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Catecholate Complexes of Silicon: Synthesis and Molecular and Crystal Structures of $[Si(cat)_2]\cdot 2THF$ and $Li_2[Si(cat)_3]\cdot 3.5dme$ (cat = Catecholate Dianion)

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The neutral complex $[Si(cat)_2]$ (**1**) and the anionic complex $Li_2[Si(cat)_3]$ (**2**) (cat = catecholate dianion) have been prepared by addition of stoichiometric amounts of Li_2cat to a solution of $SiCl_4$ in THF. The THF-soluble Li_2cat starting material was obtained by deprotonation of catechol with *n*-BuLi or LiH in THF. Both the neutral complex **1** and the lithium salt **2** show good solubility in THF. The molecular structures of both **1** and **2** have been determined by X-ray diffraction. Crystals of **1**·2THF belong to the monoclinic space group $P2_1/c$ with unit cell parameters $a = 6.3428(8)$ Å, $b = 17.7274(13)$ Å, $c = 9.1437(10)$ Å, $\beta = 108.763(10)°$, $V = 973.5(4)$ Å^3, and $Z = 2$; R (R_w) = 3.89% (4.79%) for 125 refined parameters and 1142 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The silicon atom in **1**·2THF lies on an inversion center in the unit cell and is coordinated in an octahedral fashion by four catecholate and two THF oxygen atoms. Compound **2** was crystallized from dme (dme = 1,2-dimethoxyethane) in the triclinic space group $P\bar{1}$ as $Li_2[Si(cat)_3]\cdot 3.5dme$ (**2**·3.5dme) with unit cell parameters $a = 11.7680(13)$ Å, $b = 12.3986(13)$ Å, $c = 13.7981(15)$ Å, $\alpha = 79.833(9)°$, $\beta = 81.158(10)°$, $\gamma = 63.676(10)°$, $V = 1769.6(3)$ Å^3, and $Z = 2$; R (R_w) = 3.99% (5.32%) for 434 refined parameters and 4833 reflections with $F_o^2 \geq 3\sigma(F_o^2)$. The silicon atom in **2**·3.5dme is at the center of an octahedron consisting the six catecholate oxygen atoms. Each of the two lithium cations is at the center of a distorted octahedron composed of three facial oxygen atoms of the SiO_6 octahedron and three oxygen atoms from dme solvent molecules.

Introduction

Catechol (*o*-dihydroxybenzene) forms very stable complexes with transition metals and is Nature's choice as the functional group in siderophores such as enterobactin.[1,2] Because of its strong complexing ability, the catecholate binding group has been incorporated into a number of multidentate ligands[3−6] which are promising artificial sequestering agents for iron decorporation and other sequestering applications.[7,8] Most homoleptic metal complexes of the catecholate dianion[9] (cat^{2-}) carry a negative charge {e.g., eight-coordinate $[M(cat)_4]^{n-}$ (n = 4, M = Th,[10] U,[10] Ce,[11] Hf;[11] n = 5, M = Gd[12]) and six-coordinate $[E(cat)_3]^{n-}$ (n = 1, E = P;[13] n = 2, E = Mn,[14] Sn,[15] Si;[16] n = 3, E = Cr,[17,18] Fe,[17] V[19])} although a few neutral complexes of the type $[M(cat)_3]_m$ (m = 2, M = W,[20] Mo;[21] n = 1, M = Re,[22] Tc,[23] Os[24]) with the metal in the formal +6 oxidation state and tetrachlorocatecholate[20−22] or di-*tert*-butylcatecholate[22−24] ligands are known. The anionic complexes have usually been isolated as sodium, potassium, or trialkylammonium salts; generally these are only soluble in protic solvents; they are slightly soluble or insoluble in polar aprotic solvents.[15,16] They are difficult to crystallize from protic solvents; catechol ligands seem chosen by Nature to **solubilize** ferric iron as the tricatecholate in water and the formation of multiple hydrogen bonds between the anionic complex and a protic or polar solvent effectively prevents precipitation. These properties have hampered the crystallization and characterization by X-ray diffraction of catecholate complexes, especially of

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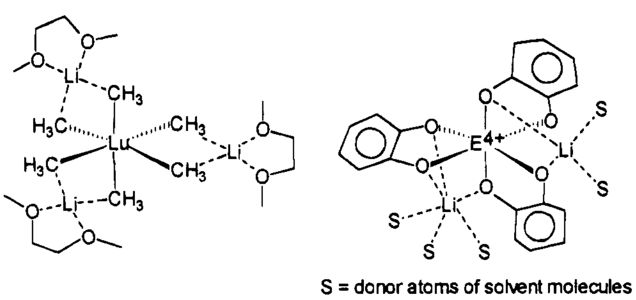

Figure 1. Coordination geometry in the ion pair $[Li(dme)]_3[Lu(CH_3)_6]$ (left) and possible geometry in the ion pair $[LiS_3][E(cat)_3]$ (right).

complexes with tripodal hexadentate tris(catecholate) ligands. Indeed, the first crystal structure of a ferric complex with a tris(catecholate) ligand was reported in 1987,[4] although the structure of $K_3[Fe(cat)_3]$ has been known since 1976.[17] Crystal structures of some additional complexes with tris(catecholate) ligands have been reported[5,6] followed by the structure of the vanadium complex of enterobaction in 1992.[25]

To faciliate the preparation of single crystals, we set out to produce ether-soluble salts of anionic catecholate complexes. We reasoned that the lithium salts of anionic catecholate complexes would form tight ion pairs, which should be soluble in ethers, in which hydrogen bond formation will not occur. This strategy was previously employed for the preparation of ether-soluble lithium salts of anionic organolanthanide complexes;[26] for example, the $[Lu(CH_3)_6]^{3-}$ anion forms an ether-soluble tight ion pair in which the lithium cations reside between the negatively charged methyl groups and complete their coordination sphere by coordination of 1,2-dimethoxyethane solvent molecule.[27] This bonding situation is schematically depicted in Figure 1 (left), where instead of dme, the diamine tmeda (tmeda = *N,N,N',N'*-tetramethylethylenediamine) can be used for coordination to the lithium cations.[28]

