2716 *Inorg. Chem.* **1994**, *33*, 2716–2718

Syntheses and Characterization of Bis(benzene-1,2-diolato)diisothiocyanatosilicon(IV) Compounds: First Stable Bicyclic Siliconate Dianion

Suraj P. Narula,* Ravi Shankar, Manish Kumar, and Meenu

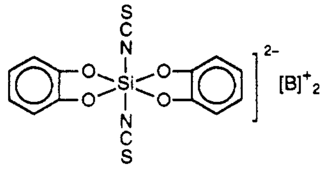
Department of Chemistry, Panjab University, Chandigarh-160014, India

Received September 29, 1993®

Syntheses of the first bicyclic dianion containing hexacoordinate silicon with several cations, $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[B]^+_2$ (B = pyH (**1**), 3-mepyH (**2**), 4-mepyH (**3**), K (**4**), Na (**5**), NH_4 (**6**), Et_2NH_2 (**7**)), are described. Complexes **1–3** are prepared from the reactions between benzene-1,2-diol and the appropriate cationic 5-coordinate silicon(IV) compounds **8–10**. Complexes **4–6** are obtained in one-step reaction between diethoxydiisothiocyanatosilane and the diol in the presence of 1 equiv amount of NCS^- anion, while **7** is formed using chemoselective metathesis of **6** with diethylamine. All the reactions occur at ambient temperature (≤25 °C). The compounds are characterized by multinuclei (^1H, ^{13}C, ^{14}N, ^{29}Si) NMR spectra besides elemental analyses, IR, and molar conductance data. FAB-mass spectra (NBA matrix) have identified the cations in **1–7** and the dianion as clusters in **1–3** and **6**.

Introduction

Anionic pentacoordinate silicon complexes are extensively studied and have found use in syntheses, study of reaction mechanisms, formation of silicon-containing ceramics, etc.[1] However, the chemistry of dianionic hexacoordinate silicon complexes is much less studied.[2–4] Recently, these compounds have assumed importance because of their role as intermediates in many nucleophilic displacement reactions at the silicon atom.[1a,5] Corriu et al. have postulated the formation of the bis(benzene-1,2-diolato)silicon(IV) dianion, $[R_2Si(O_2C_6H_4)_2]^{2-}$, in the conversion of tris(benzene-1,2-diolato)silicon(IV) complexes using organolithium/Grignand reagents.[6] There is no report in the literature about the isolation of complexes of such bicyclic siliconate dianions, though an unsuccessful attempt is briefly mentioned.[3] The complexes **1–7** containing the bis(benzene-1,2-diolato)diisothiocyanatosilicon(IV) dianion have been obtained, and the details are reported herein.



