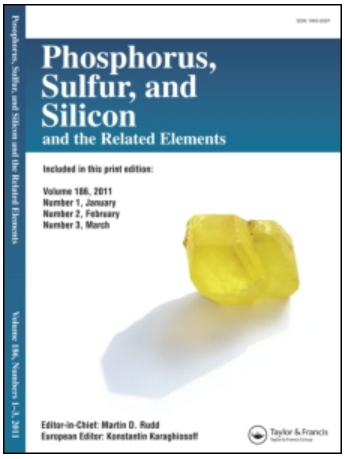


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# PREPARATION AND CHARACTERIZATION OF ALKALINE EARTH METAL SALTS OF BIS(BENZENE-1,2-DIOLATO)DIISOTHIOCYANATOSILICATE

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# PREPARATION AND CHARACTERIZATION OF ALKALINE EARTH METAL SALTS OF BIS(BENZENE-1,2-DIOLATO) DIISOTHIOCYANATOSILICATE

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Alkaline earth metal salts of hexacoordinate dianionic silicates $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}$ $M^{2+}$ [where M = Ca (**1**), Sr (**2**), Ba (**3**)] are prepared from the reaction of alkaline earth metal thiocyanates suspended in $CH_3CN$, diethoxy diisothiocyanatosilane and benzene-1,2-diol under very mild conditions. The compounds are charcterised by elemental analyses, IR, multinuclear ($^1H$, $^{13}C$, $^{29}Si$) NMR and FAB mass spectroscopy.

*Keywords:* Silicates; dianionic; hexaco-ordinate; thiocyanate; bis(benzene-1,2-diolato)diisothiocyanato

## INTRODUCTION

Pentacoordinate anionic silicates have been extensively studied[1–3] and their use in synthesis[2] and industry[4] has been highlighted. Hexacoordinate anionic silicates on the other hand, have received only scant attention. After the initial work of Rosenheim[5] and Frye[6], Corriu et al.[7] have synthesized alkali metal salts of tris (benzene-1,2 diolato)silicate and studied their reactivity towards various nucleophilic reagents. We have reported[8] the synthesis of the first hexacoordinate spirobicyclic silicate dianion $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}M^{2+}$ [M=Na,K, $NH_4$] by activating the tetracoor-

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dinate silicon center by $NCS^-$ anion. This method has an advantage over the conventional methods as the Si-NCS linkage is retained in the silicate framework. However, the isolation of alkaline earth metal salts of analogous silicon (IV) compounds remain practically unexplored as there is only one report of barium salts of tris (ethane- 1,2,-diolato) silicate.[9] Here, it is observed that the reactions of alkaline earth metal thiocyanates suspended in acetonitrile with usual reaction precursors result in the formation of title compounds **1–3**. The details of preparation and characterisation of these compounds are reported in this paper.

## RESULTS AND DISCUSSION



The compounds **1–3** have been prepared from the reaction of diethoxydiisothiocyanatosilane with benzene-1,2-diol in the presence of calcium/strontium/barium thiocyanates as given below.

$$(EtO)_2Si(NCS)_2 + M(NCS)_2 + 2C_6H_4(OH)_2 \xrightarrow[RT,5h]{CH_3CN} [(C_6H_4O_2)_2Si(NCS)_2]^{2-}M^{2+}$$

M= Ca(1), Sr(2), Ba(3)

These compounds are hygroscopic, white solids and soluble only in methanol and DMSO. Elemental analyses (Experimental section) of these compounds conform to the composition as assigned. Infrared spectra (in nujol) of these compounds reveal a $\nu_{as}$ NCS absorption at 2110–2100 $cm^{-1}$ which is 20–30 $cm^{-1}$ higher than that of the precursor diethoxydiisothiocyanatosilane (2080 $cm^{-1}$). In alkaline earth metal thiocyanates, these modes absorb in the region 2060–2030 $cm^{-1}$. Thus the $\nu_{as}$ NCS absorption mode in **1–3** may indicate the formation of Si-NCS linkage in these compounds. The bands observed at 1610–1600,1500–1495 and 1350–1345 $cm^{-1}$ are attributed to C=C ring vibrations while those at 3080–3075,1250,1035–1020,835–820,775–770, and 450–440 $cm^{-1}$ are ascribed to νCH (aromatic), νCO,$\nu_s$ NCS, νSiO,νCS and δNCS modes respectively.

