

ORGANOGERMANIUM COMPOUNDS: DESIGN, SYNTHESIS, LIGATION PROPERTIES AND OPPORTUNITY IN CHEMICAL BIOLOGY

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Abstract: The field of organogermanium in chemistry becomes important as Germanium compounds have a low mammalian toxicity and show activity against certain bacteria, which makes them useful as chemotherapeutic agents. Consideration is given to the use of organogermanium compounds (OGCs) in the development of biologically active pharmaceuticals with distinct features and a variety of pharmacological effects, such as the Panaxel drug family and the Germavit mineral vitamin complex. New biologically active materials for medical technologies have been created based on OGC, including bandages, dental floss, and surgical sutures for retention. OGC's biological activity also enables its application in the fragrance and cosmetics sectors. The present review covers the design and synthesis of Organogermanium compounds along with their biological activities. The review provides an overview of the various synthesis techniques for the synthesis of Organogermanium compounds and the synthesized compounds are further characterized by using various spectroscopic techniques like NMR, IR, XRD, and UV Visible etc. The fully characterized compounds are further evaluated for their biological activities and all the compounds shows good biological activities like antimicrobial, cytotoxicity, antitumor etc.

Keywords: Antioxidant, Bacteria, Biological activities, Organogermanium and Pathogens.

1. INTRODUCTION

The chemistry of germanium has received considerable attention over the years. The several hundred coordination compounds of this metallic element have been reviewed. The Ge atoms are mostly in oxidation states +4 or +2 with a few examples of mixed valencies and an example of +1. Coordination states (and geometries) range from seven (pentagonal bipyramidal), six (octahedral), five (trigonal bipyramidal), three (mostly trigonal) and two (bent), with the most common being four (tetrahedral) [1]. The lower coordination numbers have Ge atoms in a +2 oxidation state, and most four and all higher have the Ge atom in a +4 oxidation state. Monomers and dimers are the most abundant, with two examples of polynuclear and unique examples of hepta- and nonnuclear. There are many examples of distortion isomerism, including multiple crystallographically independent molecules in the same crystal. The most common C-donor ligands are methyl and phenyl groups. The mean Ge(II) – L bond distances are shorter than Ge(IV)-L distances, both increasing with the radius of the coordinated atom. All distances are generally shorter than equivalent distances in organotins and organolead derivatives. Germanium has wide applications in reproduction [2]. It also has an antimutagenic effect. It reduces the

mutagenicity of gamma rays. Germanium dioxide reduces the number of micronuclei and chromosome aberration in mouse bone marrow *in vivo* and inhibited the induction of sperm head abnormalities by cadmium chloride. Germanium dioxide had no effect alone in any of these assays. A number of experiments have looked at the effect of germanium compounds on the incidence of chemically induced tumours [3]. The number of intestinal tumours induced by 1,2-dimethyl hydrazine (DMH) was reduced from 91% to 64% in rats after giving organic germanium (Ge-132) for one month before and during DMH treatment or during DMH treatment only. In case the rats given "natural organic germanium" extracted from plants, the incidence of tumours was reduced to 50% and 45% in animals receiving the germanium before during DMH treatment or during DMH treatment only. Measurement of urinary Ge can detect occupational exposure to inorganic Ge and its compounds. It is prudent to recommend the monitoring of renal variables in workers exposed to germanium [4]. A histological comparison of the liver, spleen, bone marrow, circulating young erythrocytes, and differential count in mature male and female albino rats receiving germanium dioxide with their litter controls not receiving this compound was made [5]. The field of organogermanium in chemistry becomes important. Germanium compounds have a low mammalian toxicity and show activity against certain bacteria, which makes them useful as chemotherapeutic agents. Earlier due to the original synthesis of organic germanium compounds, they were used clinically in the world to treat wide spectrum of illnesses, and now has been the subject of extensive researches like pathology, biochemistry, pharmacology, immunology and neurochemistry. Certain derivatives are used as homogenous catalysts, while others find uses in agriculture as biocides. Organogermanium compounds have considerable thermal stability and chemical inertness [6-7]. The chemistry of germanium has received considerable attention over the years. Organogermanium chemistry closely resembles that of silicon, except that the later are more thermally stable and less chemically reactive [8]. The biological properties of organogermanium compounds are given in Figure 1.

