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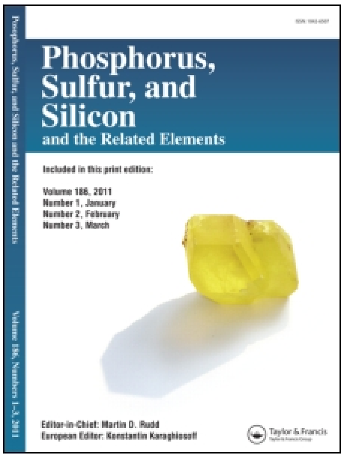

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Multinuclear Magnetic Resonance and Related Studies of Coordination Compounds of Organosilicon with Mixed Azines

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Multinuclear Magnetic Resonance and Related Studies of Coordination Compounds of Organosilicon with Mixed Azines

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New hexa-coordinated complexes of organosilicon (IV) have been synthesized by the reactions of diethoxydimethylsilane with the mixed azines. Their structures have been inferred based on elemental analysis, UV, IR, and multinuclear magnetic resonance spectral studies. The monomeric and nonelectrolytic nature of these complexes has been confirmed by molecular weight determinations and conductance measurements. The mixed azines and their silicon complexes also have been screened for their antimicrobial activities against several fungi and bacteria and were found to be quite active in this respect.

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Keywords Antimicrobial studies; mixed azines; organosilicon (IV) complexes; spectral studies

INTRODUCTION

Silicon complexes containing Si-O-C, Si-N-C, and Si-C bonding play an important role in vital processes and have specific effects on the living organisms. They are also found useful in polymer and textile chemistry, space exploration, and cosmetics. The studies on the physical, chemical and biological properties[1]of organosilicon derivatives of amino alcohols have provided valuable information about the influence of the amino group on the strength and reactivity of the Si-O bond in aminoalkoxysilanes and about the degree of intermolecular interaction between the nitrogen atom of the aminoalkoxy group, and

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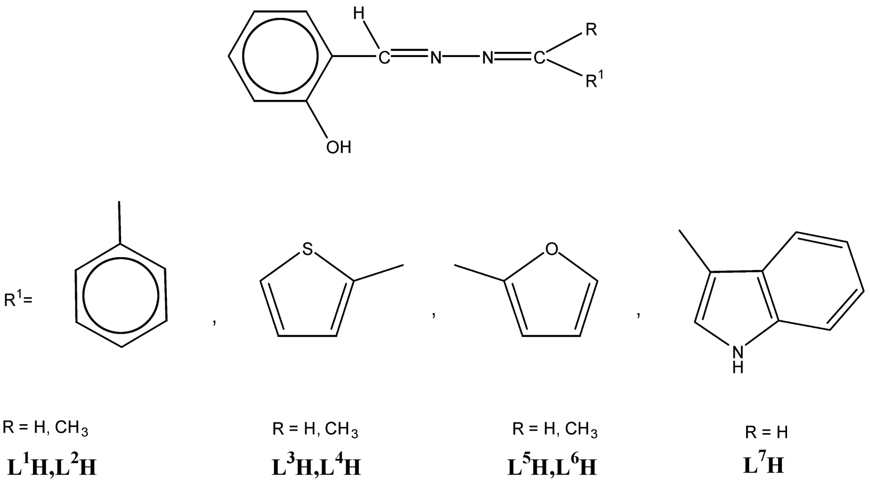

FIGURE 1 Mixed azines used as ligands in this work.

the silicon atom leading to the formation of a strong donor acceptor Si←N bond in these derivatives.[2] Azines constitute an important class of nitrogen donor ligands. Therefore, it was considered worthwhile to synthesize the organosilicon derivatives of biologically active ligands of mixed azines. The structures of the ligands are shown in Figure 1.

