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Greener synthesis and biological application of organosilicon(IV) complexes derived from semicarbazone and thiosemicarbazone of 3-acetyl-2*H*-chromen-2-one by microwave irradiation

Abstract: A new series of silicon(IV) complexes have been synthesized by adopting classical thermal- and microwave-irradiated techniques. The complexes are prepared by the reaction of dimethyldichlorosilane and triphenylchlorosilane with the sodium salts of 1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)thiosemicarbazide and 1-(1-(2-oxo-2H-chromen-3-yl)ethylidene)semicabazide in 1:1 and/or 1:2 molar ratios. Characterization of the ligands as well as of the silicon complexes has been carried out on the basis of elemental analysis, melting point determinations, molecular weight determinations, infrared, ^{1}H NMR, ^{13}C NMR, ^{29}Si NMR, and electronic and mass spectral studies. Spectral studies confirm ligands to be monofunctional bidentate and trigonal bipyramidal and octahedral environments around silicon ions. The newly synthesized ligands and their complexes have been screened for antimicrobial, minimum inhibitory concentration, and pesticidal activities. The results obtained from bioassays indicate that this class of compounds can be utilized for the design of new substances with pesticidal activity and promising antimicrobial activity.

Keywords: antimicrobial activity; minimum inhibitory concentration; pesticidal activity; silicon(IV) complexes.

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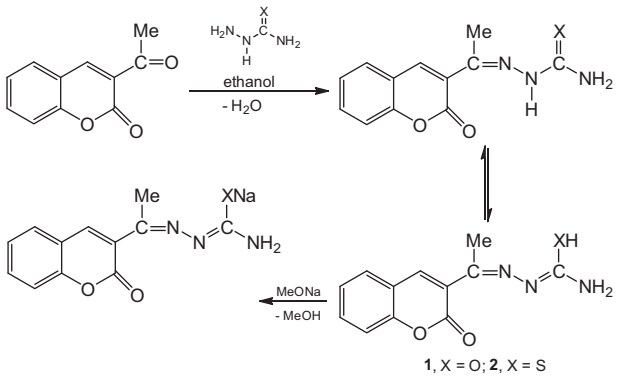
Introduction

The rapid rise in the industrial, agricultural, biological, and medical applications of organosilicon(IV) compounds during the last few decades has led to their accumulation in the environment and in biological systems. Generally, organosilicon compounds seem to owe their antitumor properties to the immuno-defensive system of the organism (Singh et al., 2011). The medical applications and effectiveness of silatranes in the treatment of wounds and tumors are thought to be related to the role of silicon in the growth of epithelial and connective tissues and hair, where its function is to impart strengths, elasticity, and impermeability to water (Singh et al., 2007; Singh and Pal 2010). Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups, and it is multiplied manyfold when the ligands have biological importance (Kulkarni et al., 2009). The number and diversity of nitrogen and sulfur chelating agents used to prepare new coordination and organometallic compounds have increased rapidly during the past few years (Baul, 2008; Li et al., 2009; Sharma et al., 2011). It is widely realized that the activity of certain natural products, drugs, and pesticides owes much to the presence of a coumarin nucleus in their molecules. Various widely used oral anticoagulants and rodenticides also incorporate the same nucleus. Schiff-base complexes of main group elements containing semicarbazones and thiosemicarbazones have remained a topic of research interest (Dawara and Singh, 2011), mainly due to the biological applications of ligands and compounds derived from them. Semicarbazones and thiosemicarbazones have attracted special attention due to their biological activities. Accordingly, synthesis, characterization, and biological evaluation of some organosilicon(IV) complexes of coumarin-based imines having substituent **1** and **2** have been reported (Scheme 1).