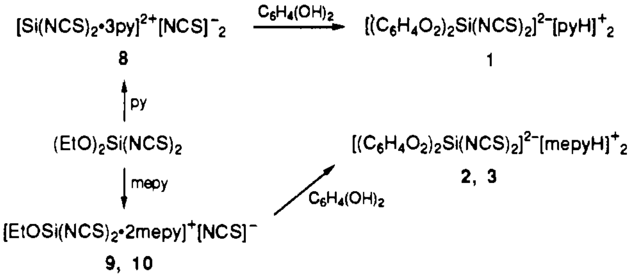
1–7

compd	B
1	pyH
2	3-mepyH
3	4-mepyH
4–6	K, Na, NH_4
7	Et_2NH_2

Results and Discussion

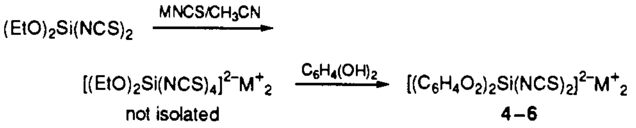
Syntheses of 1–3. The preparation of compounds **1–3** has been achieved in two steps (Scheme 1). First, the reactions of diethoxydiisothiocyanatosilane with an equimolar quantity of pyridine, 3-methylpyridine, or 4-methylpyridine in dry THF at room temperature resulted, after workup from *n*-hexane, in the formation of compounds of the composition **8–10**, respectively. Elemental analyses, molar conductance, IR, and multinuclei (^1H, ^{13}C, ^{29}Si) magnetic resonance data (Experimental Section) suggest these compounds to be cationic pentacoordinate silicon(IV) complexes of the type $[Si(NCS)_2{\cdot}3py]^{2+}[NCS]^-_2$ and $[EtOSi(NCS)_2{\cdot}2B']^+[NCS]^-$ (B′ = 3-mepy, 4-mepy). The second step involves the reactions of pure **8–10** with benzene-1,2-diol in THF yielding the desired siliconates **1–3**, respectively, in 70–75% yield. The unusual properties of cationic silicon derivatives have been reported earlier,[7] though molecular designs such as **8–10** to generate the bicyclic siliconate dianion **1–3** are demonstrated for the first time.

Scheme 1



mepy = 3-mepy, 4-mepy

Scheme 2



M = K, Na, NH_4

Syntheses of 4–7. Unlike the above methodology, the compounds **4–6** are obtained by convenient one-pot synthesis by reacting diethoxydiisothiocyanatosilane and benzene-1,2-diol (1:2 molar ratio) in the presence of a 1-equiv quantity of potassium/sodium/ammonium thiocyanate (Scheme 2). As described earlier,[8] the NCS^- ion can activate the tetracoordinate silicon center in nucleophilic displacement reactions via the intermediate

---

® Abstract published in *Advance ACS Abstracts,* May 1, 1994.

[1] (a) Chuit, C.; Corriu, R. J. P.; Reye, C.; Young, Y. C. *Chem. Rev.* **1993**, *93*, 1371. (b) Corriu, R. J. P.; Guerin, C.; Moreau, J. J. E. In *The Chemistry of Organic Silicon compounds, Part I*; Patai, S., Rappaport, Z., Eds.; Wiley & Sons: Chichester, England, 1989; p 305. (c) Holmes, R. R. *Chem. Rev.* **1990**, *90*, 17. (d) Tamao, K.; Hayashi, T.; Ito, K. In *Frontiers of Organosilicon Chemistry*; Bassindale, A. R., Gasper, P. P., Eds.; *The Royal Society of Chemistry*: Cambridge, England, 1991; p 197. (e) Tacke, R.; Becht, J.; Lopez-Mras, A.; Sheldrick, W. S.; Sebald, A. *Inorg. Chem.* **1993**, *32*, 2761. (f) Laine, R. M.; Blohowiak, K. Y.; Robinson, T. R.; Hoppe, M. L.; Nardi, P.; Kampf, J.; Uhm, J. *Nature* **1991**, *353*, 642. (g) Bassindale, A. R.; Borbaruah, M. J. *Chem. Soc., Chem. Commun.* **1993**, 352.

[2] Tandura, S. N.; Voronkov, M. G.; Alekseev, N. V. *Top. Curr. Chem.* **1986**, *131*, 99.

[3] Frye, C. L. *J. Am. Chem. Soc.* **1964**, *86*, 3170.

[4] Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *Organometallics* **1988**, *7*, 1165.

[5] Fujimoto, H.; Arita, N.; Tamao, K. *Organometallics* **1992**, *11*, 3035.

[6] Boudin, A.; Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C. *J. Organomet. Chem.* **1989**, *362*, 265.

[7] (a) Kummer, D.; Koster, H. Z. *Anorg. Allg. Chem.* **1973**, *398*, 279. (b) Kummer, D.; Seshadri, T. *Chem. Ber.* **1977**, *110*, 2355.

