

BIOLOGICAL ACTIVITIES OF NEW COMPLEXES BASED ON GERMANIUM AND SILVER COMPLEXES

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1. Introduction

In the last few years, interest in nanomaterials has been growing because of the ability to predict their properties and control their sizes. It is well known that metals like silver and germanium have antibacterial, antitoxic, anti-inflammatory properties etc. Metallic nanoparticles can enter the human body in various ways: through the skin, inhalation and injection, which allows them to be used as components of various medicinal and cosmetic products. Complex formation causes a decrease in general toxicity and an improvement in the transport of microelements to organisms. In view of this, the creation of mono- and heterometallic complexes of germanium and silver with antibacterial properties is relevant. Ethylenediaminedisuccinic acid (Edds) was chosen as the ligand. A chelating agent increases the bioavailability of metals and their biological activity.

2. Materials and Methods

The synthesis of metal complexes was carried out in aqueous solutions at equimolar ratios of reagents. Ethylenediaminedisuccinic acid was dissolved in an alkaline solution of KOH until complete dissolution with the formation of a soluble salt. An aqueous solution of the corresponding salts of metals was added to the resulting solution. In the process of complex formation, a precipitate of coordination compounds of white colour fell out. The precipitates were filtered off, washed and dried in the dark in a vacuum desiccator. IR spectra were recorded in KBr tablets in the range 250 - 4000 cm^{-1} on a PerkinElmer FTIR Spectrometer Frontier. Thermogravimetric analysis was carried out in the range of 0-600 $^{\circ}\text{C}$ on a TGA Q5000 IR. Microphotographs were recorded on a scanning electron microscope (SEM) Tescan Mira 3.