EXPERIMENTAL

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

The analyses of carbon, hydrogen, nitrogen, sulfur, and silicon in complexes were carried out as reported earlier.[3–5] The IR spectra were recorded on a Perkin-Elmer 577 IR spectrophotometer in the region 4000–4200 cm^{-1} using KBr optics. The electronic spectra (in methanol) were taken with a Toshniwal Spectrophotometer. A Perkin-Elmer Mode RB-12 Spectrometer was used to obtain the ^1H NMR spectra, DMSO-d_6 was used as the solvent. ^{13}C NMR spectra were recorded on a 90 MHz Jeol NMR spectrometer using dry DMSO as the solvent and TMS as the internal standard. The ^{29}Si NMR spectra were recorded at 17.75 MHz using DMSO as solvent. Molar conductance measurements were made in anhydrous dimethylformamide at 36 ± 1°C using a Model-305 Systronics conductivity bridge. Molecular weight determinations were carried out by the Rast camphor method.[6]

TABLE I Physical Properties and Analytical Data of Ligands

S. no.	Ligand	Color and state	M.p. (°C)	Elemental analysis (%) C found (calcd.)	H found (calcd.)	N found (calcd.)	S found (calcd.)	Mol. wt. found (calcd.)
1.	L^1H	Lemon yellow, shiny crystal	152	74.82 (74.98)	5.24 (5.39)	12.32 (12.49)	—	216.88 (224.24)
2.	L^2H	Yellow, shiny crystal	163	75.66 (75.76)	5.82 (5.92)	11.66 (11.76)	—	224.76 (238.27)
3.	L^3H	Greenish brown, shiny crystal	166	62.44 (62.59)	4.24 (4.38)	12.04 (12.16)	13.76 (13.92)	218.11 (230.27)
4.	L^4H	Brown, solid	172	63.82 (63.91)	4.79 (4.95)	11.32 (11.47)	13.02 (13.12)	236.32 (244.30)
5.	L^5H	Reddish brown, needle like crystal	198	67.20 (67.28)	4.58 (4.71)	12.96 (13.08)	—	202.12 (214.20)
6.	L^6H	Reddish brown, solid	181	68.32 (68.41)	5.22 (5.30)	12.11 (12.27)	—	220.64 (228.23)
7.	L^7H	Light red, solid	175	72.86 (72.99)	4.80 (4.98)	15.88 (15.96)	—	250.67 (263.28)

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Synthesis of Ligands

The ligands were synthesized by the condensation of salicylaldehyde and hydrazine with aldehydes/ketones *viz.* benzaldehyde, acetophenone, thiophene- 2-aldehyde[7], 2-furyl methyl ketone, indol-3-carboxaldehyde, furfuraldehyde, and 2-acetyl thiophene in 1:1:1 molar ratio using ethanol as the reaction medium. The solution was refluxed on a water bath for 3-4 hours and then allowed to cool at room temperature. The crystals that separated out were washed with ethanol, recrystallizd from the same solvent and dried in vacuo. Their elemental analysis and physical properties are given in Table I.

Synthesis of Organosilicon Complexes

The calculated amount of diethoxydimethylsilane was added to the weighed amount of ligand in 1:2 molar ratios in benzene as the reaction medium. The reactants were refluxed for about 5 hrs to complete the reaction. The ethanol liberated in the reaction was removed azeotropically with benzene. The resulting products were rendered free from solvent. The products so formed were finally dried in vacuo at 40 ± 5° for 2–3 hours after repeated washing with dry cyclohexane. The compounds were purified by recrystallization from benzene and washing with dry cyclohexane. Their physical properties and analytical data are recorded in Table II.

RESULTS AND DISCUSSION

The reactions of diethoxydimethylsilane with these ligands are as follows:

$$(CH_3)_2\,Si\,(OC_2H_5)_2 + 2LH \xrightarrow[\text{Benzene,}]{1:2} (CH_3)_2\,SiL_2 + 2C_2H_5OH. \qquad (1)$$

where LH represents the mixed azines shown in Figure 1. On refluxing for about 5 h, the resulting complexes are obtained as colored solids or semisolids. These complexes are sensitive to moisture. The molar conductance value of 10^{-3}M solutions of the complexes (10–15 ohm^{-1} cm^{2} mol^{-1}) in DMF showed them to be non-electrolytes. The monomeric nature of these complexes was confirmed by their molecular weight determinations.

