Structural Studies of Hexacoordinate Silicon. Tris(*o*-phenylenedioxy)siliconate

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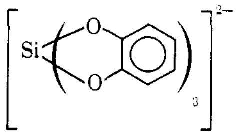
Abstract: The crystal structure of pyridinium tris(*o*-phenylenedioxy)siliconate, $[C_5H_5NH]_2{}^+[(C_6H_4O_2)_3Si]^{2-}$, has been determined by a single-crystal, three-dimensional X-ray diffraction study. This yellow salt crystallizes in the centrosymmetric space group Pbcn with lattice parameters $a = 11.430 \pm 0.005$, $b = 21.510 \pm 0.010$, and $c = 9.912 \pm 0.005$ Å ($Z = 4$). The intensity data were collected on a Picker automatic diffractometer (Cu Kα radiation), and the structure was solved by iterative application of Sayre's equation. All hydrogen atoms were located by difference synthesis. Full-matrix least-squares refinement of atom positions, hydrogen isotropic thermal parameters, and anisotropic thermal parameters for all other atoms converged at a final R of 5.8% for 1317 observed reflections. The hexacoordinate silicon dianions are only slightly distorted from octahedral (D_3) symmetry. A crystallographic twofold axis passes through one of the unique phenylenedioxy ligands (labeled A), while the other two ligands (labeled B, B′) are related by this axis. The pyridinium cations are stacked symmetrically above and below phenyl A; the distance between the centroid of phenyl A and that of pyridinium is 3.825 Å. The Si–O bond distances are 1.813 (A) and 1.765 and 1.775 Å (B), all ±0.003, while the C–O bonds average 1.357 Å.

We have undertaken to study[1–5] the structural systematics of extracoordinate silicon compounds because the properties of extracoordinate intermediates are central to the theory of organosilicon reactions.[6] Although a number of pentacoordinate silicon compounds have very recently been examined by X-ray diffraction,[1–5,7] direct structure determinations of hexavalent silicon compounds are surprisingly rare: the principal example is the familiar fluorosilicate $[SiF_6]^{2-}$ ion.[8] Among the systems in which silicon is believed to expand its valence octet to form compounds of coordination number six are congeners, $[SiF_5R]^{2-}$, of fluorosilicate,[9] donor–acceptor complexes of various bases with silicon tetrahalides,[10] and silicon acetylacetonates[11] and imidodiphosphinates.[12] We report below the X-ray structure of yet another system, the tris(*o*-phenylenedioxy)siliconate ion (I).



I

In fact, the structure of this ion has been in dispute for some time.[13–16] The preparation of salts of tris(*o*-phenylenedioxy)siliconate from silicon tetrachloride and catechol in the presence of base was reported[13] by Rosenheim as early as 1920. However, his assignment[14] of a hexavalent structure has more recently been criticized by Weiss, *et al.*,[15] on the questionable grounds that the proposed octahedral geometry is precluded by severe compressive strain in the five-membered rings. The nature of the pyridinium salt has been further obscured by Rosenheim's mistaken retraction[14] of the original (correct) formulation[13] $[C_5H_5NH]_2{}^+[Si(O_2C_6H_4)_3]^{2-}$ in favor of $[C_5H_5NH]^+[H]^+[Si(O_2C_6H_4)_3]^{2-}$ on the basis of later analyses. Our interest in the pyridinium salt was also stimulated by its bright yellow color (the simpler ammonium salts are colorless), which suggested that charge-transfer interactions[17] might occur in the solid.

Experimental Section

Well-formed needle-like crystals of pyridinium tris(*o*-phenylenedioxy)siliconate weres upplied to us by C. L. Frye. The orthorhombic space group Pbcn ($D_{2h}{}^{14}$) was established from the reciprocal lattice symmetry D_{2h} and the reflection conditions $0kl$ ($k = 2n$), $h0l$ ($l = 2n$), and $hk0$ ($h + k = 2n$) as determined from preliminary Weissenberg photographs. Accurate lattice constants, $a = 11.430 \pm 0.005$, $b = 21.510 \pm 0.010$, and $c = 9.912 \pm 0.005$ Å, obtained from least-squares refinement of the setting angles of 11 reflections on a four-circle goniometer (Cu Kα radiation, λ 1.5418), give a calculated density $\rho = 1.399$ g cm^{-3} for $Z = 4$. The dianions are then constrained by symmetry to lie on the crystallographic twofold axes or the inversion centers; the latter sites are of course chemically unreasonable.