For a tight ion pair of an $[M(cat)_3]^{2-}$ dianion (as depicted in Figure 1 (right)) two geometries are possible: (i) each lithium is tetrahedrally coordinated by two adjacent catecholate oxygen atoms and two donor atoms from solvent molecules (oxygen atoms from ethers) or (ii) each lithium cation occupies a position above opposite triangular faces of the $E^{IV}O_6$ octahedron and is coordinated by three more donor atoms from solvent molecules in an octahedral fashion as depicted in Figure 1 (right).

The silicon(IV) complexes of the catecholate dianion are useful to test this because of the redox-innocent Si(IV). Another reason for studying silicon catecholates is the old controversy about planar tetracoordinated silicon. The molecular structure of monomeric $[Si(cat)_2]$[29] has been subject to speculation and disagreement.[30] Precession and Weissenberg photographs of single crystals of $[Si(cat)_2]$ led to the space group assignment $P2_1/c$ with $Z = 2$.[29] If this is the space group, each silicon atom must occupy a crystallographic inversion center, and if the structure is ordered and monomeric, the SiO_4 unit is required to be planar. This assumption was said to be supported by theoretical arguments showing only a small difference in the energy between tetrahedral and planar four-coordinate silicon.[31] Dunitz has challenged the proposed planar, four-coordinated silicon,[30] an opinion we share. In this contribution we report a new method for the preparation of the ether-soluble salt $Li_2[Si(cat)_3]$ and the neutral monomeric complex $[Si(cat)_2]$, together with crystal structures of the ether adducts of these complexes.

Experimental Section

General Methods. All reactions were carried out in an atmosphere of dried argon using standard Schlenk line techniques. Tetrahydrofuran (THF) and dimethoxyethane (dme) were distilled from potassium benzophenone ketyl under dry nitrogen. Dichloromethane (CH_2Cl_2) was distilled under a nitrogen atmosphere from P_2O_5. Catechol and $SiCl_4$ were purchased from Aldrich Chemical Co. Catechol was freshly sublimed prior to use. ^{1}H-NMR spectra were obtained on a UCB 200-MHz Nicolet spectrometer. Chemical shifts (δ) are referenced to solvent resonances. IR data were obtained from Nujol mulls on KBr plates on a Nicolet 5DXB FTIR spectrometer and are reported in wavenumbers. Mass spectral data were recorded as negative ion fast-atom-bombardment spectra (−FAB) using thioglycerol/glycerol as the matrix or as EI-LRMS. Elemental analyses and mass spectral characterization were performed by the Microanalytical Laboratory, College of Chemistry, University of California, Berkeley, CA.

$[Si(cat)_2]\cdot 2THF$ (1·2THF). Catechol (2.0 g, 18.2 mmol) was dried in a 250 mL Schlenk flask at oil pump vacuum and 50 °C for 30 min. Dry THF (50 mL) was added under argon, and the colorless solution was cooled to −78 °C. *n*-Butyllithium (36.4 mmol, 15.2 mL of a 2.4 M hexane solution in 30 mL of THF) was added *via* a dropping funnel at −78 °C during 15 min. A thick, colorless precipitate formed upon addition of the first half of the *n*-butyllithium which redissolved upon addition of the second half. The reaction mixture was allowed to warm to room temperature, and a slightly yellow solution was obtained. A small sample of this solution was taken to dryness. The IR spectrum showed no O−H absorptions at 3328 and 3449 cm^{-1}, which is indicative of complete deprotonation of catechol. Similar results are obtained if catechol is stirred with LiH in THF for 20 h. [NaH leads, as expected, to insoluble Na_2cat, while CaH_2 does not deprotonate catechol.] $SiCl_4$ (8.1 mmol, 1.44 g, 1.04 mL in 15 mL of dry THF) was added dropwise with a syringe to the THF solution of Li_2cat at room temperature. The reaction mixture was stirred for another 30 min, and then all solvent was removed *in vacuo*. The resulting white powder was suspended in 40 mL of dry dichloromethane, and insoluble products (LiCl) were filtered off. The dichloromethane was then removed *in vacuo*, the white powder obtained was redissolved in THF, the solution was filtered, and the filtrate was cooled to −26 °C overnight. This afforded 2.9 g (82%) of colorless, air-sensitive (loss of THF) crystals of $[Si(cat)_2]\cdot 2THF$, **1**·2THF. Anal. Calcd (found) for $C_{20}H_{24}O_6Si$: C, 61.83 (60.99); H, 6.23 (6.09). Satisfactory elemental analyses were difficult to obtain, since the crystals lose THF upon drying. ^{1}H NMR (200 MHz, $CDCl_3$): δ 6.82−6.89 (m, 8H, Ar *H*), 3.76 (t, 8H, OCH_2), 1.86 (quint, 8H, OCH_2CH_2). LRMS (70 keV): *m/e* = 244 [$Si(cat)_2^+$, 69%], 110 ($catH_2^+$, 100%). IR: 983 cm^{-1} (Si−O).

