

Dianionic Complexes with Hexacoordinate Silicon(IV) or Germanium(IV) and Three Bidentate Ligands of the Hydroximato(2–) Type: Syntheses and Structural Characterization in the Solid State

Andreas Biller, Christian Burschka, Martin Penka, and Reinhold Tacke*

Institut für Anorganische Chemie, Universität Würzburg, Am Hubland,
D-97074 Würzburg, Germany

Received March 7, 2002

Reaction of $\text{Si}(\text{OMe})_4$ with acetohydroxamic acid or benzohydroxamic acid and HNMe_2 (molar ratio 1:3:2) in MeCN yielded dimethylammonium *fac*-tris[acetohydroximato(2–)]silicate (*fac*-5) and *N,N*-dimethylacetamidinium *fac*-tris[benzohydroximato(2–)]silicate (*fac*-8), respectively. Reaction of $\text{Si}(\text{OMe})_4$ with benzohydroxamic acid and HNMe_2 (molar ratio 1:3:2) or ethane-1,2-diamine (molar ratio 1:3:1) in MeOH gave dimethylammonium *fac*-tris[benzohydroximato(2–)]silicate–methanol (*fac*-6·MeOH) and ethane-1,2-diammonium *mer*-tris[benzohydroximato(2–)]silicate–dimethanol (*mer*-9·2MeOH), respectively. Reaction of $\text{Ge}(\text{OMe})_4$ with benzohydroxamic acid and HNMe_2 (molar ratio 1:3:2) in MeOH resulted in the formation of dimethylammonium *fac*-tris[benzohydroximato(2–)]germanate–methanol (*fac*-7·MeOH). Single-crystal X-ray diffraction studies showed that the Si(Ge)-coordination polyhedra of the racemic hexacoordinate silicon (germanium) compounds *fac*-5, *fac*-6·MeOH, *fac*-7·MeOH, *fac*-8, and *mer*-9·2MeOH are distorted octahedra. All compounds were additionally characterized by solid-state VACP/MAS NMR studies (^{13}C , ^{15}N , ^{29}Si). The structural investigations were complemented by computational studies of the dianions of *fac*-5 and *mer*-5.

Introduction

In context with our studies on zwitterionic silicates with pentacoordinate silicon atoms,¹ we have recently reported on the synthesis and structural characterization of a series of neutral silicon(IV) complexes containing one or two bidentate ligands of the hydroximato(2–) type, such as compounds **1**,² **2**,² **3**,³ and **4**³ (Chart 1). We have now succeeded in synthesizing dianionic complexes with hexacoordinate silicon(IV) or germanium(IV) and three bidentate hydroximato(2–) ligands. We report here on the syntheses of compounds *fac*-5, *fac*-6·MeOH, *fac*-7·MeOH, *fac*-8, and *mer*-9·2MeOH and their structural characterization in the solid state (Chart 1). These experimental investigations were complemented by computational studies of the dianions of *fac*-5 and *mer*-5. The title compounds represent a new class

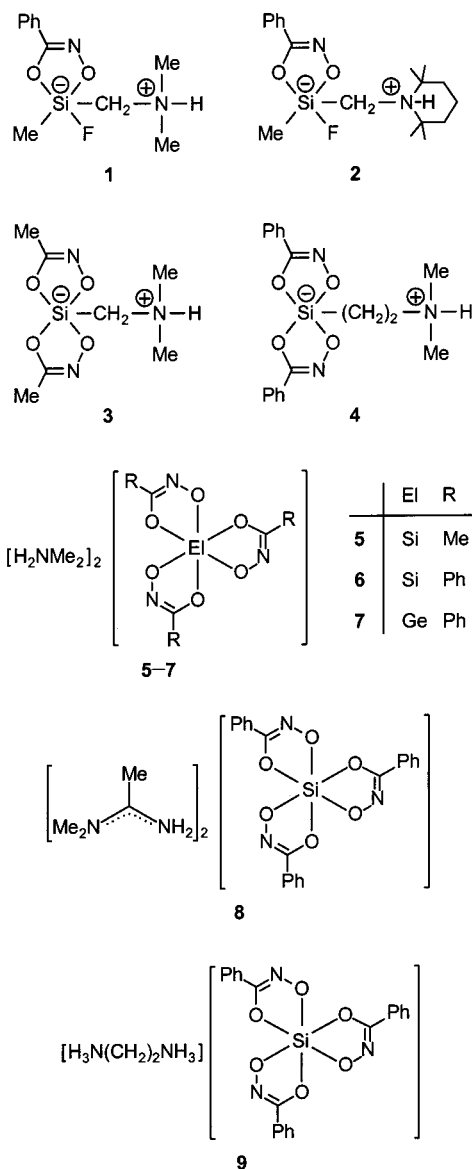
of complexes with hexacoordinate silicon or germanium (for reviews dealing with compounds of higher-coordinate silicon and germanium, see refs 4–6). Preliminary results of these studies have been reported elsewhere.⁷

- (4) Selected reviews dealing with higher-coordinate 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) Bassindale, A. R.; Taylor, P. G. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 1, pp 839–892. (d) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, U.K., 1989; Part 2, pp 1241–1288. (e) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17–31. (f) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371–1448. (g) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sperlich, J. *J. Organomet. Chem.* **1993**, *446*, 1–8. (h) Verkade, J. G. *Coord. Chem. Rev.* **1994**, *137*, 233–295. (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. (Engl. Transl.)* **1996**, *32*, 1381–1418. (k) Holmes, R. R. *Chem. Rev.* **1996**, *96*, 927–950. (l) Kost, D.; Kalikhman, I. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1339–1445. (m) Pestunovich, V.; Kirpichenko, S.; Voronkov, M. In *The Chemistry of Organic Silicon Compounds*; Rappoport, Z., Apeloig, Y., Eds.; Wiley: Chichester, U.K., 1998; Vol. 2, Part 2, pp 1447–1537.

* To whom correspondence should be addressed. E-mail: r.tacke@mail.uni-wuerzburg.de. Phone: (+49)931-888-5250. Fax: (+49)931-888-4609.

- (1) Review dealing with zwitterionic $\lambda^5\text{Si}$ -silicates: Tacke, R.; Pülm, M.; Wagner, B. *Adv. Organomet. Chem.* **1999**, *44*, 221–273 and references therein.
(2) Tacke, R.; Bertermann, R.; Dannappel, O.; Neugebauer, R. E.; Pülm, M.; Willeke, R. *Inorg. Chem.* **2001**, *40*, 2520–2527.
(3) Tacke, R.; Bertermann, R.; Biller, A.; Dannappel, O.; Penka, M.; Pülm, M.; Willeke, R. *Z. Anorg. Allg. Chem.* **2000**, *626*, 1159–1173.

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. Melting points were determined with a Büchi Melting Point B-450 apparatus using samples in sealed capillaries. Solid-state ^{13}C , ^{15}N , and ^{29}Si VACP/MAS NMR spectra were recorded at 22 °C on a Bruker DSX-400 NMR spectrometer with bottom layer rotors of ZrO_2 (diameter 7 mm) containing ca. 300 mg of sample (^{13}C , 100.6 MHz; ^{15}N , 40.6 MHz; ^{29}Si , 79.5 MHz; external standard, TMS (^{13}C , ^{29}Si ; δ 0) or glycine (^{15}N ; δ -342); spinning rate, 5–6.5 kHz; contact time, 1 ms (^{13}C), 3 ms (^{15}N), or 5 ms (^{29}Si); 90° ^1H transmitter pulse length, 3.6 μs ; repetition time, 4 s).