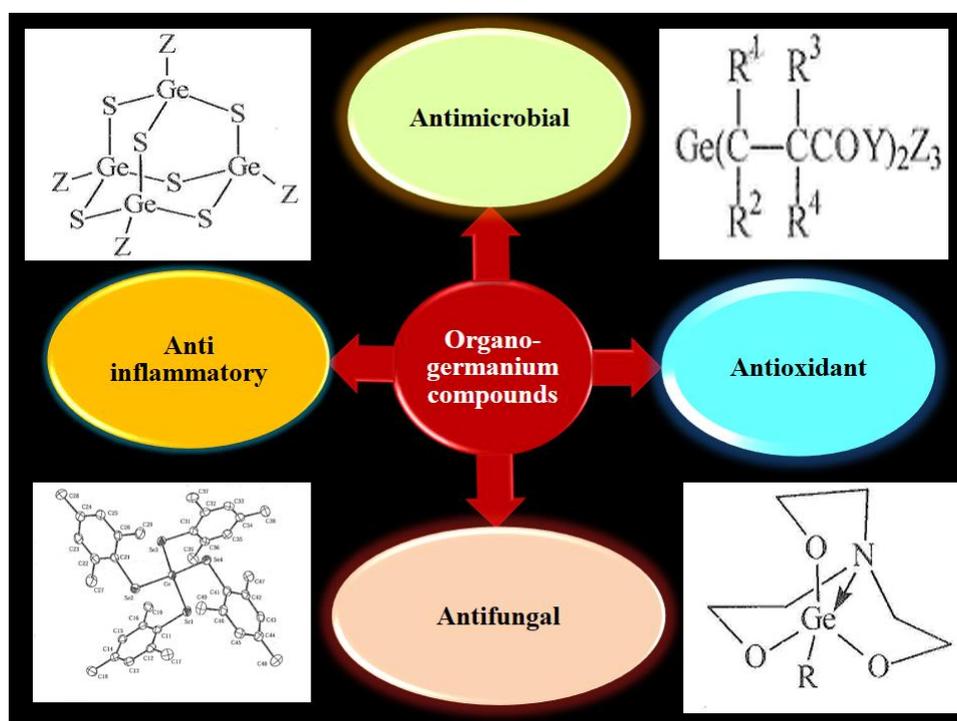
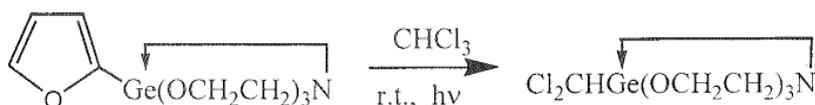


Fig. 1.

2. DESIGN AND SYNTHESIS OF ORGANOGERMANIUM COMPOUNDS

Organic derivatives of pentacoordinated germanium have attracted a great deal of interest in the recent years. Germatranes $RGe(OCH_2CH_2)_3N$ containing an intramolecular N-Ge bond are the most intensively studied class of such compounds. The analysis of Cambridge Crystallographic Data Bank has shown that the molecular structures of over 40 germatranes have been documented [9,10]. The germatrane structure consists of distorted trigonal bipyramid with nearly equatorial oxygen atoms. The transannular N-Ge bond distances for all germatranes (2.011-2.29 Å) depend on the electronic effects of the substituents bound to the all germanium atoms^{9,10}. Recently, it has been reported that the selective cleavage of Si-C

bond in hetarylsilanes proceeds with good to excellent yields [11]. It was found that 2-furylgermatrane can be quantitatively converted into dichloromethylgermatrane by simple irradiation in chloroform solution.



Lukevics et al. [12] gave the molecular structure of dichloromethylgermatrane (Figure2).