$Li_2[Si(cat)_3]\cdot 3.5dme$ (2·3.5dme). A THF solution of Li_2cat was prepared as described above from 3.0 g of catechol (27.2 mmol) in 60 mL of THF and 54.4 mmol of *n*-butyllithium (22.7 mL of a 2.4 M hexane solution in 50 mL of dry THF). To this solution was added 3.12 mL of $SiCl_4$ (4.62 g, 27.2 mmol), and the solution was stirred at room temperature for 3 h. Subsequently about 80% of the solvents were removed *in vacuo* and CH_2Cl_2 (50 mL) was added. This produced a white precipitate which was removed by filtration and was shown (precipitation with $AgNO_3$) to be mostly LiCl. At this point, the clear THF/CH_2Cl_2 solution also contained small amounts of LiCl. All solvents were removed, and the white product was recrystallized from 50 mL of dme. After one more recrystallization from this solvent, LiCl-free, colorless crystals of $Li_2[Si(cat)_3]\cdot 3.5dme$ (10.3 g) were obtained in 55.6% yield. These are slightly more stable against loss of coordinated solvent than **1**·2THF. Anal. Calcd (found) for

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Table 1. Summary of Crystallographic Data and Parameters for **1**·2THF and **2**·3.5dme

	1·2THF	**2**·3.5dme
crystal size, mm	0.25 × 0.20 × 0.10	0.40 × 0.32 × 0.16
mol formula	$C_{20}H_{24}O_6Si$	$C_{32}H_{47}Li_2O_{13}Si$
fw	388.49	681.69
cell constants		
a, Å	6.3428(8)	11.7680(13)
b, Å	17.7274(13)	12.3986(13)
c, Å	9.1437(10)	13.7981(15)
α, deg	90.0	79.833(9)
β, deg	108.763(10)	81.158(10)
γ, deg	90.0	63.676(10)
V, Å^3	973.5(4)	1769.6(3)
Z	2	2
space group	$P2_1/c$ (No. 14)	$P\bar{1}$ (No. 2)
d_{exp}, g/cm^3	1.32	1.29
d_{calc}, g/cm^3	1.325	1.279
μ, cm^{-1}	1.47	1.22
λ(Mo Kα), Å	0.710 73	
monochromator	graphite crystal ($2\theta_m = 12.2°$)	
diffractometer	Enraf-Nonius CAD-4	
data collection temp, °C	20(2)	−100(2)
2θ range, deg	$3 \le 2\theta \le 55$	$3 \le 2\theta \le 55$
reflns measd	$-8 \le h \le 8$ $0 \le k \le 23$ $-11 \le l \le 11$	$-15 \le h \le 15$ $-14 \le k \le 14$ $-17 \le l \le 17$
scan mode	2θ	2θ
scan speed	variable	variable
θ, deg/min (min/max)	1.5/6.7	1.5/6.7
scan width, deg	$0.70 + 0.35[\tan(\theta)]$	$0.70 + 0.35[\tan(\theta)]$
tot. no. of data collected	5495	16 204
no. of unique data, R_{ave}, %	2309, 1.8	8102, 2.1
no. of obsd data [$F_o^2 \ge 3\sigma(F_o^2)$]	1142	4833
R, %[a]	3.89	3.99
R_w, %[a]	4.79	5.32
p-factor[a]	0.03	0.03
GOF[b]	1.78	1.86
no. of variables	125	434

[a] Definition of residuals and refinement parameters: $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$. [b] $\mathrm{GOF} = [\sum w||F_o| - |F_c||^2/(n_o - n_p)]^{1/2}$ with n_o = number of structure factors and n_p = number of parameters, $w = 1/[\sigma(F)]^2$, $\sigma(F) = \sigma(F^2)/2F$, $\sigma(F^2) = \{[\sigma(I)]^2 + (pF^2)^2\}^{1/2}$.

$C_{32}H_{47}Li_2O_{13}Si$: C, 56.38 (55.95); H, 6.95 (6.68). FAB-MS (negative ions): m/z = 359 [$LiSi(cat)_3^-$, 62%], 353 [$HSi(cat)_3^-$, 54%). IR: 694 cm^{-1} (Si−O).

X-ray Crystallographic Determination of [Si(cat)$_2$]·2THF (1·2THF). Colorless, rhombic crystals of **1**·2THF were grown by cooling a THF solution to −26 °C. They are very sensitive toward loss of coordinated THF and turn opaque in an atmosphere of dry argon within 30 s. They were therefore mounted together with some THF in thin-walled glass capillaries for X-ray data collection. The quality of the crystal and a preliminary monoclinic unit cell were established by a series of precession photographs. The crystal was then transferred onto an automatic Enraf-Nonius CAD-4 diffractometer at room temperature. Final lattice parameters were obtained by least-squares refinement of the angular settings of 24 reflections distributed throughout reciprocal space in the 2θ range 24.1° ≤ 2θ ≤ 28.5°. Automatic indexing procedures confirmed the preliminary monoclinic cell. All data $\pm h,k,\pm l$ were collected at 20(2) °C in the 2θ range 3.0° ≤ 2θ ≤ 55.0°. Orientation and intensity control reflections were monitored every 200 reflections and every 2 h of data collection, respectively. Azimuthal (ψ) scans were recorded at the end of the data collection for four reflections near ψ = 90° at 10° increments of rotation of the crystal about the diffraction vector. Crystal data together with additional details about the diffraction experiment are listed in Table 1. The raw intensity data were converted into structure factor amplitudes (and their esd's) by correcting for scan speed, background, and Lorentz and polarization effects.[32] No decay (maximum loss of 1.2% over 50 h of X-ray exposure time) or absorption (maximum variation of 3% for averaged ψ-scan curve) correction was applied. Systematically absent reflections uniquely defined the space group to be $P2_1/c$ (No. 14). Redundant data $-h,k,\pm l$ and $+h,k,\pm l$ were averaged (R_{ave} = 1.8%), and systematically absent data were removed. The structure was solved by direct methods (MULTAN 82)[33] with Z = 2 (from density calculations). A model was obtained in which the silicon atom occupies a special position on one of the inversion centers in the unit cell. Thus the asymmetric unit contains one catecolate and one THF ligand. All non-hydrogen atoms in the asymmetric unit were first refined with isotropic and later with anisotropic thermal parameters. A difference Fourier map calculated at this stage revealed the positional parameters of all hydrogen atoms. However, these atoms were added to the structure model on calculated positions [d(C−H) = 0.95 Å][34] with their thermal parameters fixed to be 1.3 times the B_{iso} of the parent carbon atom. Neutral atomic scattering factors were used and corrections for anomalous dispersion were applied.[35] Final positional parameters for **1**·2THF are summarized in Table 2. Table 4 lists selected bond parameters.

