Main Group Met. Chem., 2011;34(3-4):69–75 © 2011 by Walter de Gruyter • Berlin • Boston. DOI 10.1515/MGMC.2011.012

Antimicrobial and pesticidal activity of some organogermanium(IV) complexes synthesized under microwave irradiation

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Abstract

Reactions of 2-hydroxy-*N*-phenylbenzamide with semicarbazide hydrochloride and thiosemicarbazide resulted in the formation of new ketimines, semicarbazone and thiosemicarbazone of 2-hydroxy-*N*-phenylbenzamide, respectively. The organogermanium(IV) complexes have been synthesized by reacting trimethylgermanium chloride and triphenylgermanium chloride in a 1:1 molar ratio with these ketimines using microwave as well as conventional heating method for comparison purposes. The authenticity of these ligands and their complexes has been established on the basis of elemental analysis, melting point determinations, molecular weight determinations, infrared, ^{1}H and ^{13}C nuclear magnetic resonance, ultraviolet, and mass spectral studies. These studies showed that the ketimines coordinated with the germanium atom and, accordingly, the trigonal bipyramidal environment around the metal atom has been established for the complexes. Both the ketimines and their complexes have been screened for their antimicrobial activities against a variety of fungal and bacterial strains and were found positive in this respect. The pesticidal activity of both the ligands and their metal complexes against the *Corcyra cephalonica* has also been tested.

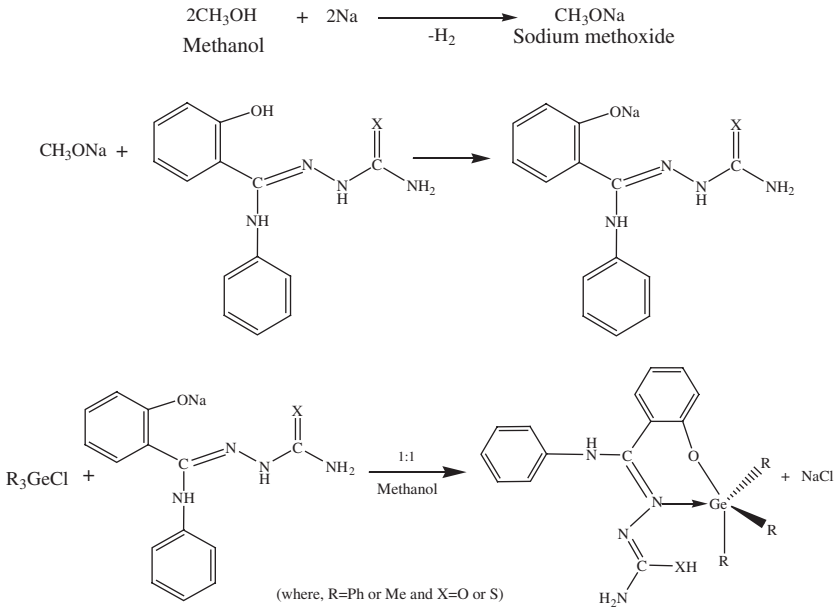
Keywords: antimicrobial; ketimines; pesticidal activity; semicarbazone; spectral studies; thiosemicarbazone.

Introduction

Microwave synthesis represents one of the important dimensions of modern chemistry attracting a considerable amount of attention. The main advantage of microwave heating is the almost instantaneous 'in-core' heating of materials in a homogenous and selective manner, coupled with the significantly shorter reaction time. This implies a considerable savings in energy (Singh et al., 2008). Recently, microwave irradiation has become popular over usual homogeneous and heterogeneous reactions because it is environmentally friendly, economical, and rapid synthetic procedure. Microwaves enhance the rate of chemical reactions and provide pure products in quantitative yield (Kidwai, 2001; Warner et al., 2004). The Schiff base complexes of main group elements containing ligands, such as semicarbazones and thiosemicarbazones have remained a topic of considerable current research interest (Nagpal and Singh, 2005). Semicarbazones and thiosemicarbazones are biologically important nitrogen and oxygen/sulfur donor ligands, and their complexes show significant activity (Fahmi and Singh, 1994). The field of organogermanium in chemistry is important. Advances in organogermanium chemistry, particularly organogermanium derivatives with extended pentacoordination spheres, most of which are biologically active compounds (Seifullina et al., 2004), have prompted our systematic studies in this area. Organic germanium has been used clinically in many parts of the world to treat a wide spectrum of illnesses and has been the subject of extensive research in many disciplines, such as pathology, biochemistry, pharmacology, immunology, oncology, and neurochemistry. Organic germanium has been used in a broad spectrum of regimes on its own, with diet and stress counseling, and as a drug in clinical trials of cancer therapy, in conjunction with chemotherapy, radiation therapy, and surgery (Swami and Singh, 2008). The chemistry of germanium has received considerable attention over the years. Organogermanium(IV) complexes have been fairly well studied and show appreciable activity against bacteria and fungi. Seeing the biological importance of nitrogen and sulfur donor ligands and their metal complexes, we decided to synthesize two new ligands and their organogermanium(IV) complexes.