Due to poor solubility of these compounds in most of the solvents, X-ray quality crystals could not be obtained. In the absence of X-ray crystallography, the solid state anion and cation composition can be estimated

through high resolution mass spectroscopy. FAB mass spectral studies have proved to be powerful tool for the identification of hexacoordinate silicate anions in the past.[8,10,11] Although the FAB mass spectra of **1–3** are complex due to divalent cations yet the identification of the cations as well as the anions could be achieved in positive and negative ion modes of these spectra. In the positive ion mode, respective cations have been identified from m/z values corresponding to cluster ions $[(C_6H_4O_2)Si(NCS)_2]^{2-}$ $3H^+$(m/z 363), $[(C_6H_4O_2)_2SiNCS]^-$ $2H^+$ (m/z 304) and $[(C_6H_4O_2)Si(NCS)_2(OCH_2C_6H_4NO_2)]^-$ $M^{2+}$ NBA (m/z 597 for M=Ca, 644 for M=Sr and 694 for M=Ba) These data provide evidence for the formation of the dianionic silicates of alkaline earth elements.

In the negative ion mode of compound **3** i.e. $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}$ $Ba^{2+}$, the dianion has been identified from peaks at m/z 514,723 and 897 corresponding to cluster ions $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}H^+$NBA, $[(C_6H_4O_2)_2Si(NCS)_2]_2^{2-}3H^+$ and $[(C_6H_4O_2)_2Si(NCS)(OCH_2C_6H_4NO_2)]^{2-}$ $Ba^{2+}$ 2NBA repectively. In the spectra of 1 and 2 peaks at m/z 723 and 761 are assigned to clusters $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}{}_2$ $3H^+$ and $[(C_6H_4O_2)_2SiNCS]^-$ 3NBA respectively. Selected FAB mass spectral data are summarized in the table.

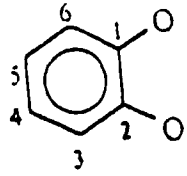
The solution state structure of a compound is generally studied through multinuclear NMR spectroscopy. $^1H$ NMR spectra of **1–3** in $CD_3OD$ reveal multiplet in the region 6.6–6.8 ppm due to $C_6H_4O_2$ groups. $^{13}C$ NMR spectra of **1–3** in $CD_3OD$ exhibit a single resonance due to NCS at 130.7-133.5 ppm whereas signals due to benzene-1,2-diolate groups appear at 144.7–146.2, 119.0–121.2 and 115.0–116.0 ppm assigned to C1/C2, C4/C5 and C3/C6 ring carbons, respectively (Experimental section). $^{29}$SiNMR spectra of these compounds reveal a single resonance in each case at –78.9 to –79.0 ppm

A comparison of these data with those of other salts[8] of the same dianion reveal the $^1H$ and $^{13}C$ NMR spectra are analogous. However, $\delta^{29}Si$ NMR values vary considerably. For example, $\delta$ $^{29}$Si NMR values of alkali metal and pyridinium salts[8] are recorded in the range –110 to –120ppm while the spectra of the compounds **1–3** show them at ~-79 ppm. In the literature, the chemical shift data of spirocyclic anionic silicates have qualitatively been related to (i) electronegativity of the substituent(s) (ii) change in ring size of cyclic group (iii) coordination number of silicon atom etc.[12] Accordingly the observed values for **1–3** are low for hexacoordinate silicates. Though a comparative interpretation of $\delta^{29}Si$ NMR values is unwar-

ranted due to the lack of NMR data of the spirobicyclic hexacoordinate silicates of varying cations, yet the present compounds being weak electrolytes in solution may promote specific effects of the cations (due to nuclear charge and the size) on the structure of anions. Alternatively the dissociation of the compound in solution during recording of $^{29}Si$ NMR (60s delay, 900 scans) spectra is also not ruled out.[13]

## EXPERIMENTAL

All operations were carried out under a dry nitrogen atmosphere. Solvents were freshly distilled under an inert atmosphere from sodium benzophenone ketyl(diethylether) or phosphorus pentaoxide(acetonitrile) before use. Postassium thiocyanate was dried under vacuum at 60°C for 2–3 days. Silicon tetrachloride (Fluka) was used as received. Diethoxydiisothiocyanatosilane[14] and calcium/ strontium/ barium thiocyanate[15] were prepared by reported procedures. Infrared spectra were routinely obtained as Nujol mulls on a Perkin Elmer Model 1430 ratio recording spectrophotometer. $^{1}H$, $^{13}C$ and $^{29}Si$ NMR were obtained on Bruker 300 MHz instrument, operating at 300MHz, 75.47 MHz and 59.63 MHz for $^{1}H$, $^{13}C$ and $^{29}Si$ nuclei respectively. Chemical shifts are quoted relative to internal TMS. FAB mas spectra were obtained on a micromass VG-7070E spectrometer in 3 nitrobenzyl alcohol (NBA). C H N analyses were carried out on Perkin Elmer Model 2400 CHN elemental analyser. S and Si were estimated gravimeterically. The numbering scheme for benzene-1,2-diolate ring is given below.




### Preparation of $[(C_6H_4O_2)_2Si(NCS)]^{2-}$ $M^{2+}$ (1–3)

Diethoxydiisothiocyanatosilane (2.0mL, 8.5 mmol) was added to the suspension of calcium/strontium/barium thiocyanate (8.5 mmol) in ace-

tonitrile (10mL). A solution of benzene-1,2-diol (1.87g, 17.0 mmol) was added dropwise to the reaction mixture. The contents were stirred at room temprature for 5h. A white solid was obtained in each case which was filtered, washed with diethyl ether and dried under vacuum.