Table 2. Positional Parameters and Isotriopic Equivalent Thermal Parameters for Non-Hydrogen Atoms in **1**·2THF

atom	x	y	z	B(iso),[a] Å^2
Si	0.500	0.000	0.000	3.39(2)
O1	0.6705(3)	0.07844(9)	0.0425(2)	3.64(4)
O2	0.3707(2)	0.0270(1)	0.1306(2)	3.70(4)
O3	0.2807(3)	0.0557(1)	−0.1592(2)	4.12(4)
C1	0.6282(4)	0.1209(1)	0.1537(3)	3.56(6)
C2	0.4567(4)	0.0924(1)	0.2019(3)	3.39(6)
C3	0.3868(4)	0.1291(2)	0.3104(3)	4.69(7)
C4	0.4951(5)	0.1953(2)	0.3736(3)	5.48(8)
C5	0.6666(5)	0.2231(2)	0.3293(3)	5.25(8)
C6	0.7371(5)	0.1864(2)	0.2173(3)	4.36(7)
C7	0.3218(5)	0.0946(2)	−0.2868(3)	5.60(8)
C8	0.1130(5)	0.1360(2)	−0.3666(4)	8.4(1)
C9	−0.0639(6)	0.0962(3)	−0.3228(4)	8.0(1)
C10	0.0479(5)	0.0605(2)	−0.1722(4)	7.03(9)

[a] The thermal parameter B(iso) given for aniosotropically refined atoms is the isotropic equivalent thermal parameter defined as $B_{eq} = {}^8/_3\pi^2[\sum_{ij}U_{ij}a_i^*a_j^*a_ia_j]$.

X-ray Crystallographic Determination of Li$_2$[Si(cat)$_3$]·3.5dme (2·3.5dme). Colorless crystals of **2**·3.5dme were grown from a dme solution at −26 °C. A suitable crystal was selected and placed on a glass fiber with the help of the device described by Veith and Bärnighausen.[36] The crystal was then directly transferred into the cold stream [−100(2) °C] of an Enraf-Nonius CAD-4 diffractometer. Final cell parameters are based on a least-squares refinement of the angular settings of 24 reflections distributed throughout reciprocal space in the 2θ range 27.5° ≤ 2θ ≤ 28.4°. Automatic indexing procedures yielded a triclinic cell. No conventional cell of higher symmetry was detected. All data $\pm h,\pm k,\pm l$ were collected at −100(2) °C in the 2θ range 3.0° ≤ 2θ ≤ 55.0°. Orientation and intensity control reflections were monitored as in the data collection for **1**·2THF. Data reduction proceeded as for **1**·2THF. A decay corrrection was applied to the data based on a linear decay of −3.2% over the 194 h of data collection time, but no absorption correction was neccessary. From the two possible triclinic space groups the centric $P\bar{1}$ with Z = 2 was chosen, and all redundant data were averaged (R_{ave} = 2.1%). This space group choice was confirmed by the subsequent structure determination, which proceeded as for **1**·2THF. Additional crystal data can be found in Table 1. Table 3 lists final positional parameters, and Table 5 contains selected bond parameters for **2**·3.5dme.

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Table 3. Positional Parameters and Isotopic Equivalent Thermal Parameters for Non-Hydrogen Atoms in **2**·3.5dme