3. Results and Discussion

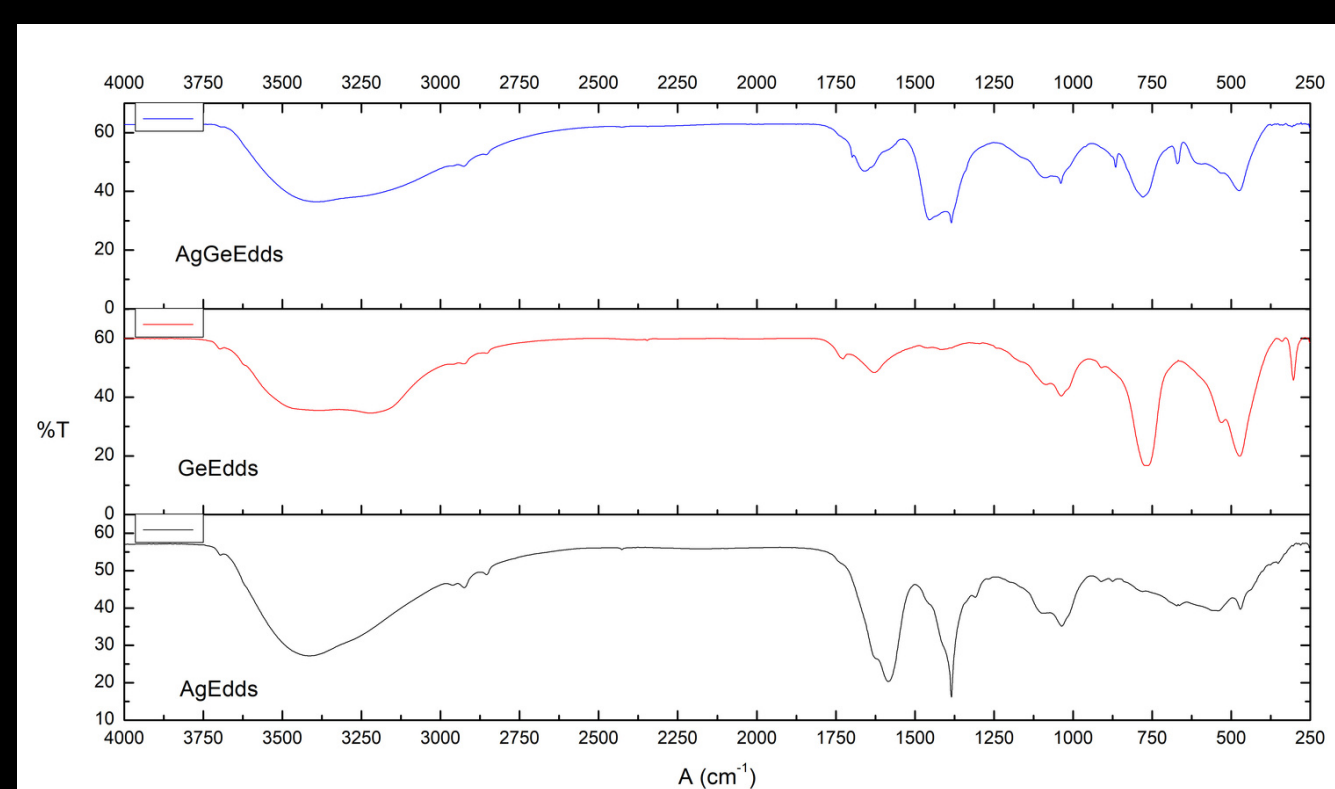


Fig. 1 - FTIR AgEdds, GeEdds and AgGeEdds

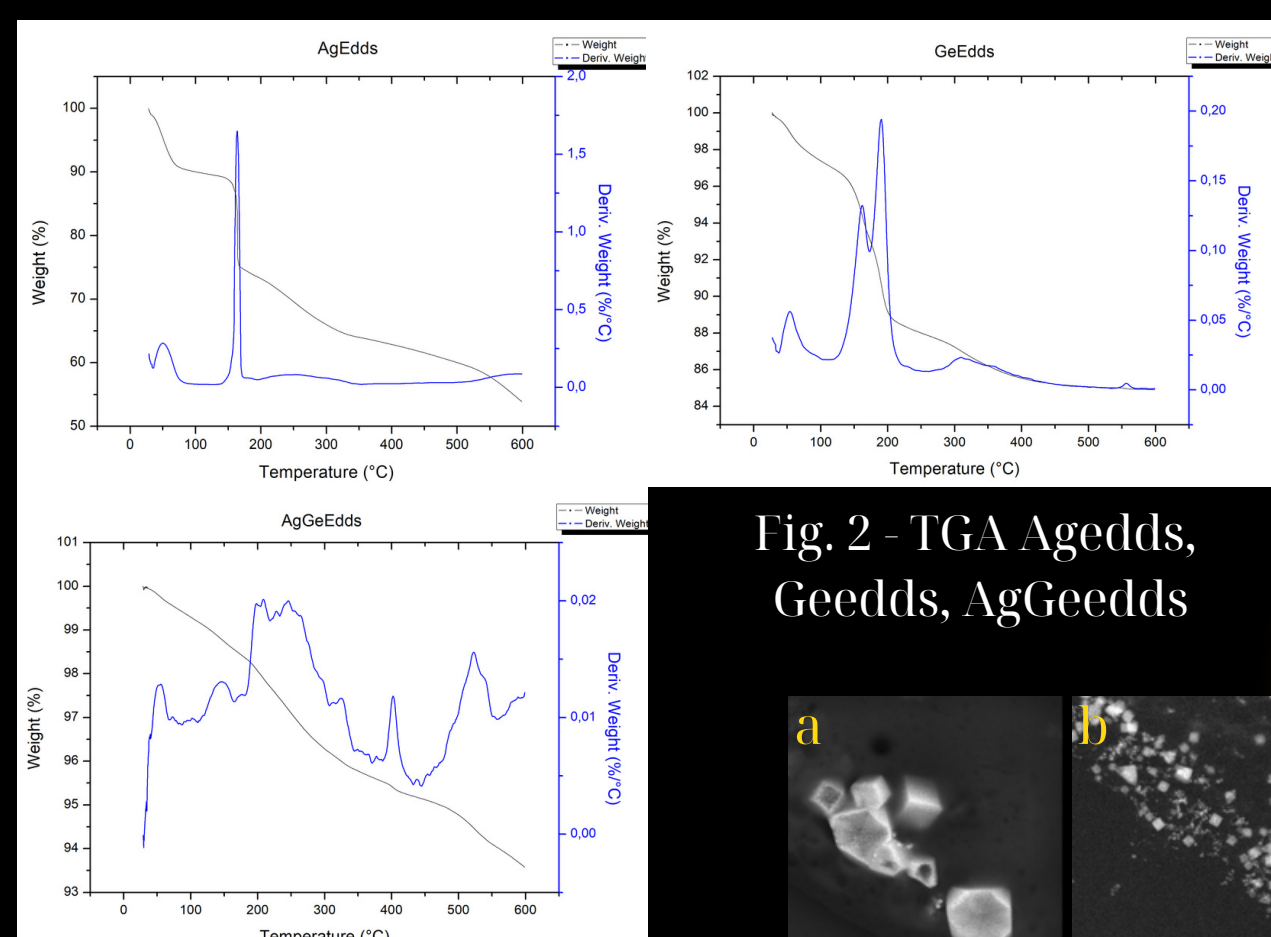


