

## IR/Raman characterization of Au-mercaptopotriazole crystals

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The aim of this study was a characterization of the crystals of gold complexes based on mercaptopotriazole, obtained from solutions with different pH values (2, 4, 7, and 9), using the methods of infrared (IR) and Raman spectroscopy. Both methods provided very useful information on the investigated systems and signaled existence of the Au-S bond in the complexes obtained at pH = 2 and 9. Recorded spectra clearly illustrated the changes that occur in the systems as a consequence of pH change. At the same time, the results also showed that the pyrrole nitrogen atoms stay protonated at pH = 9, which is not in favor of the assumption evolved from the previous UV-vis analysis of possible additional coordination between Au and possible deprotonated nitrogen atoms at this particular pH.

**Keywords:** synthesis; gold-mercaptopotriazole (Au-MT); IR and Raman spectroscopy

## INTRODUCTION

Gold coatings are widely used in many fields of industry. This is the result of their exceptional electrical, chemical and optical properties, such as excellent electrical conductivity, high abrasion resistance and excellent corrosion resistance [1]. A wide area of these applications is the subject of research of many authors [2-7].

Traditionally, gold has been plated from cyanide electrolytes, where Au<sup>+</sup> is ligated with cyanide (CN<sup>-</sup>). Cyanide electrolytes are extremely stable, but the main problem with the use of cyanide is in their poor compatibility with many standard photoresist layers on printed circuit boards, as well as the high toxicity [4,7-13].

Also, the presence of cyanides in solutions, wastewater and in atmosphere causes high costs of wastewater treatment and potential risks to the safety of workers in these facilities. Their negative redox potential makes difficult the formulation of a chemical bath, while low exchange current density leads to limits of reaction rates in cyanide complex solutions [14,15].

These disadvantages of cyanide electrolytes lead to a large number of investigations related to baths based on non-cyanide electrolytes such as: sulphite and aminosulphite, thiosulphate, thiosulphate-sulphite, thiourea, ascorbic acid, baths without a reducing agent, Au(III) halide baths, Au(I) thiomalate baths, etc.

In recent time the results of the research on formulation and characterization of a new non-cyanide electrolyte, the organic complex of gold based on mercaptopotriazole (C<sub>2</sub>H<sub>3</sub>N<sub>3</sub>S), are

published in studies of Dimitrijević *et al.* [16-24], which showed that the resulting coatings fully meet the requirements of decorative coatings.

In general, five-membered heterocyclic compounds such as triazoles are of great importance because of their wide application as anticonvulsants, but also as bactericides, insecticides, herbicides, etc. [25]. It should be mentioned here that thiazole and its derivatives were also successfully used in the synthesis of antibiotics [26].

By analogy with palladium and platinum complexes that can build colored complexes with mercaptopotriazole (MT) [27], Dimitrijević *et al.* [16] assumed that gold can also build a complex with this compound, so that the synthesis of Au-MT complex has been achieved several years ago in the chemical laboratory of the Mining and Metallurgy Institute in Bor.

Briefly, as the first step in the procedure of Au-MT synthesis, the Beyer and Kroger [28] method for MT preparation was performed using thiosemicarbazide (min 98%, Merck, Germany) and formamide (p.a. Alkaloid, Skopje) as the basic chemicals. The structure of the obtained MT crystals (melting point 215°C) was characterized by infrared (IR) and Raman spectroscopy (RS) [16]. The recorded spectra were in a good agreement with the published data of Krishnakumar and Xavier (2004) [26], who studied the vibrational spectra of 3-mercaptopotriazole using FT-IR and FT-Raman spectroscopy (Table 1). The Raman spectrum of the obtained crystals of MT provided evidence of the thione form of MT molecule, while the IR spectrum confirmed the existence of thione-thiol tautomerism (Table 1). Finally, the novel Au-MT electrolyte was synthesized in the system

