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Structural Chemistry of Pentacoordinated Silicon. Molecular Structures of the Pentafluorosilicate Anion and the Diphenyltrifluorosilicate Anion

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The X-ray structure determination of benzyltrimethylammonium pentafluorosilicate, $[C_6H_5CH_2N(CH_3)_3]^+[SiF_5]^-$ (**1**), and tetramethylammonium diphenyltrifluorosilicate $[(CH_3)_4N]^+[(C_6H_5)_2SiF_3]^-$ (**2**) shows that the anions are pentacoordinated at silicon and have a trigonal-bipyramidal geometry. The phenyl groups in **2** occupy equatorial positions of the TBP. In the diphenyl derivative **2** bond lengths to the axial and equatorial fluorine atoms are significantly longer than in **1**. Both anions display crystallographic C_2 symmetry with the axis passing through silicon and one of the equatorial ligands. **1** crystallizes in the orthorhombic space group *Pbcm*, with the following cell parameters at 170 K: $a = 12.077$ (1) Å, $b = 7.855$ (1) Å, $c = 13.297$ (1) Å, and $Z = 4$. **2** crystallizes in the trigonal space group $P3_221$, with the cell parameters $a = 8.8046$ (5) Å, $b = 18.4224$ (17) Å, and $Z = 3$. The final conventional residuals were 0.039 and 0.041 for **1** and **2**, respectively.

Introduction

It is well-known that silicon can increase its coordination number to values higher than 4 to form compounds that are penta- or hexacoordinated at the silicon atom. The fluorosilanes SiF_4, $RSiF_3$ (R = Me, Ph), and Ph_2SiF_2 react with tetraalkylammonium fluorides in a 1:1 ratio to yield stable ionic compounds.[1] From NMR[1,2] and vibration[3,4] spectroscopic data it was concluded that the anions in these compounds are pentacoordinated at silicon and have a trigonal-bipyramidal geometry.

These pentacoordinated silicon compounds have been of some interest recently because they represent model compounds for the transition state of an S_N2 reaction at tetracoordinated silicon,[5,6] which is generally believed to take place via a trigonal-bipyramidal transition state.[7]

Since it became known that the geometry around silicon in the spirobicyclic compounds $[FSi(OC_6H_4O)_2]^-$,[8] $[MeSi(OCH_2CH_2O)_2]^-$,[9] and $[FSi(OCMe_2CMe_2O)_2]^{-}$[10] can better be described as a square pyramid than as a trigonal bipyramid, the lack of accurate structural data on acyclic λ^5-silicates became especially obvious.

Several attempts were made to get accurate structural information on $[SiF_5]^-$, the most simple of the possible anions with pentacoordinate silicon. In one case the structure determination of $[Ph_4As]^+[SiF_5]^-$ failed because of a difficult kind of crystallographic disorder.[11] In another case approximate structural data of a pentafluorosilicate originating from the reaction of an iridium complex with SiF_4 was obtained. The accuracy of this structure determination, however, was reduced because of very large vibrational motion (estimated standard deviations of the bond lengths 0.04 Å and of the bond angles 4°).[12] To our knowledge $[NPr_4]^+[PhSiF_4]^-$ remains the only example of this type of compound where accurate structural information is available.[13]

In order to determine the structure of $[SiF_5]^-$, we collected a data set of the tetraethylammonium salt first but we observed at least fourfold disorder at the position of the anion whereas the atomic positions of the cation were well resolved (space group $I\bar{4}$, $Z = 2$, $a = 9.552$ Å, $c = 7.237$ Å). Benzyltrimethylammonium pentafluorosilicate finally gave well-defined positions for the atoms although vibrational motions are still rather strong (U_{eq} values for the fluorine atoms are 0.12–0.20 Å^2). In order to get more accurate bonding parameters, the data collection was repeated at 170 K. At this temperature thermal motions were reduced to normal values (U_{eq} values for the fluorine atoms are 0.05–0.08 Å^2).

