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# Fungicidal, Bactericidal and Antifertility Activities of Diorganosilicon(IV) Complexes Derived from Benzothiazolines

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**Synthetic, structural and biological aspects of trigonal-bipyramidal, $Me_2Si(N—S)Cl$ and octahedral, $Me_2Si(N—S)_2$ types of diorganosilicon(IV) complexes of heterocyclic benzothiazolines (N—SH) are described. The complexes were characterized by elemental analysis, molecular weight determination, conductance measurements and electronic, infrared, $^1H$ and $^{13}C$ NMR spectroscopic studies. Some ligands and their corresponding dimethylsilicon(IV) complexes have been tested for their effects on several pathogenic fungi and bacteria and found to be quite active in this respect. Antifertility activity in male mice of some representative ligands and their silicon complexes was also evaluated and discussed.**

**Keywords: organosilicon complexes; Schiff base ligands; benzothiazolines; antifungal, antibacterial and antifertility activities**

## INTRODUCTION

Organosilicon compounds of sulfur-containing ligands have attracted much attention recently owing to their biological importance.[1,2] Sulfur-containing ligands are well known for their anticarcinogenic,[3] antibacterial, tuberculostatic and antifungal activities.[4] It has been reported that the activities of sulfur-containing ligands increase on complexation.[5,6] In continuation of our earlier work,[7,8] on biologically active complexes, we report here some Schiff-base complexes of organosilicon(IV) chlorides.

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[9–11] moiety. It has, however, been observed that alcoholic solutions of various diketones react with mercaptoethylamine in the presence of nickel ions to give nickel complexes of the corresponding Schiff bases in good yield.[12]

## EXPERIMENTAL

All the chemicals used were dried and distilled before use. Moisture was excluded from the glass apparatus using calcium chloride drying tubes.

### Preparation of benzothiazolines

Benzothiazolines of 2-acetylfuran, 2-acetylpyridine, 2-acetylthiophene and 2-acetylnaphthalene were prepared by condensation of the appropriate ketone with 2-mercaptoaniline in a 1:1 molar ratio in benzene. The solution was stirred for 4–5 h on a magnetic stirrer.

The crystalline solid product so obtained was recrystallized from the same solvent:

(1) H. Fur. Bzt ($C_{12}H_{11}NSO$), yellow crystalline solid, m.p. 84 °C; (2) H. Pyd. Bzt ($C_{13}H_{12}N_2S$), yellow crystalline solid, m.p. 87 °C; (3) H. Thiop. Bzt ($C_{12}H_{11}NS_2$), yellow crystalline solid, m.p. 85 °C; (4) H. Naph. Bzt ($C_{18}H_{15}NS$), yellow crystalline solid, m.p. 88 °C.

### Synthesis of organosilicon(IV) complexes

For the preparation of these complexes a weighed amount of dimethyldichlorosilane in approx. 30 cm$^3$ of dry methanol in a 100 cm$^3$ round-bottom flask was added the calculated amount of the sodium salt of the ligands in 1:1 and 1:2 molar ratios. The contents were refluxed for 10–12 h. After completion of the reaction, the precipitated sodium chloride was filtered off and the excess of the solvent was removed from the mother liquor

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**Table 1** Analysis and physical characteristics of diorganosilicon(IV) complexes

