Synthesis of a Tetranuclear Macrocyclic Siliconate Ionomer. A Novel Tetraanionic Molecular Square

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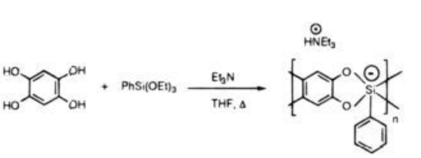
Considerable information is available regarding penta- and hexacoordinate silicon, both as reaction intermediates in organosilicon transformations[1] and as structurally interesting stable compounds.[2]

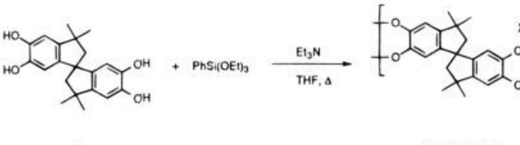
We have been involved in the synthesis of linear polymers and more highly condensed network materials that contain penta- and hexacoordinate silicon as an integral component of the polymer main chain.[3-5] The polysiliconate materials were prepared by condensation of organotriethoxysilyl derivatives with biscatechols (eq 1).



(1)

With the use of *angular* biscatechols such as spirocatechol **1**,[6] the opportunity arises for formation of macrocyclic siliconates. In this communication, we report the synthesis and characterization of the first example of a macrocyclic tetrasiliconate, a *tetraanion* containing four pentacovalent silicons.

Macrocycle **2a** was prepared by condensation of spirocatechol **1** and an equimolar amount of phenyltriethoxysilane in refluxing THF using 3 equiv of triethylamine as base (eq 2). A white precipitate formed within 48 h in 80% yield. The salt was washed with excess THF and dried *in vacuo*.



(2)

1

2a X = HNEt₃
2b X = PPN
2c X = Paraquat/2

The cyclic spirosiliconate **2a** was characterized by both spectral and analytical means. Elemental analysis was consistent with the formulation given in structure **2**.[7] A preliminary evaluation of the ^{1}H NMR (DMSO-d_6) revealed the absence of spirocatechol end groups.[8] In addition, both dilute and concentrated solutions of **2a** (DMF) exhibited equivalent viscosity. On the basis of the preceding data, a relatively low molecular weight cyclic structure was implicated.

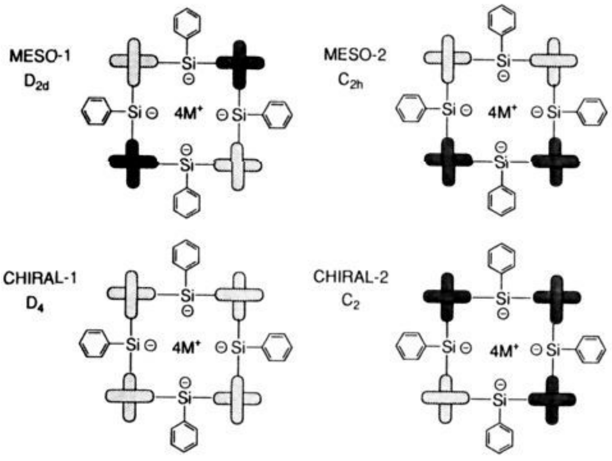


Figure 1. Schematic representation of the diastereomeric tetraspirosiliconates. The *R* and *S* enantiomers of spirocatechol **1** are represented by dark and light shading.

Mass spectrometry provided evidence in support of a cyclic tetrameric structure. The mass spectra were obtained using liquid secondary ion mass spectrometry (LSIMS) in both positive and negative ion modes. The positive ion spectra showed two apparent odd-electron molecular ions that were consistent with $[M + 4H]^+$ at 1768 Da and $[M + Et_3NH + 3H]^+$ at 1870 Da (M = tetraanion core). The negative ion spectra gave a peak at 1767 Da corresponding to $[M + 3H]^-$. The data are consistent with a tetrameric structure having a 441 Da repeat unit with appropriate counterions.[9] Vapor pressure osmometry also provides a calculated molecular weight within 89% of the value expected for **2a**.[10]

There are six stereoisomeric cyclic tetramers that can be formed from racemic (C_2 symmetric) spirocatechol **1**, two *meso* diastereomers and two pairs of chiral isomers. Their structures and point groups are given in Figure 1.[11]

NMR spectroscopy was used for a more detailed analysis of the tetranuclear macrocycle. Selected data that allowed assignment of the structure of **2** included the observation of four discrete methyl resonances (excluding those from the $[HNEt_3]^+$ counterions) in both ^{1}H and ^{13}C NMR. The intensity ratio

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(1) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, J. C. *Chem. Rev.* **1993**, *93*, 1371.

