem.* **1991**, *403*, 63−71. (b) Tacke, R.; Sperlich, J.; Strohmann, C.; Mattern, G. *Chem. Ber.* **1991**, *124*, 1491−1496. (c) Tacke, R.; Sperlich, J.; Strohmann, C.; Frank, B.; Mattern, G. *Z. Kristallogr.* **1992**, *199*, 91−98. (d) Tacke, R.; Wiesenberger, F.; Lopez-Mras, A.; Sperlich, J.; Mattern, G. *Z. Naturforsch., B* **1992**, *47*, 1370−1376. (e) Tacke, R.; Lopez-Mras, A.; Sheldrick, W. S.; Sebald, A. *Z. Anorg. Allg. Chem.* **1993**, *619*, 347−358. (f) Tacke, R.; Lopez-Mras, A.; Sperlich, J.; Strohmann, C.; Kuhs, W. F.; Mattern, G.; Sebald, A. *Chem. Ber.* **1993**, *126*, 851−861. (g) Sperlich, J.; Becht, J.; Mühleisen, M.; Wagner, S. A.; Mattern, G.; Tacke, R. *Z. Naturforsch., B* **1993**, *48*, 1693−1706. (h) Tacke, R.; Lopez-Mras, A.; Jones, P. G. *Organometallics* **1994**, *13*, 1617−1623. (i) Tacke, R.; Mühleisen, M.; Jones, P. G. *Angew. Chem.* **1994**, *106*, 1250−1252; *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1186−1188. (j) Mühleisen, M.; Tacke, R. *Chem. Ber.* **1994**, *127*, 1615−1617. (k) Mühleisen, M.; Tacke, R. *Organometallics* **1994**, *13*, 3740−3742. (l) Tacke, R.; Mühleisen, M. *Inorg. Chem.* **1994**, *33*, 4191−4193. (m) Tacke, R.; Mühleisen, M.; Lopez-Mras, A.; Sheldrick, W. S. *Z. Anorg. Allg. Chem.* **1995**, *621*, 779−788.

(2) Reviews and proceedings dealing with pentacoordinate silicon compounds: (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99−189. (b) Sheldrick, W. S. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 227−303. (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17−31. (d) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371−1448. (e) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1−8. (f) Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175−241. (g) Tacke, R.; Becht, J.; Dannappel, O.; Kropfgans, M.; Lopez-Mras, A.; Mühleisen, M.; Sperlich, J. In *Progress in Organosilicon Chemistry*; Marciniec, B., Chojnowski, J., Eds.; Gordon and Breach: Amsterdam, 1995; pp 55−68. (h) Tacke, R.; Dannappel, O.; Mühleisen, M. In *Organosilicon Chemistry II—From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, 1996; pp 427−446. (i) Tacke, R.; Dannappel, O. In *Tailor-made Silicon Oxygen Compounds—From Molecules to Materials*; Corriu, R., Jutzi, P., Eds.; Vieweg: Braunschweig/Wiesbaden, Germany, 1996; pp 75−86. (j) Lukevics, E.; Pudova, O. A. *Chem. Heterocycl. Compd.* **1996**, *353*, 1605−1646. (k) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927−950.

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Results and Discussion

Syntheses. Bis[citrato(2−)-*O*^{3},*O*^{4}](morpholiniomethyl)germanate (**2**) was synthesized by reaction of trimethoxy(morpholinomethyl)germane (**4**) with citric acid (molar ratio 1:2) in acetonitrile at room temperature (Scheme 1). The λ^5*Ge*-germanate **2** was formed spontaneously in a precipitation reaction and isolated, after crystallization from water, in 83% yield as the crystalline hydrate **2**·H_2O. Bis[citrato(2−)-*O*^{3},*O*^{4}](morpholiniomethyl)silicate (**3**) was obtained analogously by reaction of trimethoxy(morpholinomethyl)silane (**5**) with citric acid (Scheme 1) and isolated as the crystalline hydrate **3**·H_2O (yield 90%). Although citric acid contains four OH groups, it reacts chemoselectively with **4** and **5** by using only its two OH groups bound to C-3 and C-4.