| Reactants | | | | Elemental analysis (%) | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| Starting material (g) | Ligand (g) | Product formed and colour | M.p. (°C) | C Found (Calcd) | H Found (Calcd) | N Found (Calcd) | S Found (Calcd) | Cl Found (Calcd) | Si Found (Calcd) | Mol. wt. Found (Calcd) |
| $Me_2SiCl_2$ | $C_{12}H_{11}NSO$ | $C_{14}H_{16}NSOClSi$ | 99 | 54.48 | 5.51 | 4.33 | 10.06 | 11.31 | 8.84 | 330.61 |
| 0.43 | 0.73 | Light brown | | (54.26) | (5.20) | (4.52) | (10.35) | (11.44) | (9.06) | (309.89) |
| $Me_2SiCl_2$ | $C_{12}H_{11}NSO$ | $C_{26}H_{26}N_2S_2Si$ | 122 | 63.90 | 5.57 | 5.81 | 13.25 | — | 5.48 | 515.34 |
| 0.30 | 1.02 | Dark brown | | (63.64) | (5.34) | (5.71) | (13.07) | | (5.72) | (490.72) |
| $Me_2SiCl_2$ | $C_{12}H_{11}NS_2$ | $C_{14}H_{16}NS_2ClSi$ | 152 | 51.83 | 5.22 | 4.02 | 19.38 | 10.80 | 8.36 | 305.77 |
| 0.47 | 0.86 | Dirty yellow | | (51.59) | (4.95) | (4.29) | (19.67) | (10.88) | (6.62) | (325.96) |
| $Me_2SiCl_2$ | $C_{12}H_{11}NS_2$ | $C_{26}H_{26}N_2S_4Si$ | 120 | 59.96 | 5.33 | 5.44 | 24.75 | — | 5.15 | 545.60 |
| 0.46 | 1.67 | Orange brown | | (59.73) | (5.01) | (5.35) | (24.53) | | (5.37) | (522.86) |
| $Me_2SiCl_2$ | $C_{13}H_{12}N_2S$ | $C_{15}H_{17}N_2SClSi$ | 79 | 56.49 | 5.57 | 8.52 | 9.83 | 10.82 | 8.88 | 342.11 |
| 0.58 | 1.03 | Dark Yellow | | (56.14) | (5.34) | (8.73) | (9.99) | (11.05) | (8.75) | (320.92) |
| $Me_2SiCl_2$ | $C_{13}H_{12}N_2S$ | $C_{28}H_{28}N_4S_2Si$ | 146 | 65.86 | 5.78 | 11.18 | 12.26 | — | 5.22 | 534.70 |
| 0.46 | 1.40 | Orange brown | | (65.59) | (5.50) | (10.93) | (12.51) | | (5.48) | (512.78) |
| $Me_2SiCl_2$ | $C_{18}H_{15}NS$ | $C_{20}H_{20}NSClSi$ | 180(d) | 65.20 | 5.66 | 3.45 | 8.35 | 9.44 | 7.28 | 388.42 |
| 0.66 | 1.40 | Light brown | | (64.93) | (5.45) | (3.78) | (8.67) | (9.58) | (7.59) | (369.99) |
| $Me_2SiCl_2$ | $C_{18}H_{15}NS$ | $C_{38}H_{34}N_2S_2Si$ | 160 | 74.94 | 5.80 | 4.36 | 10.27 | — | 4.41 | 585.75 |
| 0.55 | 2.36 | Dark brown | | (74.71) | (5.61) | (4.59) | (10.49) | | (4.60) | (610.92) |

under reduced pressure. The complexes were subsequently dried for 3–4 h, then repeatedly washed with a mixture of dry methanol and cyclohexane so as to ensure their purity, and finally dried under reduced pressure. Their purity was further checked by TLC using silica gel-G. The analysis of these new complexes (Table 1) for silicon, carbon, hydrogen, sulfur, chlorine and nitrogen agreed with the theoretical values within the limits of experimental error.

### Analytical methods and physical measurements

Carbon and hydrogen analyses were performed in the microanalytical laboratory of this Department. Nitrogen and sulfur were estimated by Kjeldahl's and Messenger's methods, respectively. Silicon was estimated gravimetrically as silica ($SiO_2$). Conductivity was measured at 32 ± 1 °C with a conductivity bridge (Type 305 Systronics model) and molecular weights were determined by the Rast camphor method. Infrared spectra were recorded on a Perkin-Elmer 577 grating spectrophotometer in KBr pellets. The electronic spectra of the ligands and their silicon complexes were obtained using a Pye-Unicam SP-8-100 spectrophotometer in dry methanol. $^1H$ and $^{13}C$ NMR spectra were recorded on a JEOL FX902 spectrometer at 89.5 and 22.49 MHz, respectively.

## RESULTS AND DISCUSSION

The reactions of dimethyldichlorosilane with potassium salts of the benzothiazolines derived from the condensation of heterocyclic ketones and 2-aminothiophenol in 1:1 and 1:2 molar ratios in dry methanol resulted in the isolation of $Me_2Si(NS)Cl$ and $Me_2Si(NS)_2$ complexes. These are soluble in common organic solvents and have sharp melting points. The low values of molar conductance (10–12 $\Omega^{-1}$ cm$^2$ mol$^{-1}$) show them to be non-electrolytes. The monomeric nature of these complexes was confirmed by molecular weight determinations. The mode of bonding of the benzothiazolines to the silicon atom has been established on the basis of the spectroscopic studies discussed below.