Results and discussion

The 1:1 molar reactions of Me_3GeCl and Ph_3GeCl with hydrazine carboxamide and hydrazine carbothioamide have lead to the formation of $Me_3Ge(O^{\frown}N^{\frown}XH)$ and $Ph_3Ge(O^{\frown}N^{\frown}XH)$ types of complexes. These reactions were carried out in a dry methanolic medium. The reactions proceeded with the precipitation of NaCl, which was removed by filtration. These reactions can be represented by the following general equation:



The resulting complexes are colored solids that are soluble in most of the common organic solvents and susceptible to air and moisture. These complexes have been found to be monomeric, as evidenced by their molecular weights. The low molar conductivity (8–10 Ω^{-1} cm^2 mol^{-1}) of the resulting germanium complexes in anhydrous DMF shows them to be nonelectrolytes in nature.

Ultraviolet spectra

The electronic spectra of the ligands and their metal complexes were recorded in methanol.

The electronic spectra of the ligands exhibit three bands at ~230, ~270, and ~320 nm. The bands at ~230 and ~270 nm are due to π-π* transitions within the benzene ring and that around 320 nm is due to n-π* transitions of the azomethine group. However, in the metal complexes, the first two bands remain unaltered, whereas the third band undergoes a blue shift due to the coordination of the nitrogen to the central metal atom.

Infrared spectra

In the infrared spectra of the ligands, broad bands observed at 3400–3200 cm^{-1} are assigned to the phenolic OH group. These bands disappeared in the case of complexes, indicating the possible loss of protons on complexation and subsequent formation of Ge-O bond. The azomethine (C=N) stretching frequency (1590–1620 cm^{-1}) shifted by ~15 cm^{-1} to the lower frequency region due to the coordination of the azomethine nitrogen to the germanium atom. The bands at ~1680 and 1020 cm^{-1} may be assigned to ν(C=O) and ν(C=S) vibrations, respectively. The bands due to ν(C=S) and ν(C=O) remain as such in the complexes, indicating no participation of sulfur and oxygen in the bond formation at the central metal atom. Several new bands in the germanium complexes at regions 680 and 875 cm^{-1} are observed due to the (Ge←N) and (Ge-O) stretching vibrations, respectively, which further supports the proposed coordination.

^{1}H and ^{13}C nuclear magnetic resonance spectral studies

The ^{1}H nuclear magnetic resonance (NMR) spectral data of the ligands L^1H_2 and L^2H_2 and their corresponding germanium complexes have been recorded in deuterated dimethylsulfoxide (DMSO-d_6) (Table 1). In the spectra of the complexes, the disappearance of the -OH proton signal indicates the deprotonation and complexation through this functional group. The signal due to the -NH proton attached to phenyl ring remains unaltered in the complexes. The NH_2 proton signals remain almost unchanged. The ^{13}C NMR spectra of the ligands and their complexes have been recorded in Table 2. The considerable shifts in the positions of the carbon atoms adjacent to the azometine nitrogen further support the proposed coordination pattern.

Mass spectra

The electron impact mass spectrum of the $Me_3Ge(L^2H)$ complex was studied as a representative case. The molecular ion peak for the complex $Me_3Ge(L^2H)$ was observed at *m*/*z* 402.92, and this is in good agreement with its molecular weight, which suggests the monomeric nature of the complex. The molecular ion peaks of the germanium-containing fragments $[C_{17}H_{22}GeN_4OS]^+$, $[C_{17}H_{20}GeN_3OS]^+$, $[C_{16}H_{17}GeN_3OS]^+$, $[C_{15}H_{14}GeN_3OS]^+$, and $[C_{14}H_{11}GeN_3OS]^+$ are observed at 402.92, 386.89, 371.86, 356.82, and 341.79, respectively, which are accompanied by other isotopic combinations.