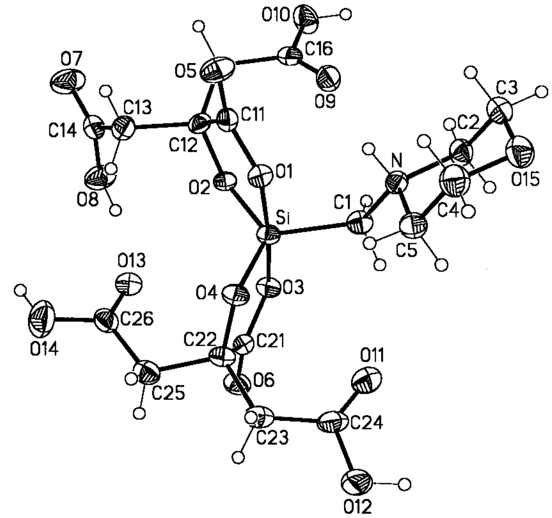
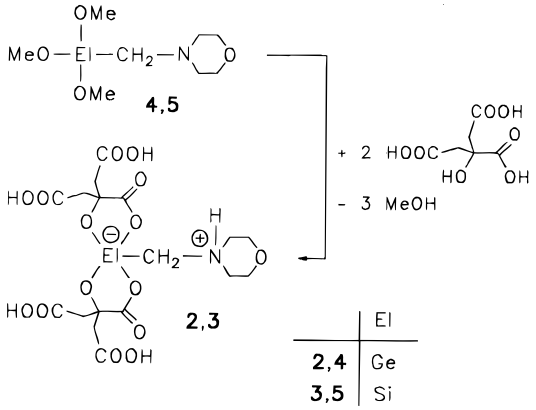


Figure 1. Molecular structure of **2** in the crystal of **2**·H_2O (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

Scheme 1



Compounds **2** and **3** as well as their hydrates **2**·H_2O and **3**·H_2O are almost insoluble in nonpolar organic solvents and also exhibit a very poor solubility in polar organic solvents. The identity of **2**, **2**·H_2O, **3**, and **3**·H_2O was established by elemental analyses (C, H, N) and solution-state ([D$_6$]DMSO) ^{1}H and ^{13}C NMR studies as well as mass spectrometric investigations (FAB MS). The silicon compounds **3** and **3**·H_2O were additionally characterized by solid-state ^{29}Si CP/MAS NMR studies and solution-state ([D$_6$]DMSO) ^{29}Si NMR experiments. In addition, the crystal structures of **2**·H_2O and **3**·H_2O were studied. These investigations unequivocally established the zwitterionic structure of **2** and **3** in the solid state and in solution (see Crystal Structure Analyses, NMR Studies, and Experimental Section).

Crystal Structure Analyses. The crystal structures of **2**·H_2O and **3**·H_2O were determined by single-crystal X-ray diffraction studies. The crystal data and experimental parameters used for these experiments are given in Table 1 (for further details, see Experimental Section). The molecular structures of the zwitterions **2** and **3** in the crystal of **2**·H_2O and **3**·H_2O are depicted in Figures 1 and 2; selected interatomic distances and angles are listed in Table 2.

The crystal structures of the Ge/Si analogues **2**·H_2O and **3**·H_2O are isotypic. Both compounds crystallize in the space group *Pbca*. The unit cell contains four Λ-enantiomers, four Δ-enantiomers, and eight water molecules each.

The coordination polyhedron around the Ge/Si atom can be described as a distorted trigonal bipyramid, each bidentate citrato(2−)-*O*^{3},*O*^{4} ligand spanning one equato-