### Electronic spectra

The electronic spectra of the benzothiazolines consist of two broad and strong bands around 280 nm and 310 nm, characteristic of the cyclic (benzothiazoline) form of the ligands; these may be attributed to the $\phi-\phi^*$ and $\pi-\pi^*$ (benzenoid) transitions respectively.[13] A new band around 400 nm due to $n-\pi^*$ electronic transitions of the azomethine group is observed in the spectra of silicon complexes.[14] This suggests the formation of the azomethine grouping on complexation and thus isomerization of the ligands to the Schiff-base form in the presence of a silicon atom.

## IR spectra

In the IR spectra of benzothiazolines, the absence of absorption bands at *ca* 2650 and 1620 cm$^{-1}$ due to $\nu$(SH) and $\nu$(C═N) vibrations, respectively, indicates the existence of the ligands in the benzothiazoline[15] rather than the Schiff-base forms. In the spectra of 1:1 and 1:2 complexes, the bands in the region 3300–3100 cm$^{-1}$ due to the NH stretching vibrations[16] of the ligands remain absent and new bands at *ca* 1615 cm$^{-1}$ are observed due to $\nu$ (C═N) vibrations. The appearance of these bands suggests that the resulting complexes are the Schiff-base derivatives of silicon. The chelation of ligands through azomethine nitrogen and thiolo sulfur receives further support from the appearance of new bands in the regions 575–550 and 530–520 cm$^{-1}$ owing to (Si←N) and (Si—S) vibrations, respectively,[17] in both types of complexes. It is known that the *cis* forms of $Me_2SiL_2$ types of complexes give rise to two $\nu$(M—N) bands whereas the *trans* complexes give rise to only one IR-active $\nu$(M—N) band. The presence of only one (Si←N) band, in the present case, suggests that 1:2 complexes exist in the *trans* form.[18]

Finally in the case of the $Me_2Si(NS)Cl$ type of complexes, a band of medium intensity at around 450 cm$^{-1}$ is caused by $\nu$(Si—Cl)[19] vibrations. The band in the region 770–740 cm$^{-1}$ may be assigned to the $\nu$(Si—CH$_3$) vibrations.[20]

## $^1$H NMR spectra

The $^1$H NMR spectra of all the ligands and their corresponding silicon complexes have been recorded in DMSO-d$_6$ using TMS as the internal standard. The chemical shift values ($\delta$, ppm) of different protons are listed in Table 2.

For the sake of exemplification, the spectra of H.Pyd.Bzt and its corresponding dimethylsilicon(IV) complexes are discussed in detail. The NH proton signal of benzothiazoline (monofunctional bidentate) appears at $\delta$ 4.55 ppm. However, this disappears in the case of silicon complexes, indicating the complete removal of the proton from the NH group and coordination of nitrogen, with simultaneously covalent bond formation by sulfur with silicon. The protons due to the $(H_3C{—}\underset{|}{C}{=}N)$ group appear at $\delta$ 2.15 ppm in the ligand and show a downfield shift ($\delta$ 2.40 and 2.51 ppm in 1:1 and 1:2 complexes, respectively) on complex formation. The aromatic protons are observed in the region $\delta$ 7.55–6.75 ppm in the spectrum of the ligand whereas in the complexes these protons undergo a downfield shift and appear between $\delta$ 7.96 and 6.86 ppm. In the spectra of complexes a downfield shift in the positions of methyl(—CH$_3$) and aromatic protons indicates deshielding as well as the coordination of azomethine nitrogen to the silicon atom. This is probably caused by the donation of the lone pair of electrons of the nitrogen atom to the central silicon atom, resulting in the formation of a coordinate linkage between silicon and nitrogen (Si←N). Further, new signals at $\delta$ 1.28 and 1.24 ppm in 1:1 and 1:2 complexes respectively are caused by the methyl protons of $Me_2Si$ group.

## $^{13}$C NMR spectra

The $^{13}$C NMR spectral data of H.Fur.Bzt and H.Pyd.Bzt, as well as their corresponding 1:1 and 1:2 complexes, have also been recorded in dry DMSO and the peak positions along with the assignments are listed in Table 3. The chemical shift values relative to TMS for the carbons attached to the azomethine nitrogen and thiolic sulfur in the ligands are observed at $\delta$148.6 and 142.5 ppm (H. Fur. Bzt) and $\delta$ 151.2 and 139.6 ppm (H. Pyd. Bzt), respectively. The noticeable change in the positions of these signals in the spectra of silicon complexes confirms the inferences drawn earlier on the basis of IR and $^1$H spectra concerning the participation of nitrogen and sulfur in bonding with the silicon atom.