Comparison of the bonding parameters of $[SiF_5]^-$, $[PhSiF_4]^-$, and $[Ph_2SiF_3]^-$ should give some information on the stability and the type of bonding in this class of compounds.

Experimental Section

Benzyltrimethylammonium pentafluorosilicate was prepared by a method that was described in ref 1 for similar compounds:

$$[C_6H_5CH_2N(CH_3)_3]^+F^- + SiF_4 \xrightarrow{\text{MeOH}}$$
$$[C_6H_5CH_2N(CH_3)_3]^+[SiF_5]^-$$
$$\mathbf{1}$$
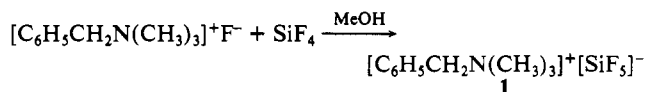
Crystal Data for 1. Suitable colorless crystals were obtained by recrystallization from CH_2Cl_2. The crystals have orthorhombic symmetry, space group *Pbcm*. The unit cell, which at 170 K has the parameters $a = 12.077$ (1) Å, $b = 7.855$ (1) Å, and $c = 13.297$ (1) Å, contains four molecules, yielding a calculated density of 1.439 g/cm^3. Data for a crystal of the dimensions 0.5 × 0.3 × 0.3 mm were measured at 170 K on a Syntex P2$_1$ diffractometer using graphite-monochromated Cu Kα (1.541 78 Å) radiation in the θ–2θ mode in the range $3° \leq 2\theta \leq 115°$ at a scan speed of 3°/min.

The data were corrected for Lorentz and polarization effects, but no absorption correction was made ($\mu = 19.42$ cm^{-1} for Cu Kα radiation). After reduction of the data 836 out of 900 measured reflections ($I \geq 1.25\sigma(I)$) were retained for the refinement of the structure. The structure was solved by Patterson and difference maps. The hydrogen atoms together with individual isotropic temperature factors were included in the refinement. After anisotropic temperature factors were introduced for the non-hydrogen atoms, the refinement converged to a final value of $R = 0.039$. In the last cycle of refinement the shifts for all parameters divided by their standard deviations were smaller than 0.001. A final difference map displayed no electron density higher than 0.31 e/Å^3.

Tetramethylammonium diphenyltrifluorosilicate was also prepared by direct reaction of the tetraalkylammonium fluoride with the tetracoordinated silicon compound:[1]

$$[(CH_3)_4N]^+F^- + (C_6H_5)_2SiF_2 \xrightarrow{\text{MeOH}} [(CH_3)_4N]^+[(C_6H_5)_2SiF_3]^-$$
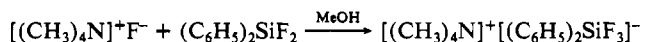
(1) Klanberg, F.; Muetterties, E. L. *Inorg. Chem.* **1968**, *7*, 155.
(2) Marat, R. K.; Janzen, A. F. *Can. J. Chem.* **1977**, *55*, 1167.
(3) Clark, H. C.; Dixon, K. R.; Nicholson, J. G. *Inorg. Chem.* **1969**, *8*, 450.
(4) Ault, B. S. *Inorg. Chem.* **1979**, *18*, 3339.
(5) E. g.: Corriu, R. J. P.; Poirier, M.; Royo, G. *J. Organomet. Chem.* **1982**, *233*, 165.
(6) Schomburg, D. *Z. Anorg. Allg. Chem.* **1982**, *493*, 53.
(7) Corriu, R. J. P.; Guerin, C. *J. Organomet. Chem.* **1980**, *198*, 231.
(8) Harland, J. C.; Day, R. O.; Vollano, J. F.; Sau, A. C.; Holmes, R. R. *J. Am. Chem. Soc.* **1981**, *103*, 5269.
(9) Schomburg, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1982**, *37B*, 195.
(10) Schomburg, D. *Z. Naturforsch., B: Anorg. Chem., Org. Chem.* **1983**, *38B*, 702.
(11) Corfield, P. W. R.; Ibers, J. A. Abstracts, Annual Meeting of the American Crystallographic Association, Summer Meeting, 1968; p 52.
(12) Bird, P.; Harrod, J. F.; Than, K. A. *J. Am. Chem. Soc.* **1974**, *96*, 1222.
(13) Schomburg, D. *J. Organomet. Chem.* **1981**, *221*, 137.