Fig. 2 - TGA AgEdds, GeEdds, AgGeEdds

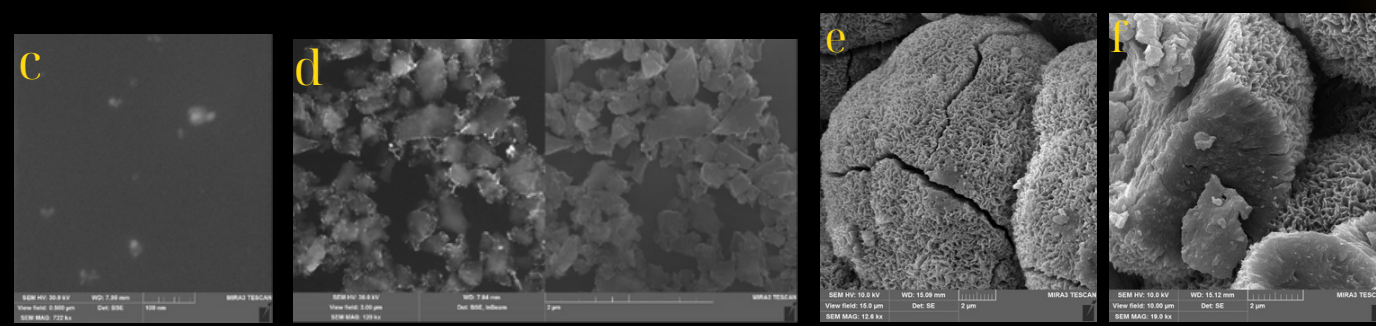


Fig. 3 - SEM: AgEdds (sol. 0.0001M a - d); GeEdds (powder e, f)

