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Coordination Behaviour of Biologically Active Benzothiazolines Towards Silicon(IV)

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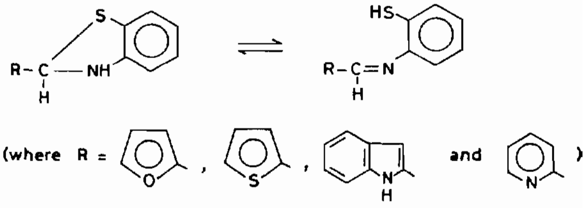
Abstract

The synthesis and structural features of some trigonal bipyramidal and octahedral complexes of silicon(IV) with biologically active benzothiazolines are described. These were derived by the condensation of pyridine-2-aldehyde, furfuraldehyde, thiophene-2-aldehyde and indole-3-carbaldehyde with 2-mercaptoaniline. The newly synthesized complexes have been characterized by elemental analyses, conductance measurements, molecular weight determinations and electronic, infrared, ^{1}H and ^{13}C NMR spectral studies. The ligand and its complexes of Si(IV) have been tested for their antifungal activity against *Helmenthosporeum gramineum* and *Rhizopus oryzae*. The growth inhibition percentage was calculated on the basis of the average diameter of the fungal colony.

Introduction

Recently, much interest has been shown in the synthesis of metal chelates of sulphur-containing ligands and it is within this particular area that rather significant advances have been made [1]. The condensation of 2-mercaptoaniline with an aldehyde or ketone does not normally lead to the isolation of the corresponding Schiff base, but rather to a thiazoline (with 2-aminobenzenethiol) or a thiazolidine (with 2-mercaptoalkylamine) [2–5] structure.

It has, however, been observed by Busch and Thompson [6] that alcoholic solutions of various β-diketones react with β-mercaptoethylamine in the presence of nickel ions to give a nickel complex of the corresponding doubly deprotonated tetradentate Schiff base in good yield. Thus the metal ion behaves as a template. Jadamus *et al.* [7] later reported that even in the absence of metal ion the condensation product of an aldehyde and ketone with 2-aminobenzenethiol forms a mixture of benzothiazoline and Schiff base and an equilibrium may exist between the two, as shown below:



Experimental

Chemicals and solvents used were dried and purified by standard methods and moisture was excluded from the glass apparatus using $CaCl_2$ guard tubes.

Preparation of Benzothiazolines

Benzothiazolines of pyridine-2-aldehyde, furfuraldehyde, thiophene-2-aldehyde and indole-3-carbaldehyde were prepared by the condensation of the appropriate aldehyde with 2-mercaptoaniline in a 1:1 molar ratio in benzene. The solution was heated under reflux for 2–3 h after which the solvent was removed *in vacuo*.

The crude solid so obtained was recrystallized from benzene: (i) Pyridine-2-aldehyde benzothiazoline (H.Py.Bzt) ($C_{12}H_{10}N_2S$), yellow solid, m.p. 81 °C; (ii) furfuraldehyde benzothiazoline (H.Furf.-Bzt) ($C_{11}H_9NSO$), yellow solid, m.p. 72 °C; (iii) thiophene-2-aldehyde benzothiazoline (H.Thiop.Bzt) ($C_{11}H_9NS_2$), yellow solid, m.p. 91 °C; (iv) indole-3-carboxaldehyde benzothiazoline (H.Indol.Bzt) ($C_{15}H_{12}N_2S$), yellow solid, m.p. 154 °C.

Synthesis of Silicon(IV) Complexes

To a weighed amount of trimethylchlorosilane (1 mol) and dimethylsilicon dichloride (1 mol) was added the requisite amount of sodium salt of the ligand (1 or 2 mol) in dry methanol. The mixture was heated under reflux for 5–6 h and the precipitate of sodium chloride so formed was filtered off. The solvent was removed and the product dried *in vacuo*. It was repeatedly washed with dry cyclohexane and again dried *in vacuo*. The physical properties and analytical data of these complexes are recorded in Table I.

