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# Synthesis, Characterization and Biological Activity of Monometallic Complexes of Germanium

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**Abstract**

Monometallic Complexes of germanium(IV) with macrocyclic ligands have been synthesized and characterized by elemental analysis, molar conductance , infrared spectra, $^1$H NMR and $^{13}$C NMR spectral studies. The molar conductance of $10^{-3}$ M solutions of these complexes at the room temperature indicates that the complexes are 1:2 electrolytes in nature. On the basis of chemical composition there presentation of the complexes as $[Ge(OAML)_nCl_2]Cl_2$ (n=1-5) has been proposed. These synthesized complexes have also been tested against several species of pathogenic fungi and bacteria in order to evaluate their antimicrobial properties.

**Keywords:** Monometallic complexes, macrocyclic, pathogenic, antimicrobial properties.

## Introduction

Recently a prodigious interest has been observed in the area of synthesis and characterization of metal complexes with macrocyclic ligands. There has been an escalating interest in the study of this branch of chemistry due to its prominence in supramolecular chemistry, material chemistry, and biochemistry[1]. Macrocyclic complexes have also received special attention because of their versatile coordination behaviour and their pharmacological properties [2, 3]. To overcome the alarming problem of microbial resistance to antibiotics, the discovery of novel active compounds against new targets is a matter of urgency [4]. Metal based drugs represent a novel group of antifungal agents with potential applications for the control of fungal and bacterial infections [5]. In view of biological importance of macrocyclic complexes, biological screening of the synthetic macrocyclic metal complexes has also been carried out [6].

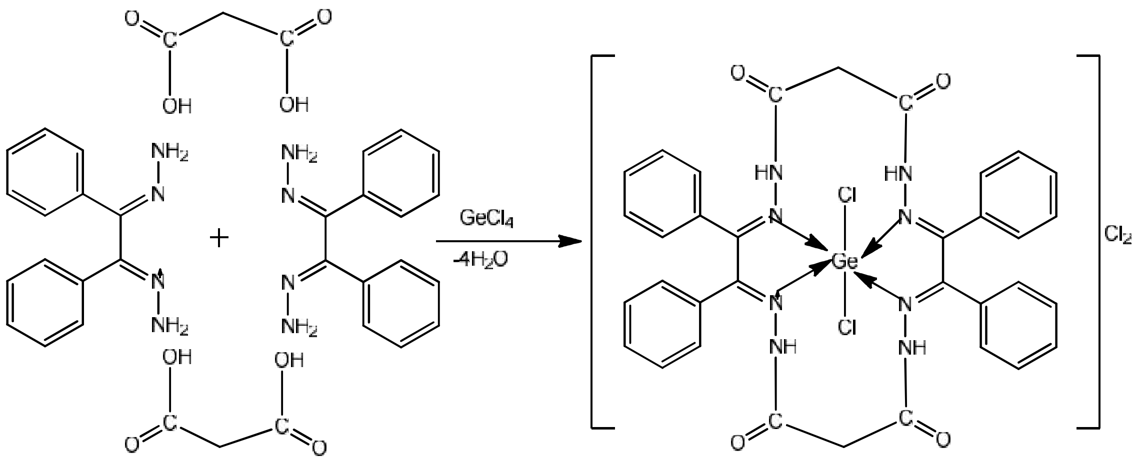
The macrocyclic complexes exhibiting antimicrobial activity have resulted in the discovery of new chemical classes of antibiotics that could serve as selective agent for the maintenance of human health and provide biochemical tools for the study of infectious diseases. In this paper we report the synthesis of macrocyclic complexes of Ge(IV) by the template process using benzildihydrazone as precursor. Metal chlorides react with Benzildihydrazone and dicarboxylic acids in a 1:2:2 molar ratio in methanol to give several solid metal complexes of the general formula $[Ge(OAML)_nCl_2]Cl_2$,n=1,2,3,4 or 5. The complexes show a broad spectrum of antimicrobial activityagainst both gram–positive and gram–negative human pathogenic bacterial isolates. From the results it is imperative that the synthesized macrocyclic complexes exhibit potent broadspectrum antimicrobial activity.