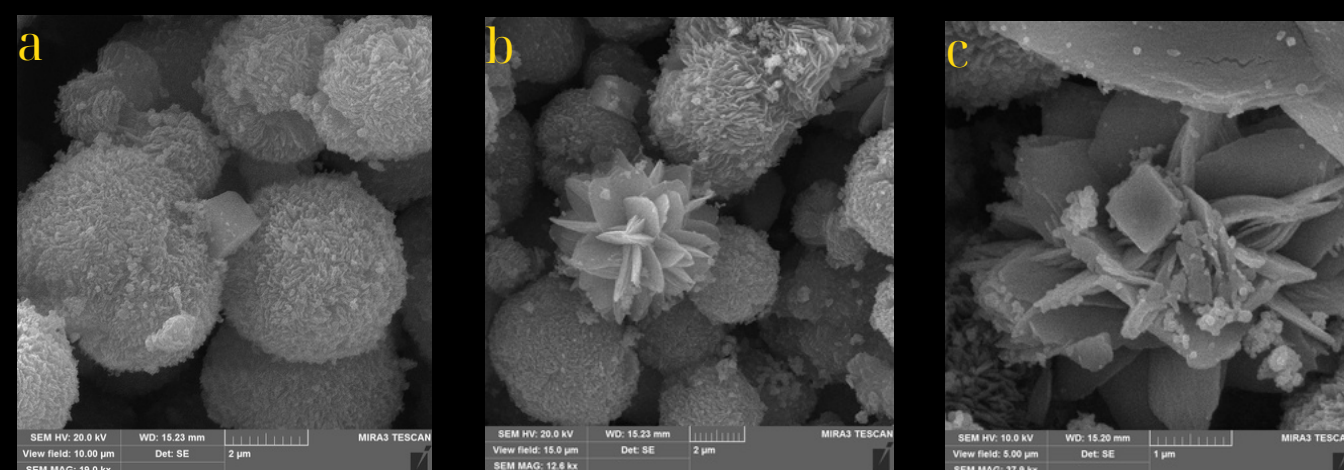


Fig. 4 - SEM (a - c) AgGeEdds (powder)