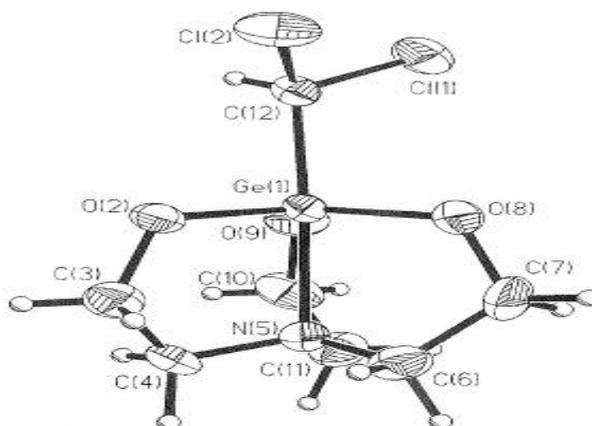


Fig. 2. Molecular structure of dichloromethylgermatrane

Schroeder et al. [13] reported that germanium, tin and arsenic effect on growth, survival, pathological lesions and life span of rats .Life term studies on mice and rats exposed to several abnormal trace metals have been reported [14-17]. A more recent study involved germanium, tin and arsenic in mice [18]. To confirm and extend these observations, rats were maintained on identical regimens. One purpose of these studies is to discover, if possible, recondite toxic effects in terms of growth, survival and extreme life span; another is to discover which elements, given orally, accumulate in several organs with age. In mice, tin was found to accumulate in heart muscle, as it does in man [19], and in spleen, and arsenic given as arsenite to a small extent in liver, heart and lung. Mice fed germanium and arsenic had shorter survival times than their controls.

Toru et al. [20] reported chronic tubulointerstitial changes induced by germanium dioxide in comparison with carboxyethyl germanium sesquioxide. Chronic nephrotoxicity was investigated in rats orally administered germanium dioxide (GeO_2) and carboxyethylgermanium sesquioxide (Ge-132) for 24 weeks. Increased BUN and serum phosphate as well as decreased creatinine clearance, weight loss, anemia and liver dysfunction were apparent at week 24 only in the GeO_2 treated group. On the other hand, neither toxic effects nor renal histological abnormalities were manifested in either the Ge-132 or the control group. Andreae et al. [21] measured arsenic, antimony, tin, germanium, silica, and supporting parameters in water samples collected along a section through the estuary of the Tejo River, Portugal. Arsenic and antimony showed substantial inputs when the data were analyzed with an estuarine model. Froelich et al. [22] measured the concentrations of dissolved nutrients, germanium species, arsenic species, tin, barium, dimethylsulfide and related parameters along the salinity gradient in charbtt Harbor (Florida). Phosphate enrichment from the phosphate industry on the Peace River promotes a productive diatom bloom near the river mouth where nitrate and silicon are completely consumed. Inorganic germanium is completely depleted in this bloom by uptake into biogenic apal. The Ge / Si ratio taken up by diatoms is about 0.0000007, the same as that provided by the river flux, confirming that silceons organisms incorporate germanium as an accidental trace replacement for silica. Monomethylgermanium and dimethylgermanium concentrations are undetectable in the Peace River, and increase linearly with increasing salinity to the seawater and of the bay. They suggested that these organogermanium species behave conservatively in estuaries and are neither produced nor consumed during estuarine biogenic apart formation or dissolution. Inorganic arsenic displays slight removal in the bloom. Tiekink et al. [23] have reported the X-ray crystal structure of Ph_3GeCl (Figure3).