Thus, on the basis of above discussion, the following pentacoordinated (Holloway and Melnik, 2002) structure for the germanium complexes has been established (Figure 1).

Table 1 ^{1}H NMR spectral data (δ, ppm) of the ligands (L^1H_2 and L^2H_2) and their triorganogermanium(IV) complexes.

Compound	OH	-NH (bs)	Φ-NH	$-NH_2$ (bs)	Aromatic (m)	Me_3Ge/Ph_3Ge
L^1H_2	12.00	10.90	10.50	2.70	6.90–8.10	–
$Me_3Ge(L^1H)$	–	10.88	10.45	2.50	6.78–7.95	0.9–1.32
$Ph_3Ge(L^1H)$	–	10.85	10.50	2.69	6.80–7.90	[a]
L^2H_2	12.12	10.84	10.64	2.80	6.75–8.30	–
$Me_3Ge(L^2H)$		10.83	10.39	2.60		0.9–1.35
$Ph_3Ge(L^2H)$	–	10.80	10.60	2.78	6.60–8.00	[a]

bs, broad singlet; m, multiplet. [a]Merged with aromatic protons.

Table 2 ^{13}C NMR spectral data (δ, ppm) of the ligands (L^1H_2 and L^2H_2) and their triorganogermanium(IV) complexes.

Compound	>C=S/>C=O	>C=N	Me_3Ge	Ph_3Ge				Aromatic carbons
				C_o	C_i	C_m	C_p	
L^1H_2	176.40	166.10	–	–	–	–	–	160.15, 138.70, 134.70, 129.90, 129.30, 125.60, 122.50, 120.70, 118.90, 119.90
$Me_3Ge(L^1H)$	176.15	163.00	16.58	–	–	–	–	158.80, 137.56, 133.56, 128.76, 128.22, 124.45, 121.34, 120.54, 119.89, 118.78
$Ph_3Ge(L^1H)$	176.00	162.52	–	133.65	131.52	130.64	132.32	159.86, 138.62, 134.68, 129.85, 129.23, 125.56, 122.47, 119.68, 118.83, 119.87
L^2H_2	179.52	168.00	–	–	–	–	–	160.86, 138.90, 130.18, 129.80, 129.95, 125.50, 122.60, 120.68, 118.90, 119.98
$Me_3Ge(L^2H)$	179.20	164.40	16.82	–	–	–	–	158.76, 137.87, 129.56, 128.98, 128.74, 124.63, 121.78, 119.56, 117.87, 118.54
$Ph_3Ge(L^2H)$	178.80	163.82	–	134.54	132.25	131.13	132.26	159.57, 138.86, 130.12, 129.74, 129.87, 125.43, 122.54, 120.61, 118.83, 119.92

Antimicrobial screening

Screening of antimicrobial activity of the synthesized ligands and their corresponding metal complexes on selected fungi, *Alternatria alternata*, *Aspergillus niger*, *Fusarium oxysporum*, and *Macrophomina phaseolina*, and four bacteria, *Staphylococcus aureus*, *Klebsiella aerogenes*, *Escherichia coli*, and *Pseudomonas cepacicola* was carried out (Tables 3 and 4). The complexes show moderate activity as compared with standard fungicide and bactericide, but all complexes are more active than their respective ligands, which thus indicates that complexation enhances the activity of the ligand. This may be explained by the chelation theory (Geeta et al., 2010), which say that chelation reduces the polarity of the ligand and the central metal atom because of the delocalization of electrons over the whole chelate ring, which favors permeation of the complexes through the lipid layer of the cell membrane. The variation in the activity of the complexes against various organisms depends either on the impermeability of the cells of the microbes or differences in ribosome in microbial cells.

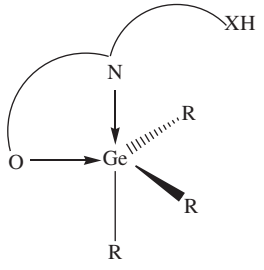


Figure 1 Structure of the complexes.
HO⌒N⌒XH is the donor set of the ligands, X=O or S and R=Me or Ph.

Minimum inhibitory concentration

The minimum inhibitory concentration (MIC) values calculated for the ligands and their germanium(IV) complexes (Table 5) indicate that the ligands and their metal complexes were most active in inhibiting the growth of the tested bacteria and fungi between 15 and 40 mg ml^{-1}.