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TABLE I. Analyses and Physical Characteristics of Silicon(IV) Complexes

Compounds	Colour	Melting point (°C)	Yield (%)	Analyses				
				C Found (Calc.)	H Found (Calc.)	N Found (Calc.)	S Found (Calc.)	Si Found (Calc.)
$Me_3Si(Furf.Bzt)$	dark brown	85	87	64.74 (65.09)	6.38 (6.59)	5.31 (5.42)	12.17 (12.40)	9.97 (10.49)
$Me_3Si(Thiop\text{-}2\text{-}al.Bzt)$	dark yellow	78	86	57.51 (57.91)	5.75 (5.86)	4.38 (4.83)	21.83 (22.06)	9.32 (9.34)
$Me_3Si(Indol\text{-}3\text{-}al.Bzt)$	dark yellow	89	81	66.65 (66.86)	6.00 (6.19)	8.31 (8.67)	9.55 (9.90)	8.15 (8.38)
$Me_3Si(Py\text{-}2\text{-}al.Bzt)$	green	100	85	62.89 (63.14)	6.11 (6.31)	9.65 (9.82)	11.02 (11.22)	9.00 (9.50)
$Me_2Si(Furf.Bzt)_2$	dark brown	166	87	66.71 (67.12)	4.65 (5.13)	6.33 (6.53)	14.73 (14.92)	6.10 (6.31)
$Me_2Si(Thiop\text{-}2\text{-}al.Bzt)_2$	dark yellow	105	82	58.12 (58.41)	4.21 (4.46)	5.25 (5.68)	25.56 (25.96)	5.16 (5.49)
$Me_2Si(Indol\text{-}3\text{-}al.Bzt)_2$	yellowish brown	110	86	68.24 (68.68)	4.65 (5.01)	9.67 (10.01)	11.12 (11.45)	4.32 (4.84)
$Me_2Si(Py\text{-}2\text{-}al.Bzt)_2$	dark green	180	87	64.25 (64.58)	4.62 (4.97)	11.13 (11.59)	13.03 (13.25)	5.21 (5.61)

TABLE II. Fungicidal Activity of Pyridine-2-aldehyde Benzothiazoline and its Complexes (temperature = 27 ± 1 °C)

Compounds	Average percentage inhibition after 96 h					
	Helminthosporeum gramineum			*Rhizopus oryzae*		
	25 ppm	50 ppm	75 ppm	25 ppm	50 ppm	75 ppm
H.Py.Bzt	79	83	89	17	32	45
$Me_2Si(Py.Bzt)_2$	81	86	91	30	43	49
$Me_3Si(Py.Bzt)$	87	93	96	38	56	60

Analytical Methods and Physical Measurements

Silicon was estimated gravimetrically and nitrogen by Kjeldahl's method. Carbon and hydrogen analyses were performed at the microanalytical laboratory of the department. Sulphur was estimated by Messenger's method.

IR spectra were recorded on a Perkin-Elmer 577 grating spectrophotometer in KBR pellets. The electronic spectra of the ligands and their silicon compounds were obtained on a Perkin-Elmer 202 spectrophotometer in dry methanol. PMR spectra were recorded on a Jeol FX90Q spectrometer in $CDCl_3$ using TMS as the internal standard at 89.55 MHz, and ^{13}C NMR spectra in methanol at 22.49 MHz.

Molar conductance measurements were made using a Systronic conductivity bridge, Model 305. Molecular weights were determined by the Rast camphor method.

The antifungal activities of the ligand and its complexes of silicon(IV) were evaluated against the fungi by the agar plate technique [8] at 75, 50 and 25 ppm. The number of replications in each case was three. The percentage inhibition given in Table II was calculated using the formula:

$$\%\ \text{inhibition} = \frac{(C - T) \times 100}{C}$$

where C = diameter of the fungus colony in the control plate after 96 h; T = diameter of the fungus colony in tested plates after the same period.

Results and Discussion

The reactions of trimethylchlorosilane and dimethylchlorosilane with benzothiazolines (NS) in 1:1 and 1:2 molar ratios proceed as follows:

TABLE III. ^1H NMR (δ ppm) Spectral Data of Benzothiazolines and the Corresponding Si(IV) Complexes

Compound	NH	H–C–N or H–C=N	Aromatic	Si–CH$_3$
H.Furt.Bzt	4.20	7.92	7.20	
$Me_3SiFurf.Bzt$		8.19	7.45	0.36
$Me_2Si(Furf.Bzt)_2$		8.16	7.24	0.16
H.Thiop-2-al.Bzt	4.36	7.84	7.32	
$Me_3SiThiop$-2-al.Bzt		8.20	7.64	0.32
$Me_2Si(Thiop$-2-al.Bzt$)_2$		8.08	7.52	0.20

$$Me_3SiCl + \overset{\frown}{NS}Na \xrightarrow[(1:1)]{MeOH} Me_3Si(\overset{\frown}{NS}) + NaCl$$

$$Me_2SiCl_2 + 2\overset{\frown}{NS}Na \xrightarrow[(1:2)]{MeOH} Me_2Si(\overset{\frown}{NS})_2 + 2NaCl$$

All the newly synthesized complexes are coloured solids, soluble in most of the common organic solvents and are non-electrolytes (15–20 ohm^{-1} cm^2 mol^{-1}) in anhydrous dimethyl formamide at 25 ± 1 °C. They are monomeric in nature.

