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SYNTHESIS, CHARACTERIZATION AND REACTIVITY OF BIS (BENZENE-1,2-DIOLATO)ISOTHIOCYANATO SILICON (IV) COMPOUNDS

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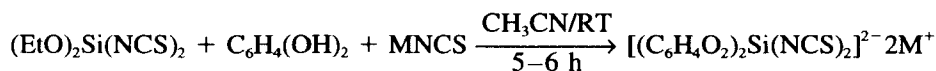
Some spirobicyclic anionic siliconates with isothiocyanate group linked to silicon atom, i.e. $[(C_6H_4O_2)_2SiNCS]^-M^+$ [$M = K$ (1), Na (2), $K(18\text{-crown-}6)$ (3), NH_4 (4)] are prepared from the reactions of triethoxyisothiocyanato silane and benzene-1,2-diol in presence of the corresponding alkali metal/ammonium thiocyanates. The reaction of 1–4 with diethylamine results in the formation of intermolecular coordination complexes containing hexacoordinate siliconate anion, $[(C_6H_4O_2)_2SiNCS.Et_2NH]^-M^+$ [$M = K$ (5), Na (6), $K(18\text{-crown-}6)$ (7), Et_2NH_2 (8)]. The reactions of 1–3 with dimethylsulfite afford new pentaoxy siliconate derivatives, $[(C_6H_4O_2)_2SiOMe]^-M^+(solv)$ [$M(solv) = K(Me_2SO_3)$ (9), $Na(Me_2SO_3)$ (10), $K(18\text{-crown-}6)$ (11)]. All the compounds isolated here are characterized by elemental analyses, IR, multinuclei (1H , ^{13}C and ^{29}Si) NMR and FAB-mass spectroscopy.

Key words: Anionic siliconates, thiocyanate, dimethylsulfite, reactivity.

INTRODUCTION

Spirobicyclic pentacoordinate siliconate salts of alkali-metal cations are usually prepared through (a) condensation reaction of alkyl/aryl triethoxy silane with appropriate 1,2-diol in presence of alkali-metal ethoxide^{1–4} or (b) nucleophilic addition on tetra-coordinate spirocyclic silane.^{1,5–7} Depolymerization of SiO_2 under strongly basic conditions is also reported to yield pentacoordinate siliconates.⁸

Recently, we have reported⁹ the syntheses of hexacoordinate dianionic siliconates $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}2M^+$ ($M = K, Na, NH_4$) from the condensation reaction between diethoxy diisothiocyanato silane and benzene-1,2-diol in the presence of alkali-metal/ammonium thiocyanates under extremely mild conditions.

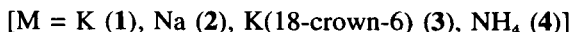


During this time, the X-ray crystal structure of the dianionic siliconate $[(C_6H_4O_2)_3Si]^{2-}2Li^+ \cdot 3.5dme$ ($dme = 1,2\text{-dimethoxyethane}$) has also appeared.¹⁰

The new synthetic strategy adopted by us⁹ has now been extended to prepare the title pentacoordinate siliconates, $[(C_6H_4O_2)_2Si(NCS)]^-M^+$ [$M = K$ (1), Na (2), $K(18\text{-crown-}6)$ (3), NH_4 (4)]. These compounds react with diethylamine and dimethylsulfite separately to afford new siliconate derivatives. The details are reported in this paper.

RESULTS AND DISCUSSION

The compounds **1–4** are prepared in a one-pot reaction between triethoxy isothiocyanato silane, benzene-1,2-diol and the corresponding alkali metal/ammonium thiocyanates in 1:2:1 molar ratio under mild conditions.



These are white, hygroscopic solids and are soluble in solvents such as CH_3CN , DMF, DMSO etc. Elemental analyses of these compounds conform to the composition as suggested. Conductance of millimolar solutions in acetonitrile (Λ_{M} 125.0–135.2 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$) suggest them to be 1:1 electrolytes.¹¹ The compounds have been characterized by IR, multinuclei (^1H , ^{13}C and ^{29}Si) NMR and FAB-mass spectral data.