## Experimental

### Synthesis of macrocyclic complexes $[Ge(OAML)_1Cl_2]Cl_2$–$[Ge(OAML)_5Cl_2]Cl_2$

For the preparation of germanium complexes an ice cold solution of $GeCl_4$ in methanol (25 mL) was reacted with benzildihydrazone in methanol at $0^oC$ and put in magnetically stirred 100 mL round bottom flask.

This was followed by the addition of methanolic solution (25 mL) of malonic acid. It was stirred for 8–10 h. The reaction is carried out in 1:2:2 molar ratios (scheme 1).




**Scheme 1.** Synthetic scheme for synthesis of complex $[Ge(OAML)_1Cl_2]Cl_2$.

The resulting solid product was recovered by filteration, washed with methanol and dried in *vacuo.* This was further subjected to check its purity by T.L.C. using silica gel–G. The other products of the series have also been synthesized by same procedure using succinic, glutaric, adipic and phthalic acids.

## Results and Discussion

### Physical properties and analytical data

The reactions proceed easily and all the complexes are coloured solids. All the complexes are soluble in DMSO, DMF and $CHCl_3$ and insoluble in common organic solvents (Table 1). The complexes are monomers as revealed by their molecular weight determinations. The molar conductance of $10^{-3}$M solutions of complexes at the room temperature lie in the range of 170–180 $ohm^{-1}mol^{-1}cm^2$, indicating that they behave as 1:2 electrolytes[7].

### Infrared Spectra

The IR spectra of octahedral complexes have been studied in order to characterize their structures. The IR spectra of the free ligand and its metal complexes were carried out in the 4000–400 $cm^{-1}$ range (Table 2). A close perusal of infrared spectra exhibit a pair of the strong band at 3200–3250 $cm^{-1}$ corresponding to ν(N–H)[8], is present in the spectrum of benzildihydrazone but absent in the spectra of all the complexes The infrared spectra of the metal complexes show the absence of uncondensed functional groups (–$NH_2$ and >C=O),stretching modes of the starting material and the appearance of bands characteristic of the imine group. The bands presents at 2915–3130 $cm^{-1}$may be assigned due to ν(C–H) vibrations of benzildihydrazone [9]. This fact is further supported by the appearance of a new strong absorption band in the region 1635–1644 $cm^{-1}$ which may be attributed due to ν(C=N) vibrations [10]. The presence of new bands in the spectra of the metal complexes in the region at 419–439 $cm^{-1}$ due to theν (Ge–N) vibrations supports the coordination of the iminenitrogen to the metal ion [11].

### $^1$H NMR spectra

The bonding pattern in the resulting complexes has been further substantiated by the proton magnetic resonance spectra of the precursor and the metal complexes of the macrocycles (Table 3). The $^1$H NMR spectra of the complexes do not show any signal corresponding to primary amino protons. This suggested that the proposed macrocyclic skeleton has been formed. In the spectra of all the complexes, a broad signal, observed in the region δ8.11-8.20 ppm is due to amide (CO-NH) protons. Singlets observed at δ2.97-3.17 ppm are attributed to the methylene protons of malonic and succinic acid respectively while multiplets assigned at δ3.26-3.31 ppm are due to the methylene protons of glutaric and adipic acid. The compounds derived from phthalic acid show a multiplet in the region δ7.15-8.13 ppm attributed to phenyl ring protons[10].

### $^{13}$C NMR Spectra

The inferences drawn from infrared and proton NMR spectra are in well coordination with $^{13}$C NMR spectra (Table 4). Thus, the most plausible structures that can be suggested for germanium complexes on the basis of spectral evidences and their monomeric nature as shown in Figure 1.