Table I. Atomic Coordinates in Crystalline $[BzlNMe_3]^+[SiF_5]^-$

	x/a	y/b	z/c
Si	0.3602 (1)	0.75	0.0
F(1)	0.3595 (1)	0.7296 (2)	0.1232 (1)
F(2)	0.2914 (1)	0.9236 (2)	0.0096 (1)
F(3)	0.4910 (2)	0.75	0.0
N	0.6872 (2)	0.6927 (3)	0.25
C(1)	0.5731 (3)	0.6196 (5)	0.25
C(2)	0.7016 (2)	0.8001 (3)	0.1583 (2)
C(10)	0.7680 (2)	0.5443 (4)	0.25
C(11)	0.8882 (3)	0.5907 (4)	0.25
C(12)	0.9463 (2)	0.6059 (3)	0.3400 (2)
C(13)	1.0589 (2)	0.6361 (3)	0.3393 (3)
C(14)	1.1150 (4)	0.6515 (5)	0.25

Table II. Atomic Coordinates in Crystalline $[NMe_4]^+[Ph_2SiF_3]^-$

	x/a	y/b	z/c
Si	-0.3873 (1)	0.0	0.1667
F(1)	-0.2002 (3)	0.0	0.1667
F(2)	-0.3993 (2)	-0.0491 (2)	0.0775 (1)
C(1)	-0.6009 (3)	-0.2084 (3)	0.1864 (1)
C(2)	-0.6385 (3)	-0.2909 (3)	0.2538 (1)
C(3)	-0.7957 (4)	-0.4427 (4)	0.2673 (2)
C(4)	-0.9212 (4)	-0.5143 (4)	0.2155 (2)
C(5)	-0.8911 (4)	-0.4362 (4)	0.1482 (2)
C(6)	-0.7309 (4)	-0.2862 (4)	0.1338 (1)
N	-0.0845 (3)	0.0	-0.3333
C(7)	0.0710 (10)	0.1135 (10)	-0.2915 (4)
C(8)	-0.1213 (11)	0.1101 (14)	-0.3820 (5)

Table III. Bond Lengths (Å) and Angles (deg) for 1^a

F(1)-Si	1.646 (1)	F(2)-Si	1.602 (2)
F(3)-Si	1.579 (2)	C(1)-N	1.492 (4)
C(2)-N	1.493 (3)	C(10)-N	1.520 (4)
C(11)-C(10)	1.497 (4)	C(12)-C(11)	1.392 (3)
C(13)-C(12)	1.380 (4)	C(14)-C(13)	1.373 (5)

F(2)-Si-F(1)	90.0 (1)	F(3)-Si-F(1)	90.3 (1)
F(3)-Si-F(2)	121.2 (1)	F(1)-Si-F(1')	179.4 (0)
F(2)-Si-F(2')	117.5 (1)	C(2)-N-C(1)	109.0 (2)
C(10)-N-C(1)	107.3 (2)	C(10)-N-C(2)	111.0 (2)
C(2)-N-C(2')	109.5 (2)	C(11)-C(10)-N	115.9 (2)
C(12)-C(11)-C(10)	120.6 (2)	C(13)-C(12)-C(11)	120.4 (3)
C(12)-C(11)-C(12)	118.5 (3)	C(14)-C(13)-C(12)	120.5 (4)
C(13)-C(14)-C(13')	119.8 (4)		

^{a} For librationally corrected values, see Table V.