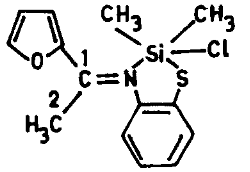
**Table 2** $^1$H NMR spectral data ($\delta$, ppm) of ligands and their corresponding diorganosilicon(IV) complexes

| Compound | —NH | $\underset{\displaystyle CH_3}{\underset{|}{—C{=}N}}$ | Aromatic | Si—Me |
|---|---|---|---|---|
| H.Fur.Bzt | 4.38 | 1.95 | 7.50–6.75 | — |
| H.Pyd.Bzt | 4.55 | 2.15 | 7.55–6.70 | — |
| H.Thiop.Bzt | 4.42 | 2.10 | 7.60–6.52 | — |
| H.Naph.Bzt | 4.50 | 2.06 | 7.52–6.60 | — |
| $Me_2Si$(Fur.Bzt)Cl | — | 2.20 | 7.68–6.80 | 0.75 |
| $Me_2Si$(Fur.Bzt)$_2$ | — | 2.34 | 7.76–6.88 | 0.94 |
| $Me_2Si$(Pyd.Bzt)Cl | — | 2.40 | 7.62–6.77 | 0.68 |
| $Me_2Si$(Pyd.Bzt)$_2$ | — | 2.51 | 7.81–6.84 | 0.88 |
| $Me_2Si$(Thiop.Bzt)Cl | — | 2.35 | 7.86–6.65 | 0.96 |
| $Me_2Si$(Thiop.Bzt)$_2$ | — | 2.38 | 7.88–6.68 | 1.05 |
| $Me_2Si$(Naph.Bzt)Cl | — | 2.25 | 7.73–6.70 | 1.10 |
| $Me_2Si$(Naph.Bzt)$_2$ | — | 2.30 | 7.78–6.74 | 1.15 |

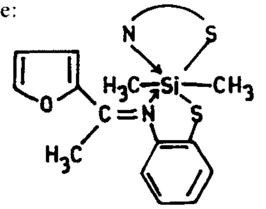
**Table 3** $^{13}$C NMR spectral data (δ, ppm) of ligands and their corresponding complexes

| Compound | C(1) | C(2) | C(3) | Aromatic | Si—CH |
|---|---|---|---|---|---|
| H.Fur.Bzt. | 146.6 | 13.8 | 142.5 | 120.4, 121.8, 122.3, 123.7 126.5, 127.2, 127.8, 128.5 | — |
| $Me_2Si(Fur.Bzt)Cl$[a] | 158.5 | 15.0 | 152.7 | 121.6, 122.8, 123.0, 124.5 126.8, 127.8, 128.3, 129.4 | 14.3 |
| $Me_2Si(Fur.Bzt)_2$[b] | 160.2 | 15.4 | 154.5 | 122.0, 123.1, 123.5, 124.7 127.2, 128.3, 128.8, 129.7 | 13.0 |
| P.Pyd.Bzt | 151.2 | 13.1 | 139.6 | 123.2, 121.3, 120.4, 121.8 125.2, 126.5, 125.6, 125.8 | — |
| $Me_2Si(Pyd.Bzt)Cl$ | 161.4 | 14.7 | 154.8 | 124.3, 121.7, 121.3, 122.4 125.6, 127.0, 126.0, 126.5 | 15.4 |
| $Me_2Si(Pyd.Bzt)_2$ | 163.5 | 15.2 | 156.6 | 125.4, 122.3, 121.9, 122.7 126.0, 127.7, 126.6, 126.8 | 14.7 |

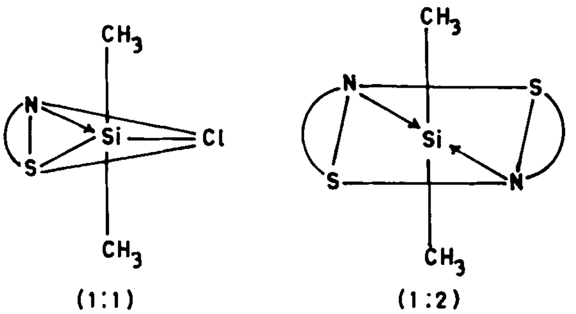
[a] Structure:



[b] Structure:



On the basis of the above spectral studies, trigonal bipyramidal and octahedral geometries are suggested for $Me_2Si(N—S)Cl$ and $Me_2Si(N—S)_2$ types of complexes respectively (illustrated in Scheme 1).



