



## Synthesis and spectroscopic characterization of gallic acid and some of its azo complexes

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### ABSTRACT

A series of gallic acid and azo gallic acid complexes were prepared and characterized by elemental analysis, IR, electronic spectra and magnetic susceptibility. The complexes were of different geometries: Octahedral, Tetrahedral and Square Planar. ESR was studied for copper complexes. All of the prepared complexes were of isotropic nature. The thermal analyses of the complexes were studied by DTA and DSC techniques. The thermodynamic parameters and the thermal transitions, such as glass transitions, crystallization and melting temperatures for some ligands and their complexes were evaluated and discussed. The entropy change values,  $\Delta S^\ddagger$ , showed that the transition states are more ordered than the reacting complexes. The biological activities of some ligands and their complexes are tested against Gram positive and Gram negative bacteria. The results showed that some complexes have a well considerable activity against different organisms.

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### 1. Introduction

Gallic acid, an organic acid, known as 3,4,5-trihydroxybenzoic acid ( $C_6H_2(OH)_3COOH$ ), is found widely throughout the plant kingdom. High gallic acid contents can be found in gallnuts, grapes, sumac, witch hazel, tea leaves, hops, and oak bark. Gallic acid exists in two forms as the free molecule and as part of tannins. Pure gallic acid is a colorless crystalline organic powder, salts and esters of gallic acid are termed gallates [1]. It has many applications in chemical research and industry such as being used as a standard for determining the phenol content of various analytes by the Folin–Ciocalteu assay [2] and also used for making dyes and inks [3].

Gallic acid is commonly used in the pharmaceutical industry because many *in vivo* and *in vitro* studies in humans, animals, and cell culture have provided evidence for the following actions of gallic acid. It shows cytotoxicity against cancer cells, without harming healthy cells [4] and it can be used to treat albuminuria and diabetes [5], also it seems to have antifungal and antiviral properties [6], which is used as an antioxidant and helps to protect human cells against oxidative damage [7]. It can be used as a remote astringent in cases of internal hemorrhage [8] and can also be used to treat psoriasis and external hemorrhoids containing gallic

acid [9]. Gallic acid molecule is essentially planar and has two intramolecular hydrogen bonds between hydroxyl groups, the hydrogen atoms of the three hydroxyl groups are oriented in the same direction around the ring and form intra- and intermolecular hydrogen bonds. The crystal structure is stabilized by all available intermolecular hydrogen bonds [10]. The two adjacent hydroxyl groups are engaged in a complex [11] and the remaining hydroxyl group is suggested to form hydrogen bonding with  $COO^-$  of the other legend presented on the same molecule forming a ring like structure.

Gallic acid is a strong chelating agent and forms complexes of high stability with iron [12,13]. The complex starts from pH = 3 and continues to pH = 9. The degree of chelating increases as the pH increases. Iron is attached to gallic acid through two adjacent hydroxyl groups presented on aromatic ring. Neodymium gallates were reported as a solid in which, metal to legend ratio was 1:2 and phenolic hydroxyl group vibrations were defined at 1282 and 1212  $cm^{-1}$  [14]. Complexes of lanthanides (III), from (La–Lu) and Y (III) with gallic acid were obtained as solids with general formula  $Ln(C_7H_5O_5)(C_7H_4O_5)_n \cdot nH_2O$  ( $n = 2$  for La–Ho and  $Y: n = 0$  for Er–Lu). The infrared spectrum of gallic acid shows a sharp absorption band of carboxylic group  $-COOH$  at 1664  $cm^{-1}$  [14], absorption bands of  $\delta_{OH}$  at 1428 and at 864  $cm^{-1}$  as well as  $\nu_{C-OH}$  at 1320  $cm^{-1}$ , while, lanthanides gallic acid complexes give  $\nu_{as OCO^-}$  at 1544–1528  $cm^{-1}$  and  $\nu_{as OCO^-}$  for dihydrated complexes, which are shifted to lower frequencies of about 8–12  $cm^{-1}$  and have not changed their position for anhydrous complexes (Er–Lu).