atom	*x*	*y*	*z*	*B*(iso),[a] Å^2
Si	0.36865(6)	0.31503(5)	0.30007(5)	1.79(1)
Li1	0.4351(4)	0.2752(4)	0.1060(3)	2.9(1)
Li2	0.3221(4)	0.3435(3)	0.5027(3)	2.48(9)
O1	0.2433(1)	0.2834(1)	0.3664(1)	1.97(3)
O2	0.4158(1)	0.1845(1)	0.2388(1)	1.91(3)
O3	0.2804(1)	0.4041(1)	0.1967(1)	2.05(3)
O4	0.3099(1)	0.4504(1)	0.3574(1)	2.03(3)
O5	0.5034(1)	0.3325(1)	0.2341(1)	2.00(3)
O6	0.4609(1)	0.2375(1)	0.4025(1)	1.88(3)
O7	0.3194(1)	0.2043(1)	0.6111(1)	2.54(4)
O8	0.1451(2)	0.4310(1)	0.5716(1)	2.74(4)
O9	0.3082(2)	0.2510(2)	0.0300(1)	3.65(4)
O10	0.0927(2)	0.1753(2)	0.0388(1)	4.17(5)
O11	0.6164(1)	0.1387(1)	0.0609(1)	2.68(4)
O12	0.4902(2)	0.3678(1)	−0.0150(1)	2.90(4)
O13	0.4229(2)	0.4035(1)	0.5659(1)	2.59(4)
C1	0.2427(2)	0.1830(2)	0.3417(2)	1.88(5)
C2	0.1565(2)	0.1356(2)	0.3798(2)	2.31(5)
C3	0.1682(2)	0.0310(2)	0.3459(2)	2.75(6)
C4	0.2657(2)	−0.0250(2)	0.2755(2)	2.77(6)
C5	0.3530(2)	0.0225(2)	0.2372(2)	2.43(5)
C6	0.3399(2)	0.1268(2)	0.2706(2)	1.92(5)
C7	0.2189(2)	0.5227(2)	0.2086(2)	1.98(5)
C8	0.1427(2)	0.6148(2)	0.1429(2)	2.38(5)
C9	0.0855(2)	0.7338(2)	0.1656(2)	2.72(6)
C10	0.1067(2)	0.7599(2)	0.2533(2)	2.63(6)
C11	0.1828(2)	0.6677(2)	0.3201(2)	2.38(5)
C12	0.2371(2)	0.5493(2)	0.2989(2)	1.92(5)
C13	0.6049(2)	0.2820(2)	0.2887(2)	1.85(5)
C14	0.7218(2)	0.2820(2)	0.2592(2)	2.34(5)
C15	0.8179(2)	0.2248(2)	0.3242(2)	2.88(6)
C16	0.7947(2)	0.1705(2)	0.4169(2)	2.94(6)
C17	0.6757(2)	0.1715(2)	0.4467(2)	2.33(5)
C18	0.5817(2)	0.2278(2)	0.3835(2)	1.83(5)
C19	0.3870(3)	0.0811(2)	0.5909(2)	3.19(7)
C20	0.1910(2)	0.2328(2)	0.6467(2)	3.35(7)
C21	0.1295(2)	0.3641(2)	0.6625(2)	3.19(6)
C22	0.0807(3)	0.5580(2)	0.5767(3)	4.42(8)
C23	0.3566(3)	0.1558(3)	−0.0296(2)	4.85(8)
C24	0.1742(3)	0.3211(3)	0.0315(2)	4.81(8)
C25	0.0959(3)	0.2617(3)	0.0905(2)	4.19(7)
C26	0.0185(3)	0.1163(3)	0.0921(2)	4.57(8)
C27	0.6976(2)	0.0514(2)	0.1321(2)	3.07(6)
C28	0.6840(2)	0.1941(2)	−0.0091(2)	3.44(7)
C29	0.5906(2)	0.2892(2)	−0.0763(2)	3.18(6)
C30	0.3993(3)	0.4682(2)	−0.0718(2)	3.65(7)
C31	0.4724(3)	0.3547(3)	0.6582(2)	4.82(8)
C32	0.4349(2)	0.5139(2)	0.5250(2)	2.86(6)

[a] The thermal parameter *B*(iso) given for aniosotropically refined atoms is the isotropic equivalent thermal parameter defined as $B_{eq} = {}^{8}/_{3}\pi^2[\sum_{ij}U_{ij}a_i^*a_j^*a_ia_j]$.

Table 4. Selected Bond Distances (Å) and Angles (deg) for **1**·2THF

	Distances		
Si−O1	1.7275(13)	C1−C6	1.379(3)
Si−O2	1.7193(12)	C2−C3	1.374(3)
Si−O3	1.9307(13)	C3−C4	1.389(3)
O1−C1	1.360(2)	C4−C5	1.369(4)
O2−C2	1.356(2)	C5−C6	1.403(3)
O3−C7	1.449(3)	C7−C8	1.485(3)
O3−C10	1.446(3)	C8−C9	1.486(4)
C1−C2	1.394(3)	C9−C10	1.473(4)
	Angles		
O1−Si−O2	91.37(6)	C2−C1−C6	120.5(2)
O1−Si−O2*[a]	88.63(6)	O2−C2−C1	113.1(2)
O1−Si−O3	90.26(6)	O2−C2−C3	125.4(2)
O1−Si−O3*	89.74(6)	C1−C2−C3	121.5(2)
O2−Si−O3	89.56(6)	C2−C3−C4	118.0(2)
O2−Si−O3*	90.44(6)	C3−C4−C5	121.0(2)
Si−O1−C1	110.74(12)	C4−C5−C6	121.2(2)
Si−O2−C2	111.34(12)	C1−C6−C5	117.7(2)
Si−O3−C7	125.31(13)	O3−C7−C8	105.6(2)
Si−O3−C10	124.13(13)	C7−C8−C9	105.3(2)
C7−O3−C10	110.5(2)	C8−C9−C10	106.2(2)
O1−C1−C2	113.4(2)	O3−C10−C9	105.9(2)
O1−C1−C6	126.1(2)		

[a] Starred atoms represent symmetry-equivalent positions of the type (1 − *x*, −*y*, −*z*).

Table 5. Selected Bond Distances (Å) and Angles (deg) for **2**·3.5dme

	Distances		
Si−O1	1.7723(12)	Li2−O1	2.568(3)
Si−O2	1.7840(12)	Li2−O4	2.186(3)
Si−O3	1.7930(12)	Li2−O6	2.085(3)
Si−O4	1.7867(12)	Li2−O7	2.084(3)
Si−O5	1.7836(12)	Li2−O8	2.043(3)
Si−O6	1.7797(12)	Li2−O13	2.012(3)
Li1−O2	2.012(3)	O1−C1	1.351(2)
Li1−O3	2.204(4)	O2−C6	1.356(2)
Li1−O5	2.379(4)	O3−C7	1.349(2)
Li1−O9	2.100(4)	O4−C12	1.349(2)
Li1−O11	2.136(4)	O5−C13	1.353(2)
Li1−O12	2.043(3)	O6−C18	1.360(2)
	Angles		
O1−Si−O2	88.70(6)	O3−Li1−O12	109.9(2)
O1−Si−O3	95.32(6)	O5−Li1−O9	157.2(2)
O1−Si−O4	89.14(6)	O5−Li1−O11	97.02(15)
O1−Si−O5	174.84(6)	O5−Li1−O12	100.47(15)
O1−Si−O6	88.38(6)	O9−Li1−O11	103.46(15)
O2−Si−O3	87.94(6)	O9−Li1−O12	93.41(14)
O2−Si−O4	175.57(6)	O11−Li1−O12	78.88(13)
O2−Si−O5	87.15(6)	O1−Li2−O4	62.78(9)
O2−Si−O6	96.02(6)	O1−Li2−O6	63.30(9)
O3−Si−O4	88.41(6)	O1−Li2−O7	96.47(12)
O3−Si−O5	87.60(6)	O1−Li2−O8	94.77(13)
O3−Si−O6	174.65(6)	O1−Li2−O13	158.9(2)
O4−Si−O5	95.21(6)	O4−Li2−O6	70.71(10)
O4−Si−O6	87.78(6)	O4−Li2−O7	159.1(2)
O5−Si−O6	89.01(6)	O4−Li2−O8	102.98(14)
O2−Li1−O3	72.00(11)	O4−Li2−O13	99.53(14)
O2−Li1−O5	67.51(10)	O6−Li2−O7	98.27(13)
O2−Li1−O9	100.1(2)	O6−Li2−O8	157.9(2)
O2−Li1−O11	95.56(15)	O6−Li2−O13	101.21(15)
O2−Li1−O12	166.3(2)	O7−Li2−O8	80.40(12)
O3−Li1−O5	65.25(10)	O7−Li2−O13	100.10(14)
O3−Li1−O9	93.04(15)	O8−Li2−O13	100.76(14)