(2) (a) Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Stereochem.* **1986**, *131*, 99. (b) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (c) Corriu, R. J. P.; Young, J. C. In *The Chemistry of Organic Silicon Compounds*; Patai, S., Rappoport, Z., Eds.; Wiley: Chichester, UK, 1989; Part 2, Chapter 20.

(3) (a) Shea, K. J.; Loy, D. A.; Small, J. H. *Chem. Mater.* **1992**, *4*, 255. (b) Shea, K. J.; Loy, D. A.; Small, J. H. *Better Ceramics Through Chemistry V*; MRS Symposium Proceedings; Materials Research Society: Pittsburgh, PA, 1992; Vol. 271, p 711.

(4) Small, J. H.; Shea, K. J.; Loy, D. A.; Jamison, G. M. Hybrid Organic−Inorganic Composites; ACS Symposium Series 585; American Chemical Society: Washington, DC, 1995; p 248.

(5) For related oligomers and polymers incorporating penta- and hexacovalent silicon, see: (a) Blohowiak, K. Y.; Hoppe, M. L.; Chew, K. W.; Kansal, P.; Mueller, B. L.; Scotto, C. L. S.; Hinklin, T.; Babonneau, F.; Kampf, J.; Laine, R. M. *Chem. Mater.* **1994**, *6*, 2177−2192. (b) Marks, T. J. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 857. (c) Tacke, R.; Muhleisen, M.; Jones, P. G. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1186.

(6) Goto, H. Jpn. Patent JP 02286642 A2 901126 Heisi, 1991; *Chem. Abstr.* **1991**, *114*, 163609.

(7) **2a**: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.75 (br s, 4H, $H^+N(CH_2CH_3)_3$), 7.47 (m, 8H, Ph-*H*), 7.09 (m, 12H, Ph-*H*), 6.36 (S, 4H, Ar-*H*), 6.34 (s, 4H, Ar-*H*), 5.84 (s, 4H, Ar-*H*), 5.82 (s, 4H, Ar-*H*), 2.95 (q, 24H, *J* = 7.28 Hz, $H^+N(CH_2CH_3)_3$, 2.12 (d, 4H, *J* = 12.63 Hz, C*H*H), 2.03 (d, 4H, *J* = 12.66 Hz, CH*H*), 1.95 (d, 4H, *J* = 12.44 Hz, C*H*H), 1.94 (d, 4H, *J* = 12.76 Hz, CH*H*), 1.24 (s, 12H, CH_3), 1.21 (s, 12H, CH_3), 1.19 (s, 12H, CH_3), 1.17 (s, 12H, CH_3), 1.04 (t, 36H, *J* = 7.29 Hz, $H^+N(CH_2CH_3)_3$; ^{13}C NMR (125 MHz, DMSO-d_6) δ 149.4, 149.3, 142.5, 142.3, 140.1, 139.4, 139.2, 138.1, 134.8, 134.6, 127.5, 127.4, 126.7, 104.5, 104.3, 102.5, 59.8, 59.6, 57.1, 45.7, 42.4, 42.3, 32.0, 31.6, 31.1, 30.7, 8.5; ^{29}Si NMR (99 MHz, DMSO-d_6) δ −86.3, −86.9; FT-IR (KBr) ν 3442, 2951, 2861, 1637, 1485, 1361, 1279, 1224, 1116, 865, 833, 742, 705, 601 cm^{-1}. Anal. Calcd. for $C_{132}H_{164}N_4O_{16}Si_4$: C, 72.89; H, 7.60; N, 2.58; Si, 5.16. Found: C, 72.68; H, 7.94; N, 2.13; Si, 5.24.

(8) The hydroxyl protons of spirocatechol **1** are found at 8.52 ppm (DMSO-d_6).

(9) Matrix-assisted laser desorption/ionization time-of-flight mass spectrometry (MALDI-TOF) also gave an odd-electron species in the positive ion mode [M + 3H + Na] at 1790 Da.

(10) Vapor pressure osmometry in DMF gave a number average molecular weight of 386. Assuming complete dissociation of **2a** in DMF into five particles, the calculated molecular weight of the complex is 5(386) = 1930. (1930/2175) × 100% = 89%.

(11) The analysis assigns the highest possible time-averaged symmetry to the structure.