Crystal Data for $[NMe_4]^+[Ph_2SiF_3]^-$ (2). Colorless crystals of **2**, which were obtained by recrystallization from CH_2Cl_2, have trigonal symmetry, space group $P3_221$. The unit cell, which has the parameters $a = 8.8046$ (5) Å, and $c = 18.4224$ (17) Å, contains three molecules, yielding a calculated density of 1.262 g/cm^3.

Data for a crystal of the dimensions 0.4 × 0.3 × 0.2 mm were collected on a Stoe STADI 4 diffractometer with monochromated Mo Kα radiation (λ = 0.710 69 Å) in the θ-2θ mode in the range 3° ≤ 2θ ≤ 50° at a scan speed of 3°/min. Lorentz and polarization factors were applied, but no absorption correction was made (μ = 1.26 cm⁻¹ for Mo Kα radiation). After the data reduction 1393 out of 1466 measured independent reflections ($I \geq 1.25\sigma(I)$) were retained for the refinement.

The structure was solved by heavy-atom methods and difference maps. Hydrogen atoms together with individual isotropic temperature factors were included in the refinement. For all other atoms anisotropic temperature factors were introduced. After several cycles the refinement converged to a final value of $R = 0.041$. In the last cycle of refinement the shifts for all parameters divided by their standard deviations were smaller than 0.01. Af final difference map showed no electron density higher than 0.32 $e/Å^3$. For data reduction, structure solution, and refinement the program SHELX-76[14] and our own programs were used. Complex neutral-atom scattering factors were employed.[15]

(14) Sheldrick, G. M., unpublished program.

Table IV. Bond Lengths (Å) and Angles (deg) for 2^a

F(1)-Si	1.648 (2)	F(2)-Si	1.688 (1)
C(1)-Si	1.893 (2)	C(2)-C(1)	1.393 (3)
C(6)-C(1)	1.391 (3)	C(3)-C(2)	1.383 (4)
C(4)-C(3)	1.355 (5)	C(5)-C(4)	1.377 (5)
C(6)-C(5)	1.393 (4)	C(7)-N	1.448 (6)
C(8)-N	1.471 (5)		

F(2)-Si-F(1)	86.2 (1)	C(1)-Si-F(1)	120.6 (1)
C(1)-Si-F(2)	92.0 (1)	C(2)-C(1)-Si	122.6 (2)
C(6)-C(1)-Si	121.2 (2)	C(6)-C(1)-C(2)	116.2 (2)
C(1)-Si-C(1')	118.9 (1)	C(3)-C(2)-C(1)	121.7 (3)
C(4)-C(3)-C(2)	120.8 (3)	C(5)-C(4)-C(3)	119.6 (3)
C(6)-C(5)-C(4)	119.7 (3)	C(5)-C(6)-C(1)	121.9 (3)
C(8)-N-C(7)	108.3 (6)	C(7)-N-C(7')	106.2 (9)
C(8)-N-C(8')	113.2 (5)		

^{a} For librationally corrected values, see Table V.
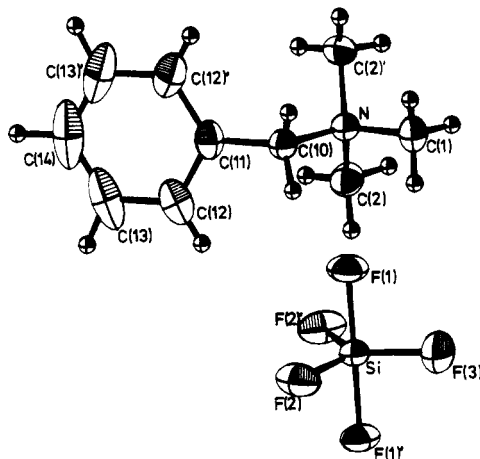
Figure 1. ORTEP plot of $[BzlNMe_3]^+[SiF_5]^-$ with thermal ellipsoids at the 50% level.
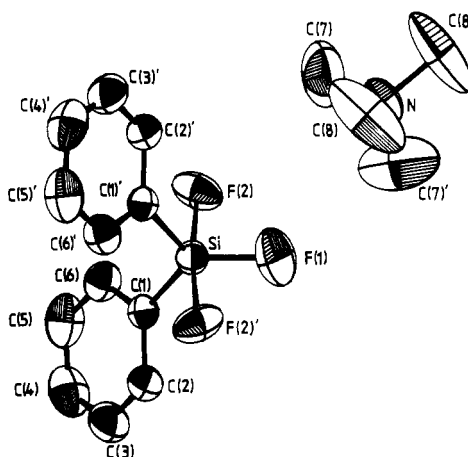
Figure 2. ORTEP plot of $[NMe_4]^+[Ph_2SiF_3]^-$ with thermal ellipsoids at the 50% level.

