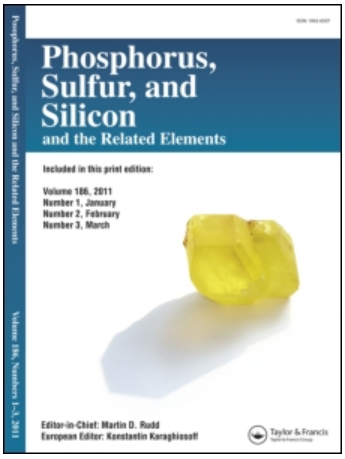

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SIX COORDINATE TRIS(CATECHOLATO)SILICATES OF PRIMARY AMINE RESIDUES—SYNTHESIS, CHARACTERIZATION, AND THERMOLYSIS STUDIES. X-RAY STRUCTURES OF $[n\text{-}C_3H_7NH_3]_2[Si(C_6H_4O_2)_3]\cdot 1/2(C_6H_{14}N_2)$ AND OF A BULKY SECONDARY AMMONIUM ION, $[(i\text{-}C_4H_9)_2NH_2]_2[Si(C_6H_4O_2)_3]\cdot H_2O$

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Synthesis of the hypervalent tris(catecholato)silicate ion, $[(C_6H_4O_2)_3\text{-}Si]^{2-}$ having five different primary ammonium cations viz. n*-propylammonium (**1**), isopropylammonium (**2**)* n*-butylammonium (**3**), cyclohexylammonium (**4**), benzylammonium (**5**), and a bulky secondary ammonium cation, namely diisobutylammonium (**6**), have been achieved by the reaction of catechol and tetraethoxysilane (TEOS) in presence of the corresponding amine. Elemental analysis, IR, NMR (^1H, ^{13}C, and ^{29}Si), and mass spectral data have been used for their characterization. Single crystal x-ray structures of **1** and **6** indicate nearly same distortion of the "SiO_6" octahedron but interesting differences in the hydrogen bonding interactions arising from the catecholato oxygens and the N–H bonds of the ammonium cations. While compound **1** exhibits hydrogen bonding more discretely and by revealing strong interaction between the* n*-propylammonium ions, compound **6** shows an extended intermolecular hydrogen bonding aided by a water molecule*

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Crystallographic data (excluding structure factors) for **1** and **6** have been deposited with the Cambridge Crystallographic Data Centre as supplementary material. The registry numbers are CCDC 194432 for compound **1** and CCDC 194433 for compound **6**. The copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ, UK. Fax: (+44) 1223-336-033; E-mail: deposit@ccdc.cam.ac.uk.

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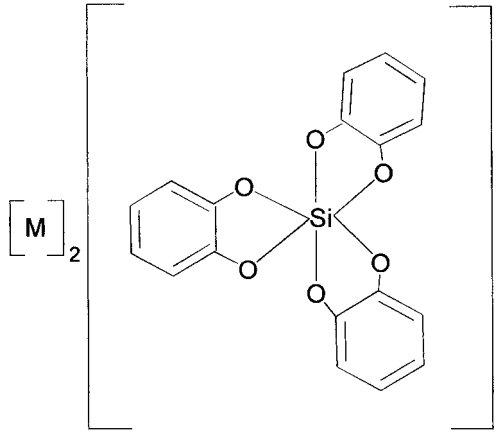
present in the lattice to lead to infinite one dimensional chain arrangement. TG and EG analyses of compounds, ***1–5*** *indicate 1) the formation of the previously observed spirosilane intermediate, [Si($C_6H_4O_2$)$_2$] and 2) their less thermal stability compared to those having secondary or tertiary ammonium cations.*

Keywords: Hydrogen bonding; primary amine residues; six coordinate silicates; thermal behavior; x-ray structure

Of late, hypervalent silicon compounds have received a great deal of attention primarily due to the interests in their structural and reactivity aspects.[1–5] Studies also have been focused on the preparation of new variety by changing both ligands and counter ions.[6–10] We also have reported recently on the preparative, structural, and reactivity features of the six coordinate tris(catecholato)silicate ion.[11–13] In the first structurally characterized example having a secondary ammonium ion, $[(C_3H_7)_2NH_2]_2[Si(C_6H_4O_2)_3]$, we observed the participation of the ammonium ion in novel and interesting modes of hydrogen bonding interactions. This result helped in providing a rationale for the thermal decomposition behavior of ammonium tris(catecholato)silicates which upon heating produced the polymeric form of the spirosilane, $[Si(C_6H_4O_2)_2]$.[13] Prompted by this, we have now considered the preparation of $[Si(C_6H_4O_2)_3]^{2-}$ derivatives possessing primary ammonium cations which are characterized by the presence of more number of NH bonds and to probe their influence on structure and thermal behaviour. We report in this article 1) the synthesis of first examples of $[Si(C_6H_4O_2)_3]^{2-}$ having different primary amino residues, 2) their thermogravimetric and evolved gas analysis behavior, 3) x-ray structure of $[n\text{-}C_3H_7NH_3]_2[Si(C_6H_4O_2)_3]$, and 4) synthesis, x-ray structure of a bulkier secondary amino derivative, $[(i\text{-}C_4H_9)_2NH_2]_2[Si(C_6H_4O_2)_3]$ and its comparison with the previous structure reported by us.