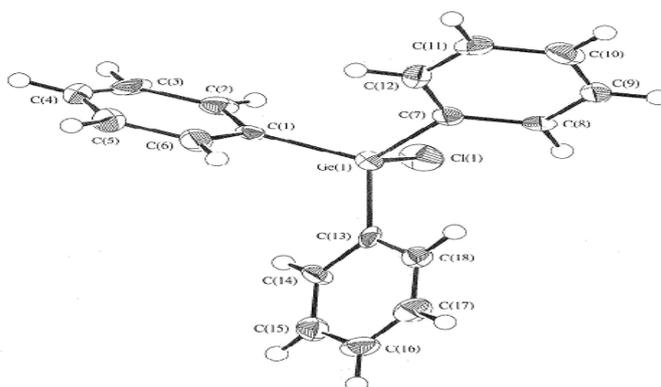


Fig. 3. The Crystal structure of triphenylgermanium(IV) chloride

Xiaoni et al. [24] synthesized thirteen tris (2-methyl-2-phenylpropyl)tingermethylpropionates and their structures characterized by elemental analysis, IR, multinuclear NMR (^1H , ^{13}C and ^{119}Sn) and MS spectroscopies. The structure of $(\text{PhC}(\text{CH}_3)_2\text{CH}_2)_3\text{SnO}_2\text{CCH}_2\text{CH}(\text{o-C}_6\text{H}_4\text{Cl})\text{GePh}_3$ has been determined by X-ray diffraction study, which indicated that the tin in the compound possess a tetrahedral geometry. Bioassay results have shown that some of the compounds have good acaricidal activity. The crystal structure of $(\text{MesSe})_4\text{Ge}$ has been determined which differs from a previous structural investigation of this complex [25] (Figure4).

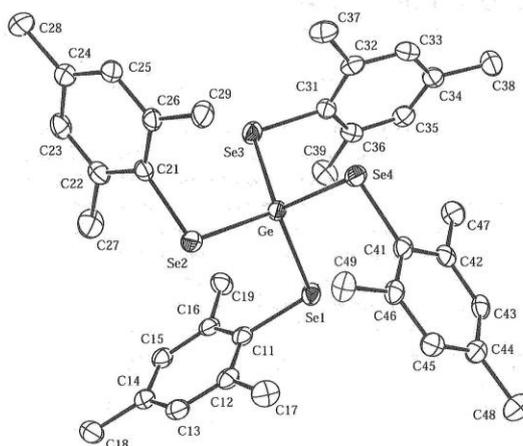


Fig. 4. ORTEP diagram of $(\text{MesSe})_4\text{Ge}$

Choudhary et al. [26] reported a series of diorganotin dicarboxylates of the general formula $(\text{CH}_3)_2\text{Sn}(\text{OCOCHR}_3\text{CHR}_2\text{GeR}_1)_2$ where $\text{R}_1 = (\text{C}_6\text{H}_5)_3$, $(\text{p-CH}_3\text{C}_6\text{H}_4)_3$ and $\text{N}(\text{CH}_2\text{CH}_2\text{O})_3$, $\text{R}_2 = \text{C}_6\text{H}_5$, H , CH_3 , $\text{p-CH}_3\text{OC}_6\text{H}_4$, $\text{p-ClC}_6\text{H}_4$ and $\text{p-CH}_3\text{C}_6\text{H}_4$, $\text{R}_3 = \text{CH}_3$ and H , which have been synthesized by the reaction of dimethyltin oxide with germanium substituted propionic acid in 1:2 molar ratios in toluene. In a search for new insect growth regulators with unusual biological properties and different activity spectrum Huang et al. [27] thought that the preservation of the bioactive unit and the introduction of 2-methyl-3-(triphenylgermanyl)propoxycarbonyl in N-tert-butyl-N,N'-dibenzoylhydrazine would enhance their larvicidal activities to a significant degree. The preliminary results indicate that some compounds have inhibitory effects against plant pathogenetic bacteria such as early blight of tomato. Further, a new series of benzylgermatranes $\text{RC}_6\text{H}_4\text{CH}_2\text{Ge}(\text{OCH}_2\text{CH}_2)_3\text{N}$, $\text{R} = \text{H}$ (I), 2-Br (II), 3-Br (III) and 4-Br (IV), has been obtained by Lukevics and coworkers [28] to study the influence of a substituent position on coordination of the germanium atom, the values of bond angles and neurotropic activity. Further, catechol and germanium tetrachloride in the presence of pyridine yielded an octahedral complex (Figure 5).

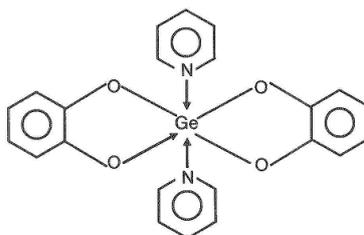


Fig. 5.

On heating the dipyrindine complex in DMF, a new complex gets precipitated (Figure 6).

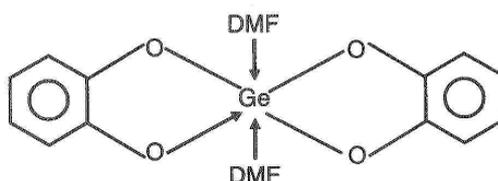


Fig. 6.