Results

Atomic coordinates for both compounds are given in Tables I and II; bond lengths and angles for compound **1** are given in Table III and for compound **2** in Table IV.

The benzyltrimethylammonium cation in compound **1** displays crystallographic mirror symmetry with the mirror plane through C(1), N, C(10), C(11), and C(14). The penta-

(15) Cromer, D. T.; Waber, J. T. *Acta Crystallogr.* **1965**, *18*, 104.
(16) A reviewer pointed to the fact that the negative charge is probably distributed over the fluorine atoms. Of course, the statement about the *formal* negative charge does not imply that silicon is really negatively charged but that the positive charge on the silicon atom in $[SiF_5]^-$ is smaller than in SiF_4.

Table V. Bond Lengths (Å) in Some Silicon-Fluorine Compounds (Mean Values)

	$[SiF_5]^-$		$[PhSiF_4]^-$		$[Ph_2SiF_3]^-$		SiF_4	$PhSiF_3$[b]	$[SiF_6]^{2-}$
Si-F$_{ax}$	1.646	1.660[a]	1.669	1.691[a]	1.688	1.705[a]	\} 1.56 (1)	1.572 (6)	1.685
Si-F$_{eq}$	1.594	1.622[a]	1.602	1.626[a]	1.648	1.662[a]			
Si-C$_{eq}$			1.871	1.896[a]	1.893	1.903[a]		1.822 (31)	
ref	this work		13		this work		17	20	27

[a] Values corrected for thermal motion.[30]   [b] Electron diffraction.

fluorosilicate anion displays crystallographic C_2 symmetry. The twofold axis passes through the silicon atom and one of the equatorial fluorine atoms (F(3)). As the anion shows rather strong thermal vibration at room temperature, the data collection was repeated at low temperature. This reduced the thermal motion significantly (U_{22} of F(3) from 0.359 Å² at room temperature to 0.148 Å², U_{11} of F(1) from 0.150 Å² to 0.060 Å²).

The overall geometry of the anion is a slightly distorted trigonal bipyramid. The largest deviation from the ideal geometry occurs at the angle F(2)–Si–F(2)′, which is 2.5° smaller than the ideal angle of 120°. This distortion can be explained by intermolecular repulsion between F(2) and three hydrogen atoms of the cation (F2)···H(10) = 2.55 Å, F(2)···H(21) = 2.65 Å, F(2)···H(13) = 2.61 Å). Other close contacts are F(1)···H(101) = 2.59 Å, F(1)···H(14) = 2.65 Å, and F(1)···H(10) = 2.53 Å.

The cation and anion of **2** are situated on crystallographic twofold axes. The geometry around silicon is a slightly distorted trigonal bipyramid with the C_2 axis passing through the silicon atom and the equatorial fluorine. The phenyl groups occupy equatorial positions. The largest deviation from the ideal trigonal bipyramid is observed at the axial Si–F bonds, which are distorted toward the equatorial silicon–fluorine bond (F_{eq}–Si–F_{ax} = 86.2°). This distortion is probably caused by intramolecular repulsions between the axial fluorine atoms and the ortho-hydrogen atoms in the phenyl rings (F_{ax}···H(1) = 2.29 Å, F_{ax}···H(6) = 2.43 Å). The angle τ between the equatorial plane and the phenyl rings (75°) is rather large.