**Table 1:** Physical properties and analytical data of macrocyclic complexes $[Ge(OAML)_1Cl_2]Cl_2$–$[Ge(OAML)_5Cl_2]Cl_2$.

| Precursers | | | Molar Ratio | Product and colour | M.P. (°C) | Analysis % Found (Calcd.) | | | | | Mol.Wt. Found (Calcd.) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| Metal Salt | Dicarboxylic Acid | Benzildihydrazone | | | | C | H | N | Cl | Sn | |
| $GeCl_4$ (0.70) | Malonic acid (0.64) | (1.48) | 1:2:2 | $C_{34}H_{28}N_8O_4Cl_4Ge$ (Orange) | 150 | 50.79 (50.90) | 3.46 (3.51) | 13.82 (13.96) | 8.72 (8.83) | 14.65 (14.79) | 789.10 (802.21) |
| $GeCl_4$ (0.53) | Succinic acid (0.56) | (1.13) | 1:2:2 | $C_{36}H_{32}N_8O_4$ $Cl_4Ge$ (Orange) | 156 | 51.92 (52.07) | 3.79 (3.87) | 13.41 (13.49) | 8.39 (8.54) | 14.18 (14.29) | 810.10 (830.25) |
| $GeCl_4$ (0.54) | Glutaric acid (0.63) | (1.15) | 1:2:2 | $C_{38}H_{36}N_8O_4$ $Cl_4Ge$ (Orange) | 179 | 53.05 (53.17) | 4.10 (4.22) | 12.91 (13.05) | 8.14 (8.26) | 13.67 (13.83) | 838.15 (858.30) |
| $GeCl_4$ (0.70) | Adipic acid (0.91) | (1.49) | 1:2:2 | $C_{40}H_{40}N_8O_4$ $Cl_4Ge$ (Orange) | 198 | 54.08 (54.20) | 4.47 (4.54) | 12.56 (12.64) | 7.84 (7.99) | 13.25 (13.39) | 867.66 (886.35) |
| $GeCl_4$ (0.63) | Phthalic acid (0.93) | (1.34) | 1:2:2 | $C_{44}H_{32}N_8O_4$ $Cl_4Ge$ (Orange) | 238 | 56.64 (57.05) | 3.35 (3.47) | 11.97 (12.09) | 7.54 (7.65) | 12.70 (12.81) | 907.65 (926.34) |

**Table 2:** Infrared spectral data of macrocyclic complexes $[Ge(OAML)_1Cl_2]Cl_2$–$[Ge(OAML)_5Cl_2]Cl_2$.

| Compound | ν(N-H) | ν(C=N) | ν(Ge–N) | ν(Ge–Cl) |
|---|---|---|---|---|
| $[Ge(OAML)_1Cl_2]Cl_2$ | 3200 | 1635 | 424 | 230 |
| $[Ge(OAML)_2Cl_2]Cl_2$ | 3220 | 1630 | 419 | 285 |
| $[Ge(OAML)_3Cl_2]Cl_2$ | 3238 | 1640 | 428 | 240 |
| $[Ge(OAML)_4Cl_2]Cl_2$ | 3250 | 1644 | 439 | 290 |
| $[Ge(OAML)_5Cl_2]Cl_2$ | 3245 | 1642 | 435 | 260 |

**Table 3:** $^1H$ NMR Spectral data (δ, ppm) of Ge(IV) macrocyclic complexes derived from benzildihydrazone and various dicarboxylic acids.

| Compound | CO–NH | $CO–(CH_2)–CO$ | $CO–(CH_2)_2–CO$ | $CO–(CH_2)_3–CO$ | $CO–(CH_2)_4–CO$ |
|---|---|---|---|---|---|
| $[Ge(OAML)_1Cl_2]Cl_2$ | 8.14 | 2.97 | – | – | – |
| $[Ge(OAML)_2Cl_2]Cl_2$ | 8.12 | – | 3.17 | – | – |
| $[Ge(OAML)_3Cl_2]Cl_2$ | 8.15 | – | – | 3.26 | – |
| $[Ge(OAML)_4Cl_2]Cl_2$ | 8.11 | – | – | – | 3.31 |
| $[Ge(OAML)_5Cl_2]Cl_2$ | 8.20 | – | – | – | – |