The intensity data were collected using the θ–2θ scan mode of a Picker automatic diffractometer with Ni-filtered Cu Kα radiation. The X-ray tube was placed at a 3° take-off angle, and a detector aperture 4.0 mm square was positioned 30 cm from the crystal. A scan angle of 2° and a scan speed of 2°/min was used throughout the range of sin θ (0.0–0.9) examined. Background counts of 15 sec were taken at each end of the scan by the stationary crystal–

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Table I. Final Structure Parameters[a] and Standard Errors[b]

Atom	x/a	y/b	z/c	$10^4\beta_{11}$	$10^4\beta_{22}$	$10^4\beta_{33}$	$10^4\beta_{12}$	$10^4\beta_{13}$	$10^4\beta_{23}$
Si	0.5000	0.3528 (1)	0.2500	75 (1)	18 (1)	80 (1)		−17 (1)	
O(1)	0.5157 (3)	0.2914 (1)	0.1261 (3)	93 (3)	17 (1)	91 (3)	0 (1)	−9 (2)	3 (1)
C(1)	0.5091 (4)	0.2337 (2)	0.1805 (4)	73 (3)	19 (1)	103 (4)	1 (1)	−14 (3)	0 (2)
C(2)	0.5197 (5)	0.1783 (2)	0.1089 (4)	118 (5)	21 (1)	131 (6)	6 (2)	−22 (5)	−13 (2)
C(3)	0.5093 (6)	0.1226 (2)	0.1825 (6)	156 (6)	18 (1)	180 (7)	10 (3)	−28 (7)	−6 (2)
O(2)	0.3480 (2)	0.3535 (1)	0.2135 (2)	81 (3)	20 (1)	93 (3)	−1 (1)	−17 (2)	−5 (1)
O(3)	0.4772 (2)	0.4086 (1)	0.3780 (3)	85 (3)	17 (1)	108 (3)	3 (1)	−24 (3)	−6 (1)
C(4)	0.2909 (3)	0.3963 (2)	0.2909 (4)	80 (3)	18 (1)	87 (4)	−2 (1)	−7 (3)	5 (2)
C(5)	0.1733 (4)	0.4097 (2)	0.2858 (4)	76 (4)	21 (1)	123 (5)	−1 (2)	−9 (4)	4 (2)
C(6)	0.1279 (5)	0.4552 (2)	0.3746 (6)	90 (5)	30 (1)	143 (6)	9 (2)	9 (4)	1 (3)
C(7)	0.2007 (5)	0.4857 (2)	0.4621 (5)	117 (5)	24 (1)	136 (6)	11 (2)	8 (5)	−2 (2)
C(8)	0.3210 (4)	0.4728 (2)	0.4678 (4)	106 (5)	18 (1)	100 (4)	4 (2)	−9 (4)	−1 (2)
C(9)	0.3647 (4)	0.4277 (2)	0.3821 (4)	88 (4)	16 (1)	88 (4)	−1 (1)	−13 (3)	3 (2)
C(10)	0.1511 (5)	0.2351 (3)	0.3266 (5)	120 (6)	28 (2)	131 (6)	−5 (2)	8 (5)	1 (2)
C(11)	0.2024 (5)	0.2217 (3)	0.2061 (5)	103 (5)	31 (2)	137 (6)	−11 (2)	15 (6)	6 (3)
C(12)	0.2184 (5)	0.1609 (3)	0.1671 (5)	117 (6)	37 (2)	109 (6)	−8 (3)	24 (4)	−5 (3)
C(13)	0.1849 (6)	0.1132 (3)	0.2547 (6)	175 (8)	34 (2)	130 (6)	−9 (3)	44 (6)	−13 (3)
C(14)	0.1311 (5)	0.1280 (2)	0.3730 (5)	134 (6)	23 (1)	130 (6)	−2 (2)	31 (5)	66 (2)
N	0.1149 (3)	0.1878 (2)	0.4051 (4)	103 (4)	25 (1)	104 (4)	1 (2)	15 (3)	−4 (2)
				B					
H(2)	0.5374 (39)	0.1775 (23)	0.0124 (50)	3.3 (1.3)					
H(3)	0.5251 (45)	0.0809 (22)	0.1236 (56)	4.8 (1.4)					
H(5)	0.1229 (42)	0.3908 (23)	0.2274 (49)	4.1 (1.4)					
H(6)	0.0470 (44)	0.4632 (21)	0.3787 (55)	4.5 (1.7)					
H(7)	0.1686 (42)	0.5164 (22)	0.5196 (49)	4.0 (1.4)					
H(8)	0.3752 (33)	0.4928 (20)	0.5287 (41)	2.0 (0.9)					
H(9)	0.0726 (57)	0.1998 (31)	0.4886 (85)	8.6 (2.5)					
H(10)	0.1429 (73)	0.2855 (36)	0.3589 (103)	12.5 (3.1)					
H(11)	0.2331 (44)	0.2549 (24)	0.1345 (54)	4.1 (1.3)					
H(12)	0.2583 (51)	0.1511 (29)	0.0720 (61)	6.8 (1.9)					
H(13)	0.1809 (59)	0.0759 (30)	0.2259 (61)	8.1 (2.5)					
H(14)	0.7686 (54)	0.0938 (34)	0.4322 (80)	9.6 (2.6)					

[a] The anisotropic thermal parameters are in the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl + 2hl\beta_{13} + 2kl\beta_{23})]$. [b] Standard errors are given in parentheses.

stationary counter technique. An error

$$\sigma(I) = [(0.03I)^2 + N_0 + k^2N_b]^{1/2}$$

was assigned to the net intensity $I = N_0 - kN_b$ of each reflection in order to establish the weights $w(F) = 4F^2/\sigma^2(F^2)$ for subsequent least-squares refinement. Here N_0 is the gross count, N_b is the background count, and k is the ratio of scan time to background time. Reflections for which either of the conditions $I > 0$ or $\sigma(I)/I < 0.2$ were not met were defined to below background and were omitted from the refinement.

