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Synthesis and characterization of mixed-ligand coordination compounds of Ge(IV) with ethyl gallate and phenanthroline/bipyridine

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In this study, new coordination compounds of Ge(IV) with ethyl gallate (H_3EtGal) and the auxiliary nitrogen-donor ligands 1,10-phenanthroline (phen) and 2,2′-bipyridine (bipy) were synthesized. Based on elemental analysis, thermogravimetric data, IR spectroscopy, and mass spectrometry, the structures of the complexes [Ge(HEtGal)$_2$(phen)] (1) and [Ge(HEtGal)$_2$(bipy)] (2) were determined. In both compounds, germanium(IV) coordinates two hydroxyl groups from each ethyl gallate ligand and two nitrogen atoms from either phen or bipy, forming a distorted octahedral coordination polyhedron.

Germanium / Ethyl gallate / Coordination compounds / IR spectroscopy / ESI mass spectrometry

1. Introduction

Among the diverse range of polyphenolic compounds, gallic acid (H_4Gal) derivatives have been widely recognized for their potent antioxidant properties. These compounds are present in various phytotherapeutic agents and exhibit a broad spectrum of biological and pharmacological effects [1]. Ethyl gallate (H_3EtGal) is considered a promising bioactive compound due to its antioxidant, anticancer, anticaries, anti-ulcerative, anti-inflammatory, and anti-HIV properties. Co-administration of ethyl gallate and pharmacological agents can enhance therapeutic efficacy while simultaneously reducing drug-induced toxicity. A significant advantage of ethyl gallate lies in its widespread natural occurrence, as it is readily found in various plant-derived products, facilitating its accessibility and potential applicability in pharmaceutical and nutraceutical formulations [2-6].

The formation of complexes is a well-established strategy employed to enhance the biological activity and biocompatibility of molecules, incorporating ligands into coordination compounds with biometals [7]. For example, metal-based coordination compounds offer distinct advantages over traditional synthetic antioxidants due to their variable geometry, oxidation states, and coordination numbers. These properties enable such compounds to effectively participate in and facilitate redox processes, broadening their potential applications in biomedical and pharmacological contexts [8].

Previous research by the authors has shown that complexation of several organic ligands with germanium(IV) leads to the formation of complexes with different types of activity: antioxidant, antihypoxic, antiviral, cardiotropic, and neurotropic [9,10]. Among polyphenolic ligands, Ge(IV) complexes have been created with gallic acid and ethyl gallate, specifically [Ge(H_2Gal)(H_3Gal)$_2$]·H_2O and [Ge(HEtGal)(H_2EtGal)$_2$]·2H_2O [11]. Additionally, the structure of a mixed-ligand Ge(IV) complex with gallic acid and 1,10-phenanthroline, [Ge(H_2Gal)$_2$(phen)], was elucidated *via* X-ray diffraction analysis [12].

The present study aimed to synthesize new coordination compounds of Ge(IV) with ethyl gallate in combination with 1,10-phenanthroline (phen) or 2,2′-bipyridine (bipy), and investigate their composition, molecular structure, and thermal properties.

2. Experimental

2.1. Main reagents

The starting reagents for the synthesis were germanium(IV) oxide (GeO_2, CAS 1310-53-8, 99.99%), ethyl gallate (H_3EtGal, CAS 831-61-8, ≥96.0%), 1,10-phenanthroline (phen, CAS 66-71-7,

99.0%), and 2,2′-bipyridine (bipy, CAS 366-18-7, 99.5%) (Sigma Aldrich).

2.2. Synthesis of [Ge(HEtGal)$_2$(phen)] (1), [Ge(HEtGal)$_2$(bipy)] (2)

Mixtures of GeO_2 (1 mmol, 0.1046 g), H_3EtGal (2 mmol, 0.396 g), and phen (1 mmol, 0.18 g) or bipy (1 mmol, 0.156 g) were dissolved in 500 mL of water under heating and evaporated to a volume of 30 mL. When the solutions were cooled to room temperature, yellow, finely dispersed precipitates of products **1** and **2** were formed. Each of them was separated on a Schott filter, washed with water and dissolved in 10 ml of dimethylformamide for recrystallization. As a salting-out agent, acetonitrile was used.

2.3. Measurements

The chemical composition (C, N, H) was determined using a CE-440 Elemental Analyzer. The germanium content in the samples was quantified by inductively coupled plasma atomic emission spectroscopy (ICP-AES) on an Optima 8000 instrument (PerkinElmer). Anal. calcd for $C_{30}H_{24}GeN_2O_{10}$ (**1**, *Mr* = 644.6): C, 55.85; H, 3.72; N, 4.34; Ge, 11.26%. Found: C, 55.75; H, 3.60; N, 4.27; Ge, 11.18%. Anal. calcd for $C_{28}H_{24}GeN_2O_{10}$ (**2**, *Mr* = 620.6): C, 54.14; H, 3.87; N, 4.51; Ge, 11.70%. Found: C, 54.07; H, 3.74; N, 4.47; Ge, 11.55%.