Results and discussion

The ligands and complexes synthesized according to Scheme 1 and to Equations (1), (2), and (3), respectively,



Scheme 1 Synthesis of ligands **1** and **2**.

are soluble in dimethylformamide (DMF) and dimethyl sulfoxide (DMSO). The reactions were carried out in perfectly dry methanol and proceed smoothly with the precipitation of NaCl.

$$Ph_3SiCl + RN{=}C(NH_2)XNa \xrightarrow[-NaCl]{methanol} Ph_3SiXC(NH_2){=}NR \quad (1)$$

3, X = O; **4**, X = S

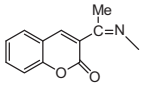
$$Me_2SiCl_2 + RN{=}C(NH_2)XNa \xrightarrow[-NaCl]{methanol} Me_2Si(Cl)XC(NH_2){=}NR \quad (2)$$

5, X = O; **6**, X = S

$$Me_2SiCl_2 + 2\,RN{=}C(NH_2)XNa \xrightarrow[-2\,NaCl]{methanol} Me_2Si[XC(NH_2){=}NR]_2 \quad (3)$$

7, X = O; **8**, X = S

R =



The low values of molar conductivity (9–17 Ω^{-1} cm^2 mol^{-1}) of the resulting silicon complexes in anhydrous DMF show them to be non-electrolytes.

Electronic spectra

The electronic spectra of ligands **1** and **2** recorded in methanol display two maxima at ~276 and ~326 nm which are due to π-π^* electronic transitions and remain almost unchanged in the spectra of the silicon complexes (**3–8**). The band around 370 nm is due to the n-π^* transitions of the >C=N chromophore which undergoes a blue shift in the complexes due to the polarization within the >C=N chromophore caused by the silicon-ligand electron interaction during the chelation. The shift of this band in the spectra of the complexes suggests the coordination of nitrogen to metal atom.

Infrared spectra

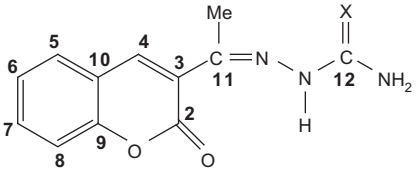
The tentative absorption frequencies of **1** and **2** and their silicon complexes (**3–8**) along with their assignments are reported in Table 1. The infrared (IR) spectra of the free ligands **1** and **2** display absorption bands at 3300–3250, 1600–1610, and 1080/1690 cm^{-1} due to –(NH), (>C=N), and (>C=S)/(>C=O), respectively. The bands at ca. 1720–1725 cm^{-1} due to (>C=O) of lactone moiety of the ligands remain almost unchanged in the complexes, indicating their non-involvement in complexation. The broad band due to –(NH) vibrations disappears in the spectra of the complexes, indicating the deprotonation of this group on coordination with the silicon atom. The negative shift (10–20 cm^{-1}) of the (>C=N) band observed in all the complexes indicates the involvement of azomethine nitrogen upon complexation. The bands due to (>C=S) and (>C=O) are shifted towards lower frequencies in the complexes, indicating coordination of sulfur and oxygen to the central silicon atom. The spectra of the free ligands display two sharp bands at 3400–3500 and 3350–3400 cm^{-1} due to the asymmetric and symmetric vibrations of the NH_2 group, respectively, which remain at almost the same positions in the spectra of the complexes, suggesting that the NH_2 group is not involved in chelation. New bands are observed in the spectra of the complexes at ca. 573–577 cm^{-1} due to the ν(Si←N) vibrations. The presence of only one ν(Si-N) band in the present case suggests that complexes exist in

Table 1 IR (cm^{-1}) and ^{1}H NMR (δ, ppm) spectral data of the ligands and their corresponding complexes.