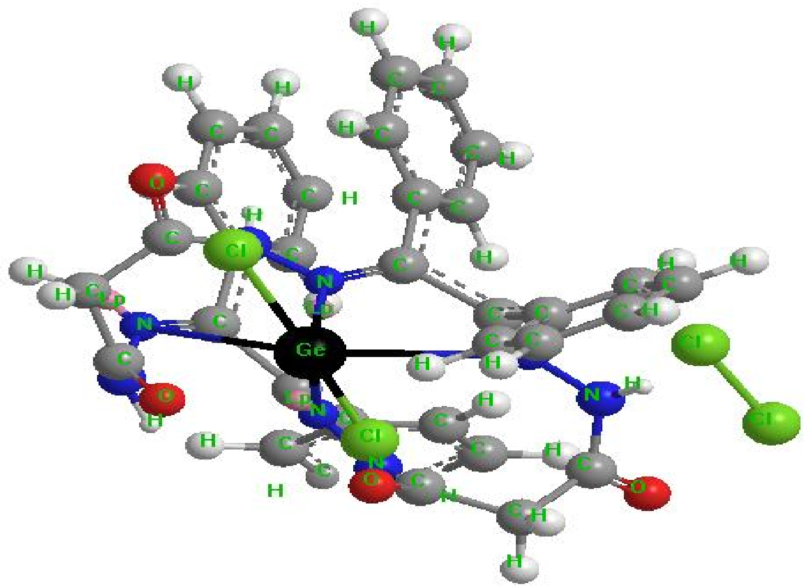


**Figure 1:** Proposed molecular structure of complex $[Ge(OAML)_1Cl_2]Cl_2$.

## Biological Activities

Currently, microbial infections have become an important clinical threat, with significant associated morbidity and mortality which is mainly due to the development to microbial resistance to the existing antimicrobial agents. Therefore, methods for anti–microbial susceptibility testing and discovering novel antimicrobial agents have been extensively used and continue to be developed [12]. Therefore, in the continuation of our research interest in biological studies the current study describes the synthesis of new tetra–coordinated mononuclear macrocyclic Ge(IV) complexes and their *in vitro* antimicrobial studies.

## Antibacterial activity

*In vitro* antibacterial screening was performed by disc diffusion method [13], for primary selection of the compounds as therapeutic agents. The antibacterial activity of the ligand and its Ge(IV) complexes were evaluated against two bacteria including Gram–positive bacteria *S. mutans, S. pyogenes and S. aureus)* and Gram–negative bacteria *P. aeruginosa, S. typhimurium* and *E. coli)* (Figure 2).

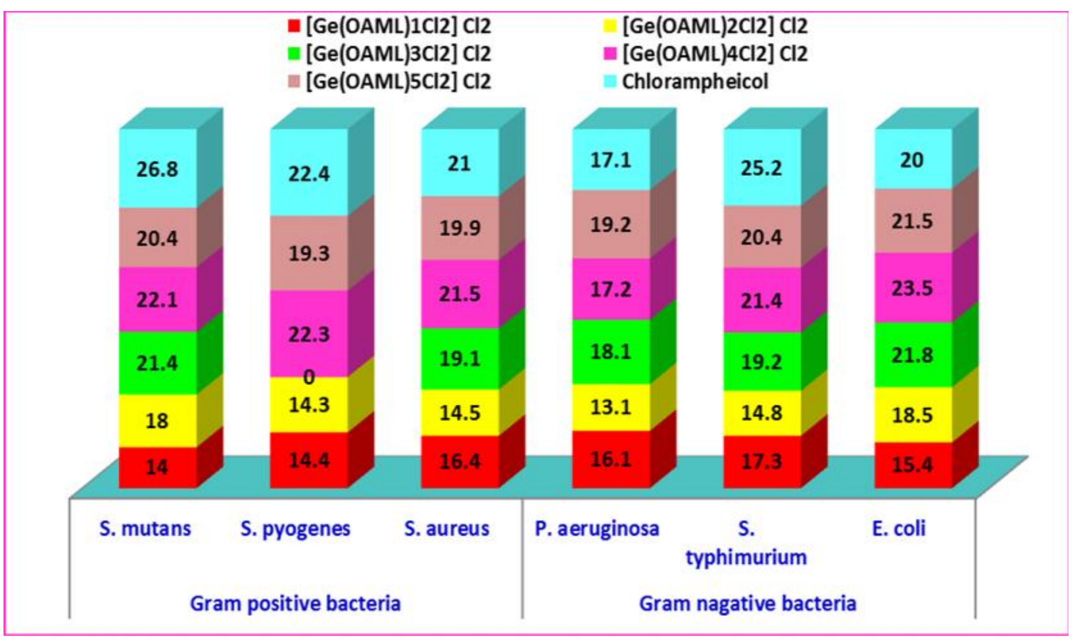
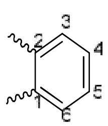
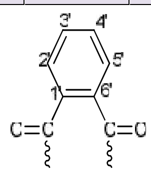


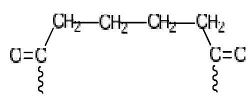

**Figure 2:** Antibacterial activity against various gram–positive and gram–negative bacterial strains with diameters of the zone of inhibition.