0020-1669/94/1333-2716$04.50/0

Table 1. Selected FAB-Mass Spectral Data (Positive Ion Mode) for 1–7[a]

compd	*m/z*	assgnts
1	80, 233, 386	$[pyH]^+$ $[pyH]^+{\cdot}NBA$, $[pyH]^+{\cdot}2NBA$
2, 3	94, 247, 400	$[mepyH]^+$, $[mepyH]^+{\cdot}NBA$, $[mepyH]^+{\cdot}2NBA$
4	192, 345	$[K]^+{\cdot}NBA$, $[K]^+{\cdot}2NBA$
5	176, 329	$[Na]^+{\cdot}NBA$, $[Na]^+{\cdot}2NBA$
6	171, 324	$[NH_4]^+{\cdot}NBA$, $[NH_4]^+{\cdot}2NBA$
7	74	$[Et_2NH_2]^+$

[a] 3-Nitrobenzyl alcohol (NBA) matrix.

Table 2. Commonly Observed Ions in the FAB-Mass Spectra (Negative Ion Mode) for 1–7[a]

m/z	assgnts
549	$[(C_6H_4O_2)_2SiOCH_2C_6H_4NO_2]^-{\cdot}NBA$
497	$[(C_6H_4O_2)Si(OC_6H_4)(NCS)_2]^-{\cdot}NBA$
396	$[(C_6H_4O_2)_2SiOCH_2C_6H_4NO_2]^-$
211	$[NCS]^-{\cdot}NBA$
169	$[(C_6H_4O_2)Si(OH)O]^-$
109	$[C_6H_4O_2H]^-$

[a] 3-Nitrobenzyl alcohol (NBA) matrix.

Table 3. Selected Multinuclei (^{13}C, ^{14}N, ^{29}Si) Magnetic Resonance Chemical Shift Data (δ) for 1–7[a]

compd	^{13}C NMR: NCS	^{14}N NMR: NCS	^{29}Si NMR: ^{29}Si
1		−234.7	−119.2
2		−236.4	−116.7
3		−234.2	−115.4
4	129.6	−237.2	−110.6
5	129.7	−238.4	−111.7
6	130.0	−230.7	−113.6
7	130.2	−234.8	−115.2
A[b]	143.0	−273.8	−104.0

[a] CD_3CN solution; chemical shifts are quoted in ppm relative to TMS (for ^{13}C and ^{29}Si NMR) and CH_3NO_2 (for ^{14}N NMR) at 25 °C. [b] A = $(EtO)_2Si(NCS)_2$ ($CDCl_3$ solution).

formation of anionic hypervalent silicon species. By analogy, the formation of **4–6** can be believed to proceed via unstable dianionic silicon intermediates $[(EtO)_2Si(NCS)_4]^{2-}M^+_2$ (M = K, Na, NH_4). Attempts to synthesize **4–6** using alkali metal ethoxides as alternate nucleophiles were unsuccessful. The reaction between diethoxydiisothiocyanatosilane and potassium or sodium ethoxide (1:2 molar ratio) in THF at −78 °C resulted in the formation of $(EtO)_4Si$ as the sole product. Compound **7** has been obtained in quantitative yield by selective metathetical reaction between compound **6** and diethylamine, shown as follows:

$$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[NH_4]^+_2 \xrightarrow[CH_3CN/RT/4\,h]{2Et_2NH} [(C_6H_4O_2)_2Si(NCS)_2]^{2-}[Et_2NH_2]^+_2 + 2NH_3$$

Characterization. The compounds **1–7** are white, hygroscopic solids and are soluble in solvents such as acetonitrile, acetone, dimethyl sulfoxide, etc. Elemental analyses of these complexes conform to the composition as described. Conductance measurements of their millimolar solutions in acetonitrile (molar conductance: 232.7–296.6 Ω^{-1} cm^2 mol^{-1}) suggest them to be 1:2 electrolytes.[9] These compounds have been characterized by FAB-mass, infrared, and multinuclei (^1H, ^{13}C, ^{14}N, ^{29}Si) NMR spectroscopy.