(5) Review dealing with higher-coordinate silicon and germanium compounds: Wong, C. Y.; Woollins, J. D. *Coord. Chem. Rev.* **1994**, *130*, 175–241.

(6) Review dealing with higher-coordinate germanium compounds: Gel'mbol'dt, V. O. *Russ. J. Coord. Chem.* **1997**, *23*, 299–310.

(7) (a) Richter, I.; Biller, A.; Burschka, C.; Penka, M.; Tacke, R. *33rd Organosilicon Symposium*; Saginaw, MI, April 6–8, 2000; Abstract PB-18. (b) Biller, A.; Richter, I.; Seiler, O.; Tacke, R. *The 9th International Conference on Inorganic Ring Systems*; Saarbrücken, Germany, July 23–28, 2000; Abstract P-111.

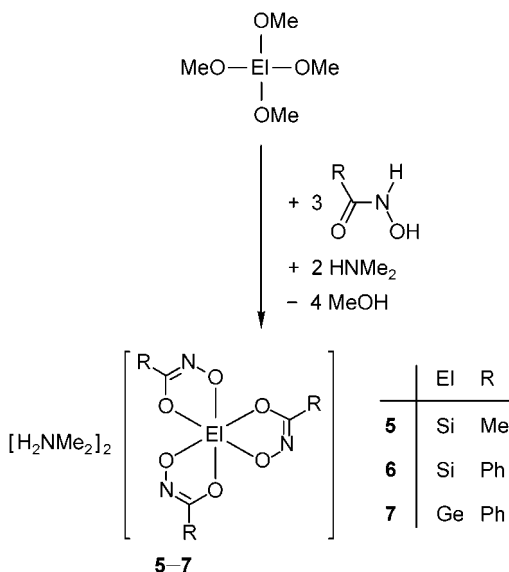
Dimethylammonium *fac*-Tris[acetohydroximato(2-)]silicate (*fac*-5). A cold solution (-20°C) of dimethylamine (5.00 g, 111 mmol) in acetonitrile (20 mL) was added dropwise at -20°C to a stirred solution of acetohydroxamic acid (1.24 g, 16.5 mmol) and tetramethoxysilane (837 mg, 5.50 mmol) in acetonitrile (50 mL). The reaction mixture was stirred at -20°C for 1 h and then allowed to warm to room temperature without further stirring and kept undisturbed for 48 h. The resulting precipitate was isolated by filtration, washed with cold acetonitrile (3×5 mL), and then dried in vacuo (0.01 Torr, 20°C , 8 h) to give 1.18 g (63% yield) of a colorless crystalline product. Mp: 130°C (dec). ^{13}C VACP/MAS NMR (878 transients): δ 15.0–15.6 and 16.5–17.0 (CCH₃); 33.5–36.8 (NCH₃); 158.9–161.5 (C=N). ^{15}N VACP/MAS NMR (15144 transients): δ -352.3 and -350.9 (br, NCH₃); -87.6, -86.7, and -85.7 (C=N). ^{29}Si VACP/MAS NMR (71 transients): δ -139.8. Anal. Calcd for $\text{C}_{10}\text{H}_{25}\text{N}_5\text{O}_6\text{Si}$: C, 35.39; H, 7.42; N, 20.63. Found: C, 35.08; H, 7.32; N, 20.84.

Dimethylammonium *fac*-Tris[benzohydroximato(2-)]silicate–Methanol (*fac*-6·MeOH). The synthesis was carried out analogously to that of compound *fac*-5 by combining a solution of dimethylamine (5.00 g, 111 mmol) in methanol (20 mL) with a solution of benzohydroxamic acid (2.26 g, 16.5 mmol) and tetramethoxysilane (837 mg, 5.50 mmol) in methanol (20 mL). The resulting precipitate was isolated by filtration, washed with cold methanol (3×5 mL), and then dried in vacuo (0.01 Torr, 20°C , 8 h) to give 1.85 g (60% yield) of a colorless crystalline product. Mp: 169°C (dec). ^{13}C VACP/MAS NMR (14064 transients): δ 34.9 and 35.6 (NCH₃); 49.4 (CH₃OH); 123.0–134.4 (C₆H₅; complex system, signals not assigned); 162.2, 163.7, and 164.2 (C=N). ^{15}N VACP/MAS NMR (3110 transients): δ -352.5 and -350.7 (NCH₃); -99.4, -94.5, and -85.4 (C=N). ^{29}Si VACP/MAS NMR (20 transients): δ -138.1. Anal. Calcd for $\text{C}_{26}\text{H}_{35}\text{N}_5\text{O}_7\text{Si}$: C, 56.00; H, 6.33; N, 12.56. Found: C, 55.68; H, 6.09; N, 12.59.

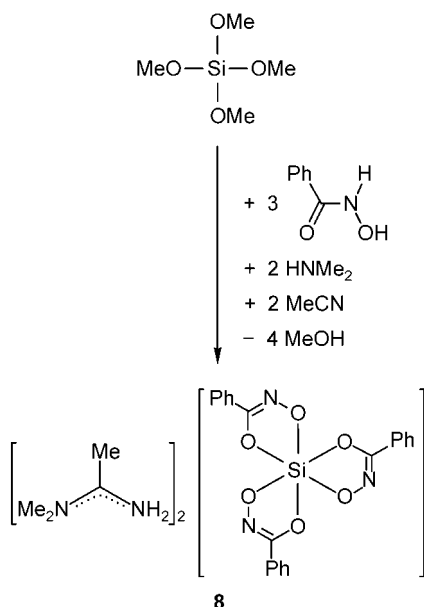
Dimethylammonium *fac*-Tris[benzohydroximato(2-)]germanate–Methanol (*fac*-7·MeOH). The synthesis was carried out analogously to that of compound *fac*-5 by combining a solution of dimethylamine (5.00 g, 111 mmol) in methanol (20 mL) with a solution of benzohydroxamic acid (2.26 g, 16.5 mmol) and tetramethoxygermane (1.08 g, 5.49 mmol) in methanol (20 mL). After the reaction mixture was stirred at -20°C for 1 h, it was kept undisturbed at -26°C for 96 h. The resulting precipitate was isolated by filtration, washed with cold methanol (3×5 mL), and then dried in vacuo (0.01 Torr, 20°C , 8 h) to give 2.41 g (73% yield) of a colorless crystalline product. Mp: 158°C (dec). ^{13}C VACP/MAS NMR (621 transients): δ 34.9 and 35.3 (NCH₃); 49.1 (CH₃OH); 120.7–134.9 (C₆H₅; complex system, signals not assigned); 161.6, 163.5, and 163.7 (C=N). ^{15}N VACP/MAS NMR (14692 transients): δ -350.8 (br, NCH₃); -101.3, -94.8, and -86.1 (C=N). Anal. Calcd for $\text{C}_{26}\text{H}_{35}\text{GeN}_5\text{O}_7$: C, 51.86; H, 5.86; N, 11.63. Found: C, 51.76; H, 5.64; N, 11.63.