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formulated of MT, glycine (Gly, min. 99%, Alkaloid, Skopje), and chloroauric acid (HAuCl<sub>4</sub>), obtained by dissolution of gold (gold powder, 99.99%, Mining and Metallurgy Institute Bor) in *aqua regia* (HCl:HNO<sub>3</sub> = 3:1); the final concentration of gold in HAuCl<sub>4</sub> was 2.5 g/dm<sup>3</sup>, which is desirable in decorative gold coating electrodeposition [16]. The experiments were performed in a wide range of pH values, so solutions with different pH (pH = 2, 4, 7, 9) were prepared (using 1 M KOH for the pH adjustment), and the obtained electrolytes were further analyzed using different methods such as: inductively coupled plasma atomic emission spectroscopy, ultraviolet–visible spectroscopy, polarization measurements, open circuit potential measurements, cyclic voltammetry [16-20]. The obtained results showed that: (1) the highest stability of the complex is at pH = 9; (2) the best coatings are obtained from the complex formed at pH = 9; and (3) the connection of gold with MT molecule is most probably formed *via* an exocyclic sulfur atom of MT [16-20].

**Table 1.** Vibrational frequencies (cm<sup>-1</sup>) and their probable assignments for the crystalline MT.

MT		Vibrational assignments*
IR	Raman	
	3155 w	N–H stretching, $\nu(\text{NH})$
3075 vs	3091 vw	C–H stretching, $\nu(\text{CH})$
2616 w	/	S–H stretching, $\nu(\text{SH})$
1558 s	1557 w	C=N stretching, $\nu(\text{CN})$
1471 s	1468 s	N–C stretching, $\nu(\text{NC})$
1430 s	1428 w	C–N stretching, $\nu(\text{CN})$
1259 w	1256 ms	N–N stretching, $\nu(\text{NN})$
1186 s	1190 s	N–H in-plane bending, $\beta(\text{NH})$
1057 ms	1065 ms	C–H in-plane bending, $\beta(\text{CH})$
/	991 s	Ring in-plane bending, $\beta(\text{ring})$
942 ms	941 ms	C–S stretching, $\nu(\text{CS})$
844 s	845 w	NCN in-plane bending, $\beta(\text{NCN})$
700 ms	708 w	CSH in-plane bending, $\beta(\text{CSH})$
665 ms	/	CNN in-plane bending, $\beta(\text{CNN})$ and CSH in-plane bending, $\beta(\text{CSH})$
/	530 s	NCS in-plane bending, $\beta(\text{NCS})$
/	354 s	NCN out-of-plane bending, $\gamma(\text{NCN})$

\* Probable vibrational assignments are in accordance with Krishnakumar and Xavier (2004) [25].

Additionally, the structures of UV–vis absorption spectra, recorded for the electrolytes

obtained at pH values of 2, 7, and 9, allowed a possibility of an assumption that, at pH = 9, the molecules of MT may interact with Au not only through sulfur, but also through the nitrogen atoms of triazole rings [16], which can be deprotonated in the circumstances of increased pH [29]. Namely, Wrzosek and Bukovska [29] demonstrated that, depending on pH change, which is followed by processes of protonation (low pH)/deprotonation (increased pH) of the rings of AMT (3-amino-MT), the orientation of these rings in the system may also be further changed affecting the complete system state and providing different possibilities for the interactions between Au and AMT.

Following these findings, our team decided to subject the crystals of Au-MT, obtained from the solutions at different pH by simple evaporation at ambient temperature, to further analysis by IR and Raman spectroscopy in terms of obtaining additional information on the Au-MT structure, and especially regarding the evidence of the established coordination between Au and sulfur, or nitrogen atoms of MT. The results of the applied methods, together with the following discussion are represented in this paper.

## EXPERIMENTAL

### IR/Raman spectroscopy

Infrared spectrometry of the crystalline Au-MT synthesized at pH = 2, 7 and 9 was performed on a Perkin-Elmer 983G Infrared spectrophotometer using the KBr technique (finely pulverized sample), in the range 100–4000 cm<sup>-1</sup>.