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(3) Publications dealing with neutral λ^5*Ge*-germanium compounds: (a) Atovmyan, L. O.; Bleidelis, J.; Kemme, A. A.; Shibaeva, R. P. *Zh. Strukt. Khim.* **1970**, *11*, 318−322; *Chem. Abstr.* **1970**, *73*, 60116j. (b) Bilton, M. S.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1972**, 722−724. (c) Kemme, A. A.; Bleidelis, J.; Shibaeva, R. P.; Atovmyan, L. O. *Zh. Strukt. Khim.* **1973**, *14*, 103−107; *Chem. Abstr.* **1973**, *78*, 129422d. (d) Dräger, M. *Chem. Ber.* **1975**, *108*, 1723−1731. (e) Dräger, M. *Z. Anorg. Allg. Chem.* **1976**, *423*, 53−66. (f) Sheldrick, W. S.; Schomburg, D.; Wolfsberger, W. *Z. Naturforsch., B* **1978**, *33*, 493−497. (g) Breliére, C.; Carré, F.; Corriu, R. J. P.; De Saxcé, A.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1981**, *205*, C1−C3. (h) Vornefeld, M.; Huber, F.; Preut, H.; Brunner, H. *Appl. Organomet. Chem.* **1989**, *3*, 177−182. (i) Chadha, R. K.; Drake, J. E.; Sarkar, A. B.; Wong, M. L. Y. *Acta Crystallogr., Sect. C* **1989**, *45*, 37−40. (j) Zaitseva, G. S.; Mohammed, N.; Livantsova, L. I.; Tafeenko, V. A.; Aslanov, L. A.; Petrosyan, V. S. *Heteroat. Chem.* **1990**, *1*, 439−442. (k) Mozzchukhin, A. O.; Macharashvili, A. A.; Shklover, V. E.; Struchkov, Yu. T.; Shipov, A. G.; Sergeev, V. N.; Artamkin, S. A.; Pestunovich, S. V.; Baukov, Yu. I. *J. Organomet. Chem.* **1991**, *408*, 305−322. (l) Gurkova, S. N.; Gusev, A. I.; Alekseev, N. V.; Dombrova, O. A.; Gar, T. K. *Metalloorg. Khim.* **1991**, *4*, 611−613; *Chem. Abstr.* **1991**, *115*, 114668x. (m) Gurkova, S. N.; Gusev, A. I.; Viktorov, N. A.; Mironov, V. F. *Metalloorg. Khim.* **1991**, *4*, 614−617; *Chem. Abstr.* **1991**, *115*, 114669y. (n) Hencsei, P.; Párkányi, L.; Mironov, V. F. *Main Group Met. Chem.* **1991**, *14*, 13−18. (o) Orlova, N. A.; Shipov, A. G.; Baukov, Yu. I.; Mozzhukhin, A. O.; Antipin, M. Yu.; Struchkov, Yu. T. *Metalloorg. Khim.* **1992**, *5*, 666−672; *Chem. Abstr.* **1992**, *117*, 251439d. (p) Mozzhukhin, A. O.; Antipin, M. Yu.; Struchkov, Yu. T.; Shipov, A. G.; Kramarova, R. P.; Baukov, Yu. I. *Metalloorg. Khim.* **1992**, *5*, 906−916; *Chem. Abstr.* **1993**, *118*, 102109q. (q) Narula, S. P.; Soni, S.; Shankar, R.; Chadha, R. K. *J. Chem. Soc., Dalton Trans.* **1992**, 3055−3056. (r) Chiang, H.-C.; Lin, S.-M.; Ueng, C.-H. *Acta Crystallogr., Sect. C* **1992**, *48*, 991−993. (s) Ovchinnikov, Yu. E.; Struchkov, Yu. T.; Baryshok, V. P.; Ovchinnikova, Z. A.; Voronkov, M. G. *Dokl. Akad. Nauk* **1993**, *330*, 464−467; *Chem. Abstr.* **1994**, *120*, 66174n. (t) Chen, D. H.; Chiang, H. C. *J. Chin. Chem. Soc.* **1993**, *40*, 373−377; *Chem. Abstr.* **1994**, *120*, 123324n. (u) Chen, D. H.; Chiang, H. C. *Synth. React. Inorg. Met.-Org. Chem.* **1993**, *23*, 383−399. (v) Hencsei, P.; Párkányi, L.; Mironov, V. F. *Z. Kristallogr.* **1994**, *209*, 630−631. (w) Párkányi, L.; Hencsei, P.; Mironov, V. F. *Z. Kristallogr.* **1994**, *209*, 632−633. (x) Lukevics, E.; Belyakov, S.; Ignatovich, L.; Shilina, N. *Bull. Soc. Chim. Fr.* **1995**, *132*, 545−550. (y) Ossig, G.; Meller, A.; Freitag, S.; Müller, O.; Gornitzka, H.; Herbst-Irmer, R. *Organometallics* **1996**, *15*, 408−414. (z) Zhang, Z.; Chen, R. *Heteroat. Chem.* **1996**, *7*, 521−524.

(4) Publications dealing with anionic λ^5*Ge*-germanates: (a) Sau, A. C.; Day, R. O.; Holmes, R. R. *J. Am. Chem. Soc.* **1980**, *102*, 7972−7973. (b) Day, R. O.; Holmes, J. M.; Sau, A. C.; Holmes, R. R. *Inorg. Chem.* **1982**, *21*, 281−286. (c) Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 193−199. (d) Holmes, R. R.; Day, R. O.; Sau, A. C.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 600−606. (e) Holmes, R. R.; Day, R. O.; Sau, A. C.; Poutasse, C. A.; Holmes, J. M. *Inorg. Chem.* **1986**, *25*, 607−611. (f) Brauer, D. J.; Wilke, J.; Eujen, R. *J. Organomet. Chem.* **1986**, *316*, 261−269. (g) Denmark, S. E.; Jacobs, R. T.; Dai-Ho, G.; Wilson, S. *Organometallics* **1990**, *9*, 3015−3019. (h) Kawashima, T.; Nishiwaki, Y.; Okazaki, R. *J. Organomet. Chem.* **1995**, *499*, 143−146. (i) Chiang, H.-C.; Hwang, S.-F.; Ueng, C.-H. *Acta Crystallogr., Sect. C* **1995**, *51*, 1258−1260.