***N,N*-Dimethylacetamidinium *fac*-Tris[benzohydroximato(2-)]silicate (*fac*-8).** The synthesis was carried out analogously to that of compound *fac*-5 by combining a solution of dimethylamine (5.00 g, 111 mmol) in acetonitrile (20 mL) with a solution of benzohydroxamic acid (2.26 g, 16.5 mmol) and tetramethoxysilane (837 mg, 5.50 mmol) in acetonitrile (50 mL). The resulting precipitate was isolated by filtration, washed with cold acetonitrile (3×5 mL), and then dried in vacuo (0.01 Torr, 20°C , 8 h) to give 1.67 g (50% yield) of a colorless crystalline product. Mp: 183°C (dec). ^{13}C VACP/MAS NMR (442 transients): δ 19.5 and 21.6 (CCH₃); 38.5, 40.4 (2 C), and 41.6 (NCH₃); 121.3–136.1 (C₆H₅; complex system, signals not assigned); 159.1, 160.4, and 161.0

Scheme 1



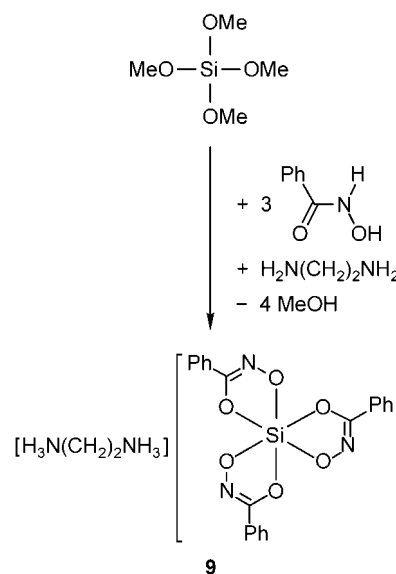
Scheme 2



(C=N); 165.0 and 167.8 (CCN₂). ¹⁵N VACP/MAS NMR (19820 transients): δ -275.4 and -271.8 (NCH₃); -258.0 and -254.3 (CCN₂); -91.1, -78.8, and -77.4 (C=N). ²⁹Si VACP/MAS NMR (75 transients): δ -137.8. Anal. Calcd for C₂₉H₃₇N₇O₆Si: C, 57.31; H, 6.14; N, 16.13. Found: C, 56.93; H, 5.99; N, 15.74.

Ethane-1,2-diammonium mer-Tris[benzohydroximato(2-)]-silicate-Dimethanol (mer-9·2MeOH). Ethane-1,2-diamine (301 mg, 5.01 mmol) was added dropwise at room temperature to a stirred solution of benzohydroxamic acid (2.06 g, 15.0 mmol) and tetramethoxysilane (761 mg, 5.00 mmol) in methanol (30 mL) and the reaction mixture then kept undisturbed at room temperature for 96 h. The resulting precipitate was isolated by filtration, washed with cold methanol (3 × 5 mL), and then dried in vacuo (0.01 Torr, 20 °C, 8 h) to give 2.17 g (78% yield) of a colorless crystalline product. Mp: 150 °C (dec). ¹³C VACP/MAS NMR (598 transients): δ 36.1 and 39.5 (NCH₂); 49.4 (br, CH₃OH); 115.8–135.6 (C₆H₅; complex system, signals not assigned); 160.5 (2 C) and 164.3 (C=N). ¹⁵N VACP/MAS NMR (20989 transients): δ -351.8 and -346.2 (NCH₂); -98.5, -93.3, and -80.1 (C=N). ²⁹Si VACP/

Scheme 3



MAS NMR (251 transients): δ -139.5. Anal. Calcd for C₂₅H₃₃N₅O₈-Si: C, 53.65; H, 5.94; N, 12.51. Found: C, 53.64; H, 5.65; N, 13.01.

Crystal Structure Analyses. Suitable single crystals of *fac*-**5**, *fac*-**6**·MeOH, *fac*-**7**·MeOH, *fac*-**8**, and *mer*-**9**·2MeOH were obtained directly from the respective reaction mixtures. The crystals were mounted in inert oil (perfluoroalkyl ether, ABCR) on a glass fiber and then transferred to the cold nitrogen gas stream of the diffractometer (*fac*-**5**, *fac*-**6**·MeOH, *fac*-**8**, and *mer*-**9**·2MeOH, Stoe IPDS diffractometer, graphite-monochromated Mo K α radiation (λ = 0.71073 Å); *fac*-**7**·MeOH, Bruker Smart-Apex CCD diffractometer, graphite-monochromated Mo K α radiation (λ = 0.71073 Å)). For the structure determination of *fac*-**7**·MeOH, an empirical absorption correction was applied.⁸ All structures were solved by direct methods.⁹ The non-hydrogen atoms were refined anisotropically.¹⁰ A riding model was employed in the refinement of the CH hydrogen atoms. The NH and OH hydrogen atoms of the cations and the solvent molecules were localized in difference Fourier syntheses and refined freely.

Computational Studies. MP2 geometry optimizations of the dianions of *fac*-**5** and *mer*-**5** were carried out at the TZP (triple- ζ plus polarization)¹¹ level using the program system TURBOMOLE.¹² For the *fac* isomer, ideal C₃ symmetry served as the starting geometry. In the case of the *mer* isomer (C₁ symmetry), a starting geometry related to the experimentally established crystal structure of the dianion of *mer*-**9** was used (replacement of the phenyl moieties by methyl groups). For both dianions, the critical points of the potential energy surfaces were characterized as local minima

- (8) Sheldrick, G. M. *SADABS 2.0*; University of Göttingen: Göttingen, Germany, 2000.
- (9) Sheldrick, G. M. *SHELXS-97*; University of Göttingen: Göttingen, Germany, 1997. Sheldrick, G. M. *Acta Crystallogr., Sect. A* **1990**, *46*, 467–473.
- (10) Sheldrick, G. M. *SHELXL-97*; University of Göttingen: Göttingen, Germany, 1997.
- (11) Schäfer, A.; Horn, H.; Ahlrichs, R. *J. Chem. Phys.* **1992**, *97*, 2571–2577.
- (12) Program system TURBOMOLE: Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kömel, C. *Chem. Phys. Lett.* **1989**, *162*, 165–169. TZP basis sets used for the dianions of *fac*-**5** and *mer*-**5** (in this context, see also: Tacke, R.; Becht, J.; Dannappel, O.; Ahlrichs, R.; Schneider, U.; Sheldrick, W. S.; Hahn, J.; Kiesgen, F. *Organometallics* **1996**, *15*, 2060–2077): Si, (12s9p1d)/[7s5p1d]; O, C, and N, (10s6p1d)/[6s3p1d]; H, (5s1p)/[3s1p].