The biological activity of the ligands exhibited a marked enhancement on coordination with the metal ions against all the test bacterial/fungal strains, which shows that metal chelates are more active than the ligands. This may be explained by chelation theory, which says that chelation reduces the polarity of the central metal atom because of partial sharing of its positive charge with the ligand, which favors permeation of the complexes through the lipid layer of cell membrane. The variation in the activities of the different complexes against various organisms depends on either the impermeability of

Table 3 Antifungal screening data of ligands and their complexes synthesized through thermal and microwave methods.

Compound	Antifungal activity: percentage of inhibition after 96 h (concentration, ppm)											
	A. alternate			*A. niger*			*F. oxysporum*			*M. phaseolina*		
	50	100	200	50	100	200	50	100	200	50	100	200
L^1H_2	20±0.92	28±0.73	30±0.67	22±1.07	25±0.60	32±0.49	20±0.66	29±0.40	35±0.4	25±1.18	28±0.45	35±0.35
$Me_3Ge(L^1H)$	35±1.41	38±0.88	42±0.54	32±0.76	35±0.55	38±0.76	25±0.57	35±0.54	38±0.73	28±0.40	35±0.89	40±0.38
$Ph_3Ge(L^1H)$	42±0.39	50±0.44	55±0.38	35±0.69	38±0.68	42±1.13	28±0.49	38±0.99	40±0.51	30±0.57	43±0.35	48±0.45
L^2H_2	22±0.50	30±0.62	35±0.30	24±0.73	28±1.05	34±0.34	23±1.03	32±0.54	42±0.40	29±0.41	30±0.45	36±0.42
$Me_3Ge(L^2H)$	35±0.28	38±0.70	43±1.04	34±0.70	39±1.42	40±0.95	28±0.50	37±0.68	40±0.37	30±1.00	38±0.73	43±0.40
$Ph_3Ge(L^2H)$	38±1.00	42±0.98	45±1.00	38±0.77	45±0.95	52±1.11	30±0.73	42±0.57	49±0.35	35±107	44±0.56	55±0.73
Bavistin	80±1.10	100±1.4	100±0.99	85±0.87	100±0.80	100±0.83	90±1.14	100±1.00	100±0.55	901.00	100±0.79	100±1.00

the cells of the microbes or the differences in ribosome in microbial cells. The enhanced effect of complexes due to chelation could increase the lipophilicity of the central metal atom, which favors the permeation through the lipid layers of the cell wall. 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 activity of the metal complexes as compared with the corresponding ligands.

Pesticidal activity

The data reported in Table 6 revealed that of the 10 compounds tested, $Ph_3Ge(L^2H)$ was highly effective as insecticide, with LC_{50} of 210 mg l^{-1} against *Corcyra cephalonica*. Other compounds also showed good insecticidal activity. Broad conclusions may become possible only after a critical appraisal of large data set.

Conclusion

Microwave irradiation is an efficient and environmentally benign method in synthesizing various inorganic products with higher yields and shorter reaction periods. Both ligands behave as bibasic tridentate with the metal atom in different reaction conditions. Germanium(IV) complexes synthesized in a 1:1 molar ratio with bibasic tridentate ligands were found to be pentacoordinated. Antimicrobial and pesticidal activity of the complexes and the ligands showed that the germanium(IV) complexes are more active than the parent ligands. The results showed that the compounds are more active than ligands but less active than standard drugs, and this was our main objective for biological screening.

Experimental

Materials and methods

The reagents Ph_3GeCl and Me_3GeCl were purchased from Alfa Aesar (Ward Hill, MA, USA). 2-Hydroxy-*N*-phenyl benzamide, semicarbazide hydrochloride (Merck, Mumbai, India), and thiosemicarbazide (Merck) were commercial products and used as such. All the reagents and the solvents used were dried, distilled, and purified using standard methods. Molecular weights were determined by the Rast camphor method (Vogel, 2004). Germanium was gravimetrically determined as GeO_2. Nitrogen was estimated by the Kjeldahl method, and sulfur was estimated by the Messenger method (Makode and Aswar, 2004). Carbon and hydrogen analyses of the ligands and their germanium complexes were carried out at Central Drug Research Institute (Lucknow, Uttar Pradesh, India). Infrared spectra of the ligands and their complexes were recorded with the help of Nicolet Magna FTIR-550 spectrophotometer on KBr pellets. The electronic spectra and mass were recorded at SAIF, IIT (Madras, Chennai, India). ^{1}H NMR spectra were recorded on a JEOL-AL-300 FT NMR spectrometer (JEOL, Tokyo, Japan) in DMSO-d_6 using tetramethylsilane as the internal standard. X-ray powder diffraction was recorded using a panalytical system with CuK_α as the radiation source (wavelength 1.542 Å, with 2θ of 10–70°).