(5) Publications dealing with zwitterionic λ^5*Ge*-germanates: (a) Tacke, R.; Sperlich, J.; Becker, B. *Chem. Ber.* **1994**, *127*, 643−646. (b) Reference 2g. (c) Heermann, J.; Tacke, R.; Jones, P. G. In *Organosilicon Chemistry III—From Molecules to Materials*; Auner, N., Weis, J., Eds.; VCH: Weinheim, Germany, in press.

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of 2·H_2O and 3·H_2O

	2·H_2O	**3**·H_2O
empirical formula	$C_{17}H_{25}GeNO_{16}$	$C_{17}H_{25}NO_{16}Si$
formula mass, g mol^{-1}	571.97	527.47
collection *T*, K	193(2)	193(2)
λ(Mo Kα), Å	0.710 73	0.710 73
cryst syst	orthorhombic	orthorhombic
space group (No.)	*Pbca* (61)	*Pbca* (61)
a, Å	18.8097(4)	18.7129(4)
b, Å	11.8550(11)	11.9262(3)
c, Å	19.8732(11)	19.6319(5)
V, $Å^3$	4431.5(5)	4381.3(2)
Z	8	8
D(calcd), g cm^{-3}	1.715	1.599
μ, mm^{-1}	1.468	0.194
F(000)	2352	2208
cryst dimens, mm	0.8 × 0.7 × 0.7	0.7 × 0.5 × 0.4
2θ range, deg	4.10−51.02	4.14−51.12
index ranges	$0 \le h \le 14$, $0 \le k \le 13$, $0 \le l \le 23$	$0 \le h \le 14$, $0 \le k \le 14$, $0 \le l \le 23$
no. of coll reflns	22 860	22 789
no. of indep reflns	2793	2812
R_{int}	0.040	0.048
max/min transmission	0.5559/0.4396	0.9399/0.9345
no. of reflns used	2793	2812
no. of params	339	339
no. of restraints	1	1
S^a	1.240	1.099
weight params a/b^b	0.0095/8.9224	0.0449/3.9208
$R1^c$ [$I > 2\sigma(I)$]	0.0309	0.0392
$wR2^d$ (all data)	0.0698	0.0964
extinction coeff	0.0069(2)	0.0078(5)
max/min res electron dens, e $Å^{-3}$	+0.298/−0.312	+0.206/−0.243

[a] $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; *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] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [d] $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

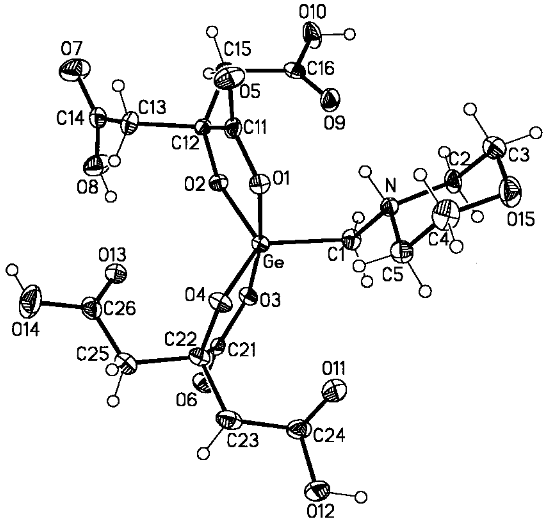

Figure 2. Molecular structure of **3** in the crystal of **3**·H_2O (probability level of displacement ellipsoids 50%), showing the atomic numbering scheme.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for 2·H_2O and 3·H_2O