A total of 2043 independent reflections were measured, on two different crystals. A total of 1316 reflections, all with sin θ values less than 0.8, were gathered from the first crystal, a nearly cylindrical needle of radius 0.06 mm. The data collection from this crystal was terminated when the intensities of the test reflections had dropped to 81% of their initial values. The remaining reflections, most of them from the region $0.8 < \sin\theta < 0.9$, were measured on a larger crystal, of radius 0.13 mm. A cylindrical absorption correction (μ (Cu Kα) = 12.26 cm^{-1}) was applied to the data from this second crystal. The cylindrical approximation appears justified since the intensities of reflections coincident with the ϕ axis (00l reflections) varied less than 5% as a function of ϕ. The two data sets were corrected for Lorentz and polarization effects and placed on a common scale using a preliminary scale factor calculated from 37 overlapping reflections. After application of the criteria cited above, 1321 reflections were deemed "above background."

Solution and Refinement of the Structure

Initial scale and temperature factors were estimated by Wilson's method, and a set of normalized structure factors (E's) was calculated for the three-dimensional set of intensities. The signs of 252 reflections for which $|E| > 1.5$ were determined using the multiple-solution computer program of Long[18a] which solves the phase problem by reiterative application of Sayre's equation[19]

$$S(E_a) = S\Big(\sum_{a=b+c} E_bE_c\Big)$$

where S means "sign of" and a, b, c are vectors representing the reflection indices hkl. The correct solution, which assumed positive signs for 311, 174, 613, 774, and 269 and negative signs for 193 and 283, gave a consistency index

$$C = \frac{\Big\langle\Big|E_a \sum_{a=b+c} E_bE_c\Big|\Big\rangle}{\Big\langle|E_a| \sum_{a=b+c} |E_b||E_c|\Big\rangle} = 0.90$$

after seven cycles. All but five signs were subsequently shown to be correct.

An E map computed[18b] from these phases revealed all the Si, O, N, and C atoms, although the nitrogen could not at this stage be distinguished unambiguously from the pyridinium carbon atoms. Two cycles of full-matrix least-squares refinement[18c,20] of the position and

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(18) We acknowledge the use of the following programs: (a) R. E. Long, "A Program for Phase Determination by Reiterative Application of Sayre's Equation," Ph.D. Thesis, University of California at Los Angeles, Los Angeles, Calif., 1965; (b) J. Gvildys "Two- and Three-Dimensional Crystallographic Fourier Summation Program," based on MIFRI, Program Library B-149, Argonne National Laboratory, Applied Mathematics Division, April 13, 1965; (c) "A Fortran Crystallographic Least-Squares Refinement Program," based on ORFLS, Program Library 14E7043, March 31, 1967; (d) "ANL FFE, A Fortran Crystallographic Function and Error Program," based on ORFFE, Program Library B 115, Sept 17, 1964; (e) C. K. Johnson, "ORTEP: A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustrations," Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., June 1965; (g) J. Gvildys, "Least-Squares Plane and Line Fitter"; see V. Schomaker, J. Waser, R. E. Marsh, and G. Bergman, *Acta Cryst.*, 12, 600 (1959), Program Library B-125, May 18, 1965.

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isotropic temperature parameters of these atoms reduced

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o|$$

from 0.33 to 0.12 and

$$R_2 = \{\sum w[F_o - F_c]^2/\sum wF_o^2\}^{1/2}$$

from 0.39 to 0.15. An electron density map calculated[18b] from these parameters showed one peak in the pyridinium ring with a density of 6.5 e/Å^3, while the other five peaks ranged from 4.5 to 5.2 e/Å^3. Nitrogen scattering factors were assigned to this atom; its identification was also consistent with somewhat shorter bond distances to the two neighboring atoms. A second electron density map, from which the heavier atoms were subtracted, revealed 12 peaks ranging between 0.20 and 0.45 e/Å^3 in chemically reasonable positions for hydrogen atoms. These were included in the subsequent refinement. At this time four intense reflections (002, 102, 122, and 109) suspected of extinction were removed from the data set. Refinement was continued assuming anisotropic thermal parameters for the Si, O, N, and C atoms and isotropic parameters for H. After four cycles R_1 was reduced from 0.014 to its final value of 0.058 for 1317 observed reflections, while R_2 dropped from 0.137 to 0.073. The mean shift of position parameters in the final cycle was 0.02σ, with a maximum shift of 0.11σ.