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Electronic Spectra

In the electronic spectra of ligands, a band at ~ 216 nm is observed due to the B band of the benzene ring, which is shifted to a higher wave number side on complexation. The band observed at ~ 340 nm in the ligand is the secondary band of benzene and which gets red shifted due to the presence of >C=N-N=C< grouping. However, this band appears at ~ 370 nm in the complexes possibly due to the polarization in >C=N- bond caused by silicon ligand electron interaction.

Infrared Spectra

The IR spectra of ligands show a broad and strong absorption band in the region 3150–2850 cm^{-1} attributable to v (OH) mode indicating that the hydroxyl groups are strongly hydrogen bonded with the azomethine nitrogen.[8] It disappears in the spectra of the silicon complexes showing thereby the deprotonation of this functional group. One strong band in all the ligands at ~ 1620 cm^{-1} due to v(C=N) gets split into two sharp bands at ~ 1630 cm^{-1} and ~ 1600 cm^{-1}on complex formation. The band at ~ 1630 cm^{-1}in the metal complexes, indicates the coordination of the azomethine nitrogen to the silicon atom,[9] whereas the other one is due to uncoordinated azomethine group. The phenolic v (C-O) and v (N-N) respectively at ~1260 and ~970 cm^{-1}are also shifted to higher frequency region because of complex formation. The appearance of new and strong medium intensity bands at ~ 625 cm^{-1} assignable to v (Si-O)

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TABLE II Physical Properties and Analytical Data of Silicon Complexes

				Elemental analysis (%)						
Reactants	Product (compound number)	Color and state	M.p. (°C)	C found (calcd.)	H found (calcd.)	N found (calcd.)	Si found (calcd.)	S found (calcd.)	Mol. wt. found (calcd)	Molar conductance (Ohm^{-1}cm^2 mol^{-1})
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^1H	$(CH_3)_2$ $Si(L^1)_2$(1)	Reddish brown solid	182	71.05 (71.40)	5.41 (5.59)	10.98 (11.10)	5.42 (5.57)	—	496.66 (504.63)	10.2
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^2H	$(CH_3)_2$ $Si(L^2)_2$ (2)	Cream solid	148 (d)	71.86 (72.15)	5.86 (6.05)	10.44 (10.52)	5.15 (5.27)	—	520.86 (532.68)	10.5
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^3H	$(CH_3)_2$ $Si(L^3)_2$ (3)	Dark brown solid	204	60.22 (60.43)	4.48 (4.68)	10.68 (10.84)	5.28 (5.44)	12.22 (12.41)	504.12 (516.69)	14.7
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^4H	$(CH_3)_2$ $Si(L^4)_2$ (4)	Dark brown solid	195	61.54 (61.73)	5.04 (5.18)	10.08 (10.28)	5.05 (5.16)	11.58 (11.77)	531.87 (544.74)	11.6
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^5H	$(CH_3)_2$ $Si(L^5)_2$ (5)	Brown solid	177	64.28 (64.44)	4.76 (4.99)	11.37 (11.56)	5.67 (5.80)	—	471.32 (484.55)	12.1
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^6H	$(CH_3)_2$ $Si(L^6)_2$ (6)	Dark brown solid	161. (d)	65.51 (65.60)	5.32 (5.51)	10.81 (10.93)	5.36 (5.48)	—	507.10 (512.60)	14.3
$(CH_3)_2$ $Si(OC_2H_5)_2$ L^7H	$(CH_3)_2$ $Si(L^7)_2$ (7)	Reddish brown semi solid	—	69.86 (70.08)	5.08 (5.19)	14.31 (14.42)	4.72 (4.82)	—	570.65 (582.70)	12.4

TABLE III H NMR Spectral Data (δ ppm) of Ligands and the Organosilicon (IV) Complexes