	2·H_2O (El = Ge)	**3**·H_2O (El = Si)
El−O1	1.964(2)	1.824(2)
El−O2	1.803(2)	1.679(2)
El−O3	1.884(2)	1.763(2)
El−O4	1.781(2)	1.666(2)
El−C1	1.955(3)	1.888(3)
O1−El−O2	85.54(9)	87.87(8)
O1−El−O3	171.19(9)	175.11(9)
O1−El−O4	86.47(8)	86.91(8)
O1−El−C1	93.93(11)	93.61(9)
O2−El−O3	90.47(9)	90.15(8)
O2−El−O4	121.31(10)	124.29(9)
O2−El−C1	114.75(12)	114.36(10)
O3−El−O4	88.92(9)	90.52(8)
O3−El−C1	94.87(11)	91.28(9)
O4−El−C1	123.76(12)	121.31(11)

rial (O2, O4) and one axial site (O1, O3). In terms of the Berry pseudorotation coordinate, the dihedral angle method[6] shows that the geometry of the coordination polyhedron for the λ^5*Ge*-germanate **2**·H_2O is displaced by 14.0% from the ideal trigonal bipyramid toward the ideal square pyramid (pivot atom C1). For the λ^5*Si*-silicate **3**·H_2O a distortion of 13.4% was determined (pivot atom C1). These distortions are somewhat smaller than that observed for the related λ^5*Si*-silicate **1**·H_2O (Berry distortion 18.7%).[1j]

As expected from the presence of 7 potential proton-donating groups (one NH and six OH functions) and 16 potential acceptor atoms (oxygen atoms) in the asymmetric unit, a complex three-dimensional hydrogen-bonding system in the crystal of **2**·H_2O and **3**·H_2O is observed. Considering the relevant geometric parameters, for both compounds the existence of three bifurcate hydrogen bonds (one intramolecular N−H···O/O, one intramolecular O−H···O/O, and one intermolecular O−H···O/O interaction) and four intermolecular nonfurcate O−H···O hydrogen bonds per asymmetric unit can be assumed. All seven proton-donating groups and the acceptor atoms O1, O2 (twice), O5, O7, O8, O9, O11, O13, and O1W (water molecule) are involved in this hydrogen-bonding system.

NMR Studies. The isotropic ^{29}Si chemical shifts obtained in the solid-state CP/MAS NMR studies of **3** (δ −97.5) and **3**·H_2O (δ −100.7) clearly characterize the ^{29}Si resonances as arising from pentacoordinate silicon atoms. As these chemical shifts are very similar to that observed for **3** in [D_6]DMSO (δ −97.6), it is concluded that pentacoordinate silicon is also present in solution. Further evidence for this assumption comes from the ^{1}H and ^{13}C NMR studies of this compound (solvent [D_6]-DMSO). In accordance with the chiral nature of the λ^5*Si*-silicate framework of **3**, the two CCH_2COOH groups of both citrato(2−)-O^3,O^4 ligands and the two NCH_2C moieties of the morpholinio group are each diastereotopic (see Experimental Section). In addition, the ^{1}H chemical shifts observed for the NCH_2C (δ 3.3−4.0), $SiCH_2N$ (δ 2.57 (δ_A), 2.78 (δ_B)), and NH group (δ 7.4) of **3** in [D_6]DMSO clearly indicate the presence of an ammonium-type nitrogen atom and thus confirm the existence of the λ^5*Si*-silicate **3** in solution.

^{1}H and ^{13}C solution-state NMR studies (solvent [D_6]-DMSO) revealed that the analogous λ^5*Ge*-germanate **2** also exists in solution. The NMR data for **2** (see Experimental Section) are quite similar to those obtained for the silicon analogue **3**, whose pentacoordinate central atom could be established directly by ^{29}Si NMR spectroscopy. As the ^{1}H and ^{13}C NMR data for the ligands bound to the germanium (**2**) and silicon atom (**3**) are very similar, we conclude that the germanium

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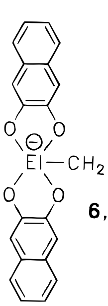
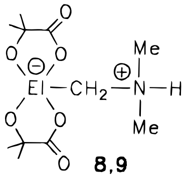
(6) (a) Muetterties, E. L.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1974**, *96*, 1748−1756. (b) Holmes, R. R.; Deiters, J. A. *J. Am. Chem. Soc.* **1977**, *99*, 3318−3326. (c) The degree of distortion was calculated by using the dihedral angle method described in ref 6a,b. All nine dihedral angles and the values for the reference geometry of the ideal square pyramid given in ref 6b were considered for this calculation.

atom is also pentacoordinated. Further evidence for the zwitterionic nature of **2** in solution comes from the characteristic resonance signal for the NH proton (δ 8.6), indicating the presence of the ammonium group.