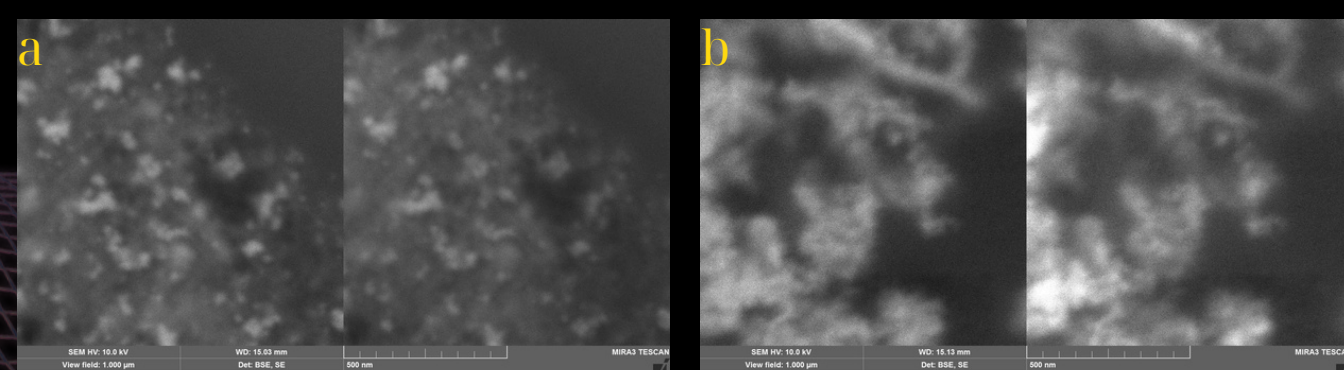
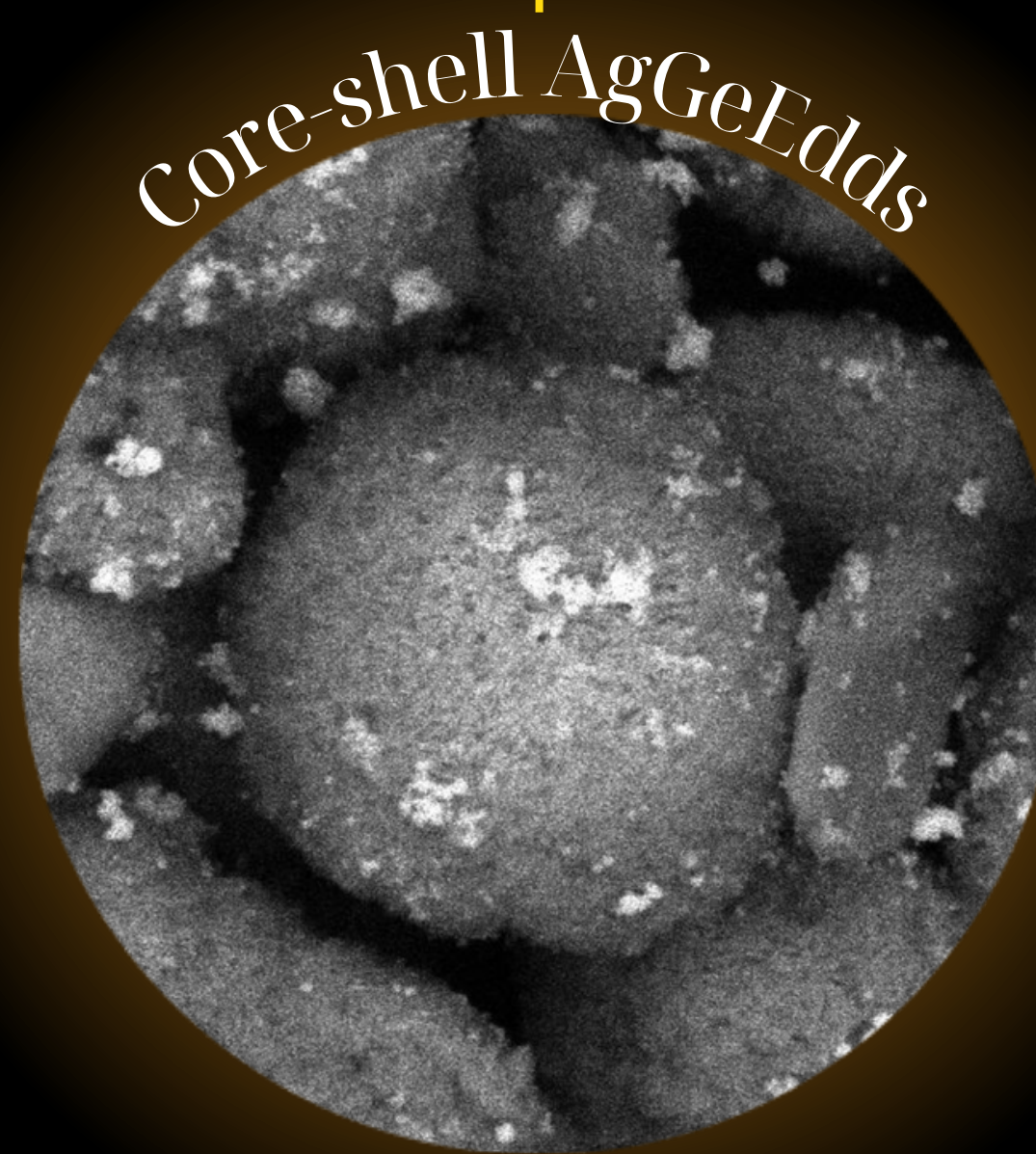


Fig. 5 - SEM: a - AgGeEdds - solution with heating; b - AgGeEdds - solution without heating