Tables of hydrogen atom positions, all bond parameters, anisotropic thermal parameters, and selected least-squares planes for **1**·2THF and **2**·3.5dme are available as supplementary material.

Results and Discussion

Synthesis of Complexes. $SiCl_4$ has been shown to react with catechol in chloroform[37] or in acetonitrile[38] to give compounds of the composition $Si(cat)_2$. The reaction of a Si/Cu mixture with catechol under hydrogen in an autoclave has also been reported[39] to give $Si(cat)_2$. The product from the reaction in chloroform is soluble in this solvent and was proposed to be a tetramer with bridging and terminal catecholate ligands.[37] The other two reactions gave only amorphous, insoluble products, which are most likely not monomeric. Sublimation of the amorphous product from the reaction in acetonitrile gave crystals containing a tetracoordinated tetrahedral silicon in a one-dimensional indefinite polymer chain of the type $[Si(O-C_6H_4-O-)_2]_\infty$.[40] So far, the synthesis of a monomeric, tetracoordinated

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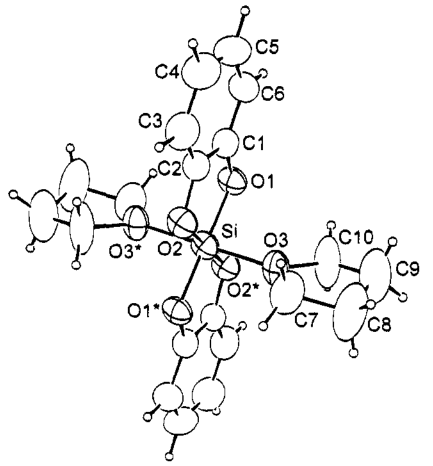

Figure 2. Molecular structure of $[Si(cat)_2]\cdot 2THF$. Starred atoms represent transformed coordinates of the type 1 − *x*, −*y*, −*z*.

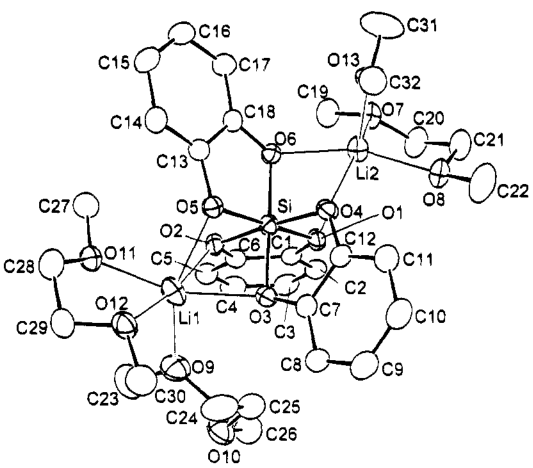

Figure 3. Contents of an asymmetric unit of $\mathbf{2}\cdot 3.5dme$ with the crystallographic numbering scheme.

complex $[Si(cat)_2]$ has not been demonstrated conclusively and the synthesis of the proposed tetracoordinated, monomeric planar complex $[Si(cat)_2]$[29] has proven to be irreproducible. However, other bidentate diols like 1,8-naphthylenediol[41] or tetramethylethylenediol[42] will react with $SiCl_4$ to give monomeric tetrahedral $[Si(diolate)_2]$ complexes. The reasons for this become apparent if bonding parameters of a $[Si(cat)_2]$ complex are compared with those of the known $[Si(diolate)_2]$ complexes (*vide infra*).

The reaction of 2 equiv of the salt Li_2cat with $SiCl_4$ reproducibly produces monomers $[Si(cat)_2]\cdot 2THF$ containing hexacoordinated silicon in good yield. Stabilization of a $Si(cat)_2$ unit by extending the coordination number at the silicon atom to 6 via pyridine coordination, in $[Si(cat)_2]\cdot 2pyridine$, has been reported by Zuckerman.[43] The product can be sublimed but it is insoluble, even in pyridine. In contrast $Li_2[Si(cat)_3]$ is soluble in ethers such as THF and dme and can be crystallized from these solvents. The good solubility is based on the formation of a tight ion pair between anion and cations, which can also be seen in the −FAB mass spectrum of $Li_2[Si(cat)_3]$, which shows a stronger peak for the $\{Li[Si(cat)_3]\}^-$ anion than for the $\{H[Si(cat)_3]\}^-$ anion. These lithium salts seem to provide a generally useful route to ether-soluble anionic catecholate complexes.