Conclusions

The studies presented here clearly indicate that the chemistry of the title compounds is characterized by distinct similarities. The Ge/Si analogues **2** and **3** can be prepared by using the same synthetic route. Both zwitterions exist in solution ([D$_6$]DMSO), showing similar ^{1}H and ^{13}C NMR data. In addition, the crystal structures of the hydrates **2**$\cdot H_2O$ and **3**$\cdot H_2O$ are isotypic. These results are in agreement with the findings already reported for the zwitterionic λ^5*Ge*-germanates **6**$\cdot{}^1/_4CH_3CN$[5a] and **8**$\cdot H_2O$[5c] and their corresponding silicon analogues **7**$\cdot{}^1/_4CH_3CN$[1b,f] and **9**$\cdot H_2O$:[5c] The crystal structures of the Ge/Si pairs **6**$\cdot{}^1/_4CH_3CN$/**7**$\cdot{}^1/_4CH_3CN$ and **8**$\cdot H_2O$/**9**$\cdot H_2O$ are isotypic, and the solution-state ^{1}H and ^{13}C NMR data ([D$_6$]DMSO) of the corresponding Ge/Si analogues are also very similar.


6,7


8,9

	El
6,8	Ge
7,9	Si

Experimental Section

General Procedures. The syntheses were carried out under dry nitrogen. The organic solvents used were dried and purified according to standard procedures and stored under nitrogen. Melting points were determined with a Leitz Biomed microscope equipped with a heater (Leitz, Model M 350). ^{29}Si CP/MAS NMR spectra were recorded on a Bruker DSX-500 spectrometer at 11.74 T with double air bearing rotors of ZrO_2 (diameter 7 mm) containing 400 mg (**3**) and 170 mg (**3**$\cdot H_2O$), respectively, of sample (99.35 MHz; external standard TMS (δ 0)). The ^{1}H, ^{13}C, and ^{29}Si solution-state NMR spectra were recorded on a Bruker AMX-400 spectrometer (^{1}H, 400.1 MHz) and a Bruker DRX-300 spectrometer (^{1}H, 300.1 MHz; ^{13}C, 75.5 MHz; ^{29}Si, 59.6 MHz). $CDCl_3$ and [D$_6$]DMSO were used as solvents. Chemical shifts (ppm) were determined relative to internal $CHCl_3$ (^{1}H, δ 7.24; $CDCl_3$), $CDCl_3$ (^{13}C, δ 77.0; $CDCl_3$), [D$_5$]DMSO (^{1}H, δ 2.49; [D$_6$]DMSO), [D$_6$]DMSO (^{13}C, δ 39.5; [D$_6$]DMSO), and TMS (^{29}Si, δ 0; $CDCl_3$, [D$_6$]DMSO). All NMR experiments were carried out at room temperature. Assignment of the ^{13}C NMR data was supported by DEPT 135 experiments. Mass spectra were obtained with a Varian MAT 711 mass spectrometer (EI MS; 70 eV) and a Finnigan MAT-8430 mass spectrometer (FAB MS; 3-nitrobenzyl alcohol or glycerol as liquid matrix, xenon as FAB source), respectively. The selected m/z values given refer to the isotopes ^{1}H, ^{12}C, ^{14}N, ^{16}O, ^{28}Si, and ^{74}Ge.

Preparation of Bis[citrato(2−)-*O*^{3},*O*^{4}](morpholiniomethyl)germanate Hydrate (2$\cdot H_2O$). Citric acid (723 mg, 3.76 mmol) was dissolved in acetonitrile (40 mL). After addition of **4** (500 mg, 1.88 mmol) over a period of 3 min at room temperature (spontaneous formation of a precipitate), the reaction mixture was stirred for 5 min and then kept undisturbed at room temperature for 48 h. The crystalline precipitate was filtered off, washed with acetonitrile (2 × 10 mL), dried in vacuo (20 °C, 0.01 Torr, 2 h) (for characterization of **2**, see below), and then recrystallized from water (slow evaporation of the solvent at room temperature; crystallization time ca. 8 days; the first crystals formed after about 2 days). The resulting crystals were isolated by filtration and dried in the atmosphere (20 °C) to give **2**$\cdot H_2O$ in 83% yield as a colorless crystalline product (890 mg, 1.56 mmol); mp 214 °C. ^{1}H NMR (400.1 MHz, [D$_6$]DMSO): δ 2.45 (δ_A) and 2.55 (δ_B) (J_{AB} = 14.1 Hz, 4 H, CH_2COOH; overlapping with the [D$_5$]-DMSO resonance signal), 2.89 (δ_A) and 3.00 (δ_B) (J_{AB} = 16.7 Hz, 4 H, CH_2COOH), 3.25 (δ_A) and 3.28 (δ_B) (J_{AB} = 13.8 Hz, 2 H, $GeCH_2N$), 3.2−3.4 and 3.7−4.0 (m, 8 H, CCH_2N and CCH_2O; overlapping with the H_2O resonance signal), 8.6 (broad s, 1 H, NH), 12.2 (broad s, 4 H, COOH). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ 41.4 (C*C*H$_2$C), 44.5 (C*C*H$_2$C), 50.4 (Ge*C*H$_2$N), 54.1 (C*C*H$_2$N), 56.0 (C*C*H$_2$N), 62.8 (2 C, C*C*H$_2$O), 74.3 (C$_3$*C*O), 171.2 (C=O), 172.6 (C=O), 176.2 (C=O). FAB MS (negative ions, glycerol as matrix): m/z 554 [3%, M(zwitterion) − H$^+$], 183 [100%, matrix]. FAB MS (positive ions, glycerol as matrix): m/z 556 [<1%, M(zwitterion) + H$^+$], 185 [100%, matrix]. Anal. Calcd for $C_{17}H_{25}GeNO_{16}$: C, 35.70; H, 4.41; N, 2.45. Found: C, 35.5; H, 4.4; N, 2.5.

