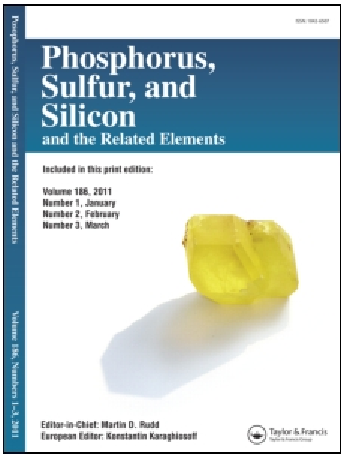

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SYNTHESIS, CHARACTERIZATION AND STRUCTURAL ELUCIDATION OF TRIORGANOSILICON (IV) COMPLEXES OF 2-AMINOCYCLOPENTENE-1-CARBODITHIOIC ACID AND ITS N-/S-ALKYL DERIVATIVES

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SYNTHESIS, CHARACTERIZATION AND STRUCTURAL ELUCIDATION OF TRIORGANOSILICON (IV) COMPLEXES OF 2-AMINOCYCLOPENTENE-1-CARBODITHIOIC ACID AND ITS N-/S- ALKYL DERIVATIVES

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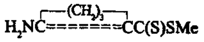
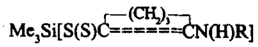
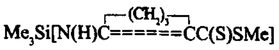
Reactions of chlorotrimethylsilane with sodium salts of 2-aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives, having the general formula  $R(H)N\overbrace{C{=\!=\!=\!=}C}^{(CH_2)_3}C(S)SH$ (R=H, Me, Et, n-Bu) and  $H_2N\overbrace{C{=\!=\!=\!=}C}^{(CH_2)_3}C(S)SMe$ in 1 : 1 molar ratio in refluxing benzene solution lead to the formation of triorganosilicon(IV) derivatives,  $Me_3Si[S(S)\overbrace{C{=\!=\!=\!=}C}^{(CH_2)_3}N(H)R]$ and  $Me_3Si[N(H)\overbrace{C{=\!=\!=\!=}C}^{(CH_2)_3}C(S)SMe]$, respectively. Characterization of these complexes by elemental analysis, molecular weight measurements, and IR, NMR (^1H, ^{13}C and ^{29}Si) spectral analysis reveals a four coordination around the silicon atom in trimethylsilicon(IV) derivatives of 2N-alkylaminocyclopentene-1-carbodithioic acid and five coordination in the S-alkyl 2-aminocyclopentene-1-carbodithioic acid derivative.

Keywords: Silicon complexes; NMR spectra; IR spectra

INTRODUCTION

2-Aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives are an important class of nitrogen and sulfur containing ligands. These ligands show a remarkable diversity in coordination pattern with various transition and non-transition metals.

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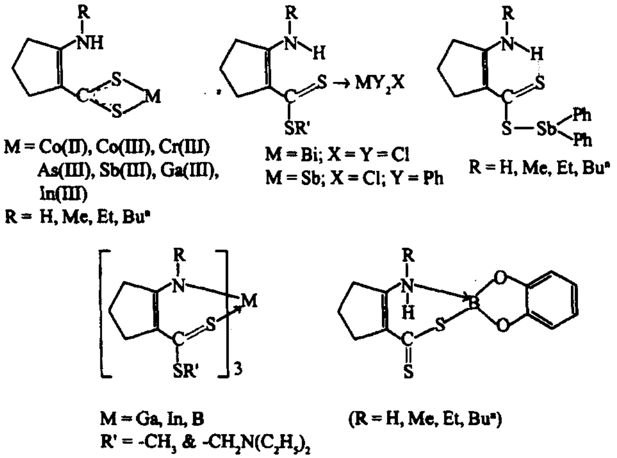
* Correspondence Author.



