

Reactivity of 1-Isothiocyanato Six Membered Silatrane towards Lewis Acids

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ABSTRACT: This manuscript deal with the reaction of the 1-Isothiocyanato six membered silatrane with different Lewis acids. The adducts **1**, **2**, **3** and **4** so formed were characterized by elemental analysis, infrared spectroscopy, ^1H , ^{13}C , ^{29}Si NMR spectroscopy. $\eta^1\text{-S}$ and $\eta^1\text{-N}$ bonding pattern were observed the coordination modes of the isothiocyanato group.

KEYWORDS: Lewis acid, silatrane, isothiocyanato

I. INTRODUCTION

The coordination behaviour of organic isothiocyanato has been extensively studied in the past [1-4]. The isothiocyanato group exhibits a variety of coordination modes depending upon the nature of Lewis acid used in most of the known coordination compounds of this class [5]. The results have been amply rationalized on the basis of hard/soft acid-base character (in Pearson's sense) of nitrogen as well as sulphur site respectively amongst the wide variety of coordination modes of isothiocyanato group. The $\eta^1\text{-N}$, $\eta^1\text{-S}$ bonding pattern are found to be the most common in the absence of X-ray crystal data. IR spectroscopy has remained the most versatile tool to identify these coordination modes [6-9].

In contrast to the organic isothiocyanato, little is known about the coordination behavior of silyl isothiocyanates partially due to the fragile nature of Si-N bond in these compounds [6,10-11]. It is in this context that the reactivity of 1-Isothiocyanato six membered towards Lewis acids has been undertaken.

II. EXPERIMENTAL

All operations were carried out under dry nitrogen atmosphere. Solvents were freshly distilled under inert atmosphere from sodium (hexane), and phosphorus pentoxide (dichloromethane) before use. Hydrous iron(III) chloride, nickel(II) chloride, cobalt(II) chloride, copper(II) chloride were converted to their anhydrous form using thionyl chloride. 1-Isothiocyanato six membered ring silatrane was synthesized according to procedure reported in literature [6]. IR spectra were obtained as thin films or nujol mulls on Perkin-Elmer RX-1 FTIR spectrophotometer. ^1H (300.4 MHz), ^{13}C (75.45 MHz), ^{29}Si NMR (59.60 MHz) spectra were obtained on JEOL AL 300 instrument. Chemical shifts were reported with respect to TMS as an external standard.

III. SYNTHESIS

Reaction of of 1-Isothiocyanato six membered silatrane and iron(III) chloride (1)

1-Isothiocyanato six-membered ring silatrane (1.00 g, 1.99 mmol) was dissolved in dry dichloromethane in a two-necked round-bottomed flask. The solution was stirred with the help of magnetic stirrer. Iron(III) chloride (0.32 g, 1.99 mmol) was added to the solution of 1-Isothiocyanato six-membered ring silatrane. A dark brownish black solid was precipitated out. The reaction mixture was stirred at room temperature for 4 h. The solid thus obtained was filtered washed with n-hexane and dried under reduced pressure.

Reaction of of 1-Isothiocyanato six membered silatrane and cobalt(II) chloride (2)

1-Isothiocyanato six-membered ring silatrane (1.00 g, 1.99 mmol) was dissolved in dry dichloromethane in a two-necked round-bottomed flask. The solution was stirred with the help of magnetic stirrer. Cobalt(II) chloride (0.25 g,

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1.99 mmol) was added to the solution of 1-Isothiocyanato six-membered ring silatrane. A white solid immediately precipitated out. The reaction mixture was stirred at room temperature for 4 h. The solid, thus obtained was filtered washed with n-hexane and dried under reduced pressure.

Reaction of of 1-Isothiocyanato six membered silatrane and nickel(II) chloride (3)

1-Isothiocyanato six-membered ring silatrane (1.00 g, 1.99 mmol) was dissolved in dry dichloromethane in a two-necked round-bottomed flask. The solution was stirred with the help of magnetic stirrer. Nickel(II) chloride (0.25 g, 1.99 mmol) was added to the solution of 1-Isothiocyanato six-membered ring silatrane. A yellowish white solid immediately precipitated out. The reaction mixture was stirred at room temperature for 4 h. The solid thus obtained, was filtered washed with n-hexane and dried under reduced pressure.