RESULTS AND DISCUSSION

The use of different metal ions[14–17] and ammonium ions[11,13,18,19] to serve as counter cations in the isolation of the six-coordinate tris(catecholato)silicate ion, $[Si(C_6H_4O_2)_3]^{2-}$ has been reported in literature. However, reports on their structural studies are limited. A recent study from our laboratory revealed that the counter cations do influence the structure, stability, and properties of the tris(catecholato)silicate derivatives.[13] The use of a primary amine in this synthesis was hitherto not known. We have now synthesized five such derivatives by the



SCHEME 1 Ammonium tris(catecholato)silicates synthesized in this work.

use of our reported method (Scheme 1) and studied their structure and behavior.

$$Si(OEt)_4 + 3C_6H_4(OH)_2 + 2RNH_2 \rightarrow [(RNH_3)_2][Si(C_6H_4O_2)_3] + 4EtOH$$

Cation =	Compound No.	%yield
n-Propylammonium [*n*-$C_3H_7NH_3$]	**1**	98
Isopropylammonium [*i*-$C_3H_7NH_3$]	**2**	98
n-Butylammonium [*n*-$C_4H_9NH_3$]	**3**	95
Cyclohexylammonium [$C_6H_{11}NH_3$]	**4**	95
Benzylammonium [$C_6H_5CH_2NH_3$]	**5**	95

Besides, the derivative of diisobutyl ammonium cation, [(*i*-C_4H_9)$_2$ NH_2]$_2$[$Si(C_6H_4O_2)_3$] (**6**) also was prepared. Contrary to the reported synthesis, these room temperature reactions are found to proceed smoothly in toluene and bulk of the products were isolated as precipitates of the reactions. Compounds **1–6** are air and moisture stable white or near-white powdery solids that are only sparingly soluble in a few solvents like acetone, methanol, and acetonitrile. Among these, **6** is found to be most soluble. However, its solution at room temperature slowly developed brown coloration implying its unstable nature over long periods. Upon heating, they are found to decompose at relatively high temperatures. The IR spectra of **1** to **6** resemble considerably and a comparison reveals that peaks at around 1585, 1440, 1250, 1095, 1025, 875, 815, 740, 685, and 590 cm^{-1} are characteristic vibrations of the tris(catecholato)silicate ion. The vibrations at 1250 and 685 cm^{-1} seem to be sensitive to cation variation as evidenced by small shifts in

TABLE I ^{1}H and ^{13}C NMR Assignments of **1–6** in d_6-Acetone

Compound	^{1}H NMR (δ ppm)	^{13}C NMR (δ ppm)	
		Aliphatic	Aromatic
1	0.90 (t, $-CCH_3$, 6H), 1.60 (m, $-CCH_2$, 4H), 2.90–3.50 (br[a], $-NCH_2$ & $-NH_3$, 10H), 6.60 (m, ArH, 6H), 6.75 (m, ArH, 6H)	42.29, 21.54, 11.36	145.95, 120.51, 116.11
2	1.00 (d, $-C(CH_3)_2$, 12H), 3.65 (septet, $-CH$, 2H), 3.10 (br, $-NH_3$, 6H), 6.65 (m, ArH, 6H), 6.80 (m, ArH, 6H)	[b]	146.00, 120.57, 116.07
3	0.90 (t, $-CCH_3$, 6H), 1.35 (m, $-CCH_2C-$, 4H), 1.55 (m, $-CCH_2C-$, 4H), 3.01 (t, $-NCH_2$, 4H), 3.00 (s, $-NH_3$, 6H), 6.65 (m, ArH, 6H), 6.79 (m, ArH, 6H)	21.36, 14.19	145.92, 120.56, 116.02
4	1.00–1.80 (m, $C_5H_{10}-$, 20H), 2.86 (t, $CH-$, 2H) 3.25 (br, $-NH_3$, 6H), 6.54 (m, ArH, 6H), 6.67 (m, ArH, 6H)	59.55, 34.07, 29.22, 25.38	145.97, 120.62, 116.06
5	4.30 (s, $-CH_2$, 4H), 2.80 (br, $-NH_3$,6H), 6.70–7.25 (m, ArH, 22H)	55.45	145.90, 141.87, 128.88, 128.52, 126.99, 120.57, 116.02
6	0.91 (d, $-C(CH3)2$, 12H), 2.05 (m, $-CH$, 2H), 2.70 (d, $-CCH_2$, 4H), 3.40 (br, $-NH_2$,4H), 6.64 (m, ArH, 6H), 6.79 (m, ArH, 6H)	56.62, 26.80, 20.65	145.95, 120.56, 116.06