Compound	IR spectral data (cm^{-1})				^{1}H NMR spectral data (δ, ppm)			
	(>C=N)	ν(NH)	ν (Si←N)	ν (Si-Cl)	–NH	–NH_2	M-CH_3	Aromatic protons (m)
2	1600	3150–3300	–	–	8.69	3.45	–	6.45–8.12
4	1592	–	574	–	–	3.42	–	6.95–8.18
6	1593	–	575	435	–	3.43	1.10	7.70–8.24
8	1595	–	573	–		3.44	1.21	6.99–8.40
1	1610	3100–3300	–	–	8.49	3.42	–	6.42–8.02
3	1600	–	575	–	–	3.40	–	7.15–8.38
5	1605	–	577	438	–	3.41	1.08	7.36–9.40
7	1598	–	576	–		3.44	1.20	7.32–9.40

Table 2 ^{13}C NMR (δ, ppm) spectral data of the ligands and their corresponding complexes.

Compound	Azomethine	>C=O/>C=S	Si-CH_3	C_2–C_7	C_3–C_8	C_4–C_9	C_5–C_{10}	C_6–
2	154.35	163.50	–	160.75–128.16	101.46–114.66	157.71–154.12	127.21–132.76	125.30–
4	150.58	–	–	160.10–128.38	102.00–114.13	157.10–153.35	125.66–132.10	124.50–
6	149.63	–	14.20	160.24–129.45	101.00–114.55	158.22–154.44	126.56–133.01	123.89–
8	148.15	–	15.21	161.02–129.32	102.00–115.40	157.65–154.56	125.65–133.14	125.40–
1	153.35	169.50	–	161.95–129.56	100.36–115.36	158.91–154.32	127.58–133.56	125.36–
3	150.98	–	–	160.26–128.98	102.01–114.65	157.32–153.26	126.36–132.85	124.58–
5	148.32	–	14.50	160.14–129.01	101.02–114.95	158.32–154.84	126.56–132.99	124.69–
7	149.95	–	15.30	161.02–129.32	102.03–115.52	157.65–154.01	125.65–133.01	125.00–



the *trans* form. It has been reported that the *cis* form of 1:2 complexes gives rise to two ν(Si-N) bands, whereas in the *trans* form only one IR-active ν(Si-N) band is observed. These remain absent in the spectrum of the ligand. In the dimethylsilicon(IV) complexes, a band at ca. 1420 cm^{-1} has been ascribed to the asymmetric deformation vibrations of the CH_3-Si group, whereas the band at ca. 1270 cm^{-1} is ascribed to the symmetric deformation mode of the CH_3-Si group (Jain and Singh, 2003).

^{1}H NMR spectra

Further evidence for the coordinating mode of the ligands was obtained from ^{1}H NMR spectra (Table 1). The broad signal due to the –NH proton in the ligand disappears in the case of silicon complexes, showing the coordination of silicon to nitrogen after the deprotonation of the functional group. The additional signal in region δ (1.08 and 1.21 ppm) of type **6**, **8**, **3**, and **5** complexes is due to the Me_2Si group. The ligands show a complex pattern in the region δ 8.02–6.45 ppm for the aromatic protons, and this is observed in the region δ 9.40–6.95 ppm in the spectra of organosilicon(IV) complexes. This shifting also supports the coordination through the nitrogen atom.

^{13}C NMR spectra

The conclusions drawn from the ultraviolet (UV), IR, and ^{1}H NMR spectra are concurrent with the ^{13}C NMR spectral data regarding the confirmation of the proposed structures. ^{13}C NMR spectra of the ligands and their silicon complexes were also recorded in dry DMSO-d_6. The shifting of the signals due to carbon attached to the azomethine nitrogen in the spectra of the complexes further supports the involvement of this group in complexation (Table 2).

^{29}Si NMR spectra

The ^{29}Si NMR spectra of **4**, **6**, **3,** and **5** give sharp signals at δ-1 to δ-98 ppm, and the spectra of **7** and **8** give sharp signals at δ-28 to δ-10 ppm, which clearly indicates the penta- and hexa-coordinated environments, respectively, around the silicon atom (Singh et al., 2004).

Mass spectra

The electron ionization mass spectrum of complex **4** was studied as a representative case. The molecular ion peak for complex **4** was observed at *m/z* 503.40, and this is in good agreement with its molecular weight, which suggests the monomeric nature of the complex.