Thermogravimetric analysis (TGA) was carried out using a Q-1500D analyzer under an air atmosphere at a heating rate of 10°C/min over a temperature range of 20-1000°C. IR spectra were recorded in the range 4000-400 cm^{-1} using potassium bromide pellets on a Frontier FT-IR spectrometer (PerkinElmer). Electrospray ionization mass spectrometry (ESI-MS) was performed using a TSQ Fortis Triple Quadrupole Mass Spectrometer (ThermoFisher Scientific, USA). Measurements were performed in methanol–water (1:1, v/v) solutions of the complexes at concentrations of 20-50 µg/mL. The sample solutions were introduced *via* a Chemyx Fusion 100T2 syringe pump equipped with a 500 µL Hamilton gas-tight syringe at a flow rate of 20 µL/min.

3. Results and discussion

Based on the results of the chemical analysis, the synthesized coordination compounds exhibit a molar ratio of germanium : ethyl gallate : 1,10-phenanthroline (or 2,2′-bipyridine) of 1:2:1. The thermal decomposition of both compounds is similar (Fig. 1). The thermogravimetric analysis indicates that these compounds are not crystalline hydrates, as no significant mass loss is observed up to 260-300°C. At temperatures above 300°C, exothermic processes corresponding to thermal degradation of the complexes are recorded. Evaluation of the mass loss from the thermogravimetric data at 850°C confirms that the final decomposition product of both compounds is GeO_2 (Δm_{TG} = 85.00%, Δm_{theor} = 83.77% (**1**, Fig. 1a), Δm_{TG} = 81.5%, Δm_{theor} = 83.15% (**2**, Fig. 1b)).

The IR spectra of the synthesized compounds were analyzed in comparison with published data on characteristic absorption bands of organic molecules and coordination compounds of germanium(IV) and other metal ions [9-13]. The results indicate that the hydroxyl groups in the complex molecules are deprotonated and coordinated to the germanium(IV) atoms. This is clearly evidenced by the absence of a O–H stretching vibration band at 3296 cm^{-1}, observed in the IR spectrum of ethyl gallate, and the appearance of Ge–O stretching vibrations at 829 cm^{-1} (complex **1**) and 831 cm^{-1} (complex **2**) (Table 1). Coordination of phenolic oxygen atoms is further supported by the splitting of the C_{Ar}–O deformation vibration band from 1257 cm^{-1} (in free ethyl gallate) into two distinct bands at 1290 and 1221 cm^{-1} (**1**) and at 1291 and 1220 cm^{-1} (**2**). The C=O stretching band remains unaffected, suggesting non-involvement of the carbonyl group in coordination.

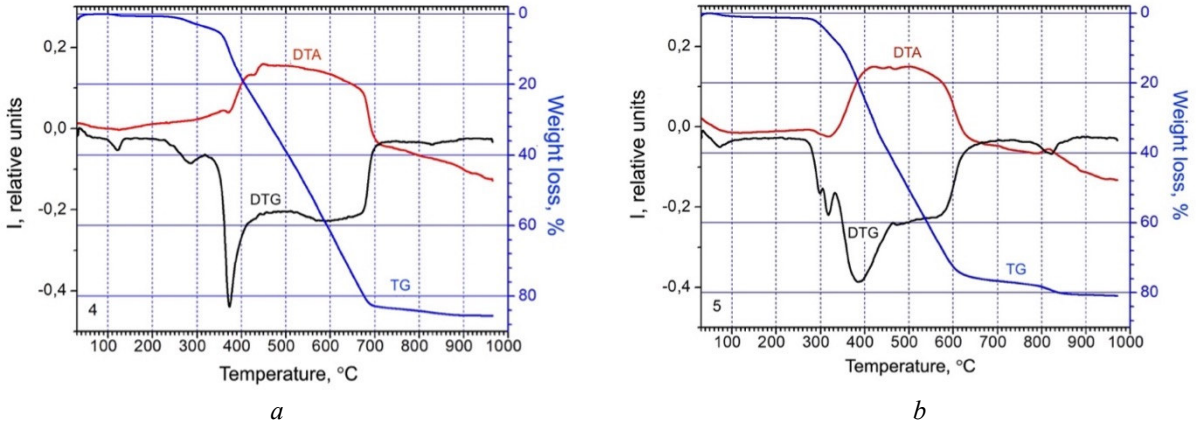

Fig. 1 Thermogravigrams of complexes: *a*) **1**; *b*) **2**.