The Raman spectra of Au-MT obtained at pH = 2, 4, 7, and 9 were acquired in "backscattering geometry", using a  $\mu$ -Raman system with a Jobin Yvon T64000 triple monochromator, and a CCD (charge-coupled-device) detector. The Ar laser 514 nm was used as a source for the excitation. All measurements were conducted at a laser power of 80 mW. The Raman spectra were recorded in the frequency range 100–3500 cm<sup>-1</sup> with a resolution of 4 cm<sup>-1</sup>.

## RESULTS AND DISCUSSION

The IR spectra of the crystalline Au-MT, synthesized at different pH: 2 (Fig. 1); 7 (Fig. 2); and 9 (Fig. 3), showed several relevant differences in comparison with the recorded IR spectrum of MT. The main indices on formation of a chemical bond between the metal and exocyclic sulfur atom of MT were evident in few cases. At the first place, according to Shalini and Sharma (2011) [26], who studied the iron and cobalt complexes with substituted MT, the appearance of a band that

reveals the conversion of C=S into C-S- (which can be positioned in the frequency range 650-700  $\text{cm}^{-1}$  in the IR spectra) may represent a basis for further conclusion of probable coordination through the sulfur atom. It is noticeable that this band is one of the strongest in the spectrum of Au-MT obtained at pH = 9: 699  $\text{cm}^{-1}$  (Fig. 3), whereas in the spectra of Au-MT, obtained at pH = 2 (Fig. 1) and pH = 7 (Fig. 2), two weak bands are present at 674  $\text{cm}^{-1}$  and 637  $\text{cm}^{-1}$ . In addition, in the IR spectra of the complexes (Figs. 1-3), as well as in the corresponding Raman spectra (Figs. 4-7), the deprotonation of a thiol group and further complexation through S atom is indicated by the absence of a band in the frequency range of 2450-2560  $\text{cm}^{-1}$ , which is usually assigned to the  $\nu(\text{S-H})$  stretching vibration [26, 30]. It should be mentioned here that this band is only found in the IR spectrum of MT (Table 1) proving the existence of thione-thiol tautomerism in the molecule.

According to Little and Ottewill (1962) [31], who studied the adsorption of MT on silver iodide by IR spectroscopy, the presence of a strong band at 1050  $\text{cm}^{-1}$  may be assigned to the  $\nu(\text{C=S})$  stretching vibration of the thione form of MT molecule, and this band was found at 1057  $\text{cm}^{-1}$  in the IR spectrum of the synthesized MT (Table 1). In the IR spectrum of Au-MT, obtained at pH = 2 (Fig. 1), this band is displaced at 995  $\text{cm}^{-1}$ , and at 1014  $\text{cm}^{-1}$  in the IR spectrum of Au-MT, obtained at pH = 9 (Fig. 3), which is most probably due to the elongation of the C=S bond caused by the complex formation [30]. However, in both latter cases, this band is rather weak. Analogous weak bands can be found in the recorded Raman spectra as follows: 995  $\text{cm}^{-1}$  for Au-MT obtained at pH = 2 and 1017  $\text{cm}^{-1}$  for Au-MT obtained at pH = 9. Finally, this band was not manifested in the IR spectrum of Au-MT obtained at pH = 7 (Fig. 2), nor in the corresponding Raman spectrum (Fig. 6). It can be said that in general, the IR spectrum of Au-MT, obtained at neutral pH (Fig. 2), has shown a notable declination with regard to the IR spectra of Au-MT obtained at pH 2 and 9 (Figs. 1 and 3, respectively), and suggested that a very specific situation may be present in the system at pH = 7, indicating a possibility of some specific molecular (re)arrangements.