All efforts to obtain X-ray-quality crystals of these compounds were not successful. In the absence of X-ray diffraction data, FAB-mass spectra have already been employed to gain evidence for the formation of anionic siliconates.[10] Positive ion FAB-mass spectra of the complexes **1–7** in 3-nitrobenzyl alcohol (NBA) matrix have identified the $[B]^+$ and also mono- and disolvated species, $[B]^+{\cdot}NBA$ and $[B]^+{\cdot}2NBA$ (Table 1). In the negative ion mode, the presence of cluster ions $A^{2-}B^+{\cdot}NBA$ (*m/z* 593 for **1** and *m/z* 607 for **2** and **3**) and $A^{2-}B^+$ (*m/z* 378 for **6**, where A^{2-} represents the dianion) identify the siliconate species. Other structurally important fragment ions remain invariably similar in the spectra of all the complexes and are summarized in Table 2.

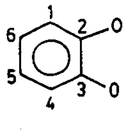
The infrared spectra of **1–7** reveal the ν(NCS) mode at 2080–2070 cm^{-1}. For **1–3**, the bands at 2600–2400 cm^{-1} indicate quaternization of the pyridine bases. The formation of these cations is also supported by the downfield ^1H NMR chemical shift values of pyridine, 3-methylpyridine, or 4-methylpyridine ring protons relative to those of the free bases. The benzene-1,2-diolato group appears as a multiplet at 6.8 ppm. The cations and $C_6H_4O_2$ groups in the anion integrate in a 1:1 ratio. ^{13}C NMR spectra of **1–3** reveal signals due to the cationic part of the compounds only while those of the anion are too weak to be assigned. However, the complexes **4–7** exhibit these signals clearly (Experimental Section) and are accordingly attributed.[12] ^{29}Si NMR spectra (delay time 90 s; 600 scans) show a single resonance in each case with the chemical shift values varying between −119.2 and −110.6 ppm. ^{14}N NMR spectra of these compounds exhibit resonances between −238.4 and −230.7 ppm, attributable to the nitrogen atom of the –NCS groups.[13] The important ^{13}C, ^{14}N, and ^{29}Si NMR data are summarized in Table 3.

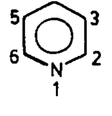
Interestingly, these results reveal significant shielding of the NCS carbon and the silicon atom and deshielding of the NCS nitrogen as compared to the precursor, diethoxydiisothiocyanatosilane. These NMR spectral changes and their implications in the chemical reactivity of these siliconates are yet to be clearly understood.

Experimental Section

All operations were carried out under dry nitrogen atmosphere. Solvents were freshly distilled under inert atmosphere from sodium (*n*-hexane), sodium benzophenone ketyl (tetrahydrofuran, diethyl ether), or phosphorus pentaoxide (acetonitrile) before use. Pyridine, 3-methylpyridine, 4-methylpyridine, or diethylamine (Aldrich) were refluxed over KOH pellets and distilled under dry nitrogen atmosphere prior to use. Potassium/sodium/ammonium thiocyanate (Qualigens) were dried under vacuum for 2–3 days at 60 °C. Silicon tetrachloride (Fluka) was used as such. 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 a Bruker 300-MHz instrument, while ^{13}C, ^{29}Si, and ^{14}N NMR spectra were carried out on a Bruker AMX-400 spectrometer. Chemical shifts are quoted relative to internal TMS for ^1H, ^{13}C, and ^{29}Si nuclei and external CH_3NO_2 for the ^{14}N nucleus. FAB-mass spectra were obtained on a Micromass VG-7070E spectrometer in the positive and negative ion FAB mode in 3-nitrobenzyl alcohol (NBA) matrix. C, H, N analyses were carried out on Perkin-Elmer Model 2400 CHN elemental analyzer. S and Si were estimated by gravimetric methods.

The ^{13}C NMR assignments are tentative and are based on reported trends.[12] The numbering scheme for the aromatic systems is shown as follows:





---

(8) Lennon, P. J.; Mack, D. P.; Thompson, Q. E. *Organometallics* **1989**, *8*, 1120.