Description of the Solid-State Structure of $[Si(cat)_2]\cdot 2THF$ ($\mathbf{1}\cdot 2THF$). The silicon atom in $\mathbf{1}\cdot 2THF$ resides on a crystallographic inversion center and is coordinated by six oxygen atoms from two THF and two catecholate ligands in a slightly distorted octahedral fashion (Figure 2). Silicon and the four catecholate oxygen atoms are required by symmetry to form an exactly planar unit. This planar unit, however, exists only as part of the pseudooctahedral coordination environment of the silicon atom. The $Si-O_{cat}$ distances in $\mathbf{1}\cdot 2THF$ [1.7275(13), 1.7193(12) Å] are longer than those in polymeric pseudotetrahedral $Si(cat)_2$ [1.602(7)−1.608(8) Å][40] or dimeric pseudotetrahedral $[Si(cat)R_2]_2$[44] compounds. However, the difference compares well with the difference in ionic radii for tetra- and hexacoordinated Si(IV).[45] Hexacoordination and the resulting slightly longer Si−O distance in $\mathbf{1}\cdot 2THF$ allow the catecholate ligands to bind in a typical chelate fashion as observed for numerous catecholate complexes. These features include O−Si−O bite angles of the catecholate ligand (dependent on the M−O distances) around 90°, Si−O−C angles of around 111°, endocyclic O−C−C angles of 113°, exocyclic O−C−C angles of 125°, and the silicon atom residing in the plane of the catecholate ligand. Deviations from these features are indicative of special geometric features of the complex. For instance, in the unique trigonal prismatic tris(catecholate) of Fe(III),[4] the iron atom lies 0.82 Å out of the C_6 catecholate plane and O−Fe−O and the C_6 catecholate plane form an angle of 30.9°. The coordination geometry of the catecholate ligands in polymeric $Si(cat)_2$ is more disturbed.[40] The O−Si−O angles vary from 104.7(4) to 116.0(6)°, and the Si−O−C angles fall in the range 131.4(7)−134.4(8)°. These are typical values for silicates, but they exclude chelate formation of the catecholate ligand as observed in $\mathbf{1}\cdot 2THF$, where the O−Si−O angles have to be around 90°. Calculations of catecholate coordination in a chelating mode on tetracoordinated silicon have predicted formation of a five-membered ring with an O−Si−O angle of 106° and a Si−O−C angle of 102° (assuming *d*(Si−O) = 1.62 Å and *d*(O−C) = 1.40 Å).[40] The required O−Si−O angle would effectively prevent the formation of a tetracoordinated planar quadratic SiO_4 core; even formation of a tetrahedral SiO_4 core would be unlikely due to the strain caused by the small angle at oxygen in a planar catecholate ring. The strain at oxygen in the five-membered chelate ring of a tetrahedral silicon can be relieved by formation of dimers[44] or polymers[40] or by participation of sp^3-hybridized carbon atoms in the five-membered chelate ring as observed in bis(tetramethylethylene)silane.[42] In addition, expansion of the chelate ring can also lead to a monomeric tetrahedral silicon complex as in bis(1,8-naphthylenedioxy)silane.[40]

All of the geometric constraints described above are relieved if the coordination number of silicon is raised to 6 with a concurrent lengthening of the Si−O distance as in $\mathbf{1}\cdot 2THF$. Then the catecholate ligand can bind without strain at either the silicon or the oxygen atoms. Thus the proposed[29] tetracoordinated, planar quadratic $Si(cat)_2$ unit can exist only as part of a pseudooctahedral coordination at silicon. Hexacoordination of silicon can be achieved by (i) coordinating solvent molecules as in $\mathbf{1}\cdot 2THF$ or (ii) polymer formation by intermolecular coordination of catecholate oxygen atoms, which will normally cause the complexes to be very insoluble. Examples of hexacoordinate Si(IV) also are known with nitrogen ligands.[46]

Description of the Solid-State Structure of $Li_2[Si(cat)_3]\cdot 3.5dme$ ($\mathbf{2}\cdot 3.5dme$). The unit cell of $\mathbf{2}\cdot 3.5dme$ contains

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(41) Bibber, J. W.; Barnes, C. L; van der Helm, D.; Zuckerman, J. J. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 501.

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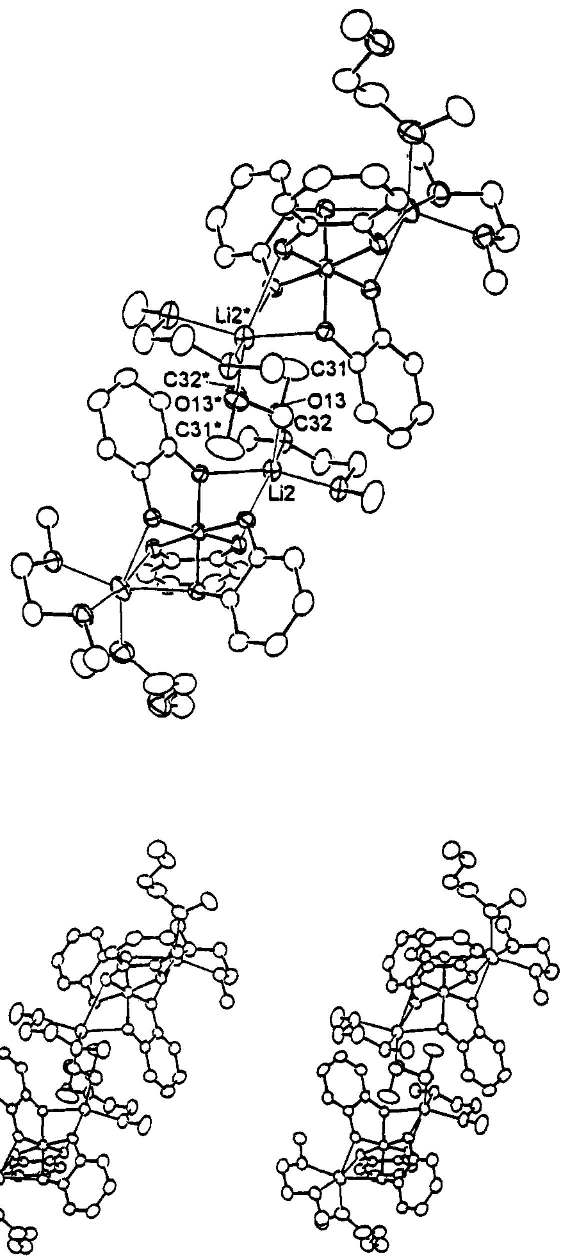