An additional support of this assumption can be found from the analysis of the recorded Raman spectra of Au-MT complexes, formed at different

pH = 2, 4, 7, and 9 (Figs. 4, 5, 6, and 7, respectively). Namely, very specific structures of the Raman spectra of Au-MT, obtained at pH 4, and 7, which are reflected in the absence of any expressive band in the spectrum for pH = 4 (Fig. 5), or in the presence of numerous bands, which are not well defined and differentiated ("noise") in the spectrum for pH = 7 (Fig. 6), are rather different in comparison with the Raman spectra of Au-MT, obtained at pH 2 and 9 (Figs. 4 and 7, respectively). Most importantly, in the latter spectra, the appearance of bands at 245  $\text{cm}^{-1}$  (for pH = 2) and 268  $\text{cm}^{-1}$  and 241  $\text{cm}^{-1}$  (for pH = 9) is noticeable, which may represent an additional and final signal of the formed bond: metal-S [30]. There were no such bands in the Raman spectrum of MT in which the band of the bending  $\beta(\text{NCS})$  vibration at 530  $\text{cm}^{-1}$  appeared as one of the strongest (Table 1). Medium strong bands, which may be ascribed to the stretching  $\nu(\text{C=S})$  vibration [29], are present in the Raman spectra of the crystalline Au-MT, as follows: at 406  $\text{cm}^{-1}$  for pH = 2 (Fig. 4), and 407  $\text{cm}^{-1}$  and 510  $\text{cm}^{-1}$  for pH = 9 (Fig. 7). Finally, it should be pointed out that both applied methods indicated that the nitrogen atoms of the triazole rings in the complex, formed at pH = 2, as well as at pH = 9, are protonated, which is not in support of previous assumptions, based on the analysis of UV-vis spectra that, at pH = 9, additional coordination between Au and deprotonated nitrogen atoms, is also possible [16]. This can be concluded on the basis of the presence of strong broad bands in the high-frequency region, which can be assigned to the NH stretching vibrations such as the bands in the range of 2600-3400  $\text{cm}^{-1}$  in the IR spectra [26], and bands at 3151  $\text{cm}^{-1}$  (Fig. 4), 3076  $\text{cm}^{-1}$  and 3122  $\text{cm}^{-1}$  (Fig. 7) in the Raman spectra [29]. The presence of bands in the frequency range 1000-1600  $\text{cm}^{-1}$ , which may be assigned not only to several modes of ring vibrations, but also to the NH deformation vibrations [25, 29], additionally supports the conclusion on protonated nitrogen. The bands from the same frequency range (1000-1600  $\text{cm}^{-1}$ ), in all recorded spectra of the obtained complexes, did not significantly change their positions in regard to the spectra of MT. It can be said that many of the bands from this region appeared as the most intensive in all spectra (except in the Raman spectra of complexes, obtained at pH 4 and 7).