(9) Geary, W. J. *Coord. Chem. Rev.* **1971**, *7*, 81.

(10) Cerveau, G.; Chuit, C.; Corriu, R. J. P.; Reye, C.; Aubagnac, J. L. *Int. J. Mass Spectromet. Ion Process.* **1989**, *91*, 145.

(11) Pugmire, R. J.; Grant, D. M. *J. Am. Chem. Soc.* **1968**, *90*, 697.

(12) Holmes, R. R.; Day, R. O.; Chandrasekhar, V.; Holmes, J. M. *Inorg. Chem.* **1985**, *24*, 2009.

(13) Mason, J., Ed. *Multinuclear NMR*; Plenum Press: New York, London, 1987; p 335.

Preparations. Diethoxydiisothiocyanatosilane. The compound was prepared as previously described[14] by reacting diethoxydichlorosilane (20.79 g, 0.11 mol) with potassium thiocyanate (24.25 g, 0.25 mol) in dry acetonitrile (100 mL). Bp: 56–57 °C/10^{-1} Torr. IR (Nujol, cm^{-1}): 2080 (ν_{as}(NCS)), 1140 (ν(CO)), 1080 (ν_{as}(Si–O)), 1010 (ν_s(NCS)), 760 (δ_{as}(NCS)). ^1H NMR ($CDCl_3$): δ 3.8 (q, 2H, OCH_2), 1.1 (t, 3H, CH_3). ^{13}C NMR (proton decoupled, $CDCl_3$): δ 58.2 (OCH_2), 10.4 (CH_3), 143.0 (NCS). ^{29}Si NMR ($CDCl_3$): δ −104.0.

$[Si(NCS)_2\cdot 3py]^{2+}[NCS]^-_2$ (8). Pyridine (1.58 g, 1.6 mL, 20.0 mmol) was added dropwise to a stirred solution of diethoxydiisothiocyanatosilane (4.72 g, 20.2 mmol) in dry THF (20 mL). The clear solution was stirred at 25 °C for 5–6 h. Thereafter, the solvent was stripped off under vacuum and *n*-hexane (50 mL) was added to it. A white solid was obtained which was filtered out, washed with *n*-hexane, and dried under vacuum. Yield: 2.25 g (45%). Mp: 125 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 302.8. Anal. Calcd for $C_{19}H_{15}N_7S_4Si$: C, 45.87; H, 3.02; N, 19.72; S, 25.75; Si, 5.63. Found: C, 45.52; H, 3.14; N, 19.62; S, 25.29; Si, 5.31. IR (Nujol, cm^{-1}): 2075 (ν_{as}(NCS)), 765 (δ(NCS)). ^1H NMR (CD_3CN): δ 9.1, 8.7, 8.2 (2H, 1H, 2H, py ring). ^{13}C NMR (CD_3CN): δ 140.3 (py-C_2/C_6), 127.0 (py-C_3/C_5), 133.2 (py-C_4), 143.2 (NCS). ^{29}Si NMR (CD_3CN): δ −234.1.

$[EtOSi(NCS)_2\cdot 2(3\text{-mepy})]^+[NCS]^-$ (9). Diethoxydiisothiocyanatosilane (4.72 g, 20.2 mmol) and 3-methylpyridine (1.86 g, 1.9 mL, 20.0 mmol) were used for the reaction. The experimental details were the same as for compound **8**. **9** was obtained as a white solid. Yield: 2.09 g (48%). Mp: >125 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 202.8. Anal. Calcd for $C_{17}H_{19}N_5OS_3Si$: C, 47.11; H, 4.38; N, 16.16; S, 22.17; Si, 6.46. Found: C, 46.24; H, 4.20; N, 16.21; S, 21.86; Si, 6.15. IR (Nujol, cm^{-1}): 2075 (ν_{as}(NCS)), 760 (δ(NCS)). ^1H NMR (CD_3CN): δ 8.8, 8.2, 7.9 (4H, 2H, 2H, mepy-ring), 4.1 (2H, OCH_2), 2.7 (6H, mepy-CH_3), 1.0 (3H, CH_3). ^{13}C NMR (CD_3CN); δ 138.9 (C_2), 136.7 (C_3), 132.2 (C_4), 125.3 (C_5), 136.0 (C_6) 142.7 (NCS), 18.3 (mepy-CH_3), 58.2 (OCH_2), 10.3 (CH_3). ^{29}Si NMR (CD_3CN): δ −236.4.