Table II. Distances and Angles[a]

A. Bond Distances (Å)

Bonds to Silicon		Carbon–Oxygen Bonds	
Si–O(1)	1.813 (3)	C(1)–O(1)	1.356 (4)
Si–O(2)	1.775 (3)	C(4)–O(2)	1.364 (4)
Si–O(3)	1.765 (3)	C(9)–O(3)	1.350 (5)
Phenyl Ring A		**Phenyl Ring B**	
C(1)–C(1)′	1.393 (7)	C(4)–C(9)	1.409 (5)
C(1)–C(2)	1.391 (5)	C(4)–C(5)	1.375 (6)
		C(8)–C(9)	1.382 (4)
C(2)–C(3)	1.408 (6)	C(5)–C(6)	1.415 (6)
		C(7)–C(8)	1.405 (6)
C(3)–C(3)′	1.355 (11)	C(6)–C(7)	1.369 (7)
C(2)–H(2)	0.976 (49)	C(5)–H(5)	0.967 (39)
		C(8)–H(8)	0.912 (47)
C(3)–H(3)	1.085 (50)	C(6)–H(6)	0.948 (48)
		C(7)–H(7)	0.946 (49)
Bonds in Pyridinium			
N–C(10)	1.345 (6)	N–H(9)	0.986 (78)
C(10)–C(11)	1.361 (7)	C(10)–H(10)	1.135 (79)
C(11)–C(12)	1.376 (7)	C(11)–H(11)	1.065 (53)
C(12)–C(13)	1.398 (7)	C(12)–H(12)	1.065 (60)
C(13)–C(14)	1.362 (7)	C(13)–H(13)	0.856 (63)
C(14)–N	1.337 (6)	C(14)–H(14)	1.131 (68)

B. Selected Interionic Contacts

Atom 1	Atom 2	Transform (atom 2)	d
Si	N	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	3.765
Si	C(14)	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	4.047
O(1)	N	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	2.688
O(1)	C(14)	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	3.479
O(1)	C(10)	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	3.574
O(2)	C(14)	$^1/_2 + x, ^1/_2 - y, 1 - z$	3.131
O(2)	N	$^1/_2 + x, ^1/_2 - y, 1 - z$	3.376
O(3)	N	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	3.212
O(3)	C(11)	x, y, z	3.287
O(3)	C(14)	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	3.407
C(1)	C(11)	$1 - x, y, ^1/_2 - z$	3.493
C(1)	N	$^1/_2 - x, ^1/_2 - y, z - ^1/_2$	3.508
C(1)	C(11)	x, y, z	3.523
C(1)	C(12)	x, y, z	3.675
C(2)	C(12)	x, y, z	3.512
C(2)	N	$1 - x, y, ^1/_2 - z$	4.184
C(3)	C(12)	x, y, z	3.429
C(3)	C(12)	$1 - x, y, ^1/_2 - z$	3.549
C(3)	C(13)	$1 - x, y, ^1/_2 - z$	3.557

Table II (*Continued*)

C. Bond Angles (Degrees)

Vertex	Atom 1	Atom 2	Angle	Vertex	Atom 1	Atom 2	Angle
Si	O(1)	O(1)′	86.4 (0.2)	O(1)	Si	C(1)	113.1 (0.2)
	O(2)	O(3)	89.8 (0.1)				
	O(1)	O(2)	89.6 (0.1)	O(2)	Si	C(4)	111.7 (0.2)
	O(1)	O(3)	88.0 (0.1)				
	O(1)	O(3)′	92.7 (0.1)	O(3)	Si	C(9)	111.1 (0.2)
	O(2)	O(2)′	94.4 (0.2)				
	O(2)	O(3)′	89.6 (0.1)				
	O(1)	O(2)′	175.4 (0.1)				
	O(3)	O(3)′	179.1 (0.2)				
C(1)	O(1)	C(1)′	113.7 (0.2)	C(9)	O(3)	C(4)	113.4 (0.4)
	C(1)′	C(2)	121.1 (0.3)		C(4)	C(8)	120.5 (0.4)
	O(1)	C(2)	125.2 (0.4)		O(3)	C(8)	126.0 (0.4)
C(2)	C(1)	C(3)	117.2 (0.4)	C(10)	N	C(11)	118.8 (0.5)
	H(2)	C(1)	122 (5)		H(10)	N	122 (3)
	H(2)	C(3)	120 (3)		H(10)	C(11)	119 (5)
C(3)	C(2)	C(3)′	121.6 (0.3)	C(11)	C(10)	C(12)	120.2 (0.5)
	H(3)	C(3)′	124 (2)		H(11)	C(10)	126 (3)
	H(3)	C(2)	114 (2)		H(11)	C(12)	113 (3)
C(4)	O(2)	C(5)	125.2 (0.4)	C(12)	C(11)	C(13)	119.1 (0.5)
	O(2)	C(9)	113.9 (0.3)		H(12)	C(11)	119 (4)
	C(5)	C(9)	120.9 (0.4)		H(12)	C(13)	121 (4)
C(5)	C(4)	C(6)	117.9 (0.4)	C(13)	C(12)	C(14)	119.1 (0.5)
	H(5)	C(4)	117 (3)		H(13)	C(12)	120 (5)
	H(5)	C(6)	124 (3)		H(13)	C(14)	118 (5)
C(6)	C(5)	C(7)	121.7 (0.5)	C(14)	N	C(13)	119.5 (0.5)
	H(6)	C(5)	119 (3)		H(14)	N	115 (4)
	H(6)	C(7)	118 (3)		H(14)	C(13)	122 (4)
C(7)	C(6)	C(8)	120.2 (0.5)	N	C(10)	C(14)	123.1 (0.4)
	H(7)	C(6)	119 (3)		H(9)	C(10)	115 (4)
	H(7)	C(8)	120 (3)		H(9)	C(14)	121 (4)
C(8)	C(7)	C(9)	118.7 (0.4)				
	H(8)	C(7)	118 (3)				
	H(8)	C(9)	123 (3)				