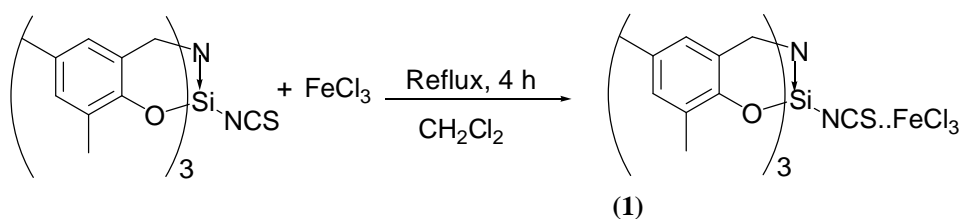
Reaction of of 1-Isothiocyanato six membered silatrane and copper(II) chloride (4)

1-Isothiocyanato six-membered ring silatrane (1.00 g, 1.99 mmol) was dissolved in dry dichloromethane in a two-necked round-bottomed flask. The solution was stirred with the help of magnetic stirrer. Copper(II) chloride (0.26 g, 1.99 mmol) was added to the solution of 1-Isothiocyanato six-membered ring silatrane. A brownish black solid immediately precipitated out. The reaction mixture was stirred at room temperature for 4 h. The solid thus obtained was filtered washed with n-hexane and dried under reduced pressure.

IV. RESULTS AND DISCUSSION

a) Reaction of 1-Isothiocyanatosilatrane possessing six membered ring with iron(III) chloride

The reaction of equimolar quantities of 1-Isothiocyanato six membered silatrane and iron(III) chloride in dichloromethane medium at room temperature (25 °C) results in the formation of a dark brown solid. Elemental analysis of this product corresponds to the composition $\text{FeCl}_3 \cdot \text{NCSSi}[(\text{OC}_6\text{H}_2\text{Me}_2)\text{CH}_2]_3\text{N}$. The isolated compound is hygroscopic in nature and insoluble in the most of the solvents except dimethyl sulfoxide. The reaction may be represented as follows (Scheme 1):



Scheme 1. Adduct formation of 1-Isothiocyanatosilatrane possessing six membered ring with iron(III) chloride.

IR Spectra: The infrared spectrum of the compound **1** in nujol mull reveals that $\nu_{\text{as}}\text{NCS}$ mode absorbs at 1996 cm^{-1} . Other characteristic absorptions due to $\nu_{\text{as}}\text{Si-O(C)}$ and νCS appear at 1036 and 801 cm^{-1} respectively and remain practically unchanged as compared to those observed in the parent silatrane. Absorptions at 2917 , 1387 , 480 cm^{-1} are ascribed to $\nu\text{Ar-H}$, νCH_2 , νNCS modes respectively. Peaks at 1611 , 1491 , 1444 cm^{-1} are attributed to $\nu\text{C=C}$ and those at 970 , 903 , 620 cm^{-1} are assigned to the skeletal mode of atrane cage in which the transannular $\text{Si}\leftarrow\text{N}$ bond is reported to contribute significantly to overall vibrations.

NMR Spectra: Though, DMSO-d_6 is suspected to dissociate the complex, it has been used as a solvent to study the multinuclei ^1H , ^{13}C and ^{29}Si NMR spectra, since the adduct is insoluble in most of the other solvents.

^1H NMR spectrum of the adduct **1** in DMSO-d_6 reveals two singlets of equal intensity at 2.18 and 2.24 ppm due to aromatic methyl protons and singlet at 4.22 ppm due to NCH_2 , two singlets of equal intensity at 6.85 and 6.89 ppm due to aromatic protons.

^{13}C NMR spectrum of the adduct **1** in DMSO-d_6 reveals two singlets at 15.97 and 19.79 ppm due to aromatic methyl carbons, singlet at 55.12 ppm due to NCH_2 . The carbon atom of the isothiocyanato group appears as a triplet at 127.13,

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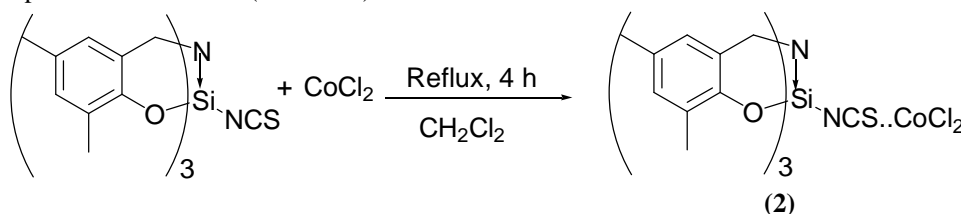
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127.32 & 127.48 ppm due to ^{13}C - ^{14}N coupling [1J (^{13}C - ^{14}N)=13.20Hz)] and singlets at 117.1, 125.18, 129.11, 131.10 and 150.96 ppm due to aromatic carbons.