M = Co(II), Co(III), Cr(III) As(III), Sb(III), Ga(III), In(III)
R = H, Me, Et, Bu^n

M = Bi; X = Y = Cl
M = Sb; X = Cl; Y = Ph

R = H, Me, Et, Bu^n

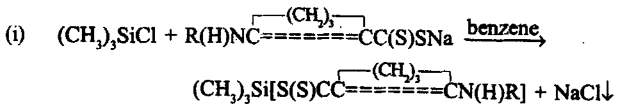
M = Ga, In, B
R' = $-CH_3$ & $-CH_2N(C_2H_5)_2$

(R = H, Me, Et, Bu^n)

In view of the interesting ligating capabilities of 2-aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives with main group elements in +3 oxidation states[1–6] developed in these laboratories it has been considered worthwhile to extend these studies to some organosilicon complexes. In this paper we report the synthesis and characterization of triorganosilicon(IV) derivatives of 2-aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives.

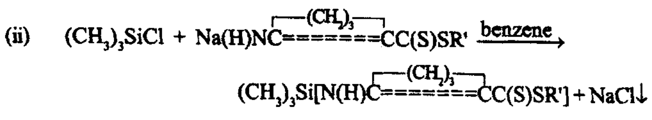
RESULTS AND DISCUSSION

The reactions of chlorotrimethylsilane with sodium salts of 2-aminocyclopentene-1-carbodithioic acid (ACDA) and its N-/S- alkyl derivatives in 1 : 1 molar ratio in refluxing benzene solution yield the corresponding derivatives :



$$\text{(i)}\quad (CH_3)_3SiCl + R(H)N\overset{(CH_2)_3}{\overline{C=\!=\!=\!=\!=\!=C}}C(S)SNa \xrightarrow{\text{benzene}} (CH_3)_3Si[S(S)C\overset{(CH_2)_3}{\overline{C=\!=\!=\!=\!=\!=C}}N(H)R] + NaCl\downarrow$$

where R = H(ACDA), Me(MeACDA), Et(EtACDA), n-Bu(BuACDA)



$$\text{(ii)}\quad (CH_3)_3SiCl + Na(H)N\overset{(CH_2)_3}{\overline{C=\!=\!=\!=\!=\!=C}}C(S)SR' \xrightarrow{\text{benzene}} (CH_3)_3Si[N(H)\overset{(CH_2)_3}{\overline{C=\!=\!=\!=\!=\!=C}}C(S)SR'] + NaCl\downarrow$$

Where R' = CH_3(ACDE)

All these complexes are found to be brown colored solids and soluble in common organic solvents like, benzene, chloroform and THF etc. Vapor pressure osmometric molecular weight measurements in chloroform solution at 45°C show their monomeric nature.

IR SPECTRA

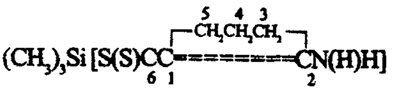
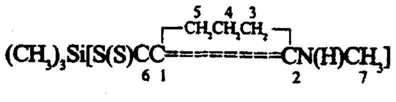
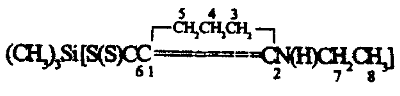
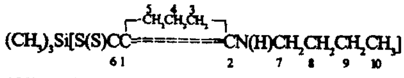
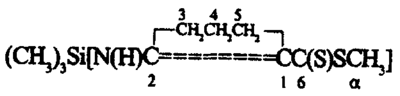
A comparision of IR spectra of these complexes with the spectra of the corresponding ligands shows the absence of $\nu_{S\text{-}H}$ band (observed at ~2500 cm^{-1} in the spectra of ligands[4,7]) indicating deprotonation of -SH and formation of Si-S bond. This has been further confirmed by the appearance of a new band at 425–405 cm^{-1} which may be assigned to $\nu_{Si\text{-}S}$ mode.[8,9] The appearance of two bands for $\nu_{S\text{-}(C=S)}$ and $\nu_{(S=C)\text{-}S}$ at 955–900 cm^{-1}, suggests the involvement of only one sulfur atom of the ligand moiety in complexation.[10] No significant shift has been observed in the position of ν_{NH_2} band in comparison to its position in parent ligand (3420–3280 cm^{-1}), this indicates the non involvement of the amino group of the ligand moiety in bonding. The strong bands observed in the range 1350–1340 cm^{-1} and 1280–1270 cm^{-1} may be assigned to $\nu_{C=N+C=S}$ and $\nu_{C=S+C=N}$ modes respectively. The band observed at 620-610 cm^{-1} may be assigned to $\nu_{sym_{CSS}}$.