Infrared spectra of the compounds **1–4** reveal $\nu_{\text{as}}\text{NCS}$ mode at 2110–2085 cm^{-1} . ^1H NMR spectrum of each compound shows a multiplet at δ 6.8 ppm due to $\text{C}_6\text{H}_4\text{O}_2$ group. An additional singlet at δ 3.5 ppm in compound **3** identifies the 18-crown-6 moiety. As expected the relative integrated intensity of $\text{C}_6\text{H}_4\text{O}_2$ and 18-crown-6 protons are in the ratio 1:3. ^{13}C NMR spectral data (experimental section) are in agreement with the composition as described. ^{29}Si NMR spectrum of each compound reveals a single resonance with chemical shift values in the range –112.6 to –110.4 ppm and suggest pentacoordinate environment around silicon atom.¹²

Selected FAB-mass spectral data (positive and negative ion modes) of the compounds **1**, **2** and **4** are given in Table I. Positive ion FAB-mass spectra in 3-nitrobenzyl alcohol (NBA) matrix reveal the corresponding mono and disolvated cations, $\text{M}^+\cdot\text{NBA}$ and $\text{M}^+\cdot 2\text{NBA}$ ($\text{M} = \text{K}, \text{Na}, \text{NH}_4$). In the negative ion mode, a few cluster ions, (e.g. A_2^-K^+ , m/z 643 for **1**; $\text{A}^-\cdot\text{Na}^+\cdot\text{NBA}\cdot\text{H}^+$, m/z 477 for **2**; $\text{A}^-\cdot\text{NH}_4\text{NO}_2$, m/z 366 for **4**; where A^- represents the parent silicate anion) have been identified which are in accord with the fragmentation pattern reported for related anionic pentacoordinate silicate derivatives.¹³ Other structurally important fragment ions (Table I, footnote) remain invariably similar in the spectra of all the compounds.

Reactions with Diethylamine

The compounds **1–3** react with diethylamine under mild conditions to afford intermolecular coordination compounds **5–7** respectively featuring hexacoordinate silicate anion. The reaction of **4** with the base proceeds with the concomitant transamination reaction to yield the silicate **8**.

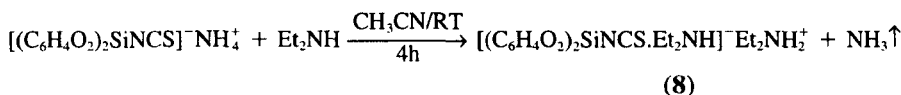
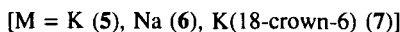
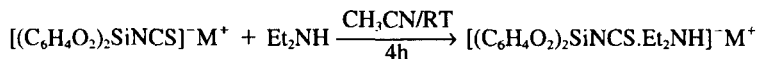


TABLE I
Selected Fab-mass spectral data of the siliconates

Complex	m/z	Positive ion mode Assignment	m/z	Negative ion mode Assignment
1	192, 345	K ⁺ NBA, K ⁺ 2NBA	211, 643	NCS ⁻ NBA, (A) ⁻ K ⁺
2	176, 329, 482	Na ⁺ NBA, Na ⁺ 2NBA, Na ⁺ 3NBA	211, 477	NCS ⁻ NBA, A ⁻ Na ⁺ (NBA-H ⁺)
4	171, 324, 477	NH ₄ ⁺ NBA, NH ₄ ⁺ 2NBA, NH ₄ ⁺ 3NBA	211, 366	NCS ⁻ NBA, A ⁻ NH ₄ ⁺ NO ₂ ⁻
5	74, 112, 119, 415	NH ₄ Et ₃ ⁺ , K ⁺ Et ₃ NH ⁺ , K ⁺ NBA, A ⁻ K ⁺ Et ₃ NH ₂ ⁺	211, 302 375, 493	NCS ⁻ NBA, A ⁻ A ⁻ Et ₃ NH ₄ , A ⁻ K ⁺ (NBA-H ⁺)
8	74, 227, 450	Et ₃ NH ₂ ⁺ , Et ₃ NH ₂ ⁺ NBA, A ⁻ (Et ₃ NH ₂) ₂	211, 375, 455, 528	NCS ⁻ NBA, A ⁻ Et ₃ NH ₄ ⁺ A ⁻ NBA, A ⁻ Et ₃ NH ₄ ⁺ NBA
9	192, 345, 498	K ⁺ NBA, K ⁺ 2NBA, K ⁺ 3NBA	95, 345, 423, 742	OSO ₂ Me ⁻ , B ⁻ K ⁺ OMe ⁻ , B (K ⁺ DMS)-H ⁺ , B ₂ ⁻ K ⁺ NBA
10	176, 329, 561	Na ⁺ NBA, Na ⁺ 2NBA, B ⁻ Na ⁺ DMS NBA	95, 297, 329, 551	OSO ₂ Me ⁻ , B ⁻ Na ⁺ -H ⁺ , B ⁻ Na ⁺ OMe ⁻ , B ₂ ⁻ H ⁺