**Table 4:** $^{13}$C NMR Spectral data (δ, ppm) of Ge(IV) macrocyclic complexes derived from benzildihydrazone and various dicarboxylic acids.

| Compound | >C=N | C=O | $C_{1,2}$ | $C_{3,6}$ | $C_{4,5}$ | $C_{\alpha}$ | $C_{\beta}$ | $C_{1',6'}$ | $C_{2',5'}$ | $C_{3',4'}$ |
|---|---|---|---|---|---|---|---|---|---|---|
| $[Ge(OAML)_1Cl_2]Cl_2$ | 155.01 | 175.13 | 155.27 | 150.19 | 146.16 | 31.41 | – | – | – | – |
| $[Ge(OAML)_2Cl_2]Cl_2$ | 150.42 | 174.25 | 160.62 | 156.75 | 152.24 | 32.15 | 22.03 | – | – | – |
| $[Ge(OAML)_3Cl_2]Cl_2$ | 151.03 | 176.35 | 161.93 | 155.62 | 153.65 | 33.85 | 23.29 | – | – | – |
| $[Ge(OAML)_4Cl_2]Cl_2$ | 155.03 | 175.91 | 162.04 | 156.55 | 152.71 | 32.10 | 25.05 | – | – | – |
| $[Ge(OAML)_5Cl_2]Cl_2$ | 159.20 | 175.84 | 163.18 | 156.42 | 153.08 | 31.46 | – | 132.31 | 127.62 | 123.38 |




α β β α

The nutrient agar medium [14] having the composition peptone 5g, beef extract 5g, NaCl 5g, agar–agar 20g and distilled water 1000 mL was pipetted into the petridish. When it solidified, 5mL of warm seeded agar was applied. The seeded agar was prepared by cooling the molten agar and then added the 10 mL of bacterial suspension. The compounds were dissolved in methanol in 500 and 1000 ppm concentrations. Paper discs of Whatman No.1 filter paper measuring diameter of 5mm were soaked in these solutions of varied concentrations. The discs were dried and placed on the medium previously seeded with organisms in petriplates at suitable distance. The petriplates were stored in an incubator at 28±20˚C for 24 h. The diameters of the zone of inhibition produced by the compounds were compared with the standard antibiotic (Chloramphenicol). The zone of inhibition thus formed around each disc containing the test compounds was measured accurately in mm.

## Antifungal Activity

### Spore germination test and method

Antifungal activity of the $[Ge(OAML)_3Cl_2]Cl_2$, $[Ge(OAML)_4Cl_2]Cl_2$ and $[Ge(OAML)_5Cl_2]Cl_2$was studied on various fungi, namely *Alternaria riticina, Fusarium udum, Alternaria brassicae, Curvularia species, Helminthosporium oryzae, Aspergillus flavus, Alternaria brasicicola* and *Curvularia lunata* by using the spore germination technique [15,16]. A drop of compound solution was placed on a grease–free glass slide and 50–100 spores of the test fungi were placed with the help of a sterilized inoculation needle on the solution. The slides were then placed in a moisture chamber and incubated at 25 $\pm$ 2˚C, for 24 h. After incubation, the spores were fixed and stained with lectophenol cotton blue and spore germination was observed under a light microscope. Similar spore numbers of each fungus were mixed in sterilized distilled water, which served as control. For measurement of inhibition, the percentage germination was subtracted by a hundred to get percentage inhibition. All the experiments were conducted in triplicate. The data were subjected to students 't' test for statistical significance. Mycelial growth of five fungi, with or without chemicals, was observed by taking dry weight of fungi grown in 150ml conical flask. All the chemical flasks were filled with 50 mL potato dextrose broth. Required amounts of the chemicals were then added to the broth to get the desired concentrations (100, 200 and 400 ppm) individually and in the mixture and dissolved and mixed thoroughly by shaking the flasks after autoclaving for 15 min. (at 121$^{o}$C) the broth was allowed to cool down and 5mm disc of fungal mycelium was taken from the border of an actively growing fungal colony and incubated into the broth. The flasks were incubated at 25 $\pm$ 2$^{o}$C for one week, Potato dextrose broth without the chemicals served as control. After one week, the broth with the fungal colony was determined by deducting the weight of the filter paper from the total weight of the filter paper and mycelium. All the experiments were conducted in triplicate. The data were subjected to student 't' test for statistical significance. Antifungal activity measured by these methods is presented in the Tables 5, 6, 7, 8 and 9.