Kenney et al. [29-31] have reported the synthesis of germanium phthalocyanines. These compounds are important because few metal phthalocyanines are known in which the central element has as large an electronegativity as germanium. Also, they provide an opportunity for the study of hexa-coordinated germanium when it is bonded to six atoms, of which four are the nitrogen atoms, and the germanium atom can be assumed to be a planar arrangement. Due to the great stability of the phthalocyanine ring system, this unusual, partly predetermined, hexa-coordination is preserved under a wide variety of conditions. Several reports have included organogermanium compounds as members of the biologically active organometal series. The following cyclic compound shows bactericidal and fungicidal activities Figure 7.

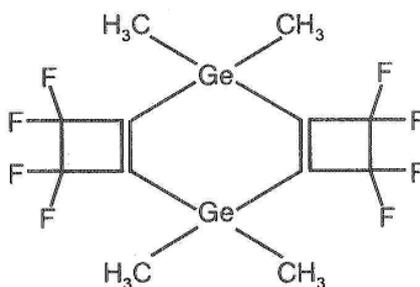


Fig. 7.

Okawa and Kubo studied the antimicrobial activity against different microorganisms of the compound shown in Figure 8.

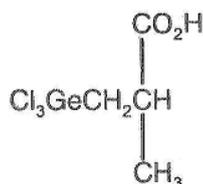
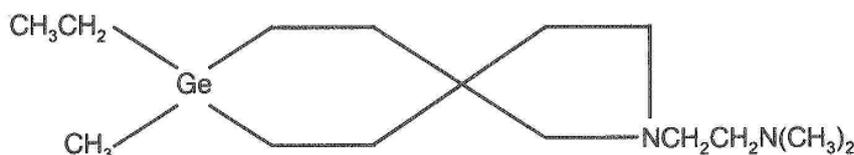


Fig. 8.

Triorganogermanium compounds have been fairly well studied and show appreciable activity against bacteria and fungi, while unsymmetrical tetraorganogermanes are found to be more active. A fair amount of work has been done on the germacyclic compounds.



In an extension to the related germanium complexes, the bis(benzenediolato)chlorogermanates and bis(benzenediolato)fluorogermanates have been structurally characterized by Holmes et al. (Figure 9).

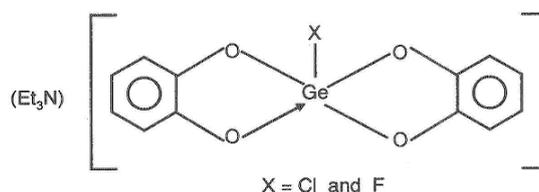


Fig. 9.

3. BIOLOGICAL PROPERTIES OF ORGANOGERMANIUM COMPOUNDS

The sulphur compounds of germanium have also been studied extensively. The crystal and molecular structures of the complex, formed by the reaction of GeCl_4 with the disodium salt of ethylenediaminetetraacetic acid in hot water, have been determined by single crystal X-ray diffraction technique. Choudhary et al. [32] have reported some new triorganotin carboxylates containing germanium with the general formula $(\text{R}_1\text{GeCHR}_2\text{CH}_2\text{COO})\text{Sn}(\text{CH}_2\text{C}(\text{CH}_3)_3)$ where $\text{R}^1 = \text{N}(\text{CH}_2\text{CH}_2\text{O})_3$ and C_6H_5 , $\text{R}^2 = \text{C}_6\text{H}_5$, $p\text{-C}_6\text{H}_4\text{OCH}_3$ and $o\text{-}/p\text{-C}_6\text{H}_4\text{F}$ (Figure 10). These were synthesized and characterized by elemental analysis, infrared, multinuclear (^1H , ^{13}C and ^{119}Sn) NMR and mass spectrometry. Antibacterial activity of these compounds was evaluated against the standard drugs ampicilline and amoxicilline, and found to be more active in some cases than the standard drugs.