$[EtOSi(NCS)_2\cdot 2(4\text{-mepy})]^+[NCS]^-$ (10). The title compound was prepared from the reaction of diethoxydiisothiocyanatosilane (4.72 g, 20.2 mmol) and 4-methylpyridine (1.86 g, 1.9 mL, 20.0 mmol) in dry THF (20 mL) by following a procedure similar to that described for **8**. **10** was obtained as a white solid. Yield: 2.00 g (46%). Mp: >125 °C dec. Λ_M (Ω^{-1} cm^2, mol^{-1}, CH_3CN): 204.2. Anal. Calcd for $C_{17}H_{19}N_5OS_3Si$: C, 47.11; H, 4.38; N, 16.16; S, 22.17; Si, 6.46. Found: C, 46.80; H, 4.42; N, 16.07; S, 21.52; Si, 6.18. IR (Nujol, cm^{-1}): 2075 (ν_{as}(NCS)), 760 (δ(NCS)). ^1H NMR (CD_3CN): δ 8.8, 8.0 (4H, 4H, mepy ring), 4.0 (2H, OCH_2), 2.7 (6H, mepy-CH_3), 1.0 (3H, CH_3). ^{13}C NMR (CD_3CN): δ 140.6 (C_2/C_6), 127.1 (C_3/C_5), 139.0 (C_4), 142.3 (NCS), 21.6 (mepy-CH_3), 58.4 (OCH_2), 10.4 (CH_3). ^{29}Si NMR (CD_3CN): δ −238.0.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[pyH]^+_2$ (1). To a solution of the complex **8** (0.60 g, 1.2 mmol) in THF (20 mL) was added benzene-1,2-diol (0.24 g, 2.2 mmol) dissolved in the same amount of the solvent. The contents were stirred for 1 h at 25 °C when a dirty white solid started precipitating. Stirring was continued for another 2 h. The solid thus obtained was filtered out, washed with the solvent, and dried under vacuum. Yield: 0.45 g (72%). Mp: >170 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 279.9. Anal. Calcd for $C_{24}H_{20}N_4O_4S_2Si$: C, 55.38; H, 3.84; N, 10.77; S, 12.30; Si, 5.38. Found: C, 55.13; H, 3.80; N, 10.84; S, 11.95; Si, 5.21. IR (Nujol, cm^{-1}): 2070 (ν_{as}(NCS)). ^1H NMR (CD_3CN): δ 10.0 (2H, pyH^+), 9.0, 8.7, 8.2 (4H, 2H, 4H, py-ring), 6.8 (8H, $C_6H_4O_2$). ^{13}C NMR (CD_3CN): δ 139.3 (py-C_2/C_6), 127.1 (py-C_3/C_5), 144.7 (py-C_4). For ^{14}N and ^{29}Si NMR data, see Table 3.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[3\text{-mepyH}]^+_2$ (2). Following the procedure previously employed for **1**, the compound **9** (0.52 g, 1.2 mmol) in dry THF (20 mL) was treated with benzene-1,2-diol (0.24 g, 2.2 mmol) also dissolved in THF (20 mL). On stirring of the reaction mixture at 25 °C for about 1 h, a dirty white solid was formed. The contents, after being stirred for another 3 h, were filtered out, washed with the solvent, and dried under vacuum. Yield: 0.47 g (75%). Mp: >170 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 257.5. Anal. Calcd for $C_{26}H_{24}N_4O_4S_2Si$: C, 56.93; H, 4.38; N, 10.22; S, 11.68; Si, 5.11. Found: C, 56.17; H, 4.22; N, 10.20; S, 11.51; Si, 4.72. IR (Nujol, cm^{-1}): 2070 (ν_{as}(NCS)). ^1H NMR (CD_3CN): δ 9.8 (2H, mepy-H^+), 8.7, 8.4, 8.0 (4H, 2H, 2H, mepy-ring), 6.8 (8H, $C_6H_4O_2$), 2.6 (6H, mepy-CH_3). ^{13}C NMR (CD_3CN): δ 138.8 (C_2), 136.9 (C_3), 141.2 (C_4), 124.9 (C_5), 136.2 (C_6), 18.7 (mepy-CH_3). The ^{14}N and ^{29}Si NMR data are given in Table 3.