Table 4 Antibacterial screening data of ligands and their complexes synthesized through thermal and microwave methods.

Compound	Antibacterial activity: diameter (mm) of inhibition zone after 24 h (concentration, ppm)							
	S. aureus (+)		*K. aerogenes* (-)		*E. coli* (-)		*P. cepacicola* (-)	
	500	1000	500	1000	500	1000	500	1000
L^1H_2	6±0.021	8±0.008	4±0.033	6±0.041	4±0.008	8±0.010	5±0.019	7±0.010
$Me_3Ge(L^1H)$	12±0.013	15±0.024	9±0.019	13±0.040	9±0.006	14±0.039	11±0.030	16±0.013
$Ph_3Ge(L^1H)$	13±0.007	16±0.046	11±0.008	15±0.040	10±0.025	15±0.040	14±0.032	16±0.009
L^2H_2	7±0.015	10±0.065	5±0.010	8±0.024	5±0.041	9±0.019	6±0.014	8±0.018
$Me_3Ge(L^2H)$	13±0.009	14±0.016	12±0.009	13±0.022	10±0.020	14±0.020	9±0.009	10±0.035
$Ph_3Ge(L^2H)$	14±0.011	16±0.008	13±0.014	15±0.008	11±0.020	16±0.018	13±0.008	15±0.027
Streptomycin	20±0.049	20±0.037	17±0.043	19±0.013	17±0.031	18±0.009	18±0.009	18±0.021

Table 5 MIC (mg ml^{-1}) of ligands and their complexes.

Compound	*E. coli*	*P. cepacicola*	*A. niger*	*F. oxysporum*
L^1H_2	28±0.1	30±0.1	38±0.1	40±0.09
$Me_3Ge(L^1H)$	22±0.2	23±0.09	29±0.1	26±0.2
$Ph_3Ge(L^1H)$	20±0.1	21±0.1	27±0.1	24±0.1
L^2H_2	24±0.09	27±0.1	32±0.09	35±0.1
$Me_3Ge(L^2H)$	19±0.1	21±0.2	28±0.1	27±0.1
$Ph_3Ge(L^2H)$	18±0.1	19±0.1	26±0.09	25±0.2

Preparation of ligands

Two different conditions were used for the synthesis of ligands.

Microwave-assisted synthesis In microwave-assisted synthesis of the ligands, hydrazine carboxamide and hydrazine carbothioamide of 2-hydroxy-*N*-phenylbenzamide were prepared by the condensation of 2-hydroxy-*N*-phenyl benzamide (0.01 mol) with semicarbazide hydrochloride (0.01 mol) (in the presence of sodium acetate) and thiosemicarbazide (0.01 mol), respectively, in a 1:1 molar ratio using a beaker through a microwave oven. The reactions were completed in a short period of 5–6 min. The solutions were then concentrated under reduced pressure, which upon cooling gave HO⌒N⌒OH($C_{14}H_{14}N_4O_2$) (off-white solid, melting point 110°C) and HO⌒N⌒SH($C_{14}H_{14}N_4OS$) (light pink solid, melting point 125°C).

Conventional thermal method For comparison, the above ligands were also synthesized by a thermal method, where, instead of few drops of alcohol, the starting materials of the ligands were dissolved in ~100 ml of alcohol and the contents were refluxed for nearly 4–5 h. The solution was then concentrated under reduced pressure. These were recrystallized twice in alcohol. A comparison between the thermal method and the microwave method is given in Table 7.

Table 6 Pesticidal data of ligands and their metal complexes.