[a]Overlap of signals due to $-NCH_2$ and $-NH_3^+$ protons, unresolved.
[b]Aliphatic carbons could not be detected clearly due to poor solubility.

their peak positions. The identity of counter ammonium ions present in **1–6** was clearly revealed by their proton NMR spectra. In all the cases, a broad signal in the range 2.8–3.5 ppm due to $-NH_3/-NH_2$ protons also appeared. ^{13}C NMR spectra corroborated the findings of the proton NMR data (Table I) by indicating the signals due to both the ions of **1–6** at the expected positions in the aliphatic and aromatic regions. ^{29}Si NMR spectra recorded in four of the six cases gave a sharp singlet around -140 ppm and revealed the presence of the six coordinate silicate ion.[20] An attempted mass spectral analysis of **1–6** under electron impact conditions showed besides the expected fragments due to the respective ions, the base peak at m/z = 244 which corresponds to the spirosilane, $[Si(C_6H_4O_2)_2]$ which has not been isolated hitherto in its monomeric form.[15]

Thermogravimetric (TG) analysis of compounds **1–6** whose results are given in Table II were carried out to know their thermal stabilities and to understand the effect of counter ion on thermolytic behavior of

TABLE II Thermoanalytical Data of Tris(catecholato)silicates[a,b]

Compound	1st decomposition[d]			2nd decomposition[e]				
	Temperature range (°C)	Weight loss (%)		Temperature range (°C)	Weight loss (%)		% of SiO_2	
		calcd	found		calcd	found	calcd	found
1[c]	70–272	48.29	48.44	272–620	38.93	40.31	12.71	11.25
2	50–240	48.29	48.43	240–550	38.93	40.31	12.71	11.25
3	109–284	51.19	50.97	284–520	36.75	35.16	12.06	13.87
4	50–237	55.78	55.63	237–600	33.29	34.37	10.87	10.00
5	80–190	56.97	56.67	190–550	32.35	35.84	10.56	7.48
6	50–243	60.13	60.31	243–600	30.02	31.56	9.80	8.13

[a]All the thermograms were recorded in air in the temperature range rt to 800°C.

[b]Bulk pyrolysis experiments afforded the corresponding amount of amorphous silica (IR and powder XRD) in all cases.

[c]$CH_3CH_2CH_2N{=}NCH_2CH_2CH_3$ is not included in the calculation, present only in the crystal.

[d]Loss of bis(ammonium) catecholate leading to the formation of spirosilane, $[Si(C_6H_4O_2)_2]$.

[e]Decomposition of spirosilane leading to the formation of silica, SiO_2.

these derivatives. The thermograms of **1–6** indicated that the onset of decomposition begins at different temperatures thereby suggesting the influence of counter ion on their thermal behavior. Their thermal stability varies in the order **3** > **5** > **1** > **4** ~ **6** ~ **2**. In general, the compounds with primary ammonium counter ions are found to be significantly less stable to those having secondary or tertiary amine residues.[13] Interestingly, they also show a two-stage decomposition with the first weight loss occurring due to the expulsion of $(M^+)_2(C_6H_4O_2)$ and leading to the formation of 1,2-phenylenedioxy spirosilane.[13] The release of catechol (m/e = 110) and the corresponding amine during thermolysis of **1–6** also was observed in their EGA plots. Bulk pyrolysis of **1–6** carried out in air using an electric Bunsen afforded the corresponding amount of silica (IR) whose x-ray powder pattern suggested amorphous nature for the silica obtained.

X-Ray Structure of Compound 1

ORTEP plot, hydrogen bonding interactions, bond length, and bond angle data as well as crystallographic parameters of compound **1** are given in Figure 1 and Tables III and V respectively. The structure reveals six coordination and slightly distorted octahedral geometry around silicon. Its bond lengths and angles are similar to those found in the reported cases.[13,15,19] The catecholato silicon rings in **1** are