Similarly, the ^{29}Si NMR spectrum of the complex reveals a triplet of equal intensity at -145.13, -145.72 and -146.25 ppm with a coupling constant [1J (^{29}Si - ^{14}N) = 33.04 Hz]. Apparently, the chemical shifts are identical to those of pure silatrane. Thus, on the basis of identical NMR chemical shift with respect to parent silatrane, it may be concluded that the adduct dissociates in DMSO- d_6 . NMR studies are quite informative since these provide irrevocable evidences in favour of retention of Si-NCS bond even in the presence of strong Lewis acid (FeCl_3).

b) Reaction of 1-Isothiocyanatosilatrane possessing six membered ring with cobalt(II) chloride

The reaction of equimolar quantities of 1-Isothiocyanato six membered silatrane and cobalt(II) chloride in dichloromethane medium at room temperature (25 °C) results in the formation of a white solid. Elemental analysis of this product corresponds to the composition $\text{CoCl}_2 \cdot \text{NCSSi}[(\text{OC}_6\text{H}_2\text{Me}_2)\text{CH}_2]_3\text{N}$. The compound isolated above is hygroscopic in nature and insoluble in the most of the solvents but soluble in dimethyl sulfoxide. The reaction may be represented as follows (Scheme 2):



Scheme 2. Reaction of 1-Isothiocyanatosilatrane possessing six membered ring with cobalt(III) chloride.

IR Spectra: The infrared spectrum of the compound **2** in nujol mull reveals that $\nu_{\text{as}}\text{NCS}$ mode absorbs at 2074 cm^{-1} . Other characteristic absorptions due to $\nu_{\text{as}}\text{Si-O(C)}$ and νCS appear at 1100 and 802 cm^{-1} respectively and remain practically unchanged as compared to those observed in the parent silatrane. Absorptions at 3100 , 1386 , 475 cm^{-1} are ascribed to $\nu\text{Ar-H}$, νCH_2 , νNCS modes respectively. Peaks at 1625 , 1491 , 1445 cm^{-1} are attributed to $\nu\text{C=C}$ and those at 971 , 911 , 680 cm^{-1} are assigned to the skeletal mode of atrane cage in which the transannular $\text{Si}\leftarrow\text{N}$ bond is reported to contribute significantly to overall vibrations.

NMR Spectra: The poor solubility of the adduct in non-coordinating solvents has precluded detailed NMR studies of the adduct. However, the multinuclei (^1H , ^{13}C and ^{29}Si) NMR spectra in DMSO- d_6 solvent have been recorded in order to gather evidences in support of retention of silatrane moiety in the adduct. The results are described below.

^1H NMR spectrum of the adduct **2** in DMSO- d_6 reveals two singlets of equal intensity at 2.21 and 2.23 ppm due to aromatic methyl protons and singlet 4.25 ppm due to NCH_2 , two singlets of equal intensity at 6.89 and 6.92 ppm due to aromatic protons.

^{13}C NMR spectrum of the adduct **2** in DMSO- d_6 reveals two singlets at 16.11 and 19.82 ppm due to aromatic methyl carbons, singlet at 55.10 ppm due to NCH_2 . The carbon atom of the isothiocyanato group appears as a triplet at 128.53, 128.72 & 128.87 ppm due to ^{13}C - ^{14}N coupling [1J (^{13}C - ^{14}N)=12.82Hz)] and singlets at 116.41, 124.28, 129.02, 129.44 and 150.96 ppm due to aromatic carbons.

Similarly, the ^{29}Si NMR spectrum of the complex reveals a triplet of equal intensity at -149.28, -149.86 and -150.41 ppm with the coupling constant [1J (^{29}Si - ^{14}N)=33.33 Hz)]. Apparently, the chemical shifts are identical to those of pure silatrane.