Table 1 Selected data for IR spectra of H_3EtGal and complexes **1**, **2**.

Vibration bands, cm^{-1}	Compounds		
	H_3EtGal	**1**	**2**
ν(O–H)	3461, 3296	3436	3422
ν(C=O)	1696	1691	1690
ν(C=C)	1467, 1462	1438	1439
ν(C_{Ar}–O)	1257	1290 1221	1291 1220
ν(C–N)	–	1586	1588
ν(Ge–O)	–	829	831
ν(Ge–N)	–	660	656

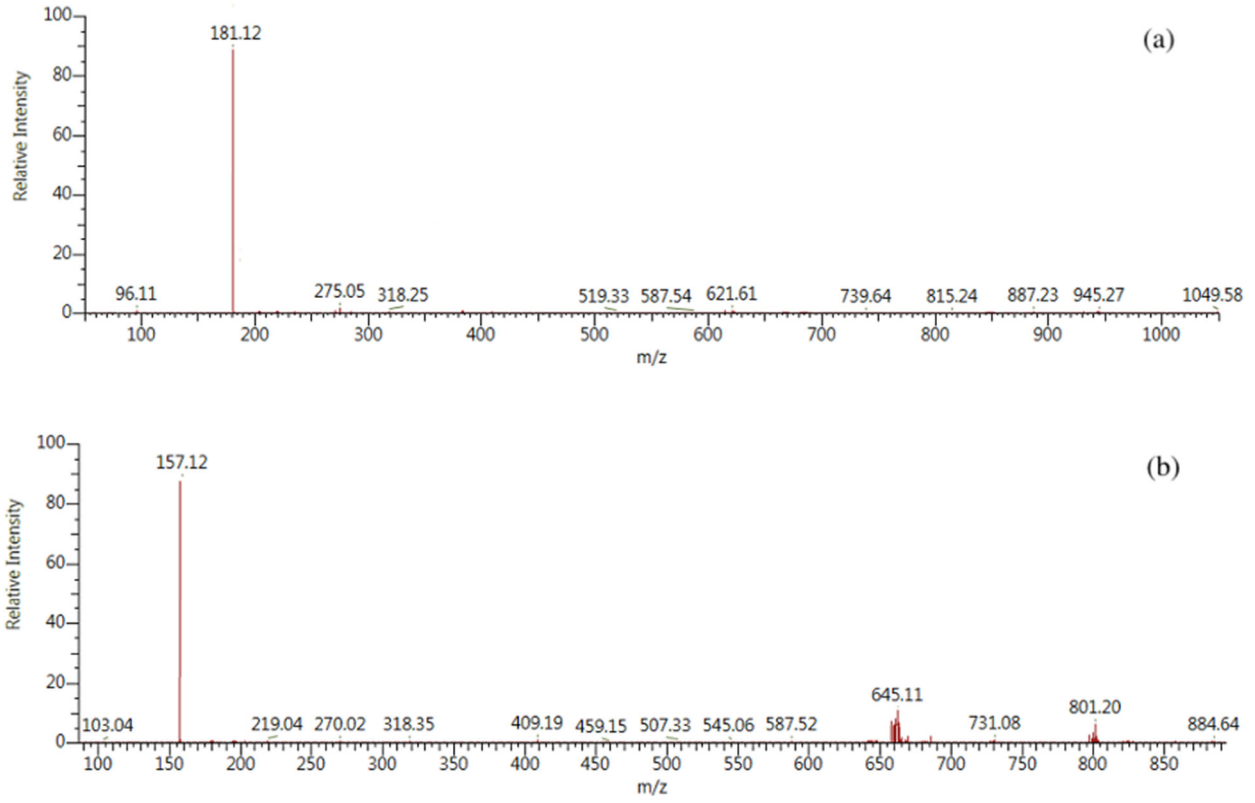

Fig. 2 ESI(+)-mass spectra of complexes: *a*) **1**; *b*) **2**.

The aromatic ligands 1,10-phenanthroline and 2,2′-bipyridine exhibit characteristic vibrational features, including C–C skeletal stretching in the range 1300-1600 cm^{-1}, in-plane C–H deformations between 1000 and 1500 cm^{-1}, out-of-plane C–H deformations between 700 and 1200 cm^{-1}, and planar skeletal deformations of the C–C framework below 700 cm^{-1} [13]. The presence of these absorption bands in the IR spectra of the complexes confirms the successful incorporation of *phen* and *bipy* into the coordination environment. Furthermore, the appearance of stretching vibration bands corresponding to C–N and Ge–N bonds (Table 1) provides evidence of nitrogen atom coordination to the Ge(IV) atoms.