Table 1. Crystal Data and Experimental Parameters for the Crystal Structure Analyses of *fac-5*, *fac-6*·MeOH, *fac-7*·MeOH, *fac-8*, and *mer-9*·2MeOH

	<i>fac-5</i>	<i>fac-6</i> ·MeOH	<i>fac-7</i> ·MeOH	<i>fac-8</i>	<i>mer-9</i> ·2MeOH
empirical formula	C ₁₀ H ₂₅ N ₅ O ₆ Si	C ₂₆ H ₃₅ N ₅ O ₇ Si	C ₂₆ H ₃₅ GeN ₅ O ₇	C ₂₉ H ₃₇ N ₇ O ₆ Si	C ₂₅ H ₃₃ N ₅ O ₈ Si
formula mass, g mol ⁻¹	339.44	557.68	602.18	607.75	559.65
collection <i>T</i> , K	173(2)	173(2)	173(2)	173(2)	173(2)
λ (Mo K α), Å	0.71073	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	triclinic	triclinic	monoclinic	triclinic
space group (No.)	C2/c (15)	P1̄ (2)	P1̄ (2)	P2 ₁ /c (14)	P1̄ (2)
<i>a</i> , Å	18.833(4)	10.4703(13)	10.5258(4)	9.984(2)	8.6410(15)
<i>b</i> , Å	12.566(3)	11.404(2)	11.5067(5)	16.883(3)	11.3339(15)
<i>c</i> , Å	17.390(4)	12.3215(16)	12.3019(5)	18.019(4)	14.2957(19)
α , deg	90	89.555(18)	89.2530(10)	90	99.348(16)
β , deg	121.18(3)	76.889(15)	76.2080(10)	94.21(3)	93.218(18)
γ , deg	90	83.275(18)	83.0500(10)	90	98.806(18)
<i>Z</i>	8	2	2	4	2
μ , mm ⁻¹ /abs corr	0.167/none	0.134/none	1.118/empirical	0.132/none	0.143/none
2 θ range, deg	4.12–52.78	4.90–56.36	3.40–56.62	4.54–52.76	4.78–52.74
no. of collected rflns	9000	18620	16751	27639	8913
no. of indep rflns	3428	6343	6519	6117	5126
<i>R</i> _{int}	0.0637	0.0302	0.0308	0.0523	0.0622
<i>S</i> ^a	0.970	1.016	0.998	1.032	0.961
<i>R</i> 1 ^b [<i>I</i> > 2 σ (<i>I</i>)]	0.0362	0.0348	0.0342	0.0391	0.0419
<i>wR</i> 2 ^c (all data)	0.1047	0.0918	0.0832	0.1065	0.1077
max/min resid electron density, e Å ⁻³	+0.238/−0.254	+0.266/−0.259	+0.628/−0.292	+0.331/−0.310	+0.386/−0.329

^a $S = \{\sum[w(F_o^2 - F_c^2)^2]/(n - p)\}^{0.5}$; *n* = no. of reflections; *p* = no. of parameters. ^b $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^c $wR2 = \{\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]\}^{0.5}$.

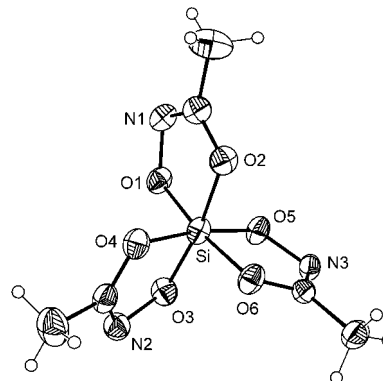
Table 2. Selected Interatomic Distances (Å) and Angles (deg) for the Dianions of *fac-5*, *fac-6*·MeOH, *fac-7*·MeOH, *fac-8*, and *mer-9*·2MeOH

	<i>fac-5</i> (El = Si)	<i>fac-6</i> ·MeOH (El = Si)	<i>fac-7</i> ·MeOH (El = Ge)	<i>fac-8</i> (El = Si)	<i>mer-9</i> ·2MeOH (El = Si)
El–O1	1.7513(13)	1.7892(10)	1.8905(12)	1.7744(12)	1.7660(14)
El–O2	1.7956(13)	1.7749(10)	1.8747(12)	1.7786(13)	1.7788(13)
El–O3	1.7744(13)	1.7868(10)	1.8906(12)	1.7819(13)	1.7846(14)
El–O4	1.7822(11)	1.7845(10)	1.8919(12)	1.7960(13)	1.7838(13)
El–O5	1.7608(11)	1.7689(11)	1.8741(12)	1.7714(13)	1.7726(14)
El–O6	1.7840(13)	1.7811(10)	1.8859(12)	1.7950(12)	1.7845(14)
O1–El–O2	85.65(6)	85.70(4)	83.59(5)	85.92(5)	86.39(6)
O1–El–O3	89.01(6)	88.69(5)	89.26(5)	88.79(5)	96.19(6)
O1–El–O4	98.24(6)	95.83(5)	96.89(5)	95.74(6)	87.31(6)
O1–El–O5	89.19(6)	87.77(5)	88.37(5)	90.31(6)	174.76(6)
O1–El–O6	172.14(5)	171.93(5)	169.47(5)	173.66(6)	89.79(6)
O2–El–O3	171.29(6)	170.88(5)	167.88(5)	172.06(6)	87.60(6)
O2–El–O4	88.48(6)	88.43(5)	88.22(5)	89.23(5)	170.63(7)
O2–El–O5	97.00(6)	97.85(5)	99.70(6)	96.13(6)	91.94(6)
O2–El–O6	89.31(6)	89.84(5)	90.40(5)	89.66(5)	95.54(6)
O3–El–O4	85.47(6)	85.00(5)	82.92(5)	85.41(5)	86.19(6)
O3–El–O5	89.79(6)	89.09(5)	89.84(5)	89.81(6)	88.69(6)
O3–El–O6	96.69(7)	96.55(5)	98.06(6)	96.07(5)	173.41(6)
O4–El–O5	171.10(6)	172.99(5)	170.97(5)	172.19(6)	94.92(7)
O4–El–O6	87.63(6)	90.76(5)	91.53(5)	88.72(5)	91.37(6)
O5–El–O6	85.44(6)	86.18(5)	84.13(5)	85.65(5)	85.42(6)

by calculation of the vibrational frequencies. The calculated energies of the dianions of *fac-5* and *mer-5* include the MP2 energies and the zero point vibrational energies obtained by HF calculations.¹³

Results and Discussion

Syntheses. Compound *fac-5* was obtained according to Scheme 1 by reaction of tetramethoxysilane with 3 molar equiv of acetohydroxamic acid and 2 molar equiv of dimethylamine in acetonitrile (formation of 4 molar equiv of methanol). Compound *fac-6*·MeOH (*fac-7*·MeOH) was prepared analogously, starting from tetramethoxysilane (tetramethoxygermane), benzohydroxamic acid, and dimethylamine and using methanol as the solvent (Scheme 1).

**Figure 1.** Structure of the dianion in the crystal of *fac-5* (probability level of displacement ellipsoids 50%).

(13) Calculated energies (MP2 + E(vib0) energies (Hartree)): dianion of *fac-5*, −1137.0709310 (*C*₃ symmetry); dianion of *mer-5*, −1137.0702241 (*C*₁ symmetry).