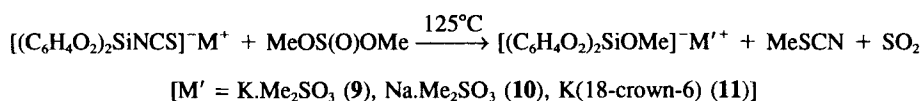
(a) A⁻ = [(C₆H₄O)₂SiNCS]⁻; B⁻ = [(C₆H₄O)₂SiOMe], NBA = 3-nitrobenzyl alcohol, DMS = Dimethylsulphite (b) In the negative ion mode, the ions at m/z = 109, 261, 396 corresponding to C₆H₄O₂H⁻, (C₆H₄O)₂SiOH⁻ and [(C₆H₄O)₂Si(OCH₂C₆H₄NO₂)]⁻ respectively are observed in the spectra of all the compounds. (c) The spectra of 5, 8, 9 and 10 also indicate fragments probably arising from tris(benzene-1,2-diolato) siliconate salts as impurity.

Infrared spectra of these compounds reveal ν_{as} NCS mode at 2070–2060 cm^{-1} . ν_{NH} mode appears at 3170–3160 cm^{-1} and undergoes a negative spectral shift of 110–100 cm^{-1} relative to the free base. In the ^1H NMR spectra, the chemical shift values of $\text{C}_6\text{H}_4\text{O}_2$, Et_2NH and 18-crown-6 (in compound **7** only) protons and their integrated intensities conform to the composition as described. Similarly, ^{13}C NMR spectra reveal the presence of organic moieties and various signals are accordingly attributed (experimental section). ^{29}Si NMR spectrum of each compound exhibits a single resonance with $\delta^{29}\text{Si}$ values lying between -156.2 to -140.7 ppm. Thus, a significant upfield shift of the $\delta^{29}\text{Si}$ values relative to those of the corresponding precursor siliconates **1–4** may suggest the coordinative association of the base with the silicon atom in these compounds. These trends are in accord with those reported for related hexacoordinate anionic siliconates.^{12,14}

The formation of these siliconates is further supported by the FAB-mass spectra of representative compounds **5** and **8**. Structurally important ions along with their possible assignments are summarized in Table I. In the positive ion mode, the respective cations, solvated by NBA matrix have been easily identified. By analogy with reported trends,¹³ a few clusters representing the siliconate anion $[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS}]^-$ or its adduct with diethylamine appear in the positive and negative ion mode FAB-mass spectra.

Reactions with Dimethylsulfite

The use of dimethylsulfite as alkylating and alkoxyating agent as well as dipolar aprotic solvent is well known in literature.¹⁵ In spite of such versatility, the reagent has not been fully exploited in the domain of organometallic chemistry. The siliconates **1–3** react with dimethyl sulfite under reflux conditions (125°C) to afford bis (benzene 1,2-diolato) methoxy siliconates of the corresponding (solvated) cations. The reactions may be represented as follows:



These reactions may be thought to involve ionic nucleophiles originating from dimethylsulfite under thermally equilibrated gas-phase conditions.^{15,16} The solvation of K and Na cations in complexes **9** and **10** is expected in view of the donor-ability of dimethylsulfite. All the compounds obtained above represent a rare class^{1,5,17} of pentaoxy siliconates. The compounds **9–11** are white, hygroscopic solids and are soluble in CH_3CN , DMSO and MeOH. These are characterized by elemental analyses, IR, multinuclei (^1H , ^{13}C and ^{29}Si) NMR and FAB-mass spectra.