Compound	Correct motility (%)	χ^2	LC_{50} (mg l^{-1})
L^1H_2	50.00	0.543	660
$Me_3Ge(L^1H)$	61.11	0.627	290
$Ph_3Ge(L^1H)$	77.77	0.246	260
L^2H_2	55.55	0.156	450
$Me_3Ge(L^2H)$	66.66	0.620	250
$Ph_3Ge(L^2H)$	88.88	0.540	210
Control	–	1.142	–

Preparation of the metal complexes

Microwave method In the microwave-assisted synthesis, the complexes were prepared by irradiating the reaction mixture of trimethylgermanium chloride (0.001 mol) and triphenylgermanium chloride (0.001 mol) and respective sodium salt of the ligands (0.001 mol) in 4–6 ml of dry methanol in a 1:1 molar ratio. The products were recovered from the microwave oven, and the dissolved minimum amount of dry methanol, where the 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 compounds were washed and recrystallized with cyclohexane.

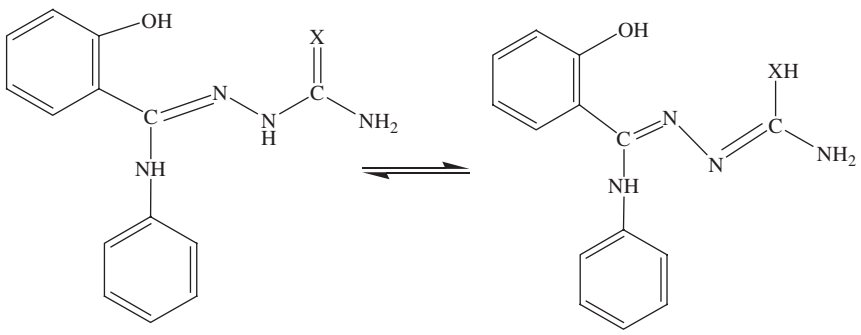


Figure 2 Equilibrium forms of the ligands.
X=O for L^1H_2/S for L^2H_2.

Table 7 Comparison between conventional and microwave methods of synthesis of ligands and their metal complexes.

Compound	Yield (%)		Solvent (ml)		Time	
	Thermal	Microwave	Thermal	Microwave	Thermal (h)	Microwave (min)
(L^1H_2)	75	90	100	5	4	6
$Me_3Ge(L^1H)$	70	92	100	5	12	5
$Ph_3Ge(L^1H)$	76	80	100	6	14	4
(L^2H_2)	72	88	100	4	4	5
$Me_3Ge(L^2H)$	75	90	100	4	12	5
$Ph_3Ge(L^2H)$	72	88	100	5	15	7

Conventional thermal method These complexes were also synthesized by the thermal method where instead of 4–7 min, reactions were completed in 12–15 h, and the yield of the products was also less than that obtained by the microwave-assisted synthesis. In this method, trimethylgermanium chloride (0.001 mol) and triphenylgermanium chloride (0.001 mol) were added with the sodium salt of the ligands (0.001 mol) in dry methanol in a 1:1 molar ratio. The resulting mixture was heated under reflux for 12–15 h, and the precipitate of the sodium chloride formed during the course of the reaction was removed by filtration and the solvent was removed under reduced pressure. The product was dried in vacuum. The complexes were washed and recrystallized with cyclohexane. The details of the products are given in Table 8.

Microbiological studies

The synthesized organogermanium compounds and ketimines were tested for the *in vitro* growth inhibitory activity against pathogenic fungi (*A. alternata*, *A. niger*, *F. oxysporum*, and *M. phaseolina*) and bacteria (*S. aureus*, *K. aerogenes*, *E. coli*, and *P. cepacicola*). Proper temperature, necessary nutrients, and growth media free from other microorganisms were used for the preparation of cultures of fungi and bacteria using aseptic techniques. The radial growth method (Chaudhary and Singh, 2004) and paper-disc plate method (Chaudhary and Singh, 2007) were used to evaluate the antifungal and antibacterial activities, respectively.

Antifungal activity

A culture of the test fungus was grown on potato dextrose agar medium (glucose, starch, agar-agar, and 1000 ml of H_2O) at 25±2°C, and the compounds, after being dissolved in methanol with concentration of 50, 100, and 200 ppm, were mixed in the medium. The linear growth of the fungus was obtained by measuring the diameter of the colony in Petri plates after 4 days, and the percentage inhibition was calculated by the following relationship:

$$\% \text{ inhibition} = 100(C\text{-}T) \times C^{-1}$$

where C and T are the diameters of the fungus colony in check and test plates, respectively.