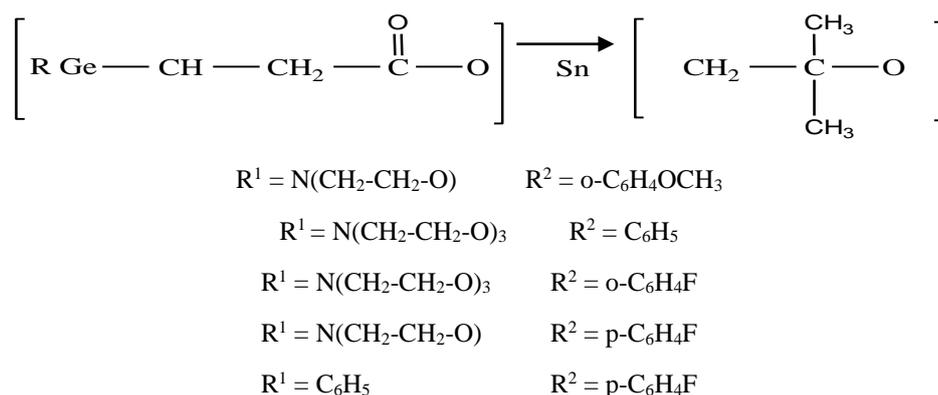
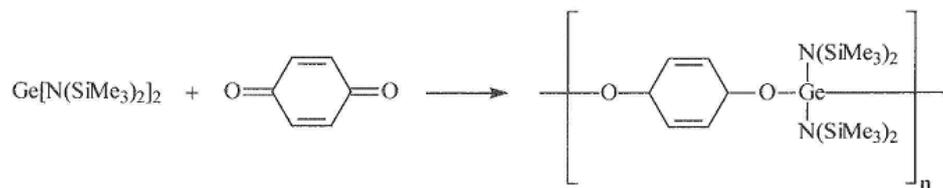


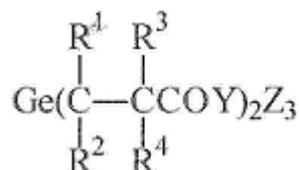
Fig. 10.

Agustin et al. [33] reported the synthesis and characterization of new stable divalent germanium, tin and lead homoleptic species L_2M ($\text{L}_2 = 2$, 2'-N, N''-bis(salicylidene)ethylenediamine, $\text{M}=\text{Ge}(1)$, $\text{Sn}(2)$, $\text{Pb}(3)$). Germanium has numerous applications in the electronic domain (semiconductors and transistors). Germanium is often supplanted by silicon which is cheaper. However, it has been shown that silicon micro chips exhibit an increase in their frequency by doping with germanium (from 1.8 to 28 GHz) [34] Monocrystalline germanium is utilized in infrared optics (metallic lens) but also for infrared detection evinces. Germanium is used for aeronautic and space applications (special alloys). GeO_2 is a component of special glasses displaying high refractive indexes and low dispersion coefficients, and is also involved in the manufacturing of optical fibers. GeO_2 is also used as a catalyst in transesterification reactions and ethylene polycondensation. Finally, GeO_2 enters the composition of ceramics with potassium or tantalum oxides, such as K_2O and Ta_2O_5 . GeH_4 is commonly used as a precursor for the production of semi conducting thin films by using the chemical vapor deposition process. Pure germanium thin films thus obtained have numerous applications, such as solar energy converters or photovoltaic cells [35]. Alkylgermanium hydrides with titanium, vanadium, chromium or molybdenum

halides as co-catalysts are superior to the Ziegler-Natta catalysts in the polymerisation of olefins [36]. The germynes react with p-benzoquinones leading to polymer in excellent yields [37]. For example, the reaction with the p-benzoquinone is shown below:



Organometallic polymers with unsaturated germanium (germylene Ge^{II} structure, e.g., germanium derivatives of thiophene or N-methylpyrrole) have shown interesting semiconducting properties. The organogermanium polymers with germanium IV, such as polygermanes (R_2Ge) $_n$, polygermyldiacetylenics, polydigermaethylenics, polygermathiophene are semiconductors but only when they are doped with small quantities of SbF_5 , FeCl_3 or NOBF_4 [38]. Germanium has been detected in a few plants or fruits, such as ginseng, litchi or garlic (at a concentration ranging from 800 to 2000 ppm). A few organic germanium derivatives have been tested in anticancer protocols. These studies are mainly led by the Asai Research Institute in Japan. For example, the sesquioxide of 2-carboxyethylgermanium $\text{Ge}(\text{CH}_2\text{CH}_2\text{COOH})_2\text{O}_3$ has been tested. A few derivatives with similar structures have also been studied as antitumor reagents but also as antibacterial agents [39].