Thus, on the basis of the above spectral features, as well as of the analytical data, the penta-coordinated trigonal bipyramidal and hexa-coordinated octahedral geometries shown in Figure 1 have been suggested for the organosilicon(IV) complexes.

Biological aspects

In the present study, the ligands and their Si(IV) complexes were evaluated for their antimicrobial activity against two bacteria, *Escherichia coli* (ATCC25922) and *Bacillus subtilis* (ATCC6633), and two fungi, *Fusarium oxysporum* (ATCC7808) and *Rhizopus nigricans* (ATCC6227b). The results are summarized in Graphs 1 and 2. The results were compared with those of standard drugs: imipinem for bacteria and Bavistin for fungi. Both the ligands and their respective Si(IV) complexes were found to be sensitive against all the fungal and bacterial strains. The

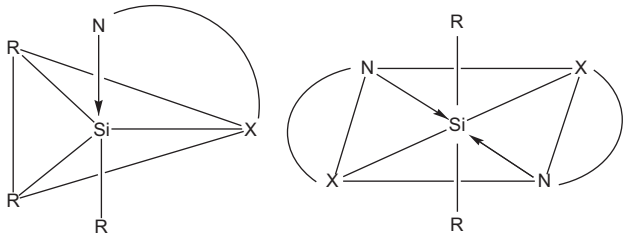
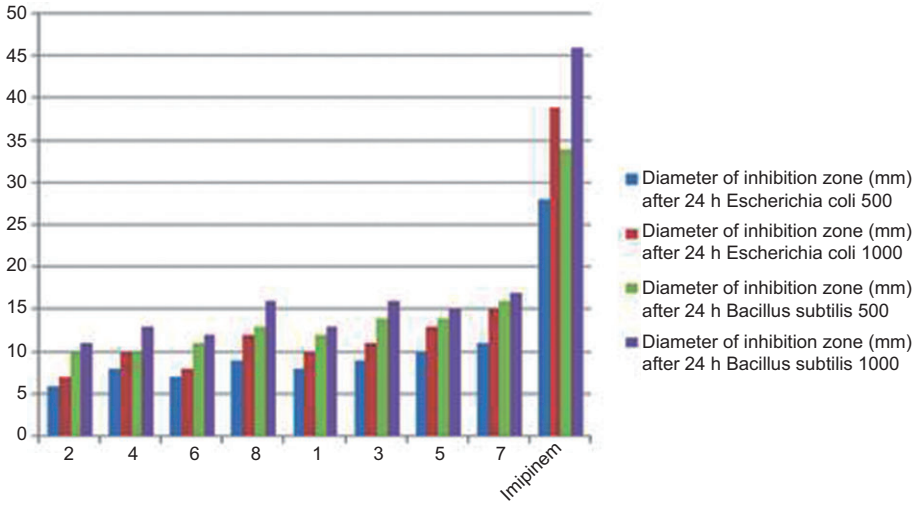


Figure 1 Structures of silicon(IV) complexes. X=O or S and R=Me or Ph.