**Table 5:** Effect of $[Ge(OAML)_5Cl_2]Cl_2$ on spore germination of some fungi.

| Fungus | Host | Control | $R_1$ 250ppm | $R_2$ 125 ppm | $R_3$ 62.5 ppm |
|---|---|---|---|---|---|
| *Fusarium udum* | *Canfanus cajan* | 96.73 | 2.51** | 11.25** | 18.86** |
| *Alternaria triticina* | *Triticum aestivum* | 99.27 | 18.03** | 24.43** | 70.15** |
| *Alternaria brassicae* | *B. campestris var. capitata* | 99.53 | 2.00** | 4.18** | 17.37** |
| *Curvularialunata* | *Oxyza sativa* | 97.33 | 68.89** | 82.73 | 87.54 |
| *Curvularia sp.* | *Brassica campestris* | 96.72 | 2.97** | 5.67** | 6.59** |
| *Helminthosporium oryzae* | *Oxyza sativa* | 96.82 | 2.99** | 5.98** | 6.88** |
| *Aspergillus flavus* | *Saprophyte* | 80.33 | 3.17** | 8.33** | 15.83** |
| *Alternaria brasicicola* | *B. Campestris* | 92.63 | 7.56** | 11.24** | 27.25** |

Row data with ** are significant at P$\geq$ 0.01

**Table 6:** Effect of the ligand ($[Ge(OAML)_4Cl_2]Cl_2$ on spore germination of some fungi.

| Fungus/Treatment | Host | Control | $S_1$ 500ppm | $S_2$ 250 ppm | $S_3$ 125 ppm |
|---|---|---|---|---|---|
| *Fusarium udum* | *Canfanus cajan* | 98.63 | 9.78** | 15.22** | 41.25** |
| *Alternaria triticina* | *Triticum aestivum* | 99.27 | 49.39** | 71.83** | 87.87** |
| *Alternaria brassicae* | *B. campestris var. capitata* | 95.53 | 14.14** | 21.69** | 33.49** |
| *Curvularia lunata* | *Oxyza sativa* | 96.44 | 73.00** | 82.73 | 87.54 |
| *Curvularia sp.* | *Brassica campestris* | 96.33 | 13.21** | 24.86** | 36.72** |
| *Helminthosporium oryzae* | *Oxyza sativa* | 97.29 | 6.57** | 9.28** | 52.15** |
| *Aspergillus flavus* | *Saprophyte* | 80.33 | 7.67** | 24.83** | 47.00** |
| *Alternaria brasicicola* | *B. Campestris* | 92.63 | 24.89** | 34.40** | 41.87** |

Row data with ** are significant at $\geq$ 0.01.

**Table 7:**Effect of $[Ge(OAML)_3Cl_2]Cl_2$, complex on spore germination of some fungi.

| Fungus / Treatment | Host | Control | $T_1$ (400 ppm) | $T_2$ (200 ppm) | $T_3$ (100 ppm) | $T_4$ (50 ppm) |
|---|---|---|---|---|---|---|
| *Fusarium udum* | *Canfanus cajan* | 98.63 | 4.72** | 9.54** | 17.34** | 24.08** |
| *Alternaria triticina* | *Triticum aestivum* | 93.32 | 0.60** | 10.72** | 27.31** | 63.11** |
| *Alternaria brassicae* | *B. campestris var. capitate* | 92.47 | 2.18** | 4.92** | 12.53** | 20.16** |
| *Curvularia lunata* | *Oxyza sativa* | 91.39 | 3.94** | 11.19** | 23.32** | 37.23** |
| *Curvularia sp.* | *Brassica campestris* | 86.39 | 1.18** | 3.37** | 10.74** | 20.59** |
| *Helminthosporium oryzae* | *Oxyza sativa* | 84.78 | 3.44 | 4.93** | 8.58** | 17.97** |
| *Aspergillus flavus* | *Saprophyte* | 94.32 | 6.17** | 13.86** | 26.06** | 29.20** |
| *Alternaria brasicicola* | *B. Campestris* | 92.63 | 11.52** | 21.58** | 29.95** | 37.76** |