Antibacterial activity

The nutrient agar medium (peptone, beef extract, agar-agar, and NaCl) and Whatman No. 1 paper discs (diameter, 5-mm) were used to evaluate bactericidal activity. The compounds were dissolved in dry methanol in 500 and 1000 ppm concentrations. The filter paper discs were soaked in different solutions of the compounds, dried, and then placed in Petri plates previously seeded with the test organism. The plates were incubated for 24–30 h at 30±1°C, and the inhibition around each disc was measured.

Determination of MIC

MIC is the lowest concentration of test agent that can inhibit visible growth of bacteria after 24 h of incubation at 37°C. The determination of MIC involves a semiquantitative test procedure that gives an approximation of the least concentration of an antimicrobial needed to prevent microbial growth. MIC was determined by liquid dilution method (Shanker et al., 2009). Stock solutions of the ligands and their complexes with concentrations of 10–50 mg ml^{-1} were prepared with aqueous methanol solvent. The inoculum of the overnight culture was prepared. In a series of tubes, 1 ml each of complex solutions with different concentrations was taken and 0.4 ml of the inoculum was added to each tubes. Sterile water (3.5 ml) was added to each of the test tubes. These test tubes were incubated for 24 h and observed for presence of turbidity. The absorbance of the suspension of the inoculum was observed with the help of a spectrophotometer

Table 8 Analytical data and physical properties of the ligands and their complexes.

Compound	Color	Melting point (°C)	Composition, found (calculated %)					Molecular weight, found (calculated)
			C	H	N	S	M	
(L^1H_2)	Off-white	110	62.00 (62.21)	5.05 (5.22)	20.55 (20.84)	–	–	265.22 (270.29)
$Me_3Ge(L^1H)$	Brown	148	52.65 (52.76)	5.30 (5.73)	14.03 (14.48)	–	18.58 (18.77)	380.52 (387.022)
$Ph_3Ge(L^1H)$	Brown	118	66.98 (67.05)	4.77 (4.92)	9.19 (9.77)	–	12.36 (12.67)	572.56 (573.20)
(L^2H_2)	Light pink	125	58.88 (58.72)	4.66 (4.93)	19.43 (19.57)	11.0 (11.20)	–	278.56 (286.35)
$Me_3Ge(L^2H)$	Cream	160	50.46 (50.65)	5.40 (5.50)	13.46 (13.90)	7.90 (7.95)	17.95 (18.02)	401.25 (403.08)
$Ph_3Ge(L^2H)$	Light brown	175	65.12 (65.22)	4.24 (4.79)	9.24 (9.51)	5.04 (5.44)	12.16 (12.33)	581.68 (589.26)

at 555 nm. The end result of the test was the minimum concentration of the antimicrobial (test materials) that gave a clear solution, i.e., no visual growth (Collins, 1964; Davidson and Parish, 1989).

Insecticidal activity

Larvae of *C. cephalonica* were obtained from stock culture maintained at the storage section of Division of Entomology, Agricultural Research Institute (Durgapura, Jaipur, India). Insects were reared on grains of wheat at 27±1°C and 70% relative humidity. Glass jars containing 500 g of wheat grains were labeled to indicate the date of introduction of larvae and new emergence. At alternate days, larvae were shifted to fresh jars so that successive rearing jars can be maintained and insects of known age can be obtained regularly. Insecticidal activity of the synthesized compounds was tested using dipping and spray methods. All synthetic compounds were weighed and dissolved in methanol to prepare 1000 mg l^{-1} stock solution. Further concentrations, viz., 900, 800, 700, 600, 500, 400, 300, 200, and 100 mg l^{-1}, were prepared by serial dilution. One milliliter of each concentration of various compounds was directly poured in each Petri plate (90 mm) using a micropipette. Petri plates with test solution were rotated vigorously to keep the preparation uniform and were allowed to dry for 3–5 min. Each concentration and control in methanol were replicated thrice. Twenty adult insects (2–5 days old) were released in each Petri plate and kept at 27±1°C and 70% relative humidity. Mortality was observed after 96 h. Adult insects were considered dead if they failed to respond to stimulus by touch. Control mortality was corrected using Abbott formula (Shaki et al., 2009) and LC_{50} was obtained by graphical method. χ^2 was calculated by statistical analysis.

Acknowledgment

The authors are thankful to U.G.C. New Delhi for financial assistance through grant no. 34-324(SR-I/08).

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Received June 27, 2011; accepted October 6, 2011