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[4\text{-mepy H}]^+_2$ (3). The title compound was prepared in a manner similar to that for **1** by the reaction of **10** (0.52 g, 1.2 mmol) with benzene-1,2-diol (0.24 g, 2.2 mmol). **3** was obtained as a dirty white solid. Yield: 0.44 g (70%). Mp: >170 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 290.1. Anal. Calcd for $C_{26}H_{24}N_4O_4S_2Si$: C, 56.93; H, 4.38; N, 10.22; S, 11.68; Si, 5.11. Found: C, 56.28; H, 4.20; N, 10.14; S, 11.25; Si, 5.02. IR (Nujol, cm^{-1}): 2070 (ν_{as}(NCS)). ^1H NMR (CD_3CN): δ 9.8 (2H, mepy-H^+), 8.8, 8.0 (4H, 4H, mepy ring), 6.8 (8H, $C_6H_4O_2$). ^{13}C NMR (CD_3CN): δ 139.0 (mepy-C_2/C_6) 126.2 (mepy-C_3/C_5), 159.9 (mepy-C_4), 21.0 (mepy-CH_3). For ^{14}N and ^{29}Si NMR data, see Table 3.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}K^+_2$ (4). Diethoxydiisothiocyanatosilane (2.08 g, 8.9 mmol) was added dropwise to a stirred solution of potassium thiocyanate (0.86 g, 8.9 mmol) in dry acetonitrile (20 mL). The reaction mixture was stirred at 25 °C for 2 h. Benzene-1,2-diol (1.96 g, 17.8 mmol) in acetonitrile (20 mL) was cannula transferred into the clear reaction mixture. Stirring was continued for another 3 h. Thereafter, the solvent was evaporated under vacuum, and diethyl ether (40 mL) was added into it. A white solid was precipitated out, which was filtered out, washed with *n*-hexane, and dried under vacuum. Yield: 1.85 g (47%). Mp: >185 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 232.7. Anal. Calcd for $C_{14}H_8N_2O_4S_2SiK_2$: C, 38.35; H, 1.82; N, 6.39; S, 14.61; Si, 6.39. Found: C. 37.88; H, 1.94; N, 6.47; S, 14.40; Si, 6.00. IR (Nujol, cm^{-1}): 2070 (ν_{as}(NCS)). ^1H NMR (CD_3CN): δ 6.8 ($C_6H_4O_2$). ^{13}C NMR (CD_3CN): δ 113.6 (C_1/C_4), 143.7 (C_2/C_3), 117.5 (C_5/C_6), 129.6 (NCS). For ^{14}N and ^{29}Si NMR data, see Table 3.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}Na^+_2$ (5). This compound was prepared by a procedure analogous to that described for **4**, using diethoxydiisothiocyanatosilane (2.08 g, 8.9 mmol), sodium thiocyanate (0.72 g, 8.9 mmol), and benzene-1,2-diol (1.96 g, 17.8 mmol) as reactants. **5** was obtained as a dirty white solid. Yield: 1.53 g (42%). Mp: >185 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 238.7. Anal. Calcd for $C_{14}H_8N_2O_4S_2SiNa_2$: C, 41.38; H, 1.97; N, 6.89; S, 15.76; Si, 6.89. Found: C, 40.81; H, 1.90; N, 6.72; S, 15.61; Si, 6.46. IR (Nujol, cm^{-1}): 2075 (ν_{as}(NCS)). ^1H NMR (CD_3CN): δ 6.7 ($C_6H_4O_2$). ^{13}C NMR (CD_3CN): δ 113.4 (C_1/C_4), 143.7 (C_2/C_3), 117.2 (C_5/C_6), 129.7 (NCS). ^{14}N and ^{29}Si NMR data are given in Table 3.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[NH_4]^+_2$ (6). Diethoxydiisothiocyanatosilane (2.08 g, 8.9 mmol), ammonium thiocyanate (0.67 g, 8.9 mmol), and benzene-1,2-diol (1.96 g, 17.8 mmol) were used for the reaction. The experimental details were the same as for compound **4**. **6** was obtained as a dirty white solid. Yield: 1.60 g (45%). Mp >130 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 240.5. Anal. Calcd for $C_{14}H_{16}N_4O_4S_2Si$: C, 42.42; H, 4.04; N, 14.14; S, 16.16; Si, 7.07. Found: C, 41.80; H, 4.27; N, 13.87; S, 15.91; Si, 6.81. IR (Nujol, cm^{-1}): 2080 (ν_{as}(NCS)), 2640 (NH_4^+). ^1H NMR (CD_3CN): δ 6.8 ($C_6H_4O_2$). ^{13}C NMR (CD_3CN): δ 114.8 (C_1/C_4), 145.0 (C_2/C_3), 111.8 (C_5/C_6), 130.0 (NCS). For ^{14}N and ^{29}Si NMR data, see Table 3.