Data for **2**: colorless crystals, mp 242 °C. ^{1}H NMR (400.1 MHz, [D$_6$]DMSO) and ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): NMR data were identical with those obtained for **2**$\cdot H_2O$ (except for the missing H_2O resonance signal in the ^{1}H NMR spectrum). FAB MS (negative ions, glycerol as matrix): m/z 554 [2%, M − H$^+$], 183 [100%, matrix]. Anal. Calcd for $C_{17}H_{23}GeNO_{15}$: C, 36.86; H, 4.18; N, 2.53. Found: C, 36.7; H, 4.2; N, 2.5.

Preparation of Bis[citrato(2−)-*O*^{3},*O*^{4}](morpholiniomethyl)silicate Hydrate (3$\cdot H_2O$). Compound **3** was prepared analogously to the synthesis of **2** by reaction of **5** (1.00 g, 4.52 mmol) with citric acid (1.74 g, 9.06 mmol) in acetonitrile (100 mL) (spontaneous formation of a precipitate; for characterization of **3**, see below) and then recrystallized from water (slow evaporation of the solvent at room temperature; crystallization time ca. 9 days; the first crystals formed after about 2 days). The resulting crystals were isolated by filtration and dried in the atmosphere (20 °C) to give **3**$\cdot H_2O$ in 90% yield as a colorless crystalline product (2.14 g, 4.06 mmol); mp 218 °C (dec). ^{1}H NMR (300.1 MHz, [D$_6$]DMSO): δ 2.47 (δ_A) and 2.56 (δ_B) (J_{AB} = 13.6 Hz, 4 H, CH_2COOH; overlapping with the [D$_5$]-DMSO resonance signal), 2.57 (δ_A) and 2.78 (δ_B) (J_{AB} = 13.2 Hz, 2 H, $SiCH_2N$), 2.85 (δ_A) and 2.98 (δ_B) (J_{AB} = 16.6 Hz, 4 H, CH_2COOH), 3.3−4.0 (m, 8 H, CCH_2N and CCH_2O; overlapping with the H_2O resonance signal), 7.4 (broad s, 1 H, NH), 12.3 (broad s, 4 H, COOH). ^{13}C NMR (75.5 MHz, [D$_6$]DMSO): δ 40.7 (C*C*H$_2$C), 43.7 (C*C*H$_2$C), 48.4 (Si*C*H$_2$N), 53.4 (C*C*H$_2$N), 55.4 (C*C*H$_2$N), 62.9 (2 C, C*C*H$_2$O), 75.1 (C$_3$*C*O), 170.9 (C=O), 172.3 (C=O), 175.2 (C=O). ^{29}Si NMR (59.6 MHz, [D$_6$]DMSO, INEPT): δ −97.6. ^{29}Si CP/MAS NMR (spinning rate 4476 Hz, 200 transients, contact time 7 ms, 90° ^{1}H transmitter pulse length 5.5 μs, repetition time 25 s): δ −100.7. FAB MS (negative ions, glycerol as matrix): m/z 508 [18%, M(zwitterion) − H$^+$], 183 [100%, matrix]. FAB MS (positive ions, glycerol as matrix): m/z 510 [3%, M(zwitterion) + H$^+$], 185 [100%, matrix]. Anal. Calcd for $C_{17}H_{25}NO_{16}Si$: C, 38.71; H, 4.78; N, 2.66. Found: C, 38.5; H, 4.8; N, 2.6.