Figure 4. Molecular structure of the dimer $\{Li_2[Si(cat)_3]\cdot 3.5dme\}_2$ with labels at the bridging dme molecule. Starred atoms represent transformed coordinates of the type 1 − *x*, 1 − *y*, 1 − *z*.

four formula units. One of these is shown in Figure 3. The silicon atom is coordinated by six catecholate oxygen atoms in a slightly distorted octahedral fashion. Each set of facial oxygen atoms coordinates to a lithium cation, thereby forming a close ion pair. The lithium cations complete their distorted octahedral coordination environment by coordination from dme oxygen atoms. Li1 binds to dme oxygen atoms O11 and O12 from one dme molecule and to O9 from a second dme molecule. The second oxygen atom of this dme molecule (O10) is not coordinated. Li2 is coordinated by O7 and O8 from one dme molecule. The last coordination site is occupied by O13. Atom O13 belongs to a dme molecule which resides on an inversion center. The midpoint of the C−C bond of this dme molecule bridges two $Li_2[Si(cat)_3]\cdot 3dme$ units, thereby creating a centrosymmetric dimer of the type $\{Li_2[Si(cat)_3]\cdot 3.5dme\}_2$. A partially labeled plot and a stereoview of the dimer are shown in Figure 4. Figure 5 depicts a schematic representation of the binding situation in the dimer.

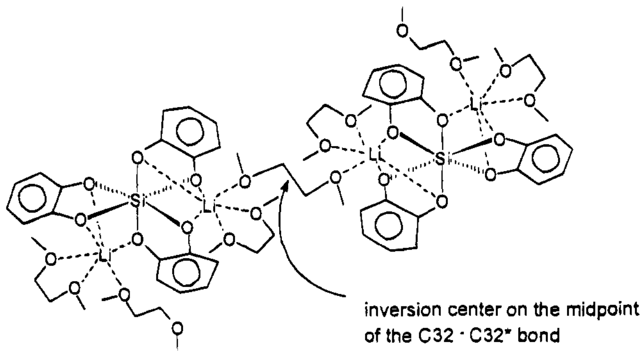

Figure 5. Schematic representation of the dimer $\{Li_2[Si(cat)_3]\cdot 3.5dme\}_2$.

The solid state structure of **2**·3.5dme explains the good solubility of this complex. In contrast to this, the salt $[C_5H_5NH]_2[Si(cat)_3]$ forms discrete ions $[C_5H_5NH]^+$ and $[Si(cat)_3]^{2-}$ in the crystal lattice,[16] and this ionic character causes poor solubility in almost all nonprotic solvents, which was also observed for the germanium and silicon complexes of a tris(catecholate) ligand.[6a]

On the basis of the previous conclusions regarding four- and six-coordinated silicon, $[Si(cat)_3]^{2-}$ should be relatively unstrained. The structure confirms this: the $Si-O_{cat}$ distances [1.7723(12)−1.7930(12) (Å)] in **2**·3.5dme fall in the range observed for $[C_5H_5NH]_2[Si(cat)_3]$[16] and are slightly longer than those in **1**·2THF, which causes the bite angles of the catecholates to shrink to values below 90° compared to a value of 91.37(6)° in **1**·2THF. The lengthening of the $Si-O_{cat}$ distances in the $[Si(cat)_3]^{2-}$ anion, compared to **1**, is also reflected in the frequencies of the Si−O IR absorptions. The angles at silicon deviate somewhat more from an octahedron than in **1**·2THF with the exocyclic O−Si−O angles larger than the endocyclic ones. For all three ligands the six carbon atoms of the catecholate rings form an almost planar unit with the catecholate oxygen atoms and the silicon atom, with dihedral angles between these planes ranging from 92.24(8) to 94.95(7)°. The Li−O distances vary over a broad range [2.012(3)−2.379(4) Å for Li1 and 2.012(3)−2.568 (3) Å for Li2], which we ascribe to packing forces. However, the shorter Li−O distances demonstrate the strong interaction between anion and cations.

Summary

Catechol can be deprotonated with *n*-butyllithium or alkali metal hydrides in ethers. Only the lithium salt Li_2cat is soluble in these solvents. They provide an easy access to ether-soluble catecholate complexes. This provides a general route to prepare and crystallize catecholate complexes in aqueous solvents. The octahedral tris(catecholate) $Li_2[Si(cat)_3]\cdot 3.5dme$ is highly soluble in THF or dme. The complex $[Si(cat)_2]\cdot 2THF$ apparently is the only monomeric bis(catecholate) complex of silicon with catecholate ligands bound in a chelating fashion. Its bonding parameters show that chelation of silicon by two pairs of catecholate oxygen atoms requires the silicon to be hexacoordinated.

Acknowledgment. We dedicate this paper to Professor Herbert Schumann on the occasion of his 60th birthday. We thank the National Institutes of Health for partial support of this research through Grant AI11744 and the Alexander von Humboldt Stiftung for an award to K.N.R.

Supplementary Material Available: Tables of hydrogen atom positions, bond distances and angles, least-squares planes, and thermal parameters for **1**·2THF and **2**·3.5dme (12 pages). Ordering information is given on any current masthead page.

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