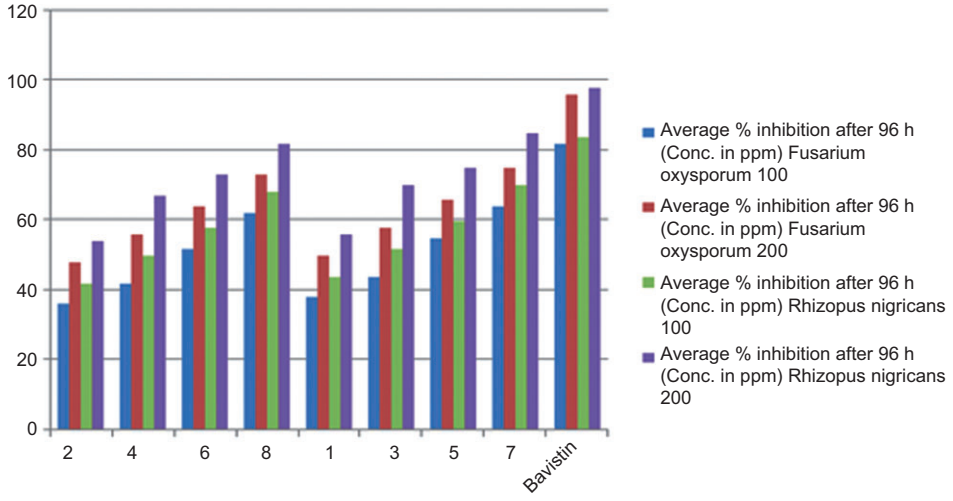
antimicrobial screening data indicate that the silicon complexes are more potent antimicrobial agents than the free ligands.

Minimum inhibitory concentration (MIC) values for the ligands and their Si(IV) complexes are shown in Table 3, which indicate that the ligands and their silicon complexes were the most active in inhibiting the growth of the tested organisms between 15 and 35 MIC values (mg ml^{-1}) against selected bacteria and fungi.

The biological activity of the ligands exhibited a marked enhancement on coordination with the silicon ions against all the test bacterial/fungal strains which shows that silicon chelates are more active than the ligands. This may be explained by Tweedy's chelation theory (Geeta et al., 2010) which states that chelation reduces the polarity of the central silicon atom because of partial sharing of its positive charge with the ligand (Keshavan and Gowda, 2002), which favors permeation of the complexes through the lipid layer of cell membranes (Varnes et al., 1972). Other factors such as solubility, conductivity, and dipole moment, which are affected by the presence of metal ions, may also be possible reasons for the increasing biological



Graph 1 Antibacterial screening of the ligands and their complexes.



Graph 2 Antifungal screening of the ligands and their complexes.

Table 3 Minimum inhibitory concentration (μg ml^{-1}) of the ligands and their complexes.

Compound	*E. coli*	*B. subtilis*	*A. niger*	*F. oxysporum*
2	25	24	33	32
4	21	20	25	27
6	20	18	30	24
8	18	17	23	18
1	26	24	30	29
3	21	18	22	23
5	22	18	20	19
7	18	17	19	18

activity of metal complexes as compared to the corresponding ligands. It was further noted that an increase in the concentration of the compounds increases the activity.

Both the ligands and their silicon complexes were also evaluated for pesticidal activity, and they have a potent inhibitory effect on growth and development of *Corcyra cephalonica* larva. The LC_{50} values in milligrams per liter are shown in Table 4. The data indicate that all Si(IV) complexes exhibit greater pesticidal activity than the respective ligands, but compound $Me_2Si(L^2)_2$ was highly effective as a pesticide with an LC_{50} value of 175 mg l^{-1} against *C. cephalonica*. A possible explanation is that the compound inhibits the molting hormone of pest larva i.e., ecdysis disruption.

For recording the biological activity of the synthesized compounds, our main objective was to determine which is more active between ligands and complexes, as well as the effect of concentration on the activity. In the present case, we have observed that complexes are more active than ligands. Now, if this is the case, then the question that arises is, to what extent are complexes more active than ligands? For this, we used two standard compounds which have already been studied in detail for such an activity. The results showed that the compounds are more active than ligands but are less active than standard drugs, and this was our main objective for biological screening.

Table 4 Pesticidal data of the ligands and their metal complexes.

Compound	Correct motility (%)	χ^2	LC_{50} (mg l^{-1})
2	55.55	0.274	630
4	66.66	0.284	406
6	72.22	0.358	460
8	77.77	0.640	230
1	61.11	0.960	410
3	77.77	0.359	320
5	83.33	0.541	265
7	88.88	0.225	175
Control	–	1.142	–

Conclusions

We have synthesized biologically relevant ligands and their Si(IV) complexes. Based on various physicochemical investigations, the penta- and hexa-coordinated environment around the silicon atom have been proposed. The complexes showed higher antimicrobial and pesticidal activities as compared to the parent ligands. A large number of other coordination complexes of nitrogen/oxygen/sulfur donor ligands have been extensively screened for their biological activity.