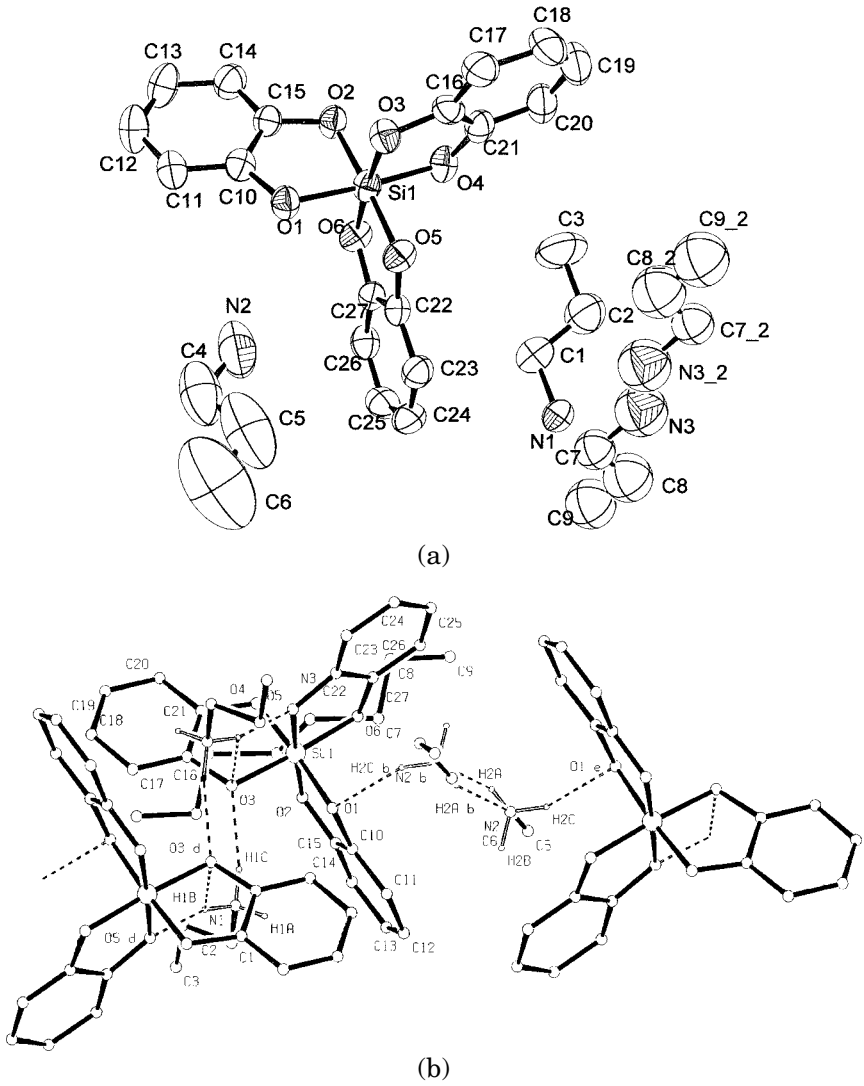


FIGURE 1 (a) ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for $[n\text{-}C_3H_7NH_3]_2[Si(C_6H_4O_2)_3] \cdot 1/2(C_6H_{14}N_2)$. (b) Hydrogen bonding interaction in **1**, the dashed line indicate hydrogen bond details between the anion and cation.

planar and the dihedral angle between the rings Si—O1—O2—C10—C15 and Si—O3—O4—C16—C21 is 80.8°. They subtend a near orthogonal angle with the remaining Si—O5—O6—C22—C27 plane (89.2° and 87.1°). The corresponding dihedral angles for the reported structure,

TABLE III Selected Bond Lengths [A°] and Bond Angles [°] of **1** and **6**

	1	**6**	
Bond lengths			
O(1)—Si(1)	1.808(2)	O(1)—Si(1)	1.797(2)
O(2)—Si(1)	1.777(2)	O(2)—Si(1)	1.760(2)
O(3)—Si(1)	1.794(2)	O(3)—Si(1)	1.803(2)
O(4)—Si(1)	1.782(2)		
O(5)—Si(1)	1.796(2)		
O(6)—Si(1)	1.779(2)		
Bond angles			
O(6)—Si(1)—O(3)	175.44(11)	O(2)′—Si(1)—O(2)	177.04(15)
O(6)—Si(1)—O(5)	88.25(11)	O(2)—Si(1)—O(1)	88.07(10)
O(3)—Si(1)—O(5)	87.53(11)	O(2)—Si(1)—O(1)′	89.91(11)
O(6)—Si(1)—O(1)	92.98(11)	O(1)—Si(1)—O(1)′	94.32(15)
O(3)—Si(1)—O(1)	88.70(11)	O(2)′—Si(1)—O(3)	88.27(10)
O(5)—Si(1)—O(1)	89.56(11)	O(2)—Si(1)—O(3)	93.86(10)
O(6)—Si(1)—O(2)	89.76(11)	O(1)—Si(1)—O(3)	88.75(9)
O(3)—Si(1)—(O2)	94.54(12)	O(1)′—Si(1)—O(3)	175.22(10)
O(5)—Si(1)—O(2)	176.80(10)	O(3)—Si(1)—O(3)′	88.42(14)
O(1)—Si(1)—O(2)	88.05(11)		
O(6)—Si(1)—O(4)	90.12(11)		
O(3)—Si(1)—O(4)	88.45(11)		
O(5)—Si(1)—O(4)	93.81(12)		
O(1)—Si(1)—O(4)	175.49(11)		
O(2)—Si(1)—O(4)	88.70(12)		
C(10)—O(1)—Si(1)	110.69(18)	C(1)—O(1)—Si(1)	111.64(18)
C(15)—O(2)—Si(1)	112.48(18)	C(6)—O(2)—Si(1)	112.64(18)
C(16)—O(3)—Si(1)	111.7(2)	C(7)—O(3)—Si(1)	111.46(18)
C(21)—O(4)—Si(1)	111.7(2)		
C(22)—O(5)—Si(1)	111.71(18)		
C(27)—O(6)—Si(1)	112.37(19)		