[a] Standard errors calculated from the variance–covariance matrix obtained in the final least-squares cycle are given in parentheses.

Final atomic parameters and their standard deviations as calculated in the last least-squares cycle are listed in Table I. A table of observed and calculated structure factors[21] is available on request. Interatomic distances and angles with standard deviations calculated[18d] from the variance–covariance matrix obtained in the final cycle of least-squares are shown in Table II. Table III lists the root-mean-square components of thermal displacement along the principal axes, as defined by the anisotropic thermal parameters. The direction of these axes may be inferred from Figure 1, in which the three-dimensional structure[18e] is shown using 50% probability ellipsoids to represent the thermal motion.

Description and Discussion of the Structure

The results confirm that the anion is indeed the hexacoordinate tris(*o*-phenylenedioxy)siliconate ion, and that each ion is associated with two pyridinium cations.

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[21] Material supplementary to this article has been deposited as Document No. NAPS-00436 with the ASIS National Auxiliary Publication Service, ℅ CCM Information Sciences, Inc., 22 West 34th St., New York, N. Y. 10001. A copy may be secured by citing the document number and remitting $1.00 for microfiche or $3.00 for photocopies. Advance payment is required. Make checks or money orders payable to: ASIS–NAPS.

Table III. Root-Mean-Square Thermal Displacement along Principal Axes[a] (Å)

Atom	Axis 1	Axis 2	Axis 3
Si	0.184	0.203	0.237
O(1)	0.198	0.213	0.251
C(1)	0.204	0.210	0.241
C(2)	0.200	0.247	0.302
C(3)	0.201	0.281	0.342
O(2)	0.193	0.206	0.266
O(3)	0.190	0.223	0.247
C(4)	0.189	0.205	0.248
C(5)	0.205	0.220	0.269
C(6)	0.221	0.261	0.292
C(7)	0.230	0.266	0.282
C(8)	0.219	0.221	0.255
C(9)	0.193	0.213	0.236
N	0.217	0.246	0.268
C(10)	0.247	0.258	0.287
C(11)	0.225	0.273	0.290
C(12)	0.218	0.272	0.311
C(13)	0.226	0.277	0.363
C(14)	0.218	0.250	0.314

[a] Ordered on increasing magnitude.

The anion most probably has D_3 symmetry when unassociated (but in the crystal this symmetry is lowered to C_2) with the six oxygen atoms placed at the vertices of a nearly regular octahedron centered on silicon. The crystallographic twofold axes, which are parallel to *y*, pass successively through the midpoints of the C(3)–C(3)′ and C(1)–C(1)′ bonds and the silicon atom. As a result, one of the three phenylenedioxy ligands (labeled A) is bisected by this symmetry axis while the other two ligands (labeled B and B′) become symmetry equivalent. The pyridinium cations lie directly above and below the phenyl group of ligand A, and are thus also related by the twofold axis.

Table IV

A. Least-Square Planes[a]	Group A	Group B	Pyr	Phenyl A	Phenyl B
Atom 1	Si	Si	N	C(1)	C(4)
Atom 2	O(1)	O(2)	C(10)	C(1)′	C(5)
Atom 3	O(1)′	O(3)	C(11)	C(2)	C(6)
Atom 4	C(1)	C(4)	C(12)	C(2)′	C(7)
Atom 5	C(1)′	C(5)	C(13)	C(3)	C(8)
Atom 6	C(2)	C(6)	C(14)	C(3)′	C(9)
Atom 7	C(2)′	C(7)			
Atom 8	C(3)	C(8)			
Atom 9	C(3)′	C(9)			
m_1	11.295	−1.999	10.218	11.288	−1.976
m_2	0.000	−15.175	0.179	0.000	−15.102
m_3	1.515	6.807	4.440	1.555	6.847
d	6.026	−4.618	3.021	6.033	−4.568
Δ*d*(atom 1)	0.000	−0.034	−0.015	−0.006	0.004
Δ*d*(atom 2)	0.010	0.037	0.015	0.006	−0.004
Δ*d*(atom 3)	−0.010	0.011	0.002	0.003	0.000
Δ*d*(atom 4)	−0.003	0.000	−0.019	−0.003	0.005
Δ*d*(atom 5)	0.003	−0.014	0.019	−0.003	−0.005
Δ*d*(atom 6)	0.009	−0.008	−0.003	+0.003	0.000
Δ*d*(atom 7)	−0.009	0.005			
Δ*d*(atom 8)	0.002	0.000			
Δ*d*(atom 9)	−0.002	0.004			