Carbon–hydrogen bond distances for **1** are found to be between 0.89 (4) and 1.00 (3) Å and for **2** between 0.85 (5) and 1.23 (6) Å.

Discussion

All three known fluorosilicates, $[SiF_5]^-$, $[PhSiF_4]^-$, and $[Ph_2SiF_3]^-$, have a trigonal-bipyramidal geometry at the silicon atom. As in other compounds containing a main-group element in a trigonal-bipyramidal environment,[24] the axial bond distances are longer then corresponding equatorial ones. But even the equatorial Si–F bond distances are significantly longer than the bonds in SiF_4 (1.56 Å).[17] This lengthening of the bonds may be due to the rise of the coordination number from 4 to 5, which means that the silicon–fluorine bonds have bond orders smaller than 1 or include participation of a d orbital which is higher in energy. Another explanation could be an enlargement of the bonding orbitals of silicon or decrease of (d–p) π bonding between silicon and fluorine because of the formal negative charge at silicon.[16] In order to distinguish between the mentioned possibilities, a comparison with compounds containing the neighboring element phosphorus might be helpful. In comparable phosphorus compounds only a very small difference is observed between P–F bond distances at tetracoordinate phosphorus (P–F in POF_3 1.524 (3) Å)[18] and equatorial bonds at pentacoordinate phosphorus (P–F$_{eq}$ in PF_5 1.534 (4) Å).[19] In contrast the axial P–F bond distances in

PF_5 are 0.053 Å longer[19] than the P–F bonds in POF_3.

Therefore, it may be assumed that the negative charge is mainly responsible for the lengthening of the equatorial Si–F bonds in λ^5-Si fluorosilicates compared to the bonds in SiF_4 or $PhSiF_3$ (Si–F = 1.572 (6) Å).[20]

Substitution of fluorine by one or two less electronegative phenyl groups causes a consistent lengthening of the axial Si–F bond distances of 0.031 ($[PhSiF_4]^-$)[13] and 0.045 Å.

Contrary to this observation the equatorial bond lengths in $[SiF_5]^-$ are not significantly different from those in $[PhSiF_4]^-$.

A similar trend is observed in the isoelectronic phosphoranes, where the axial P–F bonds in $PhPF_4$[23] are 0.039 Å longer than in PF_5[19] whereas no significant difference between equatorial bond lengths was observed.[21]

Whereas in the series PF_5[19]–$MePF_4$[22]–Me_2PF_2[22] weakening of the axial bonds (0.067 Å longer in Me_2PF_3) is more pronounced than of the equatorial bonds (0.009 and 0.019, respectively), the situation is more complicated for the silicates $[SiF_5]^-$–$[PhSiF_4]^-$–$[Ph_2SiF_3]^-$. In $[PhSiF_4]^-$ only for the axial bonds is a significant weakening found, but in $[Ph_2SiF_3]^-$ axial and equatorial bonds are lengthened by approximately the same amount (0.045 and 0.040 Å, respectively).

The distortions from the trigonal-bipyramidal geometry at the substituted fluorosilicates (though they are small and without doubt are partly caused by packing forces) follow some general trends:

(1) An opening of an X_{eq}–Si–X_{eq} angle causes a closing of the X_{ax}–Si–X_{ax} angle, a distortion which would finally lead to a square-pyramidal geometry. This geometry was observed in some spirobicyclic λ^5-Si compounds[8-10] and several phosphoranes[24] (e.g. in $[PhSiF_4]^-$ F_{eq}–Si–F_{eq} = 121.4°, F_{ax}–Si–F_{ax} = 174.6°, and C–Si–F_{ax} = 92.7°).