$[Li_2[Si(Cat)_3]3.5dme]$[15] deduced from its atom coordinates revealed a similar trend. The average Si—O—C, endocyclic O—C—C and exocyclic O—C—C angles for **1** are found to be 111.8°, 114.0°, and 125.3° respectively. Reported structural data of these compounds reveal different arrangement and mode of interaction among the constituent ions.[19] The recent structural work on $[(i\text{-}C_3H_7)_2NH_2]_2[Si(C_6H_4O_2)_3]$ reported by us, displayed different types of hydrogen bonding arising from the N—H bonds of the cation, $[(i\text{-}C_3H_7)_2NH_2]$with the catecholato oxygens of the anion, $[Si(C_6H_4O_2)_3]$. In contrast, the present structure, which is the first example to contain a primary ammonium cation, indicates that only one of its cations is engaged in hydrogen bonding (Table IV) with the catecholato moieties [N1-H1B—O5 = 1.972 A° and N1-H1C—O3 = 1.993 A°] while the other cation interacts strongly with its centrosymmetric nitrogen in the unit cell [N2-H2A—N2 = 1.840 A°] (Figure 1b)

TABLE IV Hydrogen Bonding Geometry in **1** and **6** [A°], [°]

Compound	D—H···A	D—H	H···A	D···A	D—H···A
1	N1—H1B···O5	0.889	1.972	2.833	162.2
	N1—H1C···O3	0.890	1.993	2.870	167.9
	N2—H2A···N2	0.890	1.840	2.699	161.4
6	N1—H1···O4	0.850	2.140	2.899	149.0
	N1—H1′···O3	0.950	1.900	2.778	152.0

using only one of its N—H bonds. Although hydrogen bonding exists only discretely in this structure, the presence of relatively weak van der Waal's contacts account for its extended structure.

The presence of an azopropane molecule in the lattice is rather a surprising feature in the present structure. It is found to be half a molecule per molecule of the compound. A typical N—N double bond distance (1.199 A°)[21] and centrosymmetric disposition of the two C_3H_7N units are clearly seen in the structure (Figure 1a). To ascertain this unexpected observation, synthesis, crystallization, and x-ray data collection were repeated and the structure was re-solved with the fresh data which again showed the appearance of the azopropane moiety at the same coordinates. Further, the structure was solved with the space group P1 to rule out the possibility of any pseudo centre of inversion in the structure which also confirmed the presence of azopropane.

Interestingly, both powdered sample of **1** obtained directly from the reaction and the vacuum dried sample of a fresh batch of crystals of **1** were identical as revealed by their powder XRD pattern and their CHN data did not support the presence of any azopropane. Further, the x-ray powder pattern of the compound **1**, simulated using the single crystal data and LAZY PULVERIX[22] program did not match with each other. These observations suggest that the azopropane molecule is present only in the crystal lattice of **1**. The origin of this molecule, though not clear, is presumably due to the oxidation of some residual propylamine present in the reaction mixture. It should be noted that a relatively long crystallization period at room temperature was involved in getting suitable crystals of **1** (Experimental). Conceivably, the formation of azopropane involves the dipropylhydrazine intermediate, $C_3H_7N(H)—N(H)C_3H_7$.[23]

X-Ray Structure of Compound 6

Prompted by the noteworthy hydrogen bonding details in the structure of the first example of tris(catecholato)silicate having the secondary ammonium cation reported by us,[13] we now have solved the