In order to establish the method of coordination of ligands to the central metal ions, the IR spectra of all synthesized compounds were recorded (Fig. 1). The IR spectra of all synthesized complexes are similar. In the spectra of all complexonates, bands in the region of 1300 - 1460 cm^{-1} and 1500 - 1650 cm^{-1} belonging to asymmetric and symmetric valence vibrations of carboxyl groups were recorded, respectively. The shift of the bands to the region of low frequencies relative to the ligand indicates the formation of a bond between metal ions and dissociated carboxyl groups of the ligand. The splitting of the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ signals is due to the difference in the coordination of the α - and β -carboxyl groups of edds, as well as the presence of $\nu(\text{NH})$ oscillations. Such splitting of the signal of COO groups can be caused by the asymmetry of the groups. The difference in the position of the $\nu_{\text{as}}(\text{COO})$ and $\nu_{\text{s}}(\text{COO})$ bands in the complexes ($\Delta\nu \sim 200 \text{ cm}^{-1}$) indicates monodentate coordination. The degree of change in the absorption frequency of the $\nu_{\text{s}}(\text{COO})$ valence vibration depends on the ionic or covalent nature of the M-O bond. A decrease in the frequency of symmetric oscillation corresponds to a greater contribution of the covalent component to the M-O bond. A broad band in the region of 3400 - 3200 cm^{-1} corresponds to valence vibrations of water molecules. The splitting of this band may indicate a different type of H_2O bond in the complexes. As a rule, the absorption band with a higher frequency corresponds to the outer sphere - adsorbed water, the band with a lower frequency refers to water molecules entering the inner coordination sphere of the complexes.



In the spectra of all studied complexes there is an absorption band in the region of 450 - 480 cm^{-1} , which corresponds to the valence vibrations of the M-N bond, and 500-520 cm^{-1} corresponds to the $\nu\text{M-O}$. The presence of a band of valence oscillations of the C-H bond in the region of 2950-2820 cm^{-1} in the IR spectra also indicates the formation of a bond between metals and edds amino groups. This band is one of the criteria for the formation of the M-N coordination bond in the complex ion. Bands at 1730 cm^{-1} in the IR spectrum of the GeEdds complex indicate the presence of a protonated carboxyl group, that is, one carboxyl group of the molecule does not take part in complex formation.

The results of the thermal analysis indicate that the dehydration of the complexes begins at 95 $^{\circ}\text{C}$ and corresponds to the separation of adsorbed water. As the temperature rises to 165 $^{\circ}\text{C}$, the process of dehydration of coordinated water molecules begins. The decomposition of the organic part of the molecule begins at 308 $^{\circ}\text{C}$ (Fig. 2).

Analysis of microphotographs suggests the formation of core-shell structures. In micrographs of powders of heterometallic complexes, we observe the formation of spherical particles with a size of 5-6 microns. A detailed study shows the self-organization of ethylene diamine disuccinate acid, which contributes to the formation of the above spherical particles. Energy-dispersive analysis shows that the nanofibers that later form layer-like particles contain silver. Therefore, we can assume that silver nanoparticles are adsorbed on the surface of edds. The latter, being adsorbed on the surface of the particle core, prevent coagulation (agglomeration) processes and AgEdds create an additional layer. The morphology of the particles is fibrous and layered.

For the monometallic (Fig. 3) complex, particles of different sizes and shapes are formed in the solution (Fig. 3 b and d), have the shape of petals, and spherical nanoparticles are adsorbed on their surface. In the AgGeEdds complex, we observe the formation of spherical particles, as well as the formation of flowers from petals, similar to the pure one (Fig. 4 b). Figure 4 c shows that in the center there is a cubic particle, which is similar to the particles AgEdds shown in Figure 3, but contains germanium in its composition.

DLS analysis also confirmed the presence of particles with a size of about 5 μm in the system. Due to the "conflict" of light scattering by a complex structure, several maxima occur, that is, the obtained results are not completely correct. It may also indicate a core-shell type structure. However, the unequivocal conclusion can be confirmed by TEM microphotographs.

4. Conclusion

Mono- and heterometallic complexes synthesized in this way are complex layered structures. All complexes that include silver have a light color from yellow to pink, which indicates the presence of silver nanowires. AgEdds exhibits high antibacterial properties. In the AgGeEdds complex, germanium will sensitize the bactericidal effect of silver, which allows it to expand the spectrum of practical application of the complexes.