Row data with ** are significant at p $\geq$ 0.01

**Table 8:** Effect of the $[Ge(OAML)_3Cl_2]Cl_2$, $[Ge(OAML)_4Cl_2]Cl_2$ and $[Ge(OAML)_5Cl_2]Cl_2$ on mycelial growth of some fungi.

| Treatment | Concentration (ppm) | *Curvularia lunata* | *Fusarium udum* | *Alternaria brassicae* | *Alternaria riticina* |
|---|---|---|---|---|---|
| Control | 200 | 0.2301 | 0.2195 | 0.2170 | 0.2486 |
| $[Ge(OAML)_3Cl_2]Cl_2$ | 100 | 0.1889 | 0.1487** | 0.1299** | 0.1440** |
| | 200 | 0.1320** | 0.1138** | 0.1140** | 0.1145** |
| | 400 | 0.1024** | 0.1015** | 0.0982** | 0.1021** |
| $[Ge(OAML)_4Cl_2]Cl_2$ | 100 | 0.1772** | 0.1576** | 0.2277** | 0.2135** |
| | 200 | 0.1488** | 0.1266** | 0.2212** | 0.1875** |
| | 400 | 0.0996** | 0.1075** | 0.2100** | 0.1477** |
| $[Ge(OAML)_5Cl_2]Cl_2$ | 100 | 0.1455** | 0.1185** | 0.1010** | 0.1245** |
| | 200 | 0.1241** | 0.0983** | 0.8260** | 0.0930** |
| | 400 | 0.0857** | 0.0481** | 0.0496** | 0.0230** |

Column data with ** are significant at $P \geq 0.01$.

**Table 9:** Effect of the $[Ge(OAML)_5Cl_2]Cl_2$, $[Ge(OAML)_4Cl_2]Cl_2$ and $[Ge(OAML)_3Cl_2]Cl_2$, complex on spore germination of some fungi (% inhibition).

| Fungus / Treatment | Host | Control | $[Ge(OAML)_3Cl_2]Cl_2$ | | $[Ge(OAML)_4Cl_2]Cl_2$ | | $[Ge(OAML)_5Cl_2]Cl_2$ | |
|---|---|---|---|---|---|---|---|---|
| | | | 1000 | 500 | 1000 | 500 | 1000 | 500 |
| *Fusarium udum* | *Canfanuscajan* | 1.35 | 98.65 | 90.0 | 99.37 | 88.2 | 100.0 | 95.4 |
| *Alternaria brassicae* | *B. campestris var. capitata* | 7.35 | 26.0 | 4.5 | 15.0 | 3.4 | 86.6 | 78.6 |
| *Curvularia lunata* | *Oxyza sativa* | 32.20 | 99.05 | 92.6 | 96.2 | 82.5 | 100.0 | 96.2 |
| *Curvularia sp.* | *Brassica campestris* | 3.65 | 98.77 | 85.19 | 99.4 | 85.3 | 100.0 | 98.8 |
| *Helminthosporium oryzae* | *Oxyza sativa* | 1.18 | 100.0 | 98.4 | 26.2 | 4.3 | 91.3 | 77.6 |
| *Aspergillus flavus* | *Saprophyte* | 19.80 | 99.7 | 92.27 | 56.7 | 27.4 | 99.2 | 94.8 |
| *Alternaria brasicicola* | *B. Campestris* | 22.24 | 99.5 | 92.5 | 48.2 | 22.4 | 77.2 | 54.2 |

## Statistical analysis

The data recorded for different concentrations of the compounds were subjected to the following statistical analysis.