Data for **3**: colorless crystals, mp 243 °C (dec). ^{1}H NMR (300.1 MHz, [D$_6$]DMSO), ^{13}C NMR (75.5 MHz, [D$_6$]DMSO), and ^{29}Si NMR (59.6 MHz, [D$_6$]DMSO): NMR data were identical with those obtained for **3**$\cdot H_2O$ (except for the missing H_2O resonance signal in the ^{1}H NMR spectrum). ^{29}Si CP/MAS NMR (spinning rate 4192 Hz, 316 transients, contact time 7 ms, 90° ^{1}H transmitter pulse length 6.8 μs, repetition time 25 s): δ −97.5. FAB MS (negative ions, 3-nitrobenzyl alcohol as matrix): m/z 508 [100%, M − H$^+$]. FAB MS (positive ions, 3−nitrobenzyl alcohol as matrix): m/z 510 [32%, M + H$^+$], 154 [100%, matrix]. Anal. Calcd for $C_{17}H_{23}NO_{15}Si$: C, 40.08; H, 4.55; N, 2.75. Found: C, 40.0; H, 4.6; N, 2.7.

Preparation of Trimethoxy(morpholinomethyl)germane (4). A solution of (chloromethyl)trimethoxygermane[5a] (21.5 g, 100 mmol) and morpholine (21.8 g, 250 mmol) in methanol (100 mL) was stirred under reflux for 20 h. After the mixture was cooled to room temperature, the solvent and the excess morpholine were removed by distillation under reduced pressure, and *n*-pentane (150 mL) was added to the residue. The resulting precipitate was filtered off and the solvent removed from the filtrate under reduced pressure. The residue was distilled in vacuo (Vigreux column) to give **4** in 77% yield as a colorless liquid (20.4 g, 76.7 mmol); bp 79 °C, 0.05 Torr. ^{1}H NMR (300.1 MHz, $CDCl_3$): δ 2.4−2.5 (m, 4 H, NCH_2C), 2.69 (s, 2 H, $GeCH_2N$), 3.6−3.7 (m, 4 H, CCH_2O), 3.64 (s, 9 H, OCH_3). ^{13}C NMR (75.5 MHz, $CDCl_3$): δ 47.5 ($GeCH_2N$), 52.5 (OCH_3), 55.8 (NCH_2C), 66.8 (CCH_2O). EI MS: *m*/*z* 267 [2%, M^+], 100 [100%, $H_2C{=}NC_4H_8O^+$]. Anal. Calcd for $C_8H_{19}GeNO_4$: C, 36.14; H, 7.20; N, 5.27. Found: C, 36.3; H, 7.3; N, 5.3.

Crystal Structure Analyses of 2·H_2O and 3·H_2O. Suitable single crystals of **2**·H_2O and **3**·H_2O were obtained by crystallization of **2** and **3**, respectively, from water (slow evaporation of the solvent at room temperature). The crystals were mounted in inert oil (RS 3000, Riedel-deHaën) on a glass fiber and then transferred to the cold gas stream of the diffractometer (Stoe-Siemens-Huber four-circle diffractometer fitted with a Siemens CCD detector; graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å); for the low-temperature attachment, see ref 7). Cell parameters were obtained from least-squares fits to the settings of 512 reflections in the range 4° ≤ 2θ ≤ 50°. A semiempirical absorption correction for all data was applied. The structures were solved by direct methods.[8] All non-hydrogen atoms were refined anisotropically.[9] A riding model was employed in the refinement of the CH hydrogen atom positions. For both compounds the positions of the NH and OH hydrogen atoms were localized in difference Fourier syntheses and refined freely. Distance restraints were used in the refinement of the hydrogen atom positions of the water molecules.

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Supporting Information Available: Tables of anisotropic thermal parameters, atomic coordinates, and additional interatomic distances and angles for **2**·H_2O and **3**·H_2O (8 pages). Ordering information is given on any current masthead page.

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[7] Kottke, T.; Lagow, R. J.; Stalke, D. *J. Appl. Crystallogr.* **1996**, *29*, 465−468.

[8] Sheldrick, G. M. SHELXS-96; University of Göttingen, Göttingen, Germany, 1996. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467−473.

[9] Sheldrick, G. M. SHELXL-96; University of Göttingen, Göttingen, Germany, 1996.