In the IR spectra of the complex of ACDE, a downfield shift of ~65 cm^{-1} in the position of ν_{NH_2} (~3260 cm^{-1} in the parent ligand) absorption band indicates the involvement of amino nitrogen of the ligand moiety in the bonding. The presence of two splitted bands for $\nu_{asym_{CSS}}$ in the range 940–910 cm^{-1} indicates the participation of only one sulfur atom of the ligand moiety in complexation. New bands observed at 430 cm^{-1} and 510 cm^{-1} have been assigned to $\nu_{Si\text{-}S}$ and $\nu_{Si\text{-}N}$ mode[10,11] respectively.

^{1}H NMR SPECTRA

A singlet observed for -SH proton in the spectra of ACDA and its N-alkyl derivatives has been found to be missing in their corresponding trimethylsilicon(IV) complexes (Table I) confirming the deprotonation of -SH group and the formation of Si-S bond. A significant shift ~1.5 ppm has been observed in the position of NH signals of NHR/NH_2 group as compared to their position in the spectra of ligands. This may be due to the weakening of the hydrogen bond(N-H----S=) during complexation. However, no appreciable shift was observed in the position of alkyl protons of NHR group which rules out the possibility of the coordination through nitrogen. Similarly the signals for CH_2 protons of the cyclopentene ring do not show any appreciable shift in their positions when compared with their positions in the ligand.

TABLE I ^1H NMR data of triorganosilicon(IV) complexes of 2-aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives

S.No.	*Compound*	*Chemical shift in (δ) ppm*
1.	 $(CH_3)_3Si[S(S)\underset{6}{C}\underset{1}{C}\overset{\overset{5\ \ 4\ \ 3}{CH_2CH_2CH_2}}{=\!=\!=\!=\!=\!=}\underset{2}{C}N(H)H]$ $(CH_3)_3Si(ACDA)$	1.64 – 2.18, q, 2H-CH_2 (4) ; 2.47 – 2.97, m, 4H – CH_2 (3&5); 6.05, bs, 1H – NH (Free); 10.42, bs, 1H – NH; (Chelated); 0.08, s, 9H – CH_3 (Si – CH_3)
2.	 $(CH_3)_3Si[S(S)\underset{6}{C}\underset{1}{C}\overset{\overset{5\ \ 4\ \ 3}{CH_2CH_2CH_2}}{=\!=\!=\!=\!=\!=}\underset{2}{C}N(H)\underset{7}{CH_3}]$ $(CH_3)_3Si(MeACDA)$	1.92 – 2.61,q, 2H – CH_2(4); 2.90 – 3.28, m, 4H – CH_2 (3&5); 3.68, s, 3H – N CH_3 (7); 10.52, bs, 1H – NH; 0.08, s, 9H – CH_3(Si – CH_3)
3.	 $(CH_3)_3Si[S(S)\underset{6}{C}\underset{1}{C}\overset{\overset{5\ \ 4\ \ 3}{CH_2CH_2CH_2}}{=\!=\!=\!=\!=\!=}\underset{2}{C}N(H)\underset{7}{CH_2}\underset{8}{CH_3}]$ $(CH_3)_3Si(EtACDA)$	1.80 – 2.17, q, 2H – CH_2 (4); 2.59 – 3.26, m, 4H – CH_2 (3&5); 3.39 – 3.64, m, 2H – CH_2(7); 1.33, t, 3H – CH_3(8); 10.68, bs, 1H – NH; 0.08, s, 9H – CH_3 (Si – CH_3)
4.	 $(CH_3)_3Si[S(S)\underset{6}{C}\underset{1}{C}\overset{\overset{5\ \ 4\ \ 3}{CH_2CH_2CH_2}}{=\!=\!=\!=\!=\!=}\underset{2}{C}N(H)\underset{7}{CH_2}\underset{8}{CH_2}\underset{9}{CH_2}\underset{10}{CH_3}]$ $(CH_3)_3Si(BuACDA)$	1.78 – 2.14, q, 2H – CH_2 (4); 2.52-3.10, m, 4H-CH_2(3&5); 0.82 – 3.52, m, 9H – CH_2 (7, 8, 9) & CH_3(10); 10.92, bs, 1H – NH; 0.08, s, 9H – CH_3 (Si – CH_3)
5.	 $(CH_3)_3Si[N(H)\underset{2}{C}\overset{\overset{3\ \ 4\ \ 5}{CH_2CH_2CH_2}}{=\!=\!=\!=\!=\!=}\underset{1}{C}\underset{6}{C}(S)S\underset{\alpha}{CH_3}]$ $(CH_3)_3Si(ACDE)$	1.74 – 2.09, q, 2H – CH_2(4); 2.56 – 2.94, m, 4H – CH_2 (3&5); 2.67, s, 3H – CH_3(α); 5.88, bs, 1H – NH