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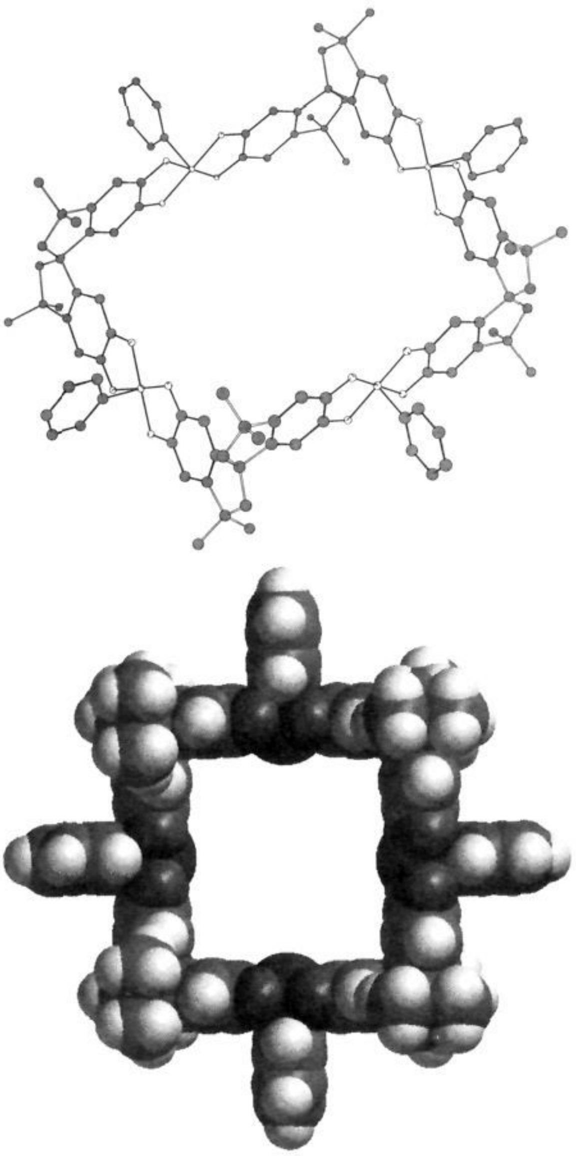

Figure 2. Framework (top) and space-filling (bottom) models of the proposed structure (*meso*-**2**) of macrocyclic tetrasiliconate **2**. The counterions have been omitted for clarity.

(1:1:1:1) of the methyl resonances remained invariant throughout recrystallization and ion exchange reactions as well as during variable temperature NMR studies (25 → 100 °C). In addition, four methylene doublets were observed in the ^{1}H NMR of **2a**. Solution ^{29}Si NMR showed two resonances at −86.3 and −86.9 ppm. These values were characteristic of an aryl-substituted pentacoordinate anionic siliconate.[12] The ^{13}C NMR of **2a** contained 25 resonances (excluding counterions). The carbon resonances associated with the tetraanionic core included eight sp^2 quaternary and eight sp^2 methine resonances. The aliphatic region's nine resonances included three quaternary and two methylene carbons in addition to the four methyl resonances.

The NMR data are consistent with a *single* diastereomer, *meso*-**2**, formed in the condensation reaction (Figure 2). The C_{2h} symmetry of this species predicts a total of 29 carbon[13] resonances (20 sp^2 and 9 sp^3) associated with the tetraanion core. The remaining four carbon resonances were "observed" upon careful examination of the ion exchanged product **2b** (*vide infra*).

Cation exchange of **2a** with PPN chloride and with paraquat iodide in acetonitrile resulted in formation of **2b** and **2c**, respectively. Both salts were recrystallized from acetonitrile. The analytical and spectroscopic properties of **2b**,**c** were also consistent with the assigned structure and were similar to those of **2a**. LSIMS of compound **2c** provided the parent molecular ion at 2137 Da.[14]

Compounds **2a**−**c** are the first examples of macrocyclic *tetraanionic* siliconates, rigid molecular squares incorporating pentacoordinate silicon. They are topologically "related" to the macrocyclic *cationic* molecular squares reported by Stang[15] and Fujita[16] and are also similar to the cyclic paraquat systems reported by Stoddart and co-workers.[17] The molecules contain a substantial cavity; the average distance between silicons is ~13.5 Å. The origin of the remarkable stereoselectivity of the condensation reaction is not known at present. We are currently exploring the properties, conformational dynamics, and synthesis of related derivatives.

Acknowledgment. Support from the National Science Foundation is gratefully acknowledged. We also thank Dr. John M. Peltier of Perceptive Biosystems for providing us with the MALDI-TOF spectra.