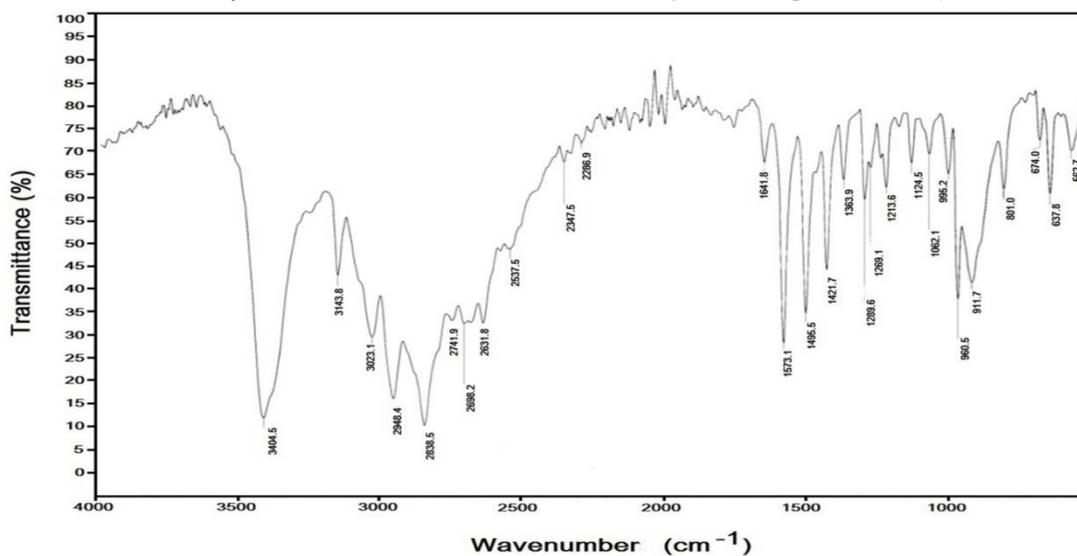


Figure 1. IR spectrum for the gold complex based on mercaptotriazole, obtained from a solution with pH = 2

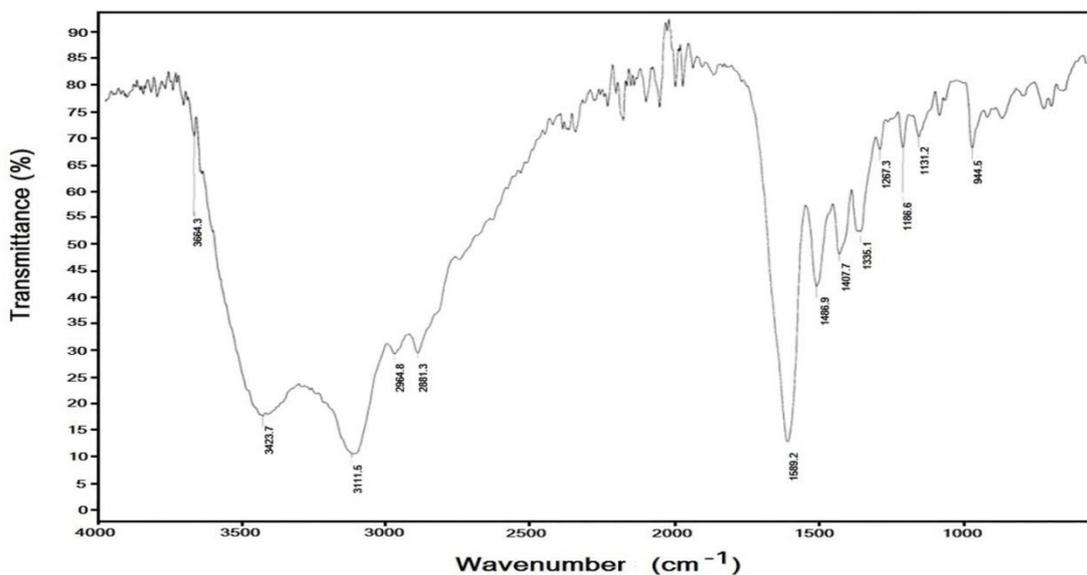


Figure 2. IR spectrum for the gold complex based on mercaptotriazole, obtained from a solution with pH = 4