(1:1) (1:2)

Scheme 1

## BIOLOGICAL STUDIES

### Antibacterial activity

The antibacterial activity of two ligands, H.Pyd.Bzt and H.Thiop.Bzt, as well as their corresponding dimethylsilicon(IV) complexes has been tested against the bacteria *Escherichia coli*, *Staphylococcus aureus*, *Enterobacter aerogenes* and *Staphylococcus citrus* at 1000 ppm concentration using the inhibition zone technique. The discs, made of Whatman No. 1 filter paper having a diameter of 5 mm, were soaked in methanolic solutions of the compounds. These discs were placed on the appropriate medium, previously seeded with organisms in Petri dishes and stored in an incubator at 30 ± 1 °C. The inhibition zone around each disc was measured after 24 h: the results of these studies are recorded in Table 4.

### Fungicidal activity

The above-mentioned compounds were also screened for their antifungal activity against the fungi *Helminthosporium graminium*, *Aspergillus niger* and *Alternaria alternata* by the agar plate technique at two different concentrations. The compounds were directly mixed with the medium (potato, dextrose, agar and distilled water) at 50 ppm and 75 ppm concentrations and the linear growth of the fungus was obtained by measuring the fungal colony diameter after five days (Table 5). The amount of growth inhibition in all the replicates was recorded and calculated by the equation:

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

**Table 4** Antibacterial activity of ligands and their corresponding diorganosilicon(IV) complexes

| | Zone of inhibition (mm) | | | |
|---|---|---|---|---|
| Compound | *E. coli* | *S. aureus* | *Enterobacter aerogenes* | *S. citrus* |
| H.Pyd.Bzt | 10 | 13 | 15 | 20 |
| H.Thiop.Bzt | 12 | 16 | 19 | 22 |
| $Me_2Si(Pyd.Bzt)Cl$ | 14 | 19 | 23 | 25 |
| $Me_2Si(Pyd.Bzt)_2$ | 17 | 22 | 24 | 29 |
| $Me_2Si(Thiop.Bzt)Cl$ | 19 | 25 | 28 | 29 |
| $Me_2Si(Thiop.Bzt)_2$ | 21 | 28 | 31 | 32 |

where $C$ = diameter of fungal colony on the control plate and

$T$ = diameter of fungal colony on the test plate.

The results reported in Tables 4 and 5 reveal that all the silicon compounds are much more toxic towards all the test organisms than are the ligands themselves. This greater toxicity of organosilicon(IV) complexes than the ligands alone can be explained in the light of chelation theory. Chelation reduces the polarity of the metal/non-metal ion ($M^+$) owing to sharing of its positive charge and possible $\pi$-electron delocalization over the whole chelate ring. This increases the lipophilic character of the complexes so that they can pass through the lipoid layers of the organism cell membrane and thus can interfere in the normal cellular processes. It has also been observed that the fungitoxicity of ligands and their complexes decreases on lowering the concentration. However the toxicity of H.Thiop.Bzt and its complexes is somewhat greater than that of other compounds studied, possibly due to the different sulfur content. It has been suggested that sulfur competes more successfully than oxygen for protons and electrons in fungal respiration and removes electrons between cytochromes *b* and *c* of the electron transport system.

## Antifertility activity

Transition metals have long been reported to possess antitesticular activity and metal complexes containing heterocyclic rings such as furan, benzofuran and pyridine have been shown to exhibit antioestrogenic and antitesticular activities.[13] A large number of silicon complexes[21] have been shown to cause atrophy of the testis, prostate and epididymis in male mice; keeping these facts in view, studies on the antifertility activity of the ligands H.Thiop.Bzt and H.Pyt.Bzt along with their silicon complexes in male mice have been undertaken (Table 6).