The complexes show better antimicrobial activities compared to the parent ligands. The compounds also inhibit the growth of fungi and bacteria to a greater extent as the concentration is increased. The newly synthesized complexes exhibited considerable pesticidal activity; however, compound **7** was found to be highly effective as a pesticide with an LC_{50} value of 175 mg l^{-1} against *C. cephalonica*.

Experimental

Materials and methods

Metal salts, Ph_3SiCl, and Me_2SiCl_2, as well as 3-acetyl coumarin were purchased from Alfa Aesar and used as such. Solvents of analytical grade were distilled from appropriate drying agents immediately prior to use. Molecular weights were determined by the Rast camphor method. Silicon was determined gravimetrically as SiO_2. Nitrogen was estimated by the Kjeldahl method, and sulfur was estimated by the Messenger method (Vogel, 2006). Carbon and hydrogen analyses of the ligands and their silicon complexes were carried out at Central Drug Research Institute, Lucknow, India. UV Spectra of the ligands and their complexes were recorded in methanol with the help of a 752 UV-Spectrophotometer (Bioage & Mohali, Punjab). Infrared spectra of the ligands and their complexes were recorded with the help of a Nicolet Magna FTIR-550 Spectrophotometer (Shimadzu) on KBr pellets. ^1H NMR and ^{29}Si NMR spectra were recorded on a JEOL-AL-300 FT-NMR Spectrometer (JEOL Ltd., Japan) in DMSO-d_6, using tetramethylsilane as the internal standard. Mass spectrum of the complex was carried out at the Indian Institute of Technology Chennai.

Preparation of the ligands

Two different methods were employed for the synthesis of ligands **1** and **2**:

Microwave-assisted synthesis

The ligands were prepared by the condensation of 3-acetylcoumarin (2.02 g, 0.01 mol) with thiosemicarbazide (0.978 g, 0.01 mol) or

semicarbazide hydrochloride (1.197 g, 0.01 mol), in the presence of sodium acetate. The reaction mixture was irradiated in a microwave oven by taking 2–3 ml of solvent. The reactions were completed in a short period (5–7 min). The resulting precipitate was then recrystallized with alcohol and dried under vacuum. These were characterized and analyzed before use. Elemental analysis (N and S) were conducted using the methods mentioned above, and their results were found to be in good agreement with the calculated values.

Conventional thermal method

For comparison purposes, the above ligands were also synthesized by the thermal method. In this method, instead of a few drops of ethanol, 100 ml of ethanol was used to dissolve the starting materials of the ligands and the contents were refluxed for nearly 3–4 h. The residue formed was separated out, filtered off, washed with water, recrystallized from ethanol, and, finally, dried in vacuum over fused calcium chloride. A comparison between the thermal method and the microwave method is given in Table 5.

Preparation of the silicon complexes

Microwave-assisted synthesis

For the synthesis of the complexes, Ph_3SiCl/Me_2SiCl_2 and sodium salt of the ligands (prepared by adding the corresponding weight of sodium to 3-acetylcoumarin semicarbazone/thiosemicarbazone) in 5 ml of dry methanol in 1:1 and/or 1:2 molar ratios were irradiated inside a microwave oven for about 5–8 min. The products were recovered from the microwave oven and dissolved in a few milliliters of dry methanol. The white precipitate of sodium chloride formed during the course of the reaction was removed by filtration, and the filtrate was dried under reduced pressure. The resulting product was repeatedly washed with petroleum ether and then finally dried at 40–60°C/0.5 mm Hg for 3–4 h. The purity was further checked by thin layer chromatography with silica gel-G using DMSO as a solvent.