Ligand/complexes	−OH	H-C=N	$-CH_3$
L^1H	12.90	8.80	—
$(CH_3)_2$ Si$(L^1)_2$ (1)	—	9.10	1.56
L^2H	13.10	8.70	—
$(CH_3)_2$ Si$(L^2)_2$ (2)	—	9.21.	1.60
L^3H	13.35	8.86	—
$(CH_3)_2$ Si$(L^3)_2$ (3)	—	9.11	1.57
L^4H	13.40	8.85	—
$(CH_3)_2$ Si$(L^4)_2$ (4)	—	9.13.	1.53
L^5H	12.99	8.88	—
$(CH_3)_2$ Si$(L^5)_2$ (5)	—	9.11	1.50
L^6H	13.05	8.90	—
$(CH_3)_2$ Si$(L^6)_2$ (6)	—	9.13	1.62
L^7H	13.15	8.84	—
$(CH_3)_2$ Si$(L^7)_2$ (7)	—	9.16	1.59

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frequencies[11], at ~ 568 cm^{-1}assignable to v (Si←N) frequencies[12–14] and at ~ 1265 and 760 cm^{-1} due to the asymmetric deformation[13] mode of CH_3-Si and stretching vibration of Si-C, respectively, in the spectra of complexes further support the formation of coordination compounds.

^{1}H NMR Spectra

The proton signal of the azomethine moiety (-HC=N) observed at δ 8.70–8.90 ppm in the spectra of the ligand and it gets shifted downfield in the spectra of silicon complexes, which is attributed to the donation of the lone pair electrons by the azomethine nitrogen to the silicon atom. The aromatic proton signal at δ 7.75–7.10 ppm remain almost unchanged. A broad signal observed at δ 12.90–13.40 ppm due to OH proton in the ligands are not observed in the spectra of the corresponding silicon complexes showing thereby the chelation of the ligand moiety through deprotonated phenolic oxygen. Further, new signals at δ1.50–1.62 ppm in the complexes are due to the methyl protons of Me_2 Si group (Table III).

^{13}C NMR Spectra

The ^{13}C NMR spectra of L^1H, L^2H and their corresponding silicon complexes have been recorded in Table IV. The signals due to the carbon atoms attached to the phenolic and the azomethine groups in

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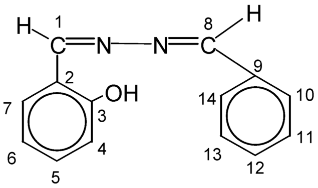
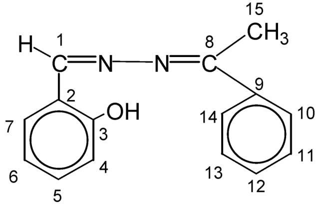
TABLE IV ^{13}C NMR Spectral Data (δ ppm) of Ligands and Their Organosilicon(IV) Complexes

	Chemical shift in δ ppm												
Compounds	1	2	3	4	5	6	7	8	9	10	11	12	15
L^1H	175.7	117.4	155.1	115.9	129.1	118.4	127.2	176.3	136.2	129.5	128.7	134.2	—
$(CH_3)_2Si(L^1)_2$	165.2	118.2	164.2	117.3	129.5	119.5	128.2	181.4	136.9	129.9	129.1	135.2	—
L^2H	173.5	115.9	153.2	118.2	129.9	119.4	128.2	168.4	135.2	129.3	128.9	133.9	13.8
$(CH_3)_2Si(L^2)_2$	167.4	117.2	161.2	119.9	130.2	121.4	129.9	171.2	136.4	130.4	129.9	134.9	14.6