Infrared spectra of **9–11**, show the absence of ν_{as} NCS mode which is quite prominent in the precursor siliconates **1–3** at 2110–2085 cm^{-1} . An additional band at 1205 cm^{-1} in the compounds **9** and **10** is attributed to νSO_3 mode of dimethylsulfite¹⁸ solvating the cations. ^1H NMR spectra of **9** and **10** exhibit signals at 6.8 (m), 3.3 (s) and 3.7–3.6 (s) ppm in 8:3:6 intensity ratio and are attributed to $\text{C}_6\text{H}_4\text{O}_2$, Si—OMe and OMe (from Me_2SO_3) groups respectively. The compound **11** manifests $\text{C}_6\text{H}_4\text{O}_2$, 18-crown-6 and Si—OMe groups at 6.8, 3.5 and 3.4 ppm respectively. ^{13}C NMR data (experimental section) also conform to the structures as suggested. ^{29}Si NMR

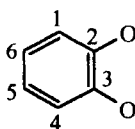
spectra of these compounds show a single resonance in each case in the region -99.1 to -99.9 ppm. These values are in fair agreement with those reported for pentaoxy siliconates.^{5,17} FAB-mass spectral data of the compounds **5** and **6** in Table I indicate the presence of a few structurally important cluster ions, thus establishing the identity of the siliconate anion i.e. $[(C_6H_4O_2)_2SiOMe]^-$. Subsequent fragmentation follows the general pathway as described here for other siliconate derivatives.

EXPERIMENTAL

All manipulations were performed under dry nitrogen atmosphere using standard glass vacuum line. Solvents were dried according to standard procedures.¹⁹ Potassium/sodium/ammonium thiocyanate (Qualigen) were dried under vacuum for 2–3 days at 50°C . Diethylamine (BDH, pure) was refluxed over KOH pellets and distilled under nitrogen atmosphere prior to use. Silicon tetrachloride (Fluka) was used as received. The deuterated solvents used for NMR spectroscopic measurements were degassed by successive "freeze-pump-thaw" cycles and dried over 4 \AA molecular sieves.

Infrared spectra were routinely obtained as thin films or nujol mulls on a Perkin-Elmer model 1430 ratio recording spectrophotometer. ^1H NMR spectra were recorded on Bruker 300 MHz instrument while ^{13}C and ^{29}Si NMR spectra were carried out on Bruker AMX-400 spectrometer with tetramethyl silane (TMS) as external reference. FAB-mass spectra were obtained on a mass spectrometer MAT 95 of finnigan MAT by SIMS method in 3-nitrobenzyl alcohol (NBA) matrix. CHN analyses were performed on Perkin Elmer Model 2400 CHN analyser. S and Si were estimated by gravimetric methods.

The ^{13}C NMR assignments for aromatic system are tentative and based on reported trends.⁹ The numbering scheme for the benzene 1,2-diolato group is shown below.



Preparations: Triethoxy isothiocyanato silane²⁰ and dimethylsulfite¹⁵ were prepared according to literature procedures. $(\text{EtO})_3\text{SiNCS}$; IR (Nujol, cm^{-1}): 2080 ($\nu_{\text{as}}\text{NCS}$), 1080 ($\nu_{\text{as}}\text{Si—O}$). $\delta^1\text{H}$ NMR (CDCl_3): 3.7 (q, 2H, OCH_2), 1.0 (t, 3H, CH_3). $\delta^{13}\text{C}$ NMR (CDCl_3): 58.2 (OCH_2), 10.4 (CH_3), 141.8 (NCS). $\delta^{29}\text{Si}$ NMR (CDCl_3): -91.7 . MeOS(O)OMe IR (Nujol, cm^{-1}): 1200 (νSO_3). $\delta^1\text{H}$ NMR (CDCl_3): 3.7 (OCH_3). $(\text{K}, 18\text{-crown-6})\text{NCS}$ was prepared by reacting equimolar quantities of potassium thiocyanate and 18-crown-6 ether in dry THF. The identity of the salt was established by elemental analyses, IR and ^1H NMR spectral data. Anal. Calcd. for $\text{C}_{13}\text{H}_{24}\text{NO}_6\text{SK}$; C, 43.21, H, 6.65, N, 3.88. Found: C, 42.30; H, 6.12; N, 3.98. IR (Nujol, cm^{-1}): 2060 ($\nu_{\text{as}}\text{NCS}$), 1100 (νOCH_2). $\delta^1\text{H}$ NMR (CDCl_3): 3.6 (OCH_2).