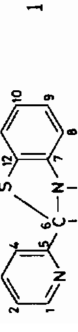
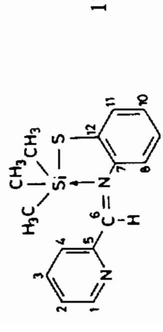
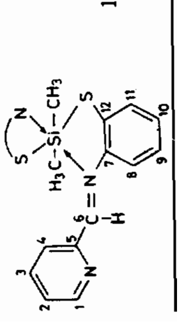
The electronic spectra of the ligands consist of two bands around 250 nm and 315 nm characteristic of benzothiazolines [9, 10]. These bands arising out of ϕ–ϕ^* and π–π^* benzenoid [11–13] transitions remain unaltered in all the silicon complexes, whereas an additional band is also observed at 410 nm due to the n–π^* electronic transitions of the azomethine group [14], which indicates isomerization of the ligands on complexation.

In the IR spectra of the ligands NH stretching and deformation bands were observed at ~3370–3200 and 1670–1705 cm^{-1}, respectively. The absence of ν(SH) at 2500–2600 cm^{-1} and ν(C=N) at 1600–1650 cm^{-1} is indicative of the benzothiazoline rather than Schiff base structure [15]. In the spectra of metalloid complexes, bands due to N–H vibrations disappear, indicating the chelation of nitrogen with the silicon atom, and a new band at *ca.* 1600 cm^{-1} is observed which may be assigned to ν(C=N) vibrations. This band suggests that the complexes are metalloid Schiff base derivatives, as the benzothiazoline ring rearranges to give the Schiff base derivative in the presence of a silicon atom [16].

Several new bands in the complexes in the region 580–555 cm^{-1} and 540–530 cm^{-1} are due to the ν(Si ← N) [17] and ν(Si–S) [18], respectively, and are absent in the spectra of benzothiazolines. Thus, the IR spectral studies of these complexes suggest that the azomethine nitrogen and the sulphur of the thiol group participate in the complexation reaction.

The PMR spectra of benzothiazolines show the N–H proton signals at δ 4.20 and 4.36 ppm, which

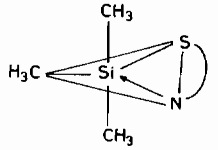
TABLE IV. ^{13}C NMR Spectral Data for Benzothiazoline and its Corresponding Silicon Complexes

Structure	1	2	3	4	5	6	7	8	9	10	11	12	Si–CH$_3$
	123.46	121.89	120.64	121.19	125.52	149.57	126.17	125.95	125.61	125.42	126.77	126.92	
	123.71	122.63	121.11	121.71	125.31	160.07	126.53	126.31	125.21	125.12	126.32	150.26	4.44
	123.51	121.94	120.70	121.71	125.25	178.23	126.22	125.57	125.41	125.22	126.37	142.93	5.34

disappear in the corresponding metalloid complexes. The azomethine proton signal shifts downfield in the spectra of the complexes due to the formation of a coordinate linkage between nitrogen and silicon. Methyl protons are also observed in the region δ 0.16–0.36 ppm in the spectra of the complexes (Table III).

^{13}C NMR spectra of pyridine-2-aldehyde benzothiazoline and its silicon complexes were also recorded (Table IV). The shifts of the carbons attached to S and N indicate their coordination with the silicon atom.

On the basis of the spectral evidence, the following tentative structures with trigonal bipyramidal and octahedral geometries around the silicon atom can be proposed.



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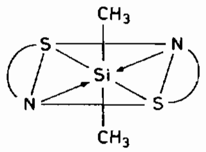

II

Antifungal Activity

Helminthosporeum gramineum and *Rhizopus oryzae* were used to check the antifungal activity of the ligand and its complexes. The results of the antifungal activity given in Table IV show that these compounds exhibit greater fungitoxicity against the *H. gramineum*, but are less active against *R. oryzae* at all three concentrations. The fungitoxicity of the ligand and its complexes decreases on lowering the concentration. It is clear from the fungicidal screening data that the metal chelates are found to be more fungitoxic than the chelating agent itself.

Acknowledgement

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