A singlet present at~δ 0.08 ppm in the spectra of all the complexes may be assigned to methyl protons attached to silicon.

In the S-methyl(ACDE) derivative of trimethylsilicon (IV)complex, the signal observed at δ 11.2 ppm and assigned to the hydrogen bonded proton of the NH_2 group in the ligand disappears and a second NH signal observed at δ 5.81 ppm in the ligand shifts down field to δ 5.88 ppm, indicating the removal of one of the protons of the amino group and the formation of Si-N bond on complexation. A downfield shift in SCH_3 signal further supports the participation of C=S in bonding.

A singlet observed at δ 0.06 ppm may be assigned to the methyl protons attached to silicon.

^{13}C NMR SPECTRA

A comparision of ^{13}C NMR spectra of the trimethylsilicon complexes of ACDA and its N-alkyl derivatives with the corresponding ligands[1] reveals the absence of any significant shift in the position of the signals for alkyl and cyclopentene ring carbons which rules out the possibility of the involvement of NHR group in bonding. This has been supported by the absence of any significant shift in the position of the C_2 carbon signal. However, a small upfield shift of ~ δ 1.5 ppm in its position as compared to free ligand may be due to the breaking of the hydrogen bonding between the amino group and free sulfur of the dithiocarboxylate group.

A singlet for methyl carbon attached to the silicon atom was observed in the range δ1.97–1.99 ppm (Table II).

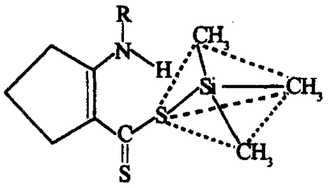
In the spectra of ligand, ACDE; the signal observed at δ 204.82 ppm has been assigned to the C_6 carbon atom. In the spectrum of the trimethylsilicon(IV) derivative, this signal shows a downfield shift and appears at δ 208.04 ppm. A shift of ~4 ppm in the position of C_6 carbon indicate the involvement of C(SR)=S group in bonding. Thus this ligand behave as bidentate moiety.

A singlet for the methyl carbon attached with silicon atom was observed at δ 2.05 ppm.

^{29}Si NMR SPECTRA

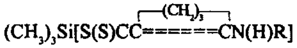
The ^{29}Si NMR spectra of N-alkyl derivatives of trimethylsilicon exhibit ^{29}Si signal (Table II) in the range δ(-)23.41 to (-) 31.83 ppm, which indicates the tetra-coordinated[11] environment around the central silicon atom.