$[(C_6H_4O_2)_2SiNCS]^-M^+$ [$M = \text{K}, \text{Na}, \text{K}(18\text{-crown-6}), \text{NH}_4(1-4)$]. Triethoxy isothiocyanato silane (9.0 mmol) was added separately to a stirred solution of potassium/sodium/potassium (18-crown-6)/ammonium isothiocyanate (9.0 mmol) in dry acetonitrile (25 mL). The clear solution was stirred at room temperature for nearly one hour. Benzene 1,2-diol (18.0 mmol) in the same solvent (25 mL) was cannula transferred into the reaction mixture. Stirring was continued for 5–6 h. Thereafter the solvent was removed under vacuum and dry diethyl ether was added to it. A white solid was precipitated out in each case which was filtered, washed with diethylether-acetonitrile mixture (3:1 ratio by volume) and dried under vacuum.

$[(C_6H_4O_2)_2SiNCS]^-K^+$ (**1**): Yield: 2.5 g (81%). Λ_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, CH_3CN): 125.0. Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{NO}_4\text{SSiK}$: C, 45.75; H, 2.35; N, 4.10; S, 9.38; Si, 8.21. Found: C, 45.33; H, 2.59; N, 4.34; S, 9.30; Si, 8.00. IR (Nujol, cm^{-1}): 2095 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.8 (m, $\text{C}_6\text{H}_4\text{O}_2$). $\delta^{13}\text{C}$ NMR (CD_3CN): 144.9 (C_2, C_3), 129.2 (NCS), 118.8 (C_5, C_6), 115.4 (C_1, C_4). $\delta^{29}\text{Si}$ NMR (CD_3CN): -110.7 .

$[(C_6H_4O_2)_2SiNCS]^-Na^+$ (**2**): Yield: 2.4 g (82%). Λ_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, CH_3CN): 126.9. Anal. Calcd. for $\text{C}_{13}\text{H}_8\text{NO}_4\text{SSiNa}$: C, 48.00; H, 2.46; N, 4.31; S, 9.85; Si, 8.61. Found: C, 47.84; H, 2.12; N, 4.10; S, 10.21; Si, 8.80. IR (Nujol, cm^{-1}): 2085 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.8 (m, $\text{C}_6\text{H}_4\text{O}_2$). $\delta^{13}\text{C}$ NMR (CD_3CN): 142.6 (C_2, C_3), 130.7 (NCS), 118.5 (C_5, C_6), 114.7 (C_1, C_4). $\delta^{29}\text{Si}$ NMR (CD_3CN): -112.6 .

$[(C_6H_4O_2)_2SiNCS]^-K^+(18\text{-crown-6})$ (**3**): Yield: 4.8 g (88%) Λ_m ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$, CH_3CN): 129.7. Anal. Calcd. for $\text{C}_{25}\text{H}_{32}\text{NO}_{10}\text{SiK}$: C, 49.58; H, 5.30; N, 2.31; S, 5.30; Si, 4.64. Found: C, 49.02; H, 5.37; N,