$[(C_6H_4O_2)_2Si(NCS)_2]^{2-}[Et_2NH_2]^+_2$ (7). To a stirred solution of compound **6** (0.71 g, 1.8 mmol) in acetonitrile (20 mL) was added diethylamine (0.26 g, 0.40 mL, 3.6 mmol) at 25 °C. After 4 h, the solvent was evaporated under vacuum and diethyl ether (40 mL) was added to precipitate a white solid. It was filtered out, washed with diethyl ether, and dried under vacuum. Yield: 0.73 g (80%). Mp: >180 °C dec. Λ_M (Ω^{-1} cm^2 mol^{-1}, CH_3CN): 296.6. Anal. Calcd for $C_{22}H_{32}N_4O_4S_2Si$: C, 51.97; H, 6.30; N, 11.02; S, 12.59; Si, 5.51. Found: C, 51.72; H, 6.28; N, 11.09; S, 12.41; Si, 5.22. IR (Nujol, cm^{-1}): 2020 (ν_{as}(NCS)). ^1H NMR (CD_3CN): δ 6.8 (8H, $C_6H_4O_2$), 3.8 (8H, NCH_2), 1.0 (12H, CH_3). ^{13}C NMR (CD_3CN): δ 115.0 (C_1/C_4), 150.9 (C_2/C_3), 118.5 (C_5/C_6), 130.2 (NCS), 41.2 (NCH_2), 9.9 (CH_3). ^{14}N and ^{29}Si NMR data are given in Table 3.

Acknowledgment. R.S. is grateful to UGC (India) for the award of Research Scientist "B"; M.K. and Meenu thank CAS in the department and Department of Atomic Energy (India), respectively, for financial assistance in the form of Junior Research Fellowships. The authors are grateful for use of the NMR National Facilities at TIFR, Bombay, and IISc, Bangalore, for the NMR spectra and are grateful to Dr. K. C. Molloy, Chemistry Department, University of Bath (Bath, U.K.), for FAB-mass spectra.

Supplementary Material Available: Figures showing mass and NMR spectra (4 pages). Ordering information is given on any current masthead page.

---

(14) Anderson, H. H. *J. Am. Chem. Soc.* **1950**, *72*, 193.