(2) A closing of the F_{eq}–Si–F_{eq} angle causes an opening of X_{ax}–Si–X_{ax} toward the third equatorial ligand. This kind of distortion is found in compound **2**[25] (e.g. in $[Ph_2SiF_3]^-$ C_{eq}–Si–C_{eq} = 118.9°, F_{ax}–Si–F_{ax} = 187.5°, and F_{eq}–Si–F_{ax} = 86.2°).

Whereas the especially small distortion in the pentafluorosilicate anion must be due to packing effects, the dis-

(17) Atoji, M.; Lipscomb, W. N. *Acta Crystallogr.* **1954**, *7*, 597.
(18) Moritani, T.; Kuchitsu, K.; Morino, Y. *Inorg. Chem.* **1971**, *10*, 344.
(19) Hansen, K. W.; Bartell, L. S. *Inorg. Chem.* **1965**, *4*, 1775.

(20) Il'enko, T. M.; Veniaminov, N. N.; Alekseev, N. V. *Zh. Strukt. Khim.* **1975**, *16*, 292.
(21) The very pronounced effect of electronegativity on the axial bond lengths becomes especially evident when the P–F$_{ax}$ bond distances in $(CH_3)_3PF_2$ (1.685 (1) Å)[28] and $(C_6F_5)_3PF_2$ (1.636 (2) Å)[29] are compared. Though the methyl groups are less space demanding, the P–F bonds in the pentafluorophenyl derivative are 0.049 Å shorter.
(22) Bartell, L. S.; Hansen, W. *Inorg. Chem.* **1965**, *4*, 1777.
(23) Dittebrandt, C.; Oberhammer, H. *J. Mol. Struct.* **1980**, *63*, 227.
(24) For a recent review on the geometry of pentacoordinted phosphorus compounds, see: Holmes, R. R. "Pentacoordinated Phosphorus"; American Chemical Society: Washington, DC, 1980; Vol. 1, ACS Monogr. No. 175, 1980; p 9 ff.
(25) With respect to R. S. Berry, who had first proposed the distortion of trigonal-bipyramidal phosphoranes toward a square pyramid for a process leading to an exchange of axial and equatorial ligands,[26] the first distortion may be called a "Berry distortion" and the second an "anti-Berry distortion".
(26) Berry, R. S. *J. Chem. Phys.* **1960**, *32*, 933.
(27) Denne, W. A.; Mathieson, A. M.; Mackay, M. F. *J. Cryst. Mol. Struct.* **1971**, *1*, 55.
(28) Yow, H.; Bartell, L. S. *J. Mol. Struct.* **1973**, *15*, 209.
(29) Sheldrick, W. S. *Acta Crystallogr.* **1975**, *B31*, 1776.
(30) Schomaker, V.; Trueblood, H. N. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1968**, *B24*, 63.

tortions in both phenyl derivatives can be explained by repulsion between the space-demanding phenyl groups and the axial ligands. In the [PhSiF$_4$]⁻ anion the axial bonds are bent away 5.4° from the phenyl ring; in [Ph$_2$SiF$_3$]⁻ the axial bonds are bent 7.5° toward the equatorial fluorine atom. Despite this distortion the F⋯H(ortho) distances are quite short (see above and ref 13).

The structural data that are now available for compounds of pentacoordinated silicon indicate that these compounds follow the same path of minimum energy as the isoelectronic phosphoranes when distortions from the trigonal-bipyramidal geometry are observed. The degree of distortion, however, (especially for spirobicyclic compounds) may be very different from that observed in similar phosphorus compounds.

Registry No. 1, 89210-88-8; **2,** 17632-46-1.