Treatment of tetramethoxysilane with benzohydroxamic acid and dimethylamine in acetonitrile (instead of methanol);

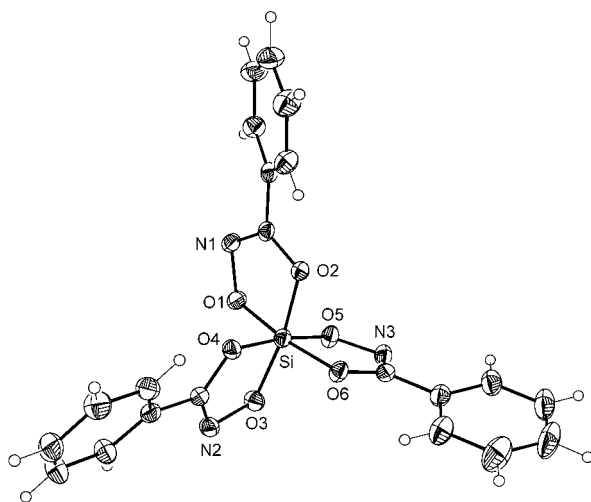


Figure 2. Structure of the dianion in the crystal of *fac-6*·MeOH (probability level of displacement ellipsoids 50%).

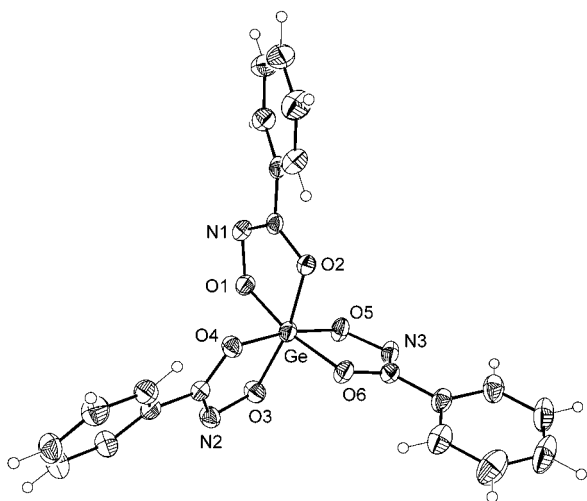


Figure 3. Structure of the dianion in the crystal of *fac-7*·MeOH (probability level of displacement ellipsoids 50%).

see synthesis of *fac-6*·MeOH) afforded compound *fac-8* (Scheme 2). Interestingly, under the reaction conditions used, dimethylamine reacted with the solvent to form *N,N*-dimethylacetamide, which upon protonation afforded the *N,N*-dimethylacetamidinium cation.

Treatment of tetramethoxysilane with 3 molar equiv of benzohydroxamic acid and 1 molar equiv of ethane-1,2-diamine in methanol gave compound *mer-9*·2MeOH (Scheme 3).

All products were isolated as crystalline solids (yield: *fac-5*, 63%; *fac-6*·MeOH, 60%; *fac-7*·MeOH, 73%; *fac-8*, 50%; *mer-9*·2MeOH, 78%). Their identities were established by elemental analyses (C, H, N), solid-state VACP/MAS NMR experiments (^{13}C , ^{15}N , ^{29}Si), and crystal structure analyses.

In conclusion, the synthetic approach used for the preparation of the title compounds can result in the formation of both *fac*- and *mer*-configured $\lambda^6\text{Si}$ -silicate dianions.¹⁴ The respective configuration of the dianions in the crystal depends in a nonpredictable manner on the specific combination of diolato(2-) ligand, cation, and solvent used.

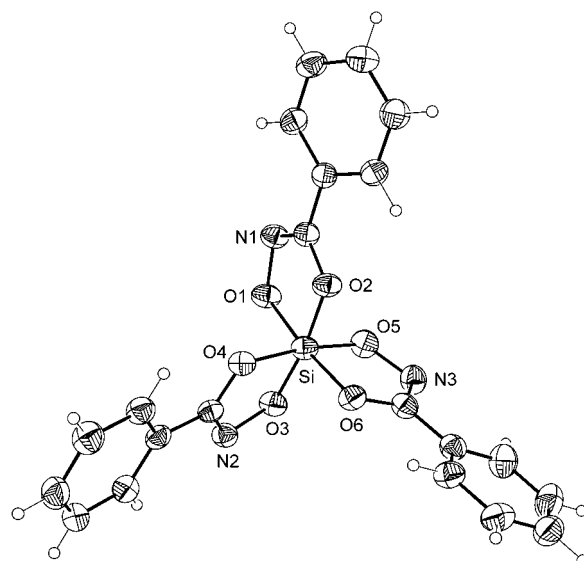


Figure 4. Structure of the dianion in the crystal of *fac-8* (probability level of displacement ellipsoids 50%).

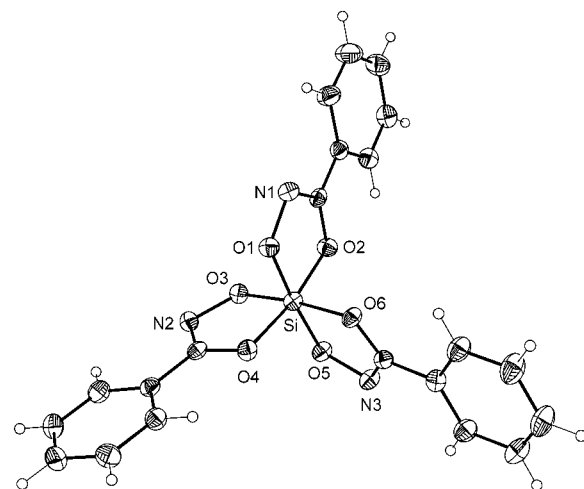


Figure 5. Structure of the dianion in the crystal of *mer-9*·2MeOH (probability level of displacement ellipsoids 50%).

Crystal Structure Analyses. Compounds *fac-5*, *fac-6*·MeOH, *fac-7*·MeOH, *fac-8*, and *mer-9*·2MeOH were structurally characterized by single-crystal X-ray diffraction. The crystal data and the experimental parameters used for these experiments are summarized in Table 1; selected interatomic distances and angles are listed in Table 2. The structures of the respective dianions in the crystal are depicted in Figures 1–5.

All dianions investigated are chiral, and the crystals contain pairs of the respective Λ - and Δ -enantiomers. As can be seen from Figures 1–5 and Table 2, all Si(Ge)-coordination polyhedra can be described as distorted octahedra. The O–Si–O (O–Ge–O) angles are in the ranges 85.00(5)–

(14) In this context it should be mentioned that treatment of tetramethoxysilane with benzohydroxamic acid and pyrrolidine (molar ratio 1:3:2) in methanol yielded pyrrolidinium *mer*-tris[benzohydroximato(2-)]-silicate—"trimethanol". The structure of this compound was established by single-crystal X-ray diffraction. As the quality of the crystal structure analysis is not sufficient to be published (three crystallographically independent methanol molecules; occupation factors 0.56, 0.86, and 1.00), the data were not included in this article.