Supporting Information Available: ^{1}H/^{13}C NMR spectra for **1** and **2b**, ^{1}H/^{13}C/^{29}Si NMR spectra for **2a**,**c**, LSIMS MS of **2a**,**c** and MALDI-TOF MS of **2a** (40 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, can be ordered from the ACS, and can be downloaded from the Internet; see any current masthead page for ordering information and Internet access instructions.

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(12) The ^{29}Si chemical shift of the triethylammonium salt of phenyl-substituted biscatechol siliconate is −87.5 ppm. Loy, D. A.; Small, J. H.; Shea, K. J. *Organometallics* **1993**, *12*, 1484.

(13) The spectroscopic data were not consistent with structures of lower symmetry. At present, we have insufficient information to locate the phenyl groups outside (Figure 1) or inside the square.

(14) **2c**: ^{1}H NMR (500 MHz, DMSO-d_6) δ 8.93 (d, 4H, J = 6.1 Hz), 8.38(d, 4H J = 6.1 Hz), 7.50−7.48 (m, 4H), 7.43 (d, 4H, J = 7.1 Hz), 7.09 (t, 8H, J = 2.9 Hz), 7.06 (t, 2H, J = 7.4 Hz), 6.90 (t, 2H, J = 7.2 Hz), 6.38 (s, 4H), 6.36 (s, 4H), 5.82 (s, 4H), 5.79 (s, 4H), 4.26 (s, 12H), 2.12 (d, 4H, J = 12.5 Hz), 2.04 (d, 4H, J = 12.5 Hz), 1.93 (2 overlapping d, 8H, J = 11.6 Hz), 1.23 (s, 12H), 1.21 (s, 12H), 1.19 (s, 12H), 1.16 (s, 12H); ^{13}C NMR (125 MHz, DMSO-d_6) δ 149.2, 149.1, 147.8, 146.4, 142.5, 142.0, 140.2, 139.8, 139.3, 138.2, 134.8, 134.3, 127.6, 127.5, 127.0, 126.7, 125.7, 104.3, 102.7, 59.6, 59.4, 57.1, 47.9, 42.4, 42.3, 31.9, 31.5, 30.9, 30.7; ^{29}Si NMR (99 MHz, DMSO-d_6) δ −86.4, −86.8; IR (KBr) ν 3130, 3066, 2964, 2974, 1654, 1577, 1500, 1371, 1294, 1243, 1127, 896, 858, 755, 717 cm^{-1}; UV (CH$_3$CN) λ_{max} (ϵ_{206} 310 000), 300 (ϵ_{300} 66 000) nm; high-resolution LSIMS calcd for $C_{132}H_{128}N_4Si_4O_{16}$ M$^+$ 2136.8, found 2136.7. VPO in DMF at 25 °C assuming complete dissociation into three particles gave a molecular weight of 1790 ± 10. This is within 84% of the calculated molecular weight.

(15) (a) Stang, P. J.; Cao, D. H.; Saito, S.; Arif, A. M. *J. Am. Chem. Soc.* **1995**, *117*, 6273. (b) Stang, P. J.; Chen, K. *J. Am. Chem. Soc.* **1995**, *117*, 1667. (c) Stang, P. J.; Cao, D. H. *J. Am. Chem. Soc.* **1994**, *116*, 4981. (d) Stang, P. J.; Zhdankin, V. *J. Am. Chem. Soc.* **1993**, *115*, 9808.

(16) (a) Fujita, M.; Kwon, Y. J.; Washizu, S.; Ogura, K. *J. Am. Chem. Soc.* **1994**, *116*, 1151. (b) Fujita, M.; Nagao, S.; Iida, M.; Ogata, K.; Ogura, K. *J. Am. Chem. Soc.* **1993**, *115*, 1574. (c) Fujita, M.; Yazaki, J.; Ogira, K. *J. Am. Chem. Soc.* **1990**, *112*, 5645.

(17) Amabilino, D. B.; Ashton, P. R.; Brown, C. L.; Córdova, E.; Godínez, L. A.; Goodnow, T. T.; Kaifer, A. E.; Newton, S. P.; Pietraszkiewicz, M.; Philip, D.; Raymo, F. M.; Reder, A. S.; Rutland, M. T.; Slawin, A. M. Z.; Spencer, N.; Stoddart, J. F.; Williams, D. J. *J. Am. Chem. Soc.* **1995**, *117*, 1271 and references therein.