B. Dihedral Angles between Least-Squares Planes

Plane 1	Plane 2	Angle
Group A	Group B	86° 5′
Group B	Group B′	89° 40′
Pyr	Group A	17° 20′
Pyr	Group B	81° 40′
Pyr	Group B′	80° 59′

[a] These planes are defined by the equation $m_1x + m_2y + m_3z = d$. The distances Δ*d* of the atoms from this plane are in Å. The calculations assumed unit weights throughout.

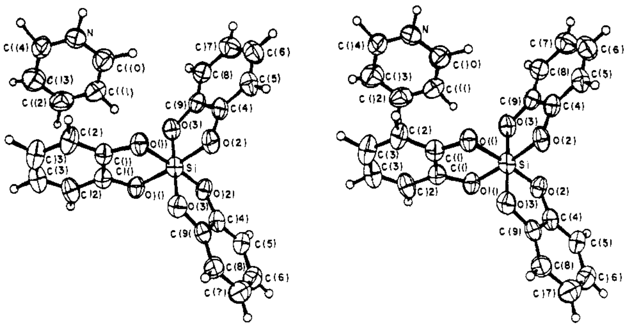


Figure 1. Three-dimensional view of the configuration of pyridinium tris(*o*-phenylenedioxy)siliconate, indicating the ellipsoids of thermal motion. Hydrogen atoms are drawn as spheres of arbitrary size. The crystallographic twofold axes are horizontal.

A. Crystal Packing. The packing arrangement in pyridinium tris(*o*-phenylenedioxy)siliconate is shown from two angles in Figures 2 and 3. Equivalent pyridinium cations stack in the *x* direction directly above and below the phenyl rings of ligand A. In Figure 3, one can see that the degree of overlap between the π systems of the pyridinium and phenyl rings is high.[17] The distance between the centroids[10f] of these rings is 3.825 Å, while the shortest unique contacts between carbon atoms (Table IIB) are 3.43, 3.51, 3.52, 3.55, 3.56, and 3.68 Å. These values may be compared to interplanar perpendicular spacings of 3.16–3.50 Å tabulated for a series of π–π donor–acceptor complexes by Prout and Wright.[17] The closest contact of the pyridinium nitrogen to the ring directly below (N · · · C(2), 4.18 Å) is somewhat longer. The variation in distances results from the relatively large[17] dihedral angle of 17° 20′ between least-squares planes[10f] through pyridinium and ligand A (see Table IV).

A second type of association between anions and cations occurs *via* the twofold screw axes parallel to *Z* (see Figure 3), which place the pyridinium nitrogen within 2.688 Å of O(1) of the siliconate ion. This contact is the only interionic distance in the crystal significantly below the van der Waals limit (2.9 Å for neutral O and N atoms), and may be favored by localization of positive charge on the nitrogen atom of the cation. The O(1)· · ·H(9) distance of 2.57 Å precludes any hydrogen-bond participation in this interaction.

In summary, the ions pack in the crystal in triads of two pyridinium ions and one siliconate, apparently bound by weak π–π interactions. These triads may in turn be linked by O· · ·N contacts. Thus, there are at least two possible paths along which charge transfer might occur. Surprisingly, all of the close interionic interactions seem to involve ligand A, while the two B ligands show no unusual contacts.

B. The Tris(*o*-phenylenedioxy)siliconate Ion. As discussed above, the geometry of the anion is essentially octahedral, but the distortions from ideal D_3 symmetry caused by electronic forces in the crystal lattice are significant. The phenylenedioxy ligands appear to deviate slightly from strict planarity: least-squares planes[10f]

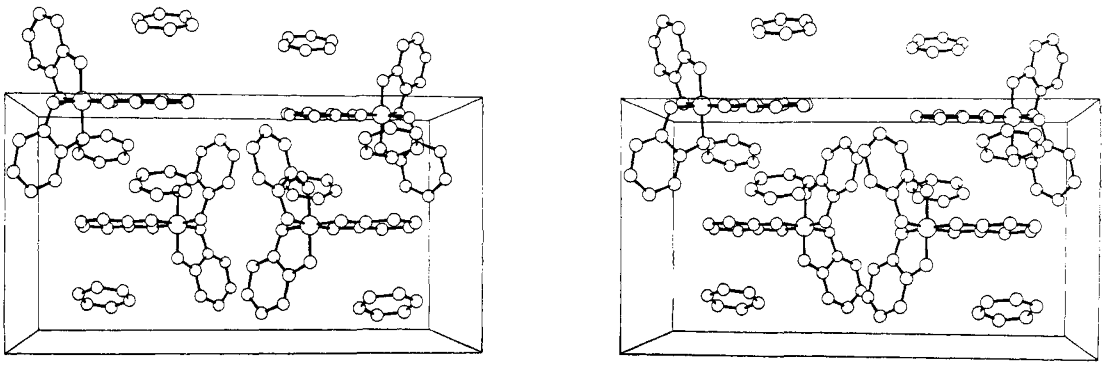


Figure 2. *Z* axis view of packing in pyridinium tris(*o*-phenylenedioxy)siliconate. The *y* axis is horizontal and *x* axis vertical.