Colony-bred adult mice were used and 75 male mice (body weight 40–50 g) were divided randomly into five groups of 15 animals each. The animals were kept in plastic cages measuring 25 cm × 20 cm × 20 cm; five animals were housed in each cage. The animals were maintained on mice feed pellets (Hindustan Lever Ltd, India),

**Table 5** Antifungal activity of ligands and their corresponding diorganosilicon(IV) complexes

| | Average percentage inhibition after 5 days | | | | | |
|---|---|---|---|---|---|---|
| | *Helminthosporium* | *graminium* | *Asp. niger* | | *Alt. alternata* | |
| Compound | 50 ppm | 75 ppm | 50 ppm | 75 ppm | 50 ppm | 75 ppm |
| H.Pyd.Bzt | 73 | 77 | 41 | 43 | 64 | 70 |
| H.Thiop.Bzt | 76 | 80 | 43 | 45 | 65 | 74 |
| $Me_2Si(Pyd.Bzt)Cl$ | 79 | 83 | 46 | 50 | 72 | 78 |
| $Me_2Si(Pyd.Bzt)_2$ | 81 | 85 | 49 | 56 | 76 | 82 |
| $Me_2Si(Thiop.Bzt)Cl$ | 84 | 88 | 55 | 60 | 79 | 85 |
| $Me_2Si(Thiop.Bzt)_2$ | 86 | 93 | 58 | 64 | 83 | 90 |

**Table 6** Antifertility activity of ligands and their dimethylsilicon(IV) complexes

| Compound | Sperm motility (%) | Sperm count in cauda epididymis ($\times 10^6$ ml$^{-1}$) |
|---|---|---|
| Vehicle alone (olive oil) | $83.4 \pm 4.8$ | $25.4 \pm 3.0$ |
| H.Pyd.Bzt | $32.6 \pm 5.5^b$ | $11.5 \pm 3.3^d$ |
| H.Thiop.Bzt | $30.2 \pm 6.0^b$ | $8.6 \pm 3.5^d$ |
| $Me_2Si(Pyd.Bzt)Cl$ | $22.5 \pm 2.8^a$ | $6.8 \pm 1.7^a$ |
| $Me_2Si$ $(Pyd.Bzt)_2$ | $20.3 \pm 2.5^a$ | $5.4 \pm 1.1^a$ |
| $Me_2Si$ $(Thiop.Bzt)Cl$ | $16.0 \pm 2.1^a$ | $4.0 \pm 1.1^a$ |
| $Me_2Si$ $(Thiop.Bzt)_2$ | $14.3 \pm 1.5^a$ | $3.2 \pm 1.6^a$ |

Values are expressed as mean ± s.e.
$^a$ $P<0.01$, $^b$ $P<0.02$, $^d$ $P<0.05$.

and water was provided *ad libitum*. Only six compounds were used separately, and each compound was administered at a dose level of 10 mg (kg body wt)$^{-1}$ day$^{-1}$ orally by gavage tube for 25 days. One group served as control, and olive oil was used as vehicle. Five animals from each group were autopsied 24 h after the last administration and reproductive organs were dissected out, freed from adherent tissues and weighed to the nearest milligram. The sperm motility and the density in the cauda epididymis were measured by using Neubar's hemocytometer according to the reported method. It was observed that motility and sperm count decreased after the administration of ligands and their complexes. Necrosis of the testis was observed in treated mice, and the spermatogenia and accessory sex organs were also affected. The prostate gland became swollen and did not become normal even after 30 days of recovery, showing the probably irreversible nature of the effects. A significant decrease ($P<0.01$) in motility from $83.4 \pm 4.8$ to $30.2 \pm 6.0\%$ was observed in animals treated with the ligands and the sperm count also decreased ($P<0.05$) from 25.4 ($\pm 3.0$) $\times 10^6$ ml$^{-1}$ to 8.6 ($\pm 3.5$) $\times 10^6$ ml$^{-1}$. A highly significant ($P<0.001$) decline in sperm motility was observed in the case of dimethylsilicon(IV) complexes derived from H.Thiop.Bzt. The sperm count was also found to decrease significantly in the treated animals. The antifertility activity data indicate that the ligands and their complexes affect the motility as well as the sperm count in male mice. Further, it is also observed that the ligands themselves are able to inhibit fertility but due to the synergistic effects of the silicon complexes their activity is enhanced. Further studies in this area might lead to the development of a safer and more acceptable male oral contraceptive.

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