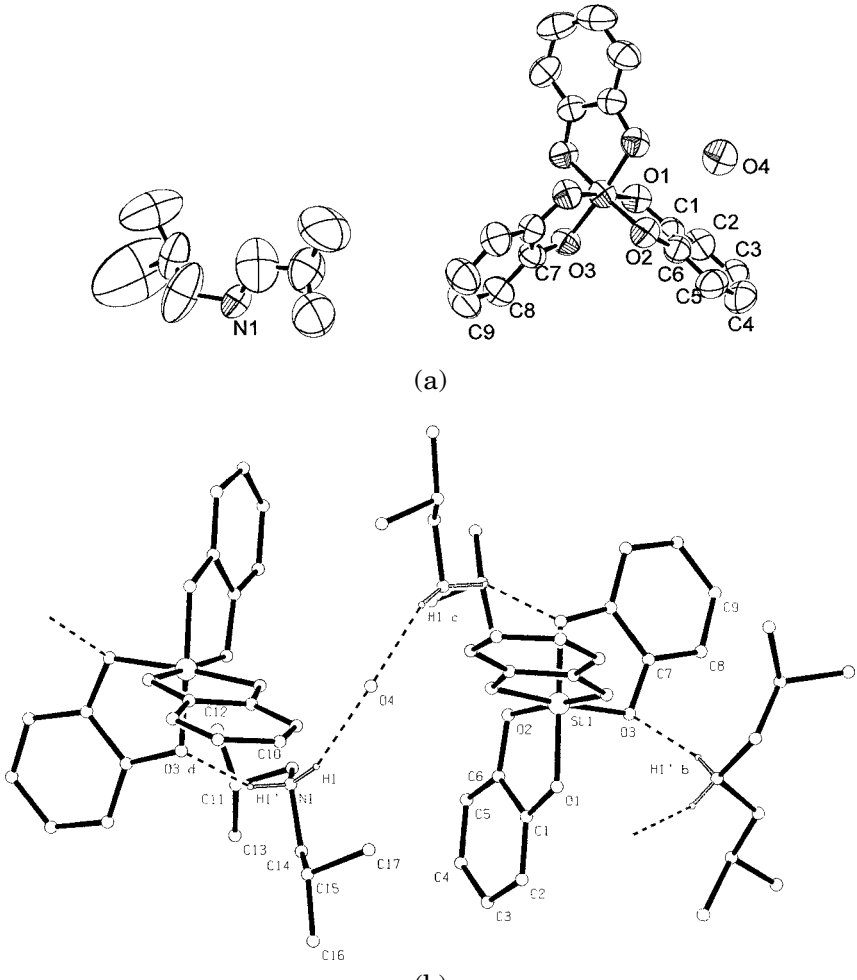


FIGURE 2 (a) ORTEP plot (50% probability ellipsoids) and atomic numbering scheme for $[(i\text{-}C_4H_9)_2NH_2]_2[Si(C_6H_4O_2)_3]\cdot H_2O$. (b) Hydrogen bonding interaction in **6**, the dashed line indicate hydrogen bond details between the anion and cation.

structure of another such example having diisobutylammonium ion which is bulkier than the previous. Figure 2a, Tables III and V provide the ORTEP plot, bond length, bond angle, and crystallographic parameters of $[(C_4H_9)_2NH_2]_2[Si(C_6H_4O_2)_3]$ (**6**). The compound crystallizes in the space group $P3_121$ and a twofold axis which bisects the tris(catecholato)silicate ion exists. Due to the crystallographic

TABLE V Crystal Data and Structure Refinement Parameters for **1** and **6**

	1	**6**
Empirical formula	$C_{54}H_{78}N_6O_{12}Si_2$	$C_{34}H_{54}N_2O_7Si$
Formula weight	1059.402	630.88
Temperature	293(2) K	293(2) K
Wavelength	0.71073 A°	1.54180 A°
Crystal system; space group	Triclinic; Pi	Trigonal; $P3_121$
a [A°]; α [°]	10.278(6); 67.81(5)	13.3369(16); 90
b [A°]; β [°]	12.365(6); 69.09(4)	13.337(2); 90
c [A°]; γ [°]	13.283(8); 67.94(5)	17.734(10); 120
V[A°^{3}]; Z	1402.3(14); 1	2731.8(16); 3
ρ_{calad} [Mg m^{-3}]	1.250	1.150
Absorption coefficient [mm^{-1}]	0.128	0.937
F(000)	568	1026
Crystal size [mm]	0.4 × 0.3 × 0.3	0.3 × 0.3 × 0.2
θrange [°]	2.14–25.04	3.83–68.01
Index ranges	$-11 \le h \le 12$, $-13 \le k \le 14$, $-14 \le l \le 15$	$-16 \le h \le 8$, $0 \le k \le 16$, $0 \le l \le 17$
Collected reflections	5524	6350
Independent reflections	4926 [R(int) = 0.0451]	3176 [R(int) = 0.0753]
Observed reflections [I > 2σ(I)]	2808	2102
Goodness-of-fit on F^2	0.661	0.933
Final R indices [I > 2σ(I)]	R1 = 0.0562, ωR2 = 0.1565	R1 = 0.0509, ωR2 = 0.1245
R indices (all data)	R1 = 0.1065, ωR2 = 0.1929	R1 = 0.0709, ωR2 = 0.1315
Largest diff. peak and hole [eA°$^{-3}$]	0.418 and –0.382	0.350 and –0.133

equivalence observed with the bulky ammonium cation in the lattice, only one of the diisobutylammonium ion is shown in the ORTEP along with the silicate anion. The geometrical parameters of the six coordinate octahedral unit, "SiO_6" anion of **6** are almost identical to those of the reported structure[13] and compound **1**. However, the dihedral angle between the planes C1—C2—C3—C4—C5—C6—O1—O2 and C1′—C2′—C3′—C4′—C5′—C6′—O1′—O2′ is 75.97° and both of these planes subtend an equal angle 88.35° with the plane O3—C7—C8—C9—C9′—C8′—C7′—O3′.