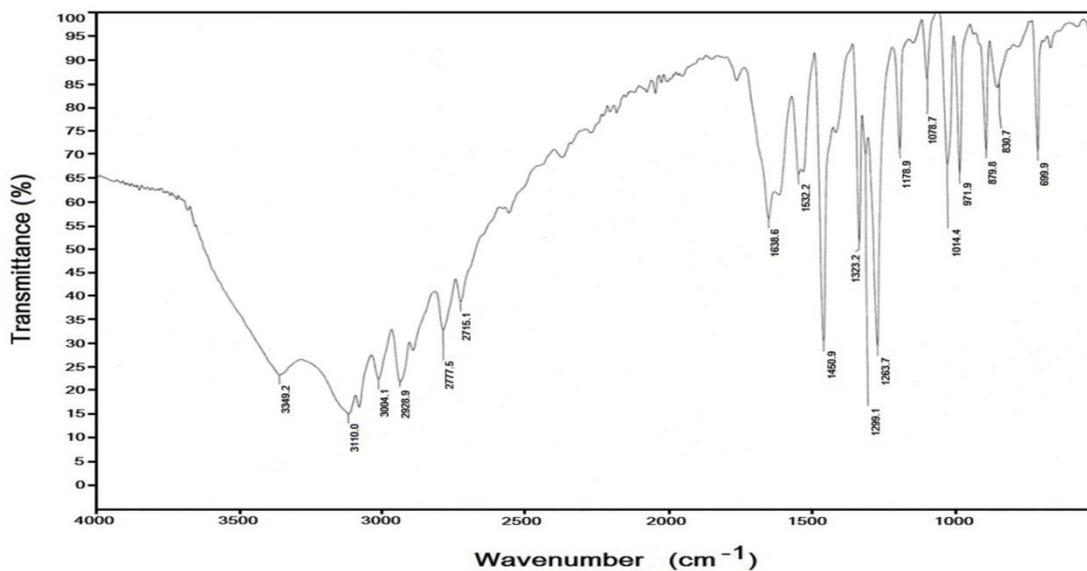
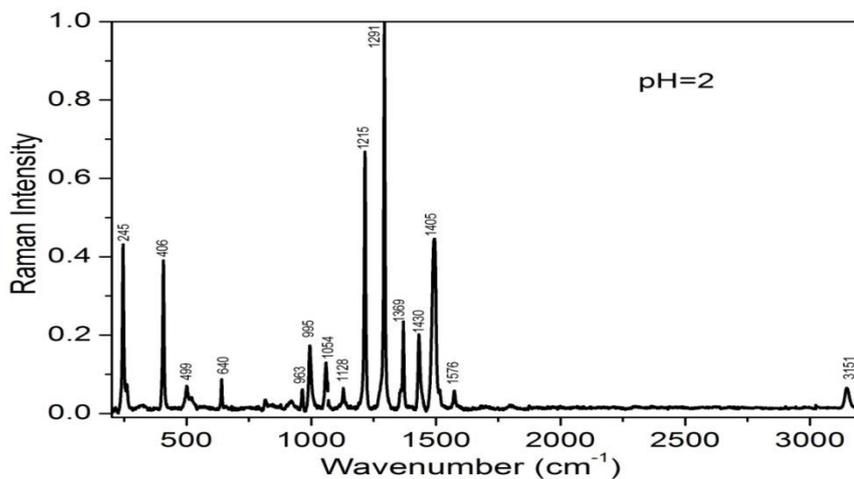
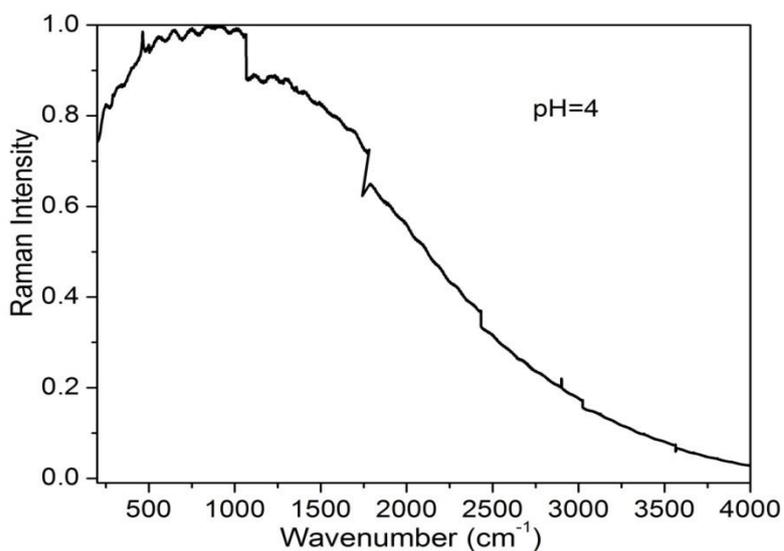