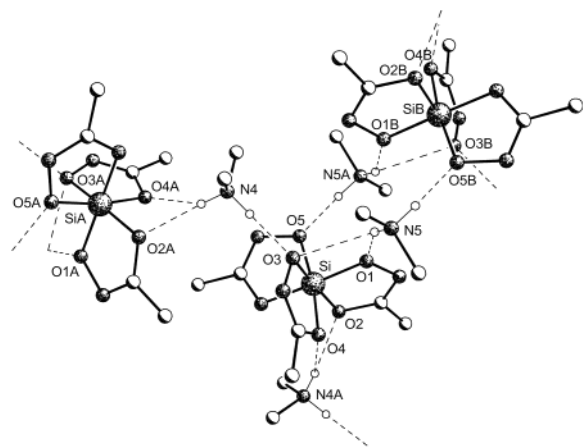


Figure 6. Hydrogen-bonding system in the crystal of *fac-5*. The dashed lines indicate intermolecular hydrogen bonds between the two crystallographically independent cations and the dianion, leading to an infinite two-dimensional network parallel to the plane [100]. The hydrogen atoms (except for the NH atoms) are omitted for clarity. Hydrogen-bonding geometries²⁰ (Å, deg): N4–H4A 0.86(2), H4A···O2 2.05(3), N4···O2 2.860(2), N4–H4A···O2 156(2), H4A···O4 2.59(2), N4···O4 3.280(2), N4–H4A···O4 138(2), O2···H4A···O4 63.8(6); N4–H4B 0.93(2), H4B···O3 1.78(2), N4···O3 2.702(2), N4–H4B···O3 171(2); N5–H5A 0.95(2), H5A···O5 1.75(2), N5···O5 2.702(2), N5–H5A···O5 177(2); N5–H5B 0.86(2), H5B···O1 2.01(2), N5···O1 2.788(2), N5–H5B···O1 149(2), H5B···O3 2.53(2), N5···O3 3.198(2), N5–H5B···O3 135(2), O1···H5B···O3 64.8(7).

98.24(6)° (82.92(5)–99.70(6)°) and 170.63(7)–174.76(6)° (167.88(5)–170.97(5)°), and the Si–O (Ge–O) distances amount to 1.7513(13)–1.7960(13) Å (1.8741(12)–1.8919(12) Å). These distances are similar to those reported for the tris[benzene-1,2-diolato(2–)]silicate^{15–18} dianion and the tris[benzene-1,2-diolato(2–)]germanate^{18,19} dianion.

As expected from the presence of the potential NH and OH (*fac-6*·MeOH, *fac-7*·MeOH, *mer-9*·2MeOH) donor functions and the potential nitrogen and oxygen acceptor atoms, complex hydrogen-bonding systems were observed in the crystals of *fac-5*, *fac-6*·MeOH, *fac-7*·MeOH, *fac-8*, and *mer-9*·2MeOH (Figures 6–9).²⁰ Undoubtedly, these hydrogen bonds play a major role for the crystal structures investigated.

Compound *fac-5* forms two intermolecular bifurcate N–H···O/O and two intermolecular nonfurcate N–H···O hydrogen bonds, leading to an infinite two-dimensional network in the crystal (Figure 6). The hydrogen-bonding systems of *fac-6*·MeOH and its germanium analogue *fac-7*·MeOH both are characterized by one intermolecular trifurcate N–H···N/O/O and one intermolecular nonfurcate N–H···N interaction as well as two intermolecular nonfurcate N–H···O hydrogen bonds, leading to centrosymmetric

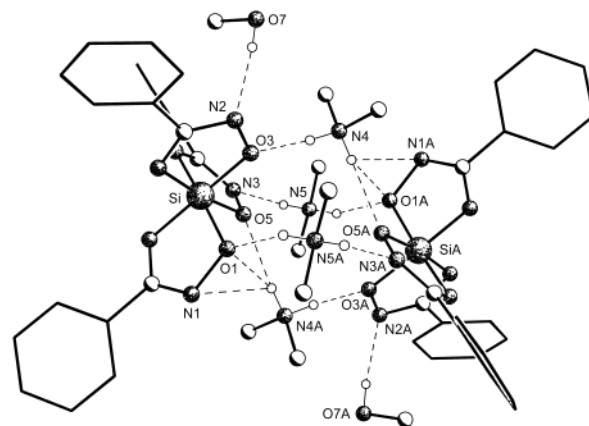


Figure 7. Hydrogen-bonding system in the crystal of *fac-6*·MeOH. The dashed lines indicate intermolecular hydrogen bonds between the two crystallographically independent cations and the dianion and between the MeOH molecule and the dianion, leading to centrosymmetric aggregates. The hydrogen atoms (except for the NH and OH atoms) are omitted for clarity, and the phenyl groups are represented as stick models. Hydrogen-bonding geometries²⁰ (Å, deg): N4–H4A 0.929(18), H4A···O3 1.784(18), N4···O3 2.7116(17), N4–H4A···O3 175.6(15); N4–H4B 0.912(18), H4B···N1 2.596(18), N4···N1 3.1910(18), N4–H4B···N1 123.5(14), H4B···O1 2.160(18), N4···O1 3.0102(16), N4–H4B···O1 154.9(16), H4B···O5 2.198(17), N4···O5 2.8986(16), N4–H4B···O5 133.1(15), N1···H4B···O1 33.7(3), N1···H4B···O5 89.2(6), O1···H4B···O5 68.9(5); N5–H5A 0.921(19), H5A···N3 1.898(19), N5···N3 2.8150(18), N5–H5A···N3 173.2(16); N5–H5B 0.927(18), H5B···O1 1.867(18), N5···O1 2.7583(16), N5–H5B···O1 160.6(16); O7–H7A 0.89(2), H7A···N2 2.00(2), O7···N2 2.8674(18), O7–H7A···N2 165(2). For the isotopic germanium analogue *fac-7*·MeOH, an analogous hydrogen-bonding system was observed: N4–H4A 0.92(2), H4A···O3 1.81(2), N4···O3 2.729(2), N4–H4A···O3 174.6(18); N4–H4B 0.82(2), H4B···N1 2.59(2), N4···N1 3.161(2), N4–H4B···N1 127.9(19), H4B···O1 2.15(2), N4···O1 2.927(2), N4–H4B···O1 159(2), H4B···O5 2.40(2), N4···O5 2.980(2), N4–H4B···O5 128.7(19), N1···H4B···O1 33.5(3), N1···H4B···O5 90.2(7), O1···H4B···O5 70.2(6); N5–H5A 0.91(2), H5A···N3 1.88(2), N5···N3 2.786(2), N5–H5A···N3 172.9(19); N5–H5B 0.85(2), H5B···O1 1.99(2), N5···O1 2.790(2), N5–H5B···O1 157(2); O7–H7A 0.81(3), H7A···N2 2.08(3), O7···N2 2.876(2), O7–H7A···N2 168(3).

aggregates consisting of four cations and two dianions (Figure 7). These aggregates are completed by two crystallographically equivalent methanol molecules, which interact with the two dianions via intermolecular nonfurcate O–H···N hydrogen bonds. Compound *fac-8* forms one intermolecular bifurcate N–H···N/O, one intermolecular nonfurcate N–H···N, and two intermolecular nonfurcate N–H···O hydrogen bonds, leading to centrosymmetric aggregates consisting of four cations and two dianions (Figure 8). The hydrogen-bonding system of *mer-9*·2MeOH is characterized by one intermolecular bifurcate interaction each of the types N–H···O/O and N–H···N/O and one intermolecular nonfurcate interaction each of the types N–H···N and N–H···O between the dication and the dianion (Figure 9). These hydrogen bonds lead to the formation of infinite one-dimensional chains in the crystal, which are completed by two crystallographically independent methanol molecules per formula unit. These molecules form intermolecular hydrogen bonds with both the dication and the dianion by acting as hydrogen acceptor and hydrogen donor (one bifurcate O–H···N/O and one nonfurcate O–H···N interaction as well as two nonfurcate N–H···O interactions).