Conventional thermal method

These Si(IV) complexes were also synthesized by the thermal method. The reaction mixtures were heated under reflux for 12–17 h and filtered to remove NaCl, and the solvent was removed by the same procedure mentioned above, which was adopted to get the complexes. The physico-chemical properties and analytical data of these complexes are listed in Table 6.

Test microorganism

All the compounds were evaluated for their antimicrobial properties. MIC was defined as the minimum concentration of an antimicrobial necessary to inhibit the growth of microorganism. The results obtained were compared with a standard antibiotic, imipinem, and a standard antifungal drug, Bavistin. The microorganisms used were *E. coli* (ATCC25922), *B. subtilis* (ATCC6633), *F. oxysporum* (ATCC7808), and *R. nigricans* (ATCC6227b). The synthesized organosilicon(IV) complexes were also tested for the pesticidal activity against fifth instar larva of *C. cephalonica*.

In vitro antibacterial activity

The newly prepared compounds were screened for their antibacterial activity against *E. coli* (ATCC25922) and *B. subtilis* (ATCC6633) by the paper disc plate method. Each compound was dissolved in DMSO, and solutions of the concentrations (500 and 1000 ppm) were prepared separately. Paper discs of Whatman filter paper (no. 42) of uniform diameter (5 mm) were cut and sterilized in an autoclave. The paper discs soaked in the desired concentration of the complex solutions were placed aseptically in Petri dishes containing nutrient agar media (agar 20 g+beef extract 3 g+peptone 5 g) seeded with *E. coli* (ATCC25922) and *B. subtilis* (ATCC6633) bacteria strains separately. The Petri dishes were incubated at 37°C, and the inhibition zones were recorded after 24 h of incubation. The antibacterial activity of imipinem was also recorded using the same procedure as above at the same concentrations and solvent. The medium with DMSO as solvent was used as a negative control, whereas media with imipinem were used as positive control. The experiments were performed in triplicates.

In vitro antifungal activity

The newly prepared complexes were also screened for their antifungal activity against *F. oxysporum* (ATCC7808) and *R. nigricans*

Table 5 Comparison between the microwave and thermal methods.

Compound	Yield (%)		Solvent (ml)		Time	
	Thermal	Microwave	Thermal	Microwave	Thermal (h)	Microwave (min)
2	83	95	100	4	3	5
4	75	82	45	2	17	8
6	75	88	50	3	12	5
8	76	86	50	2	13	5
1	81	98	100	3	4	7
3	69	81	40	3	15	5
5	71	80	40	3	14	7
7	70	83	50	2	17	6

Table 6 Analytical data and physical properties of the ligands and their silicon complexes.

Compound	Color	Melting point (°C)	Found (calcd.) (%)					Molecular weight found (calcd.)
			C	H	N	S	Si	
2	Cream	195–200	58.12 (58.77)	4.22 (4.52)	16.82 (17.13)	–	–	244.23 (245.23)
4	Mahroon	150–155	70.59 (71.55)	4.12 (5.00)	8.56 (8.34)	–	5.65 (5.58)	502.45 (503.62)
6	Brown	141–145	48.91 (49.77)	3.49 (4.77)	12.56 (12.44)	–	8.25 (8.31)	336.26 (337.83)
8	Dark brown	130–135	56.85 (57.13)	3.99 (4.74)	15.56 (15.37)	–	4.99 (5.14)	545.56 (546.61)
1	Yellow	215–218	55.09 (55.16)	4.11 (4.24)	15.92 (16.08)	11.92 (12.27)	–	260.12 (261.30)
3	Brown	250–255	65.12 (64.49)	3.88 (4.11)	7.56 (7.78)	4.25 (5.94)	4.65 (5.20)	538.45 (540.11)
5	Gray	220–225	46.25 (47.51)	3.49 (4.56)	11.96 (11.87)	9.23 (9.06)	7.25 (7.94)	352.26 (353.90)
7	Black	230–235	52.69 (53.96)	3.87 (4.53)	14.56 (14.52)	10.89 (11.08)	4.75 (4.85)	577.56 (578.74)