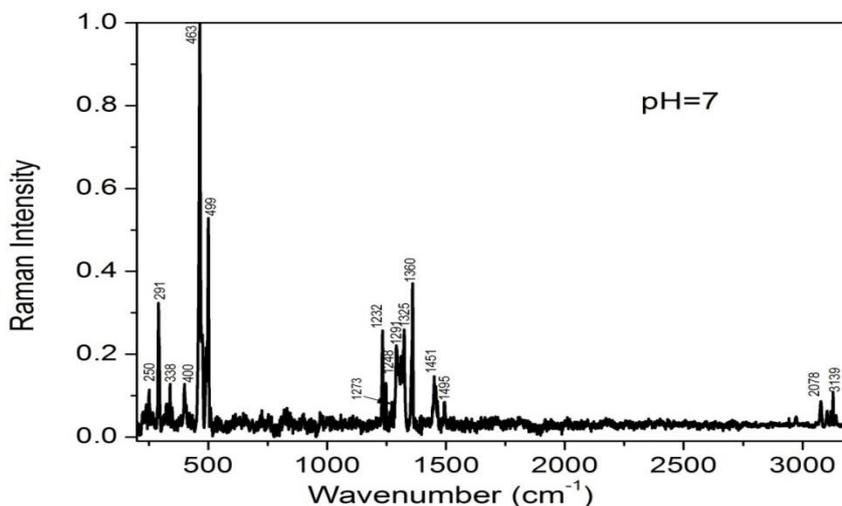
Figure 3. IR spectrum for the gold complex based on mercaptotriazole, obtained from a solution with pH = 9



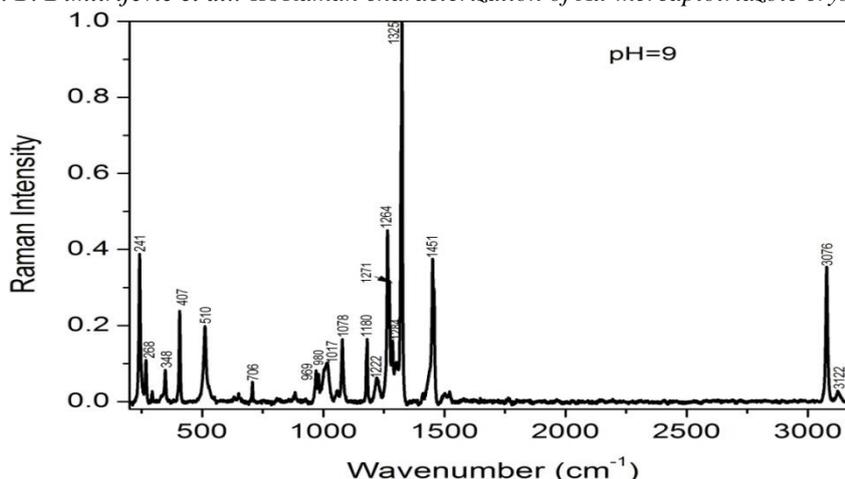
**Figure 4.** Raman spectrum for the gold complex based on mercaptoptriazole, obtained from a solution with pH = 2



**Figure 5.** Raman spectrum for the gold complex based on mercaptoptriazole, obtained from a solution with pH = 4



**Figure 6.** Raman spectrum for the gold complex based on mercaptoptriazole, obtained from a solution with pH = 7



**Figure 7.** Raman spectrum for the gold complex based on mercaptoptriazole, obtained from a solution with pH = 9

### CONCLUSION

The methods of IR and Raman spectroscopy, applied in this work for the characterization of the crystals of Au-MT obtained from the solutions at different pH, provided very useful information on their structures, and signaled the existence of Au-S bond in the complexes, obtained at pH = 2 and pH = 9. The recorded spectra clearly illustrated the changes occurring in the systems as a consequence of pH change. However, the obtained results also showed that, at pH = 9, the pyrrole nitrogen atoms more likely stay protonated, which is not in favor of the assumption evolved from the UV-vis analysis of possible additional coordination between Au and deprotonated nitrogen atoms of MT at this particular pH.

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