L^1H



L^2H



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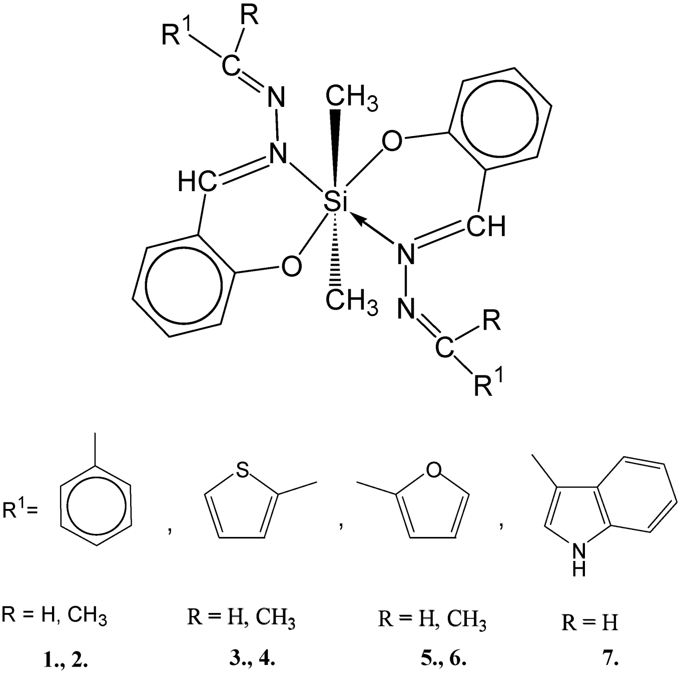

FIGURE 2 Suggested structures of the Si(IV) complexes.

the ligands appear at δ 155.1, δ 153.2 and δ 175.7, δ 173.5 ppm respectively. However, in the spectra of the corresponding silicon complexes these signals appear at δ 164.1, δ 161.2 and δ 165.2 and δ 167.4 ppm respectively. The considerable shifts in the carbon atoms attached to nitrogen and oxygen indicate the involvement of nitrogen and oxygen atom in coordination with the silicon atom.

TABLE V ^{29}Si NMR Spectral Data of Silicon Complexes

Compound number	δ ppm
$(CH_3)_2$ $Si(L^1)_2$ (1)	−157.63
$(CH_3)_2$ $Si(L^2)_2$ (2)	−157.80
$(CH_3)_2$ $Si(L^3)_2$ (3)	−158.35
$(CH_3)_2$ $Si(L^4)_2$ (4)	−158.46
$(CH_3)_2$ $Si(L^5)_2$ (5)	−157.98
$(CH_3)_2$ $Si(L^6)_2$ (6)	−157.82
$(CH_3)_2$ $Si(L^7)_2$ (7)	−158.50

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TABLE VI Antimicrobial Activity of the Ligands and Their Silicon (IV) Complexes

Microorganism		L^1H	1.	L^2H	2.	L^3H	3	L^4H	4	L^5H	5	L^6H	6	L^7H	7
S. aureus	IZ	7.5	9.0	10.1	11.6	9.1	11.6	8.2	7.9	8.4	10.4	9.6	8.7	11.3	9.5
	(AI)	(0.52)	(0.62)	(0.70)	(0.80)	(0.63)	(0.80)	(0.59)	(0.54)	(0.58)	(0.72)	(0.67)	(0.60)	(0.78)	(0.66)
E. coli	IZ	8.6	10.1	6.6	8.7	6.3	9.4	6.7	7.3	10.4	9.5	10.8	8.5	9.3	8.9
	(AI)	(0.67)	(0.79)	(0.51)	(0.67)	(0.49)	(0.73)	(0.52)	(0.57)	(0.80)	(0.74)	(0.84)	(0.66)	(0.72)	(0.69)
A. niger	IZ	6.2	7.3	5.4	6.8	6.3	8.7	8.2	7.5	6.4	8.5	6.5	6.9	7.9	6.6
	(AI)	(0.69)	(0.81)	(0.60)	(0.75)	(0.70)	(0.97)	(0.91)	(0.83)	(0.71)	(0.97)	(0.94)	(0.76)	(0.87)	(0.73)
A. flavus	IZ	4.6	6.9	7.7	6.7	6.0	6.9	6.5	7.2	5.3	6.8	7.3	7.0	7.3	5.5
	(AI)	(0.56)	(0.84)	(0.93)	(0.81)	(0.73)	(0.84)	(0.79)	(0.87)	(0.64)	(0.82)	(0.89)	(0.85)	(0.89)	(0.67)
R. phaseoli	IZ	6.0	7.9	6.2	7.8	6.2	6.3	7.4	5.5	5.6	5.9	7.2	7.4	7.5	6.4
	(AI)	(0.75)	(0.98)	(0.75)	(0.97)	(0.77)	(0.78)	(0.92)	(0.68)	(0.70)	(0.73)	(0.90)	(0.92)	(0.92)	(0.80)