On the basis of IR and NMR spectral data described in preceeding pages the following structure (Fig. 1) may be proposed for these derivatives:



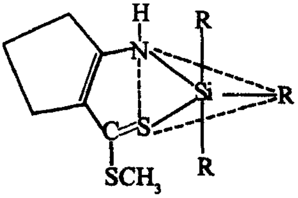
where R = H, Me, Et and n-Bu

FIGURE 1 Proposed structure for the derivatives



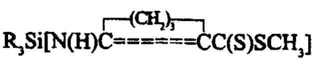
$(CH_3)_3Si[S(S)C\overbrace{C{=}{=}{=}{=}{=}{=}C}^{(CH_2)_3}N(H)R]$

The ^{29}Si NMR spectrum of $Me_3Si(ACDE)$ shows the presence of ^{29}Si signal at δ (-)131.20 ppm, indicating a penta-coordination[12] around the central silicon atom leading to the structure (Figure 2) in which the ligand behaves as a bidentate moiety.



Where R = -CH$_3$

FIGURE 2 Proposed structure for the derivative



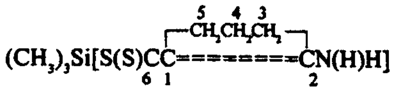
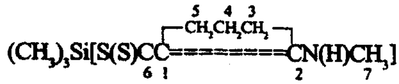
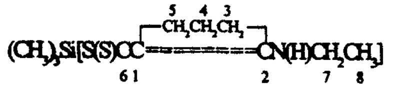
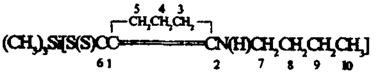
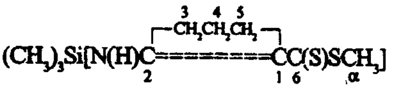
$R_3Si[N(H)C\overbrace{{=}{=}{=}{=}{=}{=}C}^{(CH_2)_3}C(S)SCH_3]$

EXPERIMENTAL

The ligands used were prepared by the literature method.[13] Me_3SiCl was distilled at 57°C. Silicon and Sulphur were estimated gravimetrically as silicon oxide and barium sulphate (Messenger's method), respectively.[14]

Nitrogen was estimated by Kjeldahl's method.[14] Molecular weights were determined with a "Knauer Vapor pressure" osmometer, using chloroform solution at 45°C.

TABLE II ^{13}C and ^{29}Si spectral data of triorganosilicon(IV) complexes of 2-aminocyclopentene-1-carbodithioic acid and its N-/S- alkyl derivatives (δ) ppm

S.No.	*Compound*	*^{13}C chemical shift values*	*^{29}Si chemical shift values*
1.		$C_{(1)}$,118.60; $C_{(2)}$,167.18; $C_{(3)}$,38.14; $C_{(4)}$,19.48; $C_{(5)}$,35.12; $C_{(6)}$, 198.02; Si-CH_3, 1.99	(-) 23.41
2.		$C_{(1)}$, 119.72; $C_{(2)}$, 168.43; $C_{(3)}$, 36.18; $C_{(4)}$, 19.31; $C_{(5)}$, 34.02; $C_{(6)}$, 193.12; $C_{(7)}$, 31.18; Si-CH_3, 1.97	-
3.		$C_{(1)}$, 117.59; $C_{(2)}$, 169.91; $C_{(3)}$, 39.59; $C_{(4)}$, 20.04; $C_{(5)}$, 33.27; $C_{(6)}$, 194.18; $C_{(7)}$, 40.04; $C_{(8)}$, 14.79; Si – CH_3, 1.99	(-) 31.83
4.		$C_{(1)}$, 117.86; $C_{(2)}$, 169.82; $C_{(3)}$, 39.52; $C_{(4)}$, 19.68; $C_{(5)}$, 33.41; $C_{(6)}$, 195.01; $C_{(7)}$, 45.21; $C_{(8)}$, 31.42; $C_{(9)}$, 19.98; $C_{(10)}$, 13.56; Si-CH_3, 1.98	(-) 29.76
5.		$C_{(1)}$, 117.66; $C_{(2)}$, 165.66; $C_{(3)}$, 36.07; $C_{(4)}$, 20.41; $C_{(5)}$, 33.04; $C_{(6)}$, 208.04; $C_{(\alpha)}$, 16.95; Si-CH_3, 2.05	(-) 131.20