The ESI(+) mass spectrum of compound **1** (Fig. 2a), recorded in positive ion mode, exhibits a signal corresponding to protonated 1,10-phenanthroline $[C_{12}H_8O_{10}+H]^+$, m/z = 181.12. In the case of compound **2** (Fig. 2b), the spectrum contains a peak assigned to protonated bipyridine $[C_{10}H_8O_{10}+H]^+$, m/z = 157.12. In the ESI(−) mass spectra (Fig. 3) of both complexes, a prominent signal corresponding to the deprotonated ethyl gallate ligand anion H_2EtGal^- $[C_9H_{10}O_5–H]^-$, m/z = 197.04. Additionally, signals at m/z = 496.81 and 494.97 are attributed to the presence of anionic species incorporating different isotopes of germanium, corresponding to the formula $[Ge(HEtGal)(H_2EtGal)\cdot MeOH–H]^-$.

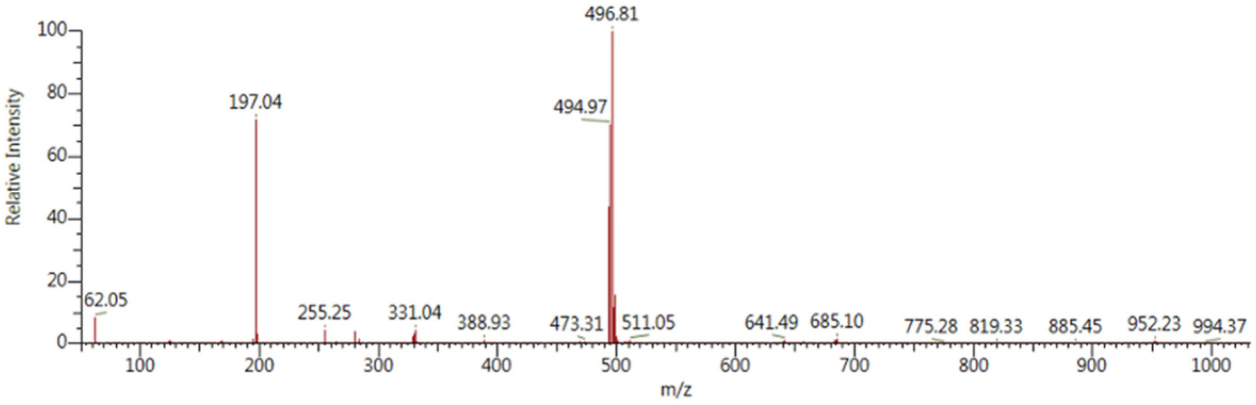

Fig. 3 ESI(-)-mass spectrum of complex **1**.

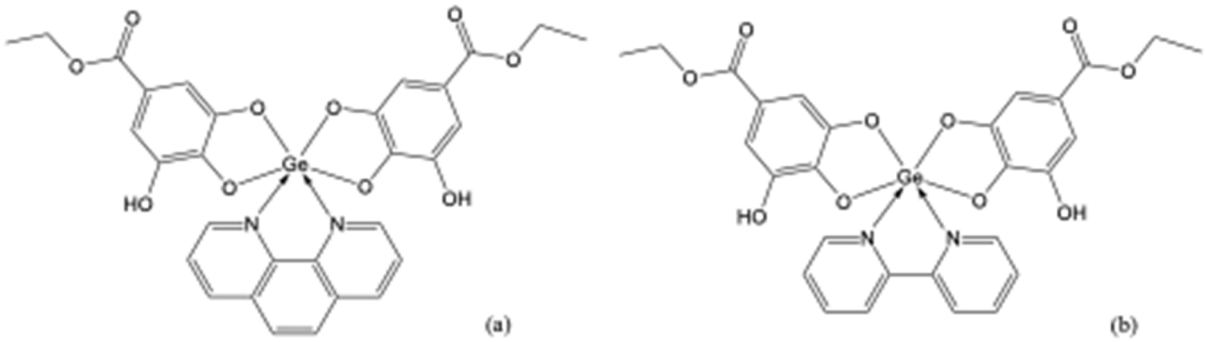

Fig. 4 Schemes of the structures: *a*) **1**; *b*) **2**.

4. Conclusion

Based on a comprehensive analysis of the chemical composition, thermogravimetric data, infrared spectroscopic features, and mass spectrometric results – along with consideration of the characteristic coordination number six for Ge(IV) and reference to previously structurally characterized germanium compounds – structural schemes were proposed for the synthesized complexes [Ge(HEtGal)$_2$(phen)] (**1**) and [Ge(HEtGal)$_2$(bipy)] (**2**) (Fig. 4). In both complexes, the coordination environment of Ge(IV) includes two hydroxyl groups from each ethyl gallate ligand and two nitrogen atoms from either 1,10-phenanthroline or 2,2′-bipyridine, resulting in octahedral coordination of the germanium atoms.

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