(ATCC6227b) in DMSO by the agar diffusion method (Singh et al., 2010). Sabouraud's agar media was prepared by dissolving peptone (10 g), D-glucose (40 g), and agar (20 g) in distilled water (1000 ml) and adjusting the pH to 5.7. Normal saline water was used to make a spore suspension of fungal strain for lawning. A loopful of particular fungal strain was transferred to 3 ml of saline to get the suspension of corresponding species. Twenty milliliters of agar media was poured into each Petri dish. The excess of suspension was decanted, and plates were dried by placing in an incubator at 37°C for 1 h using an agar punch; wells were made and each well was labeled. A control was also prepared in triplicate and maintained at 37°C for 96 h. The fungal activity of each compound was compared with Bavistin as standard drug. The medium with DMSO as solvent was used as a negative control, whereas media with Bavistin (standard antifungal) were used as positive control. The experiments were performed in triplicates. The cultures were incubated for 96 h at 35°C, and the growth was monitored and the percentage of inhibition was calculated by the following equation:

$$\% \text{ inhibition} = 100(C\text{-}T)/C,$$

where C and T are the diameters of the fungal colony in the control and the test plates, respectively.

Determination of MIC

MIC is the lowest concentration of a test agent that inhibits the visible growth of bacteria after 18 h of incubation at 37°C. Determination of the MIC involves a semi-quantitative test procedure, which gives an approximation to the least concentration of an antimicrobial needed to prevent microbial growth. The MIC was determined by the microbroth dilution method (Shanker et al., 2009). Stock solution of Si(IV) complexes with 50–3.125 μg ml^{-1} concentrations was prepared with DMSO solvent. Inoculum of the overnight culture was prepared. In a series of tubes, 1 ml each of Si(IV) complex solution with different concentrations was taken, and 0.4 ml of the inoculum was added to each tube. A further 3.5 ml of sterile water was added to each of the test tubes. These test tubes were incubated for 18 h and observed for the presence of turbidity. Absorbance of the suspension of the inoculum was observed with a spectrophotometer at 555 nm. The end result of the test was the minimum concentration of an antimicrobial agent (test materials) which gave a clear solution, i.e., no visual growth (Collins, 1964; Davidson and Parish, 1989). The zone of inhibition of compounds was considered after the subtraction of the inhibition zone of DMSO. Negative control (with no compound) was also observed.

Pesticidal activity

Fifth instar larvae of *C. cephalonica* were obtained from stock culture maintained at the storage section of the Division of Entomology, Durgapura Agricultural Research Institute, Jaipur, India. Insects were reared on wheat grain at 27±1°C and 70% relative humidity. Glass jars containing 500 g of wheat cereals were labeled to indicate the date of introduction of adults and new emergence. At alternate days, the larvae were shifted to fresh jars so that successive rearing jars can be maintained and insects of known age can be obtained regularly. Pesticidal activity of the synthesized compounds was tested by the immersion method. All the synthetic compounds were weighed and dissolved in methanol to prepare 1000 mg l^{-1} of stock solution. Further concentrations, *viz*., 900, 800, 700, 600, 500, 400, 300, 200, and 100 mg l^{-1}, were prepared by serial dilution. Twenty larvae were released into each Petri plate, then 1 ml of each concentration of various compounds was directly poured into each Petri plate with the help of a brush. Petri plates with test solution were rotated vigorously and were kept at 27±1°C and 70% relative humidity. Mortality was observed after 96 h. Larvae were considered dead if they failed to respond to stimulus by touch. Control mortality was corrected by using Abbott's formula, and data were subjected to probit analysis according to Finney (1971).

$$\text{Corrected \% mortality} = \frac{\text{\% mortality observed-\% mortality in control} \times 100}{\text{100-\% mortality in control}}$$

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