$\text{R}^1\text{-R}^4 = \text{H}$, alkyl, aryl; $\text{Z} = \text{O}$, S; $\text{Y} = \text{OH}$, OR, OM, NH_2 , N_2 , NRR'

The porphyrin dimethylgermanium complexes (Figure 11) have shown an anticancer activity for rats and mice.

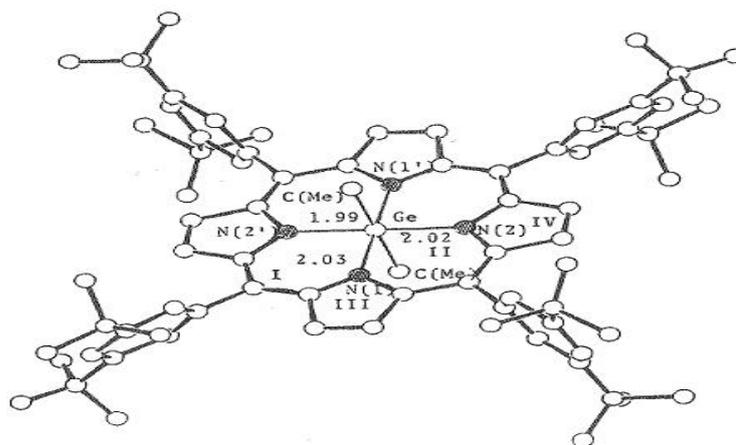


Fig. 11.

Moreover, spirogermane (Figure 12) is an active compound against prostate cancer [40].



Fig. 12.

Rijkens and Van der Kerk [41] have studied the biological activity of trialkyl germanium on fungi, yeasts and bacteria. Some organogermanium compounds present a rather strong activity against streptococcus lactis. Recently, $\text{Me}_3\text{GeCH}_2\text{CH}_2\text{NHCH}_2\text{Ph}$ has shown a high antibacteria activity with a large spectrum. The organogermanium sesquisulfur (Figure 13) has also an excellent antibacterial activity [42].

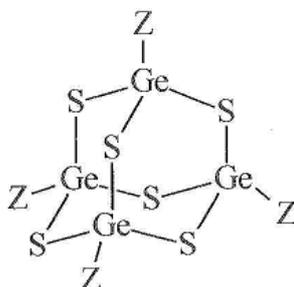


Fig. 13.

The geometries and trithiagermatranes (Figure 14) exhibit psychotropic and antitumor activities [43].

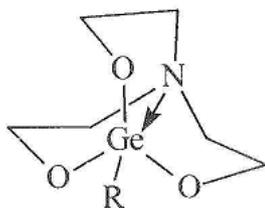
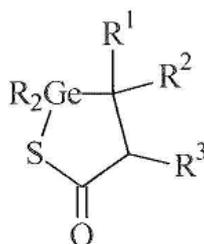


Fig. 14.

Germathiolactones (Figure 15) are active as biological antioxidants [44].



$R^1, R^2, R^3 = \text{H, alkyl group.}$

Fig. 15.

$(\text{Et}_3\text{Ge})_2\text{S}$ is an extremely strong fungicide. Its efficiency is multiplied by three compared to the best marketed fungicides [45].

4. CONCLUSION

In conclusion, we note a critical review of existing information on Ge compounds and their biological activity. The basic areas and applications of organogermanium compounds as drugs and the hope and expectations for their application are discussed in this article. Germanium is an essential trace element that is involved in global biochemical processes of living cells. This is responsible for the broad spectrum of biological activity of its compounds. The vigorous development of the chemistry of organogermanium compounds as potential drugs and the active study of their biological activity began with Ge-132. This topic was reviewed several times and was the subject of an original monograph.

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