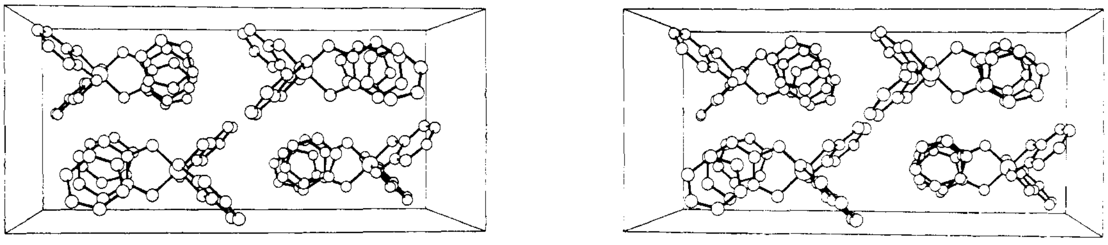
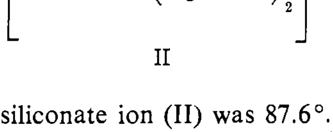


Figure 3. Packing in pyridinium tris(*o*-phenylenedioxy)siliconate as viewed down the *x* axis, with *y* horizontal and *z* vertical.

(Table IV) through the nine Si, O, and C atoms of each ligand give maximum deviations of 0.010 Å for ligand A and 0.037 Å for B. Those deviations that do occur are confined largely to the five-membered rings, for the phenyl rings alone show maximum deviations of only 0.006 (A) and 0.005 Å (B). The dihedral angle between the planes through ligand A and through ligand B, 86.5°, is one measure of the distortion produced by the crystal forces. The comparable angle between B and B′ is 89° 40′.

Some of the bond angles at silicon also differ significantly from the ideal 90 and 180° angles of a regular octahedron. Of most interest are the O–Si–O bond angles in the five-membered rings, 86.4 (A) and 89.8° (B), which differ from each other but are both *below* the 90° octahedral value. Such values are not unprecedented for extracoordinate silicon: the corresponding angle found[3] in the pentacoordinate bis(*o*-phenylenedioxy)phenylsiliconate ion (II) was 87.6°. Ring strain is evident in the O–C–C bond angles within the five-membered rings. The values measured here (113.4, 113.5, and 113.7°) are reduced substantially below the normal 120° bond angle for sp^2-hybridized carbon, and are again comparable to the average O–C–C angle of 112.7° in II.

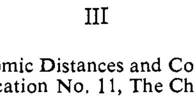


II

The unique Si–O bond lengths 1.813 (ligand A) and 1.765 and 1.775 Å (B) again differ from each other slightly. These values for an hexacoordinate silicon dianion are in fact fairly close to the axial bond length of 1.794 Å found in the pentacoordinate anion II, but are considerably longer than the equatorial bond length, 1.700 Å, in the same compound. All of these values are however substantially greater than the accepted[22] Si–O single bond distance (1.64 Å) for neutral tetrahedral silicon.

Carbon–oxygen bond distances in five-membered cyclic esters of second-row elements show large variations[3] (1.34–1.46 Å), particularly when the rings are unsaturated.[23–25] Certainly the dramatic shortening[3,23,24b] from the normal C–O single bond length[22] as in ethers and alcohols cannot be accounted for by changes in C hybridization alone. The cause of these variations is not yet known and provides one of the motivations for structural studies in this area. The present study provides a fourth example where the C–O bond lengths are near the short end of this range: the unique distances found here are 1.355, 1.356, and 1.364 Å.

The C–C bond lengths (Table IIA) in the phenyl rings also show deviations from the normal aromatic value[22] of 1.395 Å. Although such deviations do not occur in catechol itself,[26] there is growing evidence for bond localization in catechol esters of second-row elements, *e.g.*, in ions I and II, and in catechol cyclic sulfate[27] (III).



III

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In the present example, the ring bonds directly opposite the exocyclic C–O bonds are apparently shortened. Their lengths (C(3)–C(3)′, 1.355 Å, and C(6)–C(7), 1.369 Å) are, however, not nearly so short as the anomalous C(8)–C(9) bond[3] in the anion II, 1.288 Å.