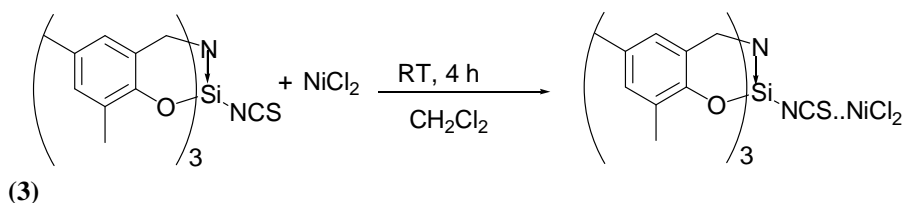
c) Reaction of 1-Isothiocyanatosilatrane possessing six membered ring with nickel(II) chloride

The reaction of equimolar quantities of 1-Isothiocyanato six membered silatrane and nickel(II) chloride in dichloromethane medium at room temperature (25 °C) results in the formation of a yellowish white solid. Elemental analysis of this product corresponds to the composition $\text{NiCl}_2 \cdot \text{SCNSi}[(\text{OC}_6\text{H}_2\text{Me}_2)\text{CH}_2]_3\text{N}$. The compound isolated above is hygroscopic in nature and is insoluble in most of the solvents except dimethyl sulfoxide. The reaction may be represented as follows (Scheme 3):

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Scheme 3. Reaction of 1-Isothiocyantosilatrane possessing six membered ring with nickel(III) chloride.

IR Spectra: The infrared spectrum of the compound **3** in nujol mull reveals that $\nu_{as}NCS$ mode absorbs at 2031cm^{-1} . Other characteristic absorptions due to $\nu_{as}Si-O(C)$ and νCS appear at 1040 cm^{-1} , 814 cm^{-1} respectively and remain practically unchanged as compared to those observed in the parent silatrane. Absorptions at 3120 , 1384 , 485 cm^{-1} are ascribed to $\nu Ar-H$, νCH_2 , νNCS modes respectively. Peaks at 1631 , 1492 , 1449 cm^{-1} are attributed to $\nu C=C$ and those at 969 , 924 and 660 cm^{-1} are assigned to the skeletal mode of atrane cage in which the transannular $Si\leftarrow N$ bond is reported to contribute significantly to overall vibrations.

NMR Spectra: Though, $DMSO-d_6$ is suspected to dissociate the complex, it has been used as a solvent to study the multinuclei 1H , ^{13}C and ^{29}Si NMR spectra, since the adduct is insoluble in most of the other solvents.

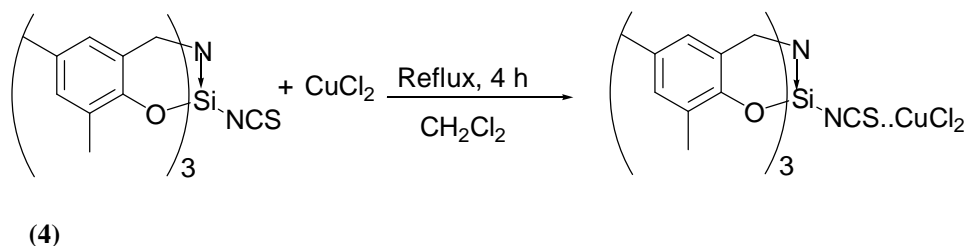
1H NMR spectrum of the adduct **3** in $DMSO-d_6$ reveals two singlets of equal intensity at 2.19 and 2.20 ppm due to aromatic methyl protons and a singlet at 4.25 ppm due to NCH_2 , two singlets of equal intensity at 6.89 and 6.91 ppm due to aromatic protons respectively.

^{13}C NMR spectrum of the adduct in $DMSO-d_6$ reveals two singlets at 16.10 and 19.11 ppm due to aromatic methyl carbons, singlet at 54.99 ppm due to NCH_2 . The carbon atom of the isothiocyanato group appears as a triplet at 127.69, 127.89 & 128.04 ppm due to $^{13}C-^{14}N$ coupling [$^1J (^{13}C-^{14}N)=13.20\text{Hz}$] and singlets at 116.47, 124.38, 129.23, 129.51 and 150.96 ppm due to aromatic carbons.