Table IV and Figure 2b show the details of the hydrogen bonding in **6**. Unlike structure **1**, the compound **6** indicates interactions involving only one of the catecholates with one of the N—H bonds of the cation (N1···H1′···O3 = 1.90 A°). The remaining N—H bond of the cation is also involved in a relatively strong interaction with the oxygen (O4) of a water molecule present in the lattice (N1···H1···O4 = 2.14 A°). Contrary to **1**, the presence of water molecule facilitates an extended

intermolecular hydrogen bond network leading to an infinite one dimensional chain arrangement in compound **6** (Figure 2b). The hydrogen atoms of water molecule could not be located in difference fourier electron density map. However, a distance of 2.829 A° observed between the oxygen atoms of water (O4) and catechol (O1) suggests the possibility of O—H—O interaction between the two. The water molecule present in the lattice sits on the twofold axis. It may be seen bridging the symmetrically disposed cations through N1-H1···O4 hydrogen bond.

CONCLUSION

Six six-coordinate silicates, $M_2[Si(C_6H_4O_2)_3]$ containing primary and secondary ammonium cations have been synthesized and characterized. Influence of counter cations on solubility, air and thermal stability has been observed. X-ray structures of **1** and **6** reveal the differences in the inter ionic interactions facilitated by hydrogen bonding and highlighting the role of counter cations.

EXPERIMENTAL

General Procedures

All syntheses and subsequent manipulations were carried out under argon by conventional Schlenk line techniques. Solvents, catechol, and amines were purified by employing standard procedure.[24] Tetraethoxysilane, TEOS (Metkem silicon, 99% pure) was used as such.

Details of facilities used for obtaining various characterization data are same as reported elsewhere.[13] ^{29}Si NMR spectra were recorded on a JEOL JNM-LA 400 instrument (400 MHz) as solutions in CD_3OD and/or CD_3CN. Perkin Elmer TGA-7 and Balzers GAM 440 were used for TG and EG analysis respectively. Powder XRD patterns were obtained by Rigaku Miniflex table top model with radiation sources CoKα ($\lambda = 1.7902$ A°) and CuKα ($\lambda = 1.5418$ A°).

Synthesis of Tris(catecholato)silicate Derivatives of Various Amines, 1–6

Catechol (5.38 g, 53.8 mmol) and amine in the mole ratio 3:2 were stirred in toluene (120 mL) and TEOS (3.74 g, 18.0 mmol) was added as neat liquid in 30 min at room temperature. After ca. 3 h (12 h in case of **6**), the reaction mixture was filtered to isolate the product **1–6** as the precipitate in ca. 75% yield. By cooling the concentrated filtrate to 0°C for 1 day ca. 15% of the same product was recovered. Compound **6** was

isolated entirely from solution as there was no precipitate. In all the cases, the compounds were washed with ether (5 × 5 mL) and dried in vacuo.

[(n-$C_3H_7NH_3)_2$][$Si(C_6H_4O_2)_3$] (**1**): IR (Nujol): 1591(s), 1460(m), 1376(s), 1251(m), 1099(m), 1017(m), 955(s), 872(s), 813(s), 738(s), 689(m), 595(m) cm^{-1}; MS (70 eV, EI): m/z(%): 244 {100, $Si(C_6H_4O_2)_2^+$}, 136 {34, $Si(C_6H_4O_2)^+$}, 110 {30, $C_6H_6O_2^+$}, 59 {10, $CH_3CH_2CH_2NH_2^+$}; ^{29}Si NMR (CD_3OD, δ in ppm): -143.9; elemental analysis calcd (%) for $C_{24}H_{32}N_2O_6Si$ (472.60): C 60.99, H 6.83, N 5.93; found: C 60.60, H 6.50, N 5.90.

[(i-$C_3H_7NH_3)_2Si(C_6H_4O_2)_3$] (**2**): IR (Nujol): 1586(s), 1457(s), 1370(s), 1243(vs), 1094(m), 1018(m), 957(m), 877(vs), 814(vs), 739(s), 692(s), 590(m) cm^{-1}; MS (70 eV, EI): m/z (%): 244 {80, $Si(C_6H_4O_2)_2^+$}, 136 {18, $Si(C_6H_4O_2)^+$}, 110 {74, $C_6H_6O_2^+$}, 59 {66, $(CH_3)_2CHNH_2^+$}; ^{29}Si NMR (CD_3OD): no signal observed due to poor solubility; elemental analysis calcd (%) for $C_{24}H_{32}N_2O_6Si$ (472.60): C 60.99, H 6.83, N 5.93; found: C 60.80, H 6.65, N 5.80.

[(n-$C_4H_9NH_3)_2Si(C_6H_4O_2)_3$] (**3**): IR (Nujol): 1588(s), 1455(s), 1376(s), 1248(vs), 1103(m), 1016(m), 957(m), 916(vs), 883(vs), 872(vs), 814(vs), 738(m), 685(s), 598(m) cm^{-1}; MS (70 eV, EI): m/z (%): 244 {100, $Si(C_6H_4O_2)_2^+$}, 136 {30, $Si(C_6H_4O_2)^+$}, 110 {36, $C_6H_6O_2^+$}, 73 {12, $CH_3(CH_2)_3NH_2^+$}; ^{29}Si NMR (CD_3OD, δ in ppm): -141.3; elemental analysis calcd (%) for $C_{26}H_{36}N_2O_6Si$ (500.66): C 62.37, H 7.24, N 5.59; found: C 62.60 H 6.99, N 5.60.