C. The Pyridinium Ion. Bond distances in the pyridinium ion appear quite normal. The C–N distances, 1.337 and 1.345 Å, compare closely with 1.340 Å in pyridine,[28] as do our distances between β and γ carbons, 1.376 and 1.398 Å (pyridine, 1.394 Å). The distances between the α and β carbons, 1.361 and 1.362 Å, appear, however, to be slightly shorter than the 1.394-Å value in pyridine. Distortions from planarity, if any, are small: the maximum deviation from the least-squares plane through the ring atoms (Table IV) is 0.019 Å. The six hydrogen atoms were clearly resolved in chemically reasonable positions.

Acknowledgment. Our thanks go to C. L. Frye who recognized[16] the problems associated with the structure of these ions and who supplied us with the crystals.

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Four- and Five-Coordinate Nickel(II) Complexes with Monodentate Phosphines

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Abstract: Four- and five-coordinate nickel(II) complexes of phenyldimethylphosphine, $C_6H_5P(CH_3)_2$ (L), and pentafluorophenyldimethylphosphine, $C_6F_5P(CH_3)_2$ (L_F), have been synthesized and characterized. Whereas L gives both square-planar and five-coordinate complexes, L_F gives only square-planar $[Ni(L_F)_2X_2]$ complexes except for the five-coordinate $[Ni(L_F)_3(CN)_2]$. The intensely red-orange $[NiL_3(CN)_2]$ and $[Ni(L_F)_3(CN)_2]$ complexes are diamagnetic and nonelectrolytes in nitromethane. Both are assigned a *trans*-trigonal-bipyramidal structure on the basis of their electronic and vibrational spectra and a single-crystal X-ray study on $[NiL_3(CN)_2]$. Two other pentacoordinate complexes, $[NiL_3I_2]$ and $[NiL'_3(CN)_2]$ (where $L' = (C_6H_5)_2PCH_3$), were also isolated as solids. In contrast to the $[NiL_2X_2]$ complexes, none of the $[Ni(L_F)_2X_2]$ (X = Cl, Br, I, NCS) complexes showed any tendency to coordinate a third pentafluorophenyldimethylphosphine molecule in dichloromethane solution. Electronic spectra indicate that the ligand field strengths of $C_6H_5P(CH_3)_2$ and $C_6F_5P(CH_3)_2$ are very similar in analogous complexes. Dissociation constants of $[NiL_3X_2]$ complexes in dichloromethane solution showed that the stability of the pentacoordinate complexes is influenced by the anion and decreases in the order: $CN \gg I > Br > Cl > NO_2 > NCS$. The tendency to form pentacoordinate nickel(II) complexes is correlated with the electronegativity or polarizability of the anions rather than with their relative positions in the spectrochemical series. The reduced tendency of pentafluorophenyldimethylphosphine to stabilize five-coordinate complexes, as compared with phenyldimethylphosphine, is discussed from the viewpoint of electronic and steric factors.

Previous investigations in this laboratory have suggested that electronic considerations may be more important than steric factors in the formation of diamagnetic five-coordinate nickel(II) complexes.[1] Evaluation of these electronic factors should be attempted with monodentate ligands in order to eliminate any possibility that the geometry of the resulting complex is controlled by the symmetry or steric requirements of chelating ligands.

In contrast to the numerous stable five-coordinate complexes of nickel(II) with polydentate ligands,[1,2] most of those known with monodentate ligands are dissociated in solution as, for example, $Ni(CN)_5^{3-}$,[3] $[Ni(HP(C_6H_5)_2)_3X_2]$ (X = Cl, Br, I),[4] $[Ni(C_6H_5P(C_2H_5)_2)_3(C{\equiv}CC_6H_5)_2]$,[5] $[Ni(C_{14}H_{13}P)_3X_2]$ (X = Cl, Br, I; $C_{14}H_{13}P$ = 2-phenylisophosphindoline),[6] $[Ni(RPC_{12}H_8)_3X_2]$ (X = Cl, Br, I; $RPC_{12}H_8$ = 9-alkyl-9-phosphafluorenes),[7] $[Ni(C_6H_5P(C_2H_5)_2)_3(CN)_2]$,[8] $[NiL_3(CN)_2]$ (L = $P(OCH_3)_3$, $P(O\text{-}n\text{-}C_4H_9)_3$, $C_6H_5P(OC_2H_5)_2$, $P(OCH_2)_3CCH_3$).[9] However, dissociatively stable pentacoordinate $[NiL_3(CN)_2]$ complexes (where L = $C_6H_5P(OC_2H_5)_2$,[10,11] $C_6H_5P(OCH_3)_2$, $P(OC_2H_5)_3$,[11] and $P(OC_6H_5)_3$[9]) have been reported recently. Gray, *et al.*,[11] suggested that steric interactions of some bulky tertiary phosphines, such as $(C_6H_5)_3P$, may preclude formation of $[NiL_3(CN)_2]$ complexes. However, Verkade, *et al.*,[9] concluded from spectral studies with similar phosphite ligands that the importance of steric factors with $(C_6H_5)_3P$ had been overemphasized.

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