Infrared spectra were recorded in the range 4000–200 cm^{-1} on "Nicolet Magna 550" FT IR spectrophotometer. ^1H and ^{13}C NMR spectra were recorded in $CDCl_3$ and $CHCl_3$ solution, respectively on a 90MHz JEOL FX 90Q spectrometer using TMS as an internal reference. ^{29}Si NMR spectra of complexes were recorded in $CHCl_3$ solution using Me_4Si as an external reference.

Since all complexes were synthesized in similar manner, the experimental details of a representative complex is being described below. Analytical results are summarised in Table III.

TABLE III Physical and analytical data of triorganosilicon(IV) complexes of 2-aminocyclopentene-1-carbodithioic acid and its N-/S-alkyl derivatives

S.No.	*Reactants(g)*			*Product yield (%)*	*NaCl(g) Found (Calcd.)*	*Elemental Analysis(%)*			*Molecular weight Found (Calcd.)*	*M.P. (°C)*
						Found (Calcd.)				
	Na	*LH*	*(CH₃)₃SiCl*			*Si*	*N*	*S*		
1.	0.12	ACDA 0.86	0.59	$C_9H_{17}S_2NSi$ 70	0.30 (0.30)	12.02 (12.13)	5.98 (6.05)	27.32 (27.70)	229 (231.46)	94 (decomp.)
2.	0.14	MeACDA 1.05	0.66	$C_{10}H_{19}S_2NSi$ 72	0.33 (0.35)	11.22 (11.44)	5.42 (5.71)	26.02 (26.12)	243 (245.49)	98 (decomp.)
3	0.10	EtACDA 0.81	0.47	$C_{11}H_{21}S_2NSi$ 70	0.22 (0.25)	10.64 (10.82)	5.32 (5.40)	24.64 (24.71)	256 (259.52)	124(decomp.)
4.	0.11	BuACDA 1.03	0.52	$C_{13}H_{25}S_2NSi$ 75	0.27 (0.28)	9.66 (9.77)	4.64 (4.87)	22.04 (22.30)	285 (287.57)	86(decomp.)
5.	0.15	ACDE 1.13	0.71	$C_{10}H_{19}S_2NSi$ 72	0.36 (0.38)	11.24 (11.44)	5.44 (5.71)	26.04 (26.12)	247 (245.49)	56 (decomp.)

LH = Ligand

Synthesis of $(CH_3)_3Si(ACDA)$; $(C_9H_{17}S_2NSi)$

A weighed amount of sodium metal (0.12g, 5.2 mmol) was treated with dry methanol (~5 ml) and to this, a benzene solution of 2-aminocyclopentene-1-carbodithioic acid (0.85 g, 5.3 mmol) was added dropwise with constant stirring. The reaction mixture was refluxed for ~4 hrs. and then cooled. To this solution a benzene solution of chlorotrimethylsilane (0.58g, 5.3 mmol) was added dropwise with constant stirring. The reaction mixture was stirred for ~4 hrs. and then refluxed for ~3 hrs. The NaCl that formed was filtered and the excess solvent was removed from the filtrate under reduced pressure. The crude product was recrystallised from chloroform pet.-ether mixture. The compound on analysis was found to have Si, 12.02; N, 5.98; S, 27.32% Calcd. for $C_9H_{17}S_2NSi$: Si, 12.13; N, 6.05; S, 27.70%. Mol.Wt. Found 229, Calcd. 231.46.

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