Computational Studies. MP2 studies of the silicate dianions of *fac-5* and *mer-5* revealed only a small difference

(15) Flynn, J. J.; Boer, F. P. *J. Am. Chem. Soc.* **1969**, *91*, 5756–5761.

(16) Hahn, F. E.; Keck, M.; Raymond, K. N. *Inorg. Chem.* **1995**, *34*, 1402–1407.

(17) Sackerer, D.; Nagorsen, G. *Z. Anorg. Allg. Chem.* **1977**, *437*, 188–192.

(18) Tacke, R.; Stewart, A.; Becht, J.; Burschka, C.; Richter, I. *Can. J. Chem.* **2000**, *78*, 1380–1387.

(19) Parr, J.; Slawin, A. M. Z.; Woollins, J. D.; Williams, D. J. *Polyhedron* **1994**, *13*, 3261–3263.

(20) The hydrogen-bonding systems were analyzed by using the program PLATON: Spek, A. L. *PLATON*; University of Utrecht: Utrecht, The Netherlands, 1998. In this context, see also: Jeffrey, G. A.; Saenger, W. *Hydrogen Bonding in Biological Structures*; Springer-Verlag: Berlin, Germany, 1991; pp 15–24.

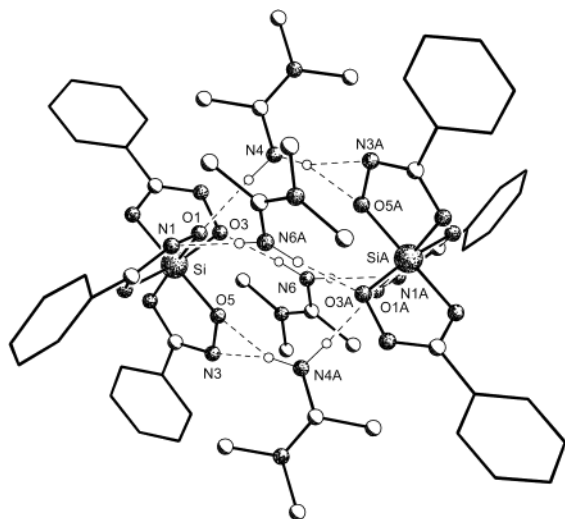


Figure 8. Hydrogen-bonding system in the crystal of *fac-8*. The dashed lines indicate intermolecular hydrogen bonds between the two crystallographically independent cations and the dianion, leading to centrosymmetric aggregates. The hydrogen atoms (except for the NH atoms) are omitted for clarity, and the phenyl groups are represented as stick models. Hydrogen-bonding geometries²⁰ (Å, deg): N4–H4A 0.89(2), H4A···N3 2.44(2), N4···N3 3.165(2), N4–H4A···N3 138.3(19), H4A···O5 1.95(2), N4···O5 2.782(2), N4–H4A···O5 155(2), N3···H4A···O5 35.4(4); N4–H4B 0.91(2), H4B···O1 1.86(2), N4···O1 2.770(2), N4–H4B···O1 177.0(19); N6–H6A 0.91(2), H6A···O3 1.87(2), N6···O3 2.7655(19), N6–H6A···O3 169(2); N6–H6B 0.90(2), H6B···N1 2.19(2), N6···N1 3.086(2), N6–H6B···N1 172.9(19).

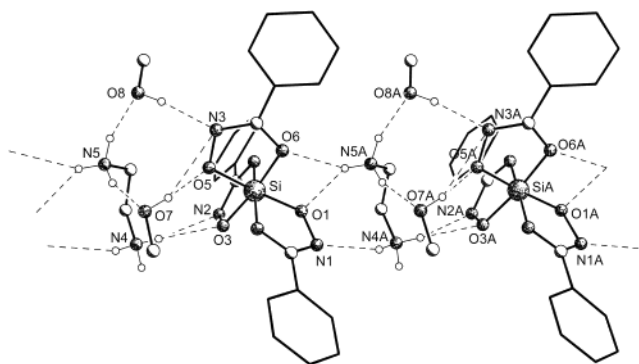


Figure 9. Hydrogen-bonding system in the crystal of *mer-9*·2MeOH. The dashed lines indicate intermolecular hydrogen bonds between the dication, the dianion, and the two crystallographically independent MeOH molecules, leading to infinite one-dimensional chains along the base vector [100]. The hydrogen atoms (except for the NH and OH atoms) are omitted for clarity, and the phenyl groups are represented as stick models. Hydrogen-bonding geometries²⁰ (Å, deg): N4–H4A 0.88(3), H4A···N2 2.62(3), N4···N2 3.106(2), N4–H4A···N2 115.6(18), H4A···O3 2.16(3), N4···O3 2.947(2), N4–H4A···O3 148(2), N2···H4A···O3 33.2(4); N4–H4C 0.88(2), H4C···N1 2.22(3), N4···N1 3.015(2), N4–H4C···N1 150(2); N5–H5A 0.95(3), H5A···O7 1.83(2), N5···O7 2.755(2), N5–H5A···O7 162(2); N5–H5B 0.95(3), H5B···O8 1.88(3), N5···O8 2.798(2), N5–H5B···O8 163(2); N5–H5C 0.86(3), H5C···O1 2.04(3), N5···O1 2.786(2), N5–H5C···O1 145(2), H5C···O6 2.34(3), N5···O6 3.064(2), N5–H5C···O6 142(2), O1···H5C···O6 69.3(8); O7–H7A 0.85(3), H7A···N3 2.60(3), O7···N3 3.396(2), O7–H7A···N3 154(3), H7A···O5 1.82(3), O7···O5 2.642(2), O7–H7A···O5 162(3), N3···H7A···O5 31.5(5); O8–H8A 0.82(3), H8A···N3 1.94(3), O8···N3 2.749(2), O8–H8A···N3 169(2).

in energy for the respective local minima, the dianion of the *fac*-isomer being energetically more stable by 1.9 kJ mol⁻¹. This result is in accordance with the finding that the same synthetic approach can lead to both *fac*- and *mer*-configured products, the configuration being dependent on the nature

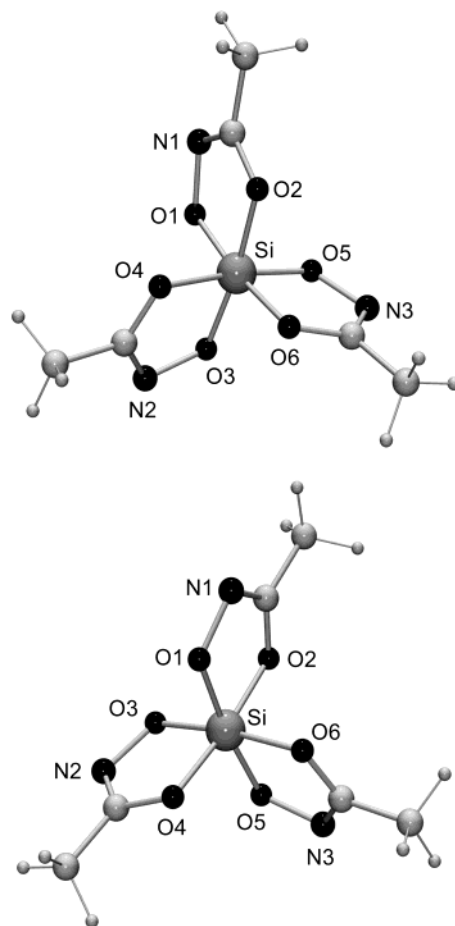


Figure 10. Calculated structures of the dianions of *fac-5* (above) and *mer-5* (below).