Similarly, the ^{29}Si NMR spectrum of the complex reveals a triplet of equal intensity at -151.24 , -151.76 and -152.36 ppm with the coupling constant [$^1J (^{29}Si-^{14}N)=33.04\text{ Hz}$]. Apparently, the chemical shifts are identical to those of pure silatrane.

d) Reaction of 1-Isothiocyantosilatrane possessing six membered ring with copper(II) chloride

The reaction of equimolar quantities of 1-Isothiocyanto six membered silatrane and copper(II) chloride in dichloromethane medium at room temperature ($25\text{ }^\circ\text{C}$) results in the formation of brown black solid. The compound isolated above is hygroscopic in nature and insoluble in the most of the solvents except dimethyl sulfoxide. Elemental analysis of this product corresponds to the composition $CuCl_2 \cdot SCNSi[(OC_6H_2Me_2)CH_2]_3N$. The reaction may be represented as follows (Scheme 4):



Scheme 4. Reaction of 1-Isothiocyantosilatrane possessing six membered ring with copper(III) chloride.

IR Spectra: The infrared spectrum of the compound **4** in nujol mull reveals that $\nu_{as}NCS$ mode absorbs at 2141cm^{-1} . Other characteristic absorption is due to $\nu_{as}Si-O(C)$ and νCS appear at 1096 cm^{-1} , 805 cm^{-1} respectively and remain practically unchanged as compared to those observed in the parent silatrane. Absorptions at 3122 , 1403 , 468 cm^{-1} are

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ascribed to $\nu_{\text{Ar-H}}$, ν_{CH_2} , ν_{NCS} modes respectively. Peaks at 1611, 1492, 1447 cm^{-1} are attributed to $\nu_{\text{C}=\text{C}}$ and those at 963, 931, 679 cm^{-1} are assigned to the skeletal mode of atrane cage in which the transannular Si \leftarrow N bond is reported to contribute significantly to overall vibrations.

NMR Spectra: The poor solubility of the adduct **4** in non-coordinating solvents has precluded detailed NMR studies of the adduct. However, the multinuclei (^1H , ^{13}C and ^{29}Si) NMR spectra in DMSO- d_6 solvent have been recorded in order to gather evidences in support of retention of silatrane moiety in the adduct. The results are described below.

^1H NMR spectrum of the adduct **4** in DMSO- d_6 reveals two singlets of equal intensity at 2.19 and 2.22 ppm due to aromatic methyl protons and a singlet 4.24 ppm due to NCH_2 , two singlets of equal intensity at 6.91 and 6.93 ppm due to aromatic protons respectively.

^{13}C NMR spectrum of the adduct in DMSO- d_6 reveals two singlets at 16.10 and 19.87 ppm due to aromatic methyl carbons, singlet at 55.11 ppm due to NCH_2 . The carbon atom of the isothiocyanato group appears as a triplet at 128.31, 128.52 & 128.67 ppm due to ^{13}C - ^{14}N coupling [1J (^{13}C - ^{14}N)=13.50 Hz)] and singlets at 116.07, 124.33, 129.01, 129.04 and 150.96 ppm appear due to aromatic carbons.

Similarly, the ^{29}Si NMR spectrum of the complex reveals a triplet of equal intensity at -149.31, -149.86 and -150.44 ppm with the coupling constant [1J (^{29}Si - ^{14}N)=33.33 Hz)]. Apparently, the chemical shifts are identical to those of pure silatrane.

Table 1 summarizes the results obtained from the present study along with the possible mode of coordination of the title silatrane with Lewis acids.

Table 1. Possible site of coordination of 1-Isothiocyanato silatrane with various Lewis acids.

Lewis acid	Composition of adduct	Coordination site
FeCl_3	Sil. FeCl_3	$\eta^1\text{-N}$
CoCl_2	Sil. CoCl_2	$\eta^1\text{-N}$
NiCl_2	Sil. NiCl_2	$\eta^1\text{-N}$
CuCl_2	Sil. CuCl_2	$\eta^1\text{-S}$

V. CONCLUSIONS

The reactivity of 1-Isothiocyanato six membered towards Lewis acids (iron(III) chloride, nickel(II) chloride, cobalt(II) chloride, copper(II) chloride) has been studied successfully. The spectroscopic data has helped to establish possible site of coordination of 1-Isothiocyanato silatrane with various Lewis acids

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