## Analysis of variance (ANOVA)

The analysis of variance was carried out separately for each fungus against all the compounds at various concentrations according to the procedure of Randomized Block Design Analysis (Table 10) [17].

**Table 10:** Analysis of Variance (ANOVA).

| Source of Variance | Replication | Concentration | Error | Total |
|---|---|---|---|---|
| Degree of Freedom | (r–1) | (c–1) | (r–1) (c–1) | (rc–1) |
| Sum of squares | RSS | CSS | ErSS | TSS |
| Mean sum of squares | RMS | CMS | ErMS | – |
| $F_{cal}$ = Calculated value of F | RMS/ ErMs | CMS/ErMs | – | – |

The results showed that the spore germination inhibited significantly even at the lowest concentration $T_4$ (50 ppm). Similar results were obtained when selected fungi were taken for their mycelial growth on potato dextrose broth supplemented with the chemicals. The spores which showed sensitivity against the chemicals also showed a similar trend in the production of mycelial dry weight. Out of the tested fungi, *Alternaria triticina* showed maximum sensitivity when the chemicals were mixed, followed by *Alternaria brassicae* and *Fusarium udum* (Table 8). The results of the present experiments showed the probable synergistic effect of the two compounds in the mixture. Such compounds may inhibit development of resistance since they have multisite action majority in comparison to widely used fungicides with single site of action. Further experimentation with these compounds in glasshouse and under field conditions is suggested for practical application of plant disease control. In case of *Fusarium udum* and *Aspergillus niger* the effect of the ligand $[Ge(OAML)_3Cl_2]Cl_2$, $[Ge(OAML)_4Cl_2]Cl_2$and $[Ge(OAML)_5Cl_2]Cl_2$were very significant showing inhibition upto 100% in many these cases (Table 9).

From an overall study of the effect of the $[Ge(OAML)_3Cl_2]Cl_2$, $[Ge(OAML)_4Cl_2]Cl_2$and $[Ge(OAML)_5Cl_2]Cl_2$, in certain cases the complex, $[Ge(OAML)_5Cl_2]Cl_2$ is more effective i.e., show more fungi–toxicity in comparison to the individual $[Ge(OAML)_4Cl_2]Cl_2$ or $[Ge(OAML)_3Cl_2]Cl_2$. For practical utility of this compound, the inhibiting capacity of the complexes were compared with the commercially available fungicide, dithane–M–45 (a broad fungicide) which is used in the inhibition of spore germination in the 0.1 – 0.2% in the field condition limit for many fungi. It was found that in the case of $[Ge(OAML)_5Cl_2]Cl_2$against *Fusarium udum* and *Curvularia* species, the effect of the complex was found to be better than that of commercially available fungicide dithane M–45. This observation is quite significant and opens, up a new field of research as the metal complex $[Ge(OAML)_5Cl_2]Cl_2$is better fungi toxic than commercial products, showing greater possibility of applicability of the complex under field conditions.

## Conclusion

In this work, series of macrocyclic complexes of Ge(IV) were designed and synthesized. These macrocyclic monometallic complexes of Ge(IV) were then investigated against a number of microbial species. All the complexes were physicochemically characterized using elemental analysis, IR spectrum, $^1$HNMR and $^{13}$C NMR spectrum. All the complexes were evaluated for antimicrobial property against Gram–positive bacteria (*S. mutans, S. pyogenes and S. aureus)* and Gram–negative bacteria *(P. aeruginosa, S. typhimurium and E. coli)* along with this antifungal activity of the $[Ge(OAML)_3Cl_2]Cl_2$, $[Ge(OAML)_4Cl_2]Cl_2$ and $[Ge(OAML)_5Cl_2]Cl_2$ was studied on various fungi, namely *Alternariat riticina, Fusarium udum, Alternaria brassicae, Curvularia species, Helminthosporium oryzae, Aspergillus flavus, Alternaria brasicicola* and *Curvularia lunata* by using the spore germination technique. The effect of complex $[Ge(OAML)_5Cl_2]Cl_2$ against *Fusarium udum* and *Curvularia* species was found to be better than that of commercially available fungicide dithane M–45. Our data indicated that these complexes were effective to combat the growth of selective drug resistant pathogenic microorganisms.

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