of the hydroxamic acid, amine, and solvent used for the synthesis. The structures of the calculated minima of the dianions of *fac-5* and *mer-5* are shown in Figure 10; selected calculated interatomic distances and angles are listed in Table 3. As can be seen from Figure 10 and Table 3, the calculated and experimentally established structure of the dianion of *fac-5* are in good agreement.²¹

Solid-State NMR Studies. Compounds *fac-5*, *fac-6*·MeOH, *fac-7*·MeOH, *fac-8*, and *mer-9*·2MeOH were characterized by solid-state VACP/MAS NMR experiments (¹³C, ¹⁵N, ²⁹Si) at 22 °C.²² All NMR spectra obtained (see Experimental Section) are compatible with the respective crystal structures of these compounds (see Crystal Structure Analyses).²³ The solid-state ¹³C, ¹⁵N, and ²⁹Si NMR spectra of *fac-5* are depicted in Figure 11 as examples.²⁴ The iso-

(21) A perfect agreement between the calculated and experimentally established structure of the dianion cannot be expected because the latter is influenced by intermolecular interactions (including hydrogen bonds) with the neighboring cations in the crystal.

(22) Because of the poor solubility of these compounds in organic solvents, attempts to characterize them by solution NMR experiments gave unsatisfactory results. Thus, no information about *fac/mer* isomerism in solution could be obtained.

(23) Crystal structure analyses at room temperature gave the same results as those obtained by measurements at 173 K. Therefore, it can be assumed that no phase transition occurs on cooling of the crystals from room temperature to 173 K. Thus, the crystal structures established at 173 K can be correlated with the solid-state NMR data obtained at room temperature.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for the Dianions of *fac-5* (Experimentally Established and Calculated) and *mer-5* (Calculated)

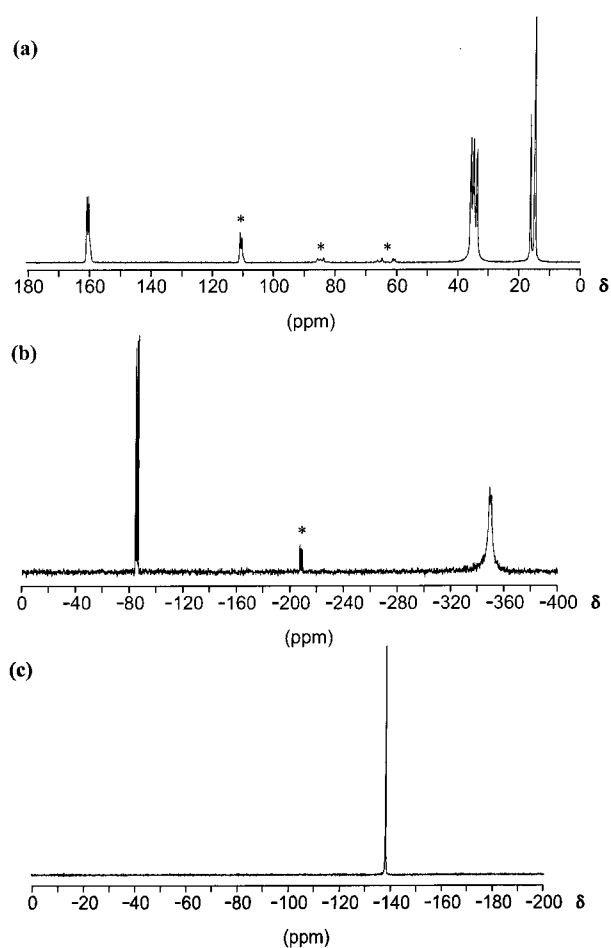
	<i>fac-5</i>		<i>mer-5</i> (calcd)
	exptl	calcd	
Si–O1	1.7513(13)	1.791	1.803
Si–O2	1.7956(13)	1.845	1.829
Si–O3	1.7744(13)	1.791	1.792
Si–O4	1.7822(11)	1.845	1.829
Si–O5	1.7608(11)	1.791	1.803
Si–O6	1.7840(13)	1.845	1.846
O1–Si–O2	85.65(6)	85.5	85.4
O1–Si–O3	89.01(6)	92.1	97.3
O1–Si–O4	98.24(6)	95.1	88.5
O1–Si–O5	89.19(6)	92.1	172.6
O1–Si–O6	172.14(5)	172.4	88.8
O2–Si–O3	171.29(6)	172.4	91.1
O2–Si–O4	88.48(6)	87.6	173.0
O2–Si–O5	97.00(6)	95.1	91.6
O2–Si–O6	89.31(6)	87.6	93.1
O3–Si–O4	85.47(6)	85.5	86.3
O3–Si–O5	89.79(6)	92.1	89.5
O3–Si–O6	96.69(7)	95.1	172.9
O4–Si–O5	171.10(6)	172.4	94.8
O4–Si–O6	87.63(6)	87.6	90.2
O5–Si–O6	85.44(6)	85.5	84.7

tropic ^{29}Si chemical shifts of the compounds studied ($\delta^{29}\text{Si} = -137.8$ to -139.8) are typical of SiO_6 skeletons and are very similar to those reported for the tris[benzene-1,2-diolato(2-)]silicate dianion (see for example ref 18).

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie.

Supporting Information Available: Tables of atomic coordinates and equivalent isotropic displacement parameters, anisotropic displacement parameters, experimental details of the X-ray diffraction studies, and bond lengths and angles for *fac-5*, *fac-6*·MeOH, *fac-7*·MeOH, *fac-8*, and *mer-9*·2MeOH. This material is available free of charge via the Internet at <http://pubs.acs.org>. In addition,

(24) As the ^{13}C and ^{15}N VACP/MAS NMR spectra of *fac-5* at 22 °C look more complicated than expected (see Figure 11), low-temperature ^{13}C , ^{15}N , and ^{29}Si VACP/MAS NMR experiments were performed in the temperature range 155–293 K. The sharp ^{29}Si resonance signal did not change in this temperature range, whereas the broad ^{15}N site arising from the ammonium nitrogen atoms splitted into two sharp signals upon cooling, in accordance with the presence of two crystallographically independent ammonium cations. In contrast, the ^{13}C NMR data did not change significantly on cooling.

**Figure 11.** Solid-state VACP/MAS NMR spectra of *fac-5*: (a) ^{13}C ; (b) ^{15}N ; (c) ^{29}Si . The signals marked by an asterisk are spinning sidebands. For experimental details, see Experimental Section.

crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC-180396 (*fac-5*), CCDC-180397 (*fac-6*·MeOH), CCDC-180398 (*fac-7*·MeOH), CCDC-180399 (*fac-8*), and CCDC-180400 (*mer-9*·2MeOH). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax, (+44) 1223/336033; e-mail, deposit@ccdc.cam.ac.uk).

IC0255757