2.38; S, 5.16; Si, 4.33. IR (Nujol, cm^{-1}): 2110 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.8 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.5 (s, 24H, OCH_3). $\delta^{13}\text{C}$ NMR (CD_3CN): 147.9 (C_2 , C_3), 135.3 (NCS), 118.8 (C_5 , C_6), 112.9 (C_1 , C_4), 69.6 (OCH_2). $\delta^{29}\text{Si}$ NMR (CD_3CN): -110.4.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS}]^-\text{NH}_4^+$ (4). Yield: 2.5 g (86%). Λ_{M} ($\Omega^{-1}\text{cm}^2\text{mol}^{-1}$, CH_3CN): 135.2. Anal. Calcd. for $\text{C}_{13}\text{H}_{12}\text{N}_2\text{O}_4\text{SSi}$: C, 48.75; H, 3.75; N, 8.75; S, 10.00; Si, 8.75. Found: C, 48.24; H, 3.34; N, 8.30; S, 10.20; Si, 8.32. IR (Nujol, cm^{-1}): 2090 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.7 (m, $\text{C}_6\text{H}_4\text{O}_2$). $\delta^{13}\text{C}$ NMR (CD_3CN): 144.9 (C_2 , C_3), 129.3 (NCS), 118.7 (C_5 , C_6), 115.4 (C_1 , C_4). $\delta^{29}\text{Si}$ NMR (CD_3CN): -111.5.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS.Et}_2\text{NH}]^-\text{M}^+$ [$\text{M} = \text{K}, \text{Na}, \text{K}$ (18-crown-6), Et_2NH_2] (5–8). To a separately stirred solution of the compound 1–4 (2.0 mmol) in dry acetonitrile (20 mL) was added diethylamine (4.0 mmol). The contents were stirred at room temperature for 4 h resulting in a clear solution. Thereafter, the solvent was evaporated from the reaction mixture under vacuum and dry diethylether (50 mL) was added. A white solid was precipitated out in each case which was filtered, washed with diethylether and dried under vacuum to yield the compound 5–8 respectively.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS.Et}_2\text{NH}]^-\text{K}^+$ (5). Yield: 0.7 g (84%). Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_4\text{SSiK}$: C, 49.27; H, 4.59; N, 6.73; S, 7.72; Si, 6.76. Found: C, 48.92; H, 4.24; N, 6.62; S, 7.10; Si, 6.24. IR (Nujol, cm^{-1}): 3160 (NH), 2060 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.6 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.0 (q, 4H, NCH_2), 1.1 (t, 6H, CH_3). $\delta^{13}\text{C}$ NMR (CD_3CN): 147.5 (C_2 , C_3), 133.2 (NCS), 118.5 (C_5 , C_6), 108.8 (C_1 , C_4), 41.0 (NCH_2), 10.7 (CH_3). $\delta^{29}\text{Si}$ NMR (CD_3CN): -140.7.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS.Et}_2\text{NH}]^-\text{Na}^+$ (6). Yield: 0.6 g (81%). Anal. Calcd. for $\text{C}_{17}\text{H}_{19}\text{N}_2\text{O}_4\text{SSiNa}$: C, 51.25; H, 4.77; N, 7.04; S, 8.04; Si, 7.03. Found: C, 51.05; H, 4.64; N, 6.89; S, 7.93; Si, 6.95. IR (Nujol, cm^{-1}): 3170 (νNH), 2060 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.6 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.0 (q, 4H, NCH_2), 1.2 (t, 6H, CH_3). $\delta^{13}\text{C}$ NMR (CD_3CN): 147.2 (C_2 , C_3), 133.0 (NCS), 118.1 (C_5 , C_6), 109.5 (C_1 , C_4), 41.7 (NCH_2), 10.2 (CH_3). $\delta^{29}\text{Si}$ NMR (CD_3CN): -142.7.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS.Et}_2\text{NH}]^-\text{K}^+$ (18-crown-6) (7). Yield: 1.0 g (74%). Anal. Calcd. for $\text{C}_{29}\text{H}_{43}\text{O}_{10}\text{SSiK}$: C, 51.33; H, 6.34; N, 4.13; S, 4.72; Si, 4.13. Found: C, 50.40; H, 6.15; N, 4.20; S, 4.42; Si, 4.02. IR (Nujol, cm^{-1}): 3160 (νNH), 2060 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.6 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.6 (s, 24H, OCH_2), 2.8 (q, 4H, NCH_2), 1.2 (t, 6H, CH_3). $\delta^{13}\text{C}$ NMR (CD_3CN): 149.7 (C_2 , C_3), 133.2 (NCS), 118.2 (C_5 , C_6), 110.9 (C_1 , C_4), 69.9 (OCH_2), 42.4 (NCH_2), 10.1 (CH_3). $\delta^{29}\text{Si}$ NMR (CD_3CN): -156.2.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiNCS.Et}_2\text{NH}][\text{Et}_2\text{NH}_2]^+$ (8). Yield: 0.7 g (78%). Anal. Calcd. for $\text{C}_{21}\text{H}_{31}\text{N}_3\text{O}_8\text{SSi}$: C, 56.12; H, 6.90; N, 9.35; S, 7.13; Si, 6.23. Found: C, 56.31; H, 6.72; N, 9.17; S, 6.90; Si, 5.86. IR (Nujol, cm^{-1}): 3160 (νNH), 2070 ($\nu_{\text{as}}\text{NCS}$). $\delta^1\text{H}$ NMR (CD_3CN): 6.6 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 2.8 (q, 8H, NCH_2), 1.2 (t, 12H, CH_3). $\delta^{13}\text{C}$ NMR (CD_3CN): 151.9 (C_2 , 6C_3), 134.2 (NCS), 117.4 (C_5 , C_6), 110.8 (C_1 , C_4), 43.2 (NCH_2), 11.6 (CH_3). $\delta^{29}\text{Si}$ NMR (CD_3CN): -141.3.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiOCH}_3]^-\text{K}^+.\text{Me}_2\text{SO}_3$ (9). To the compound 1 (1.02 g, 3.0 mmol) was added excess of dimethylsulfite (5.0 mL). The compound dissolved completely resulting in a clear solution. On heating the reaction mixture at 125°C for one hour, a white solid started precipitating out. Heating was continued for 4 h. Thereafter, the solid obtained was filtered, washed with diethylether and dried under vacuum. Yield: 0.6 g (53%). Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{O}_8\text{SSiK}$: C, 42.45; H, 4.00; S, 7.56; Si, 6.66. Found: C, 42.67; H, 3.84; S, 7.40; Si, 6.14. IR (Nujol, cm^{-1}): 1080 ($\nu\text{Si—O}$), 1205 (νSO_3). $\delta^1\text{H}$ NMR ($\text{DMSO-}d_6$): 6.8 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.6 (s, 6H, Me_2SO_3), 3.3 (s, 3H, OCH_3). $\delta^{13}\text{C}$ NMR ($\text{DMSO-}d_6$): 149.9 (C_2 , C_3), 117.4 (C_5 , C_6), 109.6 (C_1 , C_4), 50.6 (Me_2SO_3), 48.4 (OCH_3). $\delta^{29}\text{Si}$ NMR ($\text{DMSO-}d_6$): -99.8.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiOCH}_3]^-\text{Na}^+.\text{Me}_2\text{SO}_3$ (10). The compound was prepared in a manner similar to that described for 9 by reacting 2 (0.97 g, 3.0 mmol) with dimethylsulfite (5.0 mL). Yield: 0.5 g (51%). Anal. Calcd. for $\text{C}_{15}\text{H}_{17}\text{O}_8\text{SSiNa}$: C, 44.11; H, 4.16; S, 7.84; Si, 6.86. Found: C, 43.80; H, 4.42; S, 7.77; Si, 6.34. IR (Nujol, cm^{-1}): 1080 ($\nu\text{Si—O}$), 1205 (νSO_3). $\delta^1\text{H}$ NMR ($\text{DMSO-}d_6$): 6.8 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.7 (s, 6H, Me_2SO_3), 3.3 (s, 3H, OCH_3). $\delta^{13}\text{C}$ NMR ($\text{DMSO-}d_6$): 149.7 (C_2 , C_3), 117.4 (C_5 , C_6), 109.6 (C_1 , C_4), 50.5 (Me_2SO_3), 48.4 (OCH_3). $\delta^{29}\text{Si}$ NMR ($\text{DMSO-}d_6$): -99.9.