Supplementary Material Available: Tables of anisotropic temperature factors, positional and isotropic temperature factors for hydrogen atoms, and observed and calculated structure factors for both compounds (20 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Harvard University, Cambridge, Massachusetts 02138

Higher Valent Manganese Chemistry. Synthetic, Structural, and Solution Studies on [Mn(catecholate)₃]ⁿ⁻ (n = 2, 3) Complexes

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The complexes (Et$_3$NH)$_2$[Mn(Cat)$_3$] and K$_2$[Mn(3,5-(*t*-Bu)$_2$Cat)$_3$]·6CH$_3$CN (Cat = catecholate) have been synthesized, and the latter has been characterized by X-ray diffraction (trigonal system, space group $R\bar{3}$, a = 14.760 (9) Å, c = 50.752 (32) Å, Z = 6, final R = 6.9%, final R_w = 7.1%). The [Mn(3,5-(*t*-Bu)$_2$Cat)$_3$]²⁻ anion has crystallographic threefold symmetry with short Mn–O bond lengths (1.922 (3) and 1.891 (3) Å) and no evidence of either dynamic or static Jahn–Teller distortion. The electron paramagnetic resonance spectrum of the [Mn(Cat)$_3$]²⁻ ion at 77 K is characteristic of a d³ system with large zero-field splitting. The magnetic behavior of K$_2$[Mn(3,5-(*t*-Bu)$_2$Cat)$_3$]·6CH$_3$CN is fully consistent with that expected for a simple d³ system. The present structural, magnetic susceptibility, and magnetic resonance results establish that these essentially identical chelates are tris(catecholate)manganese(IV) rather than (semiquinone)bis(catecholate)manganese(III) complexes. The present structural results also show that the "bite distance" of catechol (2.58 Å) is too short to offer a regular octahedral environment to Mn(IV). This fact has a pervasive influence on the chemistry of the system. It causes trigonal compression of the Mn(IV) ion and thereby gives rise to the large zero-field splitting observed. In the Mn(III)–catechol system, it actually determines the solution chemistry. Because Mn(III) is even larger than Mn(IV) and has either two or four elongated bonds (by the Jahn–Teller theorem), three catechol ligands cannot span all six coordination sites in a chelating fashion. The short bite distance of catechol therefore effectively prevents formation of [Mn^III(Cat)$_3$]³⁻. Moreover, the difficulty of forming a tris complex of Mn(III) with a catechol-like ligand may contribute significantly to stabilization of [Mn(3,5-(*t*-Bu)$_2$Cat)$_3$]²⁻ as tris(catecholate)manganese(IV) instead of (semiquinone)bis(catecholate)manganese(III).

Introduction

Relatively little is known of the chemistry of the higher valence states of manganese,[2] although Mn(III) and Mn(IV) are thought to play a central role in photosynthetic oxygen evolution.[3] Recent EXAFS results on chloroplasts and Mn(III) and Mn(IV) model compounds support this long-held presumption.[4] However, for relatively few Mn(III) or Mn(IV) complexes are either the electronic or the molecular structures known, and in particular the factors that determine their redox potentials are not well understood. In large part this is because few ligands are presently known that can complex these ions without being oxidized by them.

One ligand with remarkable ability to stabilize high oxidation states is catechol (*o*-dihydroxybenzene). Complexes of catechol with, e.g., Fe(III),[5] V(V),[6] Ti(IV),[7] and even Ce(IV)[8] are all extremely stable, and recently the Mn(IV)–catecholate complex [Mn(3,5-(*t*-Bu)$_2$Cat)$_2$(py)$_2$] (Cat = catecholate) has been reported.[9] Coordinated catechol can also
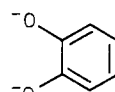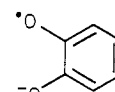
catecholate   semiquinone

be oxidized to the *o*-semiquinone, which is itself a good ligand.[10] A wide variety of metal semiquinone complexes have been prepared in the last 5 years, in particular by Razuvaev and Pierpont, Hendrickson, and their co-workers. The area has been reviewed,[10] and theoretical studies on V, Cr, and Fe quinone–semiquinone–catecholate complexes have recently been published.[11,12]

Recently Sawyer and co-workers reported that reaction of manganic acetate with 3,5-di-*tert*-butylcatechol and 3,5-di-*tert*-butyl-*o*-benzoquinone in the presence of base gave a deep

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