[($C_6H_{11}NH_3)_2Si(C_6H_4O_2)_3$] (**4**): IR (Nujol): 1590(s), 1459(m), 1368(s), 1246(vs), 1096(m), 1025(m), 942(m), 878(s), 813(vs), 738(m), 679(s), 588(m) cm^{-1}; MS (70 eV, EI): m/z(%): 244 {80, $Si(C_6H_4O_2)_2^+$}, 136 {20, $Si(C_6H_4O_2)^+$}, 110 {24, $C_6H_6O_2^+$}, 99 {16, $C_6H_{11}NH_2^+$}; ^{29}Si NMR (CD_3OD, δ in ppm): −142.0; elemental analysis calcd (%) for $C_{30}H_{40}N_2O_6Si$ (552.74): C 65.18, H 7.29, N 5.07; found: C 64.99, H 7.18, N 5.20.

[($C_7H_7NH_3)_2Si(C_6H_4O_2)_3$] (**5**): IR (Nujol): 1588(vs), 1455(m), 1376(s), 1251(s), 1060(m), 1018(vs), 950(s), 833(vs), 813(vs), 739(m), 695(vs), 595(s) cm^{-1}; MS (70 eV, EI): m/z(%): 244 {50, $Si(C_6H_4O_2)_2^+$}, 136 {24, $Si(C_6H_4O_2)^+$}, 110 {20, $C_6H_6O_2^+$}}, 106 {100, $C_6H_5CH_2NH_2^+$}; ^{29}Si NMR (CD_3OD): no signal observed due to poor solubility; elemental analysis calcd (%) for $C_{32}H_{32}N_2O_6Si$ (568.71): C 67.58, H 5.67, N 4.92; found: C 67.70, H 5.70, N 5.01.

[($\{i$-$C_4H_9\}_2NH_2)_2Si(C_6H_4O_2)_3$] (**6**): IR (Nujol): 1586(s), 1460(m), 1367(s), 1244(s), 1095(m), 1022(m), 957(m), 876(s), 813(s), 735(m), 677(m), 589(m) cm^{-1}; MS (70 eV, EI): m/z (%): 244 {75, $Si(C_6H_4O_2)_2^+$}, 136 {14, $Si(C_6H_4O_2)^+$}, 110 {20, $C_6H_6O_2^+$}, 129 {9,

$((CH_3)_2CHCH_2)_2NH_2^+\}$; ^{29}Si NMR (CD_3OD, δ in ppm): -144.0; elemental analysis calcd (%) for $C_{34}H_{52}N_2O_6Si$ (612.88): C 66.63, H 8.55, N 4.57; found: C 66.06, H 8.90, N 4.44.

Thermal Analysis

TGA: Finely powdered samples (1–3 mg) were heated in a cylindrical Pt crucible from room temperature to 800°C at the rate of 20°C/min. in static air.

EGA: The samples were heated in a furnace (previously baked at 85°C for 1.5 h.) from 50–400°C in a temperature programmed mode (scanning rate 10°C/cycle). Evolved gases were monitored by the gas analyzer.

X-Ray Structure Determination of 1 and 6

Suitable crystals of **1** were got by keeping the turbid reaction mixture for ca. 3 days at room temperature while that of **6** were obtained by slow evaporation of the reaction mixture under argon atmosphere. Crystals of **1** and **6** are highly unstable in air and on exposure, turns to light brown powder immediately. Crystals of appropriate sizes of **1** and **6** sealed in Lindemann glass capillary tubes (along with mother-liquor) were used. The diffraction intensities of **6** and **1** were collected on Enraf-Nonius CAD-4 Diffractometer equipped with a graphite monochromated radiation Cu Kα ($\lambda = 1.5418$ A°) and MoKα ($\lambda = 0.71073$ A°) radiation at 293 K respectively. Intensity measurements were performed using ω-2θ scan technique. Lattice parameters and their standard deviations were obtained by least square refinement of 25 carefully selected reflections in the θ range 20–30° and 10–15° for **6** and **1** respectively. Lorentz and polarization corrections were applied, as was an empirical absorption correction based on ψ-scans. The structure was solved by direct methods (SHELXS-97[25]). All the non-hydrogen atoms were refined with anisotropic thermal parameters using the program SHELXL-97.[26] Refinement was carried out by full-matrix least squares on $|F|$.[2] Hydrogen atoms were geometrically fixed and riding model refinement was performed. The data reduction were performed using a software package MolEN.[27] The thermal ellipsoid plots were obtained using PLATON.[28]

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