$[(\text{C}_6\text{H}_4\text{O}_2)_2\text{SiOCH}_3]^-\text{K}^+$ (18-crown-6) (11). A clear solution of the compound 3 (1.2 g, 2.0 mmol) in dimethylsulfite (5.0 mL) was heated at 125°C for 4 h. The contents were cooled and dry diethylether (50 mL) was added. On stirring the reaction mixture for nearly one hour, a white solid was precipitated out, which was filtered washed with diethylether and dried under vacuum. Yield: 0.8 g, (75%). Anal. Calcd. for $\text{C}_{22}\text{H}_{35}\text{O}_{11}\text{SiK}$: C, 51.90; H, 6.00; Si, 4.84. Found: C, 51.72; H, 5.84; Si, 4.62. IR (Nujol, cm^{-1}): 1140 (νCO), 1080 ($\nu\text{Si—O}$). $\delta^1\text{H}$ NMR (CDCl_3): 6.6 (m, 8H, $\text{C}_6\text{H}_4\text{O}_2$), 3.5 (s, 24H, OCH_2), 3.4 (s, 3H, OCH_3). $\delta^{13}\text{C}$ NMR (CDCl_3): 149.7 (C_2 , C_3), 118.0 (C_5 , C_6), 110.9 (C_1 , C_4), 69.9 (OCH_2), 51.2 (OCH_3). $\delta^{29}\text{Si}$ NMR (CDCl_3): -99.1.

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