TABLE I Selected FAB mass spectral data * of calcium/strontium/barium bis (benzene-1,2-diolato) diisothiocyanatosilicate

| *Assignments* | $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}M^{2+}$ | | |
|---|---|---|---|
| | *M=Ca* | *M=Sr* | *M=Ba* |
| **Positive ion mode** | | | |
| $M^{2+}NCS^-$ | 98 | 145 | 195 |
| $M^{2+}NCS^-NBA$ | 251 | 298 | 348 |
| $M^{2+}(OCH_2C_6H_4NO_2)^-$ | 192 | 239 | 288 |
| $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}3H^+$ | 363 | 363 | 363 |
| $[(C_6H_4O_2)Si(NCS)_2(OCH_2C_6H_4NO_2)]^-M^{2+}NBA$ | 597 | 644 | 694 |
| $[(C_6H_4O_2)Si(NCS)_2(OC_6H_5)]^-M^{2+}$ | 385 | – | 482 |
| **Negative ion mode** | | | |
| $[(C_6H_4O_2)_2SiNCS]^-3NBA$ | – | 761 | – |
| $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}{}_2 3H^+$ | – | 723 | 723 |
| $[(C_6H_4O_2)_2Si(NCS)_2]^{2-}$ $H^+NBA$ | – | – | 514 |
| $[(C_6H_4O_2)Si(NCS)_2(OCH_2C_6H_4NO_2)]^-$ | 404 | 404 | – |
| $NCS^-NBA$ | 211 | 211 | 211 |
| $[C_6H_4O_2H]^-$ | 109 | 109 | 109 |
| $NCS^-$ | 58 | 58 | 58 |

*In 3-nitrobenzyl alcohol (NBA)

## $[(C_6H_4O_2)_2Si\ (NCS)_2]^{2-}Ca^{2+}$(1)

Yield : 2.39g (70%). Mp:>160° C dec. Anal. calcd. for $C_{14}H_8N_2O_4S_2SiCa$: C,42.00; H,2.00; N,7.00; S,16.00; Si,7.00. Found: C,41.85; H,1.91; N,6.88; S,15.91; Si,6.75. IR (Nujol, $cm^{-1}$) : 2100 ($\nu_{as}$ NCS). $^1H$ NMR ($CD_3OD$) : 6.7 (m,$C_6H_4O_2$). $^{13}C$ NMR ($CD_3OD$) : δ

131.5(NCS),145.2 (C1/C2,$C_6H_4O_2$), 119.5 (C4/C5,$C_6H_4O_2$), 115.1 (C3/C6,$C_6H_4O_2$), $^{29}$Si NMR ($CD_3$ OD):δ-78.9.

### $[(C_6H_4O_2)_2\ Si(NCS)_2]^{2-}\ Sr^{2+}$(2)

Yield : 2.60g (68%) Mp.>160°C dec. Anal. *calcd. for $C_{14}H_8N_2O_4S_2SiSr$: C,37.67;H,1.79;N,6.28;S,14.35. Found*C,37.50; H,1.90; N,6.13; S,14.10. IR(Nujol, $cm^{-1}$): 2105 ($\nu_{as}$ NCS). $^1$H NMR($CD_3OD$): δ 6.8 (m,$C_6H_4O_2$). $^{13}$C NMR($CD_3OD$):δ133.1 (NCS),145.1(C1/C2,$C_6H_4O_2$),119.3 (C4/C5,$C_6H_4O_2$), 116.0(C3/C6, $C_6H_4O_2$) $^{29}$ Si NMR ($CD_3OD$): δ −79.0.

### $[(C_6H_4O_2)_2\ Si(NCS)_2]^{2-}Ba^{2+}$(3)

Yield : 2.88g (68%). Mp.> 165°C dec. Anal.* calcd. for $C_{14}H_8N_2O_4S_2SiBa$:C,33.80;H,1.61;N,5.63;S,12.88; Ba 27.56. Found: C,33.65; H,1.81; N,5.72;S12.71; Ba 27.31.IR (Nujol,$cm^{-1}$);2110 ($\nu_{as}$-NCS). $^1$HNMR ($CD_3OD$); δ 6.8 (m,$C_6H_4O_2$).$^{13}$C NMR ($CD_3OD$); δ 132.8 (NCS), 146.2 (C1/C2,$C_6H_4O_2$),121.2 (C4/C5,$C_6H_4O_2$),116.6 (C3/C6,$C_6H_4O_2$). $^{29}$ Si NMR ($CD_3OD$): δ-79.0.



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* Si could not be estimated correctly for **2** and **3** due to interference from Sr and Ba respectively.

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