IZ = Inhibition zone (in mm); and AI = activity index (inhibition zone of test compound/Inhibition zone of standard).

^{29}Si NMR Spectra

^{29}Si NMR spectra of silicon complexes have been recorded and given in Table V. A sharp signal at $\delta-$ 158.50 to $\delta-$ 157.63 ppm clearly indicates the six-coordinated environment around the silicon.[15]

Based on the above spectral studies, the following octahedral geometry has been suggested for the silicon (IV) complexes.

Antimicrobial Activity

The antimicrobial activity of a few ligands and their corresponding complexes were tested by paper disc method[16] for their antimicrobial activities at a concentration of 1 mg/disc. Streptomycin and Micostatin were used as the reference compounds for antibacterial and antifungal activities, respectively. The data are presented in Table VI. They were tested against *S. aureus, E. coli* (bacteria) and *A. niger, A. flavus, R. phaseoli* (fungi). The results have been recorded in the form of inhibition zones (diameter in mm) and activity index.

Further, the silicon complexes are more active as compared to the free ligands, indicating that complexation increases the activity, and the preliminary results achieved have led us to conclude that this type of complex should be studied in detail for their applications in diverse areas.

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REFERENCES

[1] C. Eaborn, *Organosilicon Compounds* (Butterworth Scientific Publications, London, 1960), p. 473.
[2] M. G. Voronkov and E. Y. Lukevics, *Russ. Chem. Rev*., **38,** 975 (1969).
[3] M. Sharma, H. L. Singh, S. Varshney, P. Sharma, and A. K. Varshney, *Phosphorus, Sulfur, and Silicon*, **178,** 811 (2003).
[4] A. K. Varshney, S. Varshney, M. Sharma, and H. L. Singh, *Phosphorus, Sulfur, and Silicon,* **161,** 163 (2000).
[5] H. L. Singh, M. Sharma, and A. K. Varshney, *Synth. React. Inorg. Met.-Org. Chem.,* **29,** 817 (1999).
[6] S. Glasstone and D. Lewis,*The Elements of Physical Chemistry* (MacMillan, London (1968), p. 242
[7] M. S. K. Youssef, *J. Chem. Technol. Biotechnol.,* **31,** 363 (1981).
[8] H. H. Freedman, *J. Am. Chem. Soc.*, **83,** 2900 (1961).
[9] B. Samual, R. Snaith, C. Summerford, and K. Wade, *J. Chem. Soc. (A),* 2019 (1970).
[10] N. S. Biradar and V .S. Kulkarni, *Z. Anorg. Allg. Chem.,* **281,** 312 (1971).
[11] W. Newton and E. G. Rochow, *J. Chem. Soc. (A),* 2664 (1970).
[12] A. Saxena and J. P. Tandon, *Ind. J. Chem.,* **24A,** 419 (1985).
[13] C. Gildewell and D.W.H. Rankin, *J. Chem. Soc. (A),* 753 (1969).
[14] E. A. V. Ebsworth and M. J. Mays, *J. Chem. Soc.,* 3450 (1964).
[15] M. S. Singh and P. K. Singh, *Synth. React. Inorg. Met.- Org. Chem.,* **33,** 271 (2003).
[16] N. H. Thronbery, *Phytopathology*, **40,** 419 (1950).