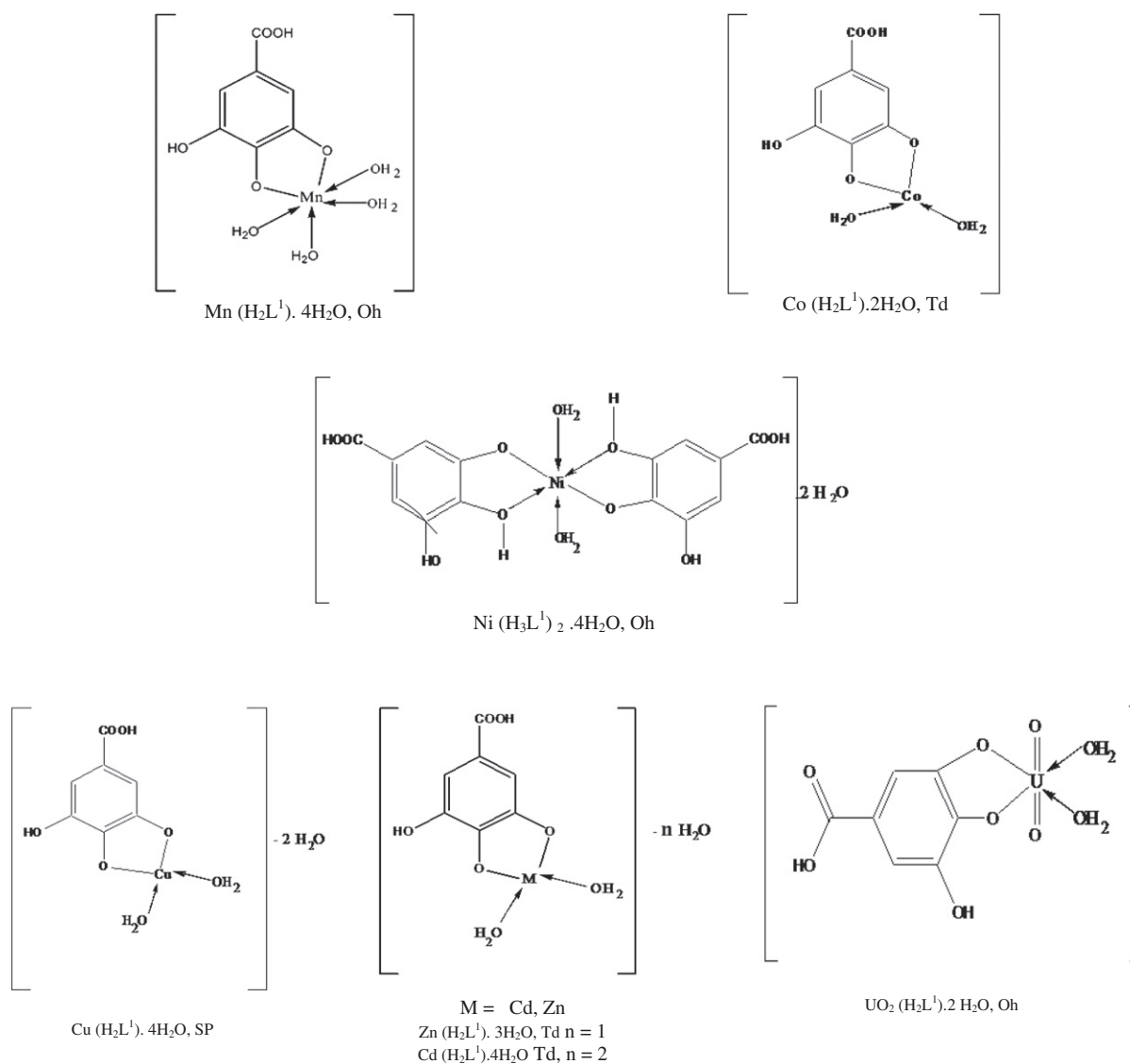
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**Table 3**  
Fundamental infrared bands ( $\text{cm}^{-1}$ ) of  $\text{H}_4\text{L}^1$  and its azo complexes.

Compound	$\nu_{\text{OH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$ and $\nu_{\text{C-C}}$	$\nu_{\text{C-OH}}$ and $\delta_{\text{OH}}$	$\delta_{\text{C-OH}}$	$\delta_{\text{C=O}}$	$\gamma_{\text{O-H}}$	$\gamma_{\text{CO}}$	H. bonding OH in COOH
$\text{H}_4\text{L}^1$	3494 3279 2669	1666	1612 1540 1426	1318 1384	1266 1098	634	865 794	558	733
$\text{Mn}(\text{H}_2\text{L}^1)\cdot 4\text{H}_2\text{O}$	3429 3287 –	1639	1593 – –	– 1388	– –	– –	– 793	– –	– –
$\text{Co}(\text{H}_2\text{L}^1)\cdot \text{H}_2\text{O}$	3417 3295	–	1606 1574	– 1383	– –	651	– 797	– –	– –
$\text{Ni}(\text{H}_3\text{L}^1)_2\cdot 4\text{H}_2\text{O}$	3446 3263	–	– 1588	– 1383	– 1115	668	– –	– –	– –
$\text{Cu}(\text{H}_2\text{L}^1)\cdot 4\text{H}_2\text{O}$	3449 2664	–	1597 –	1393 –	– –	680	– –	– –	760
$\text{Zn}(\text{H}_2\text{L}^1)\cdot 3\text{H}_2\text{O}$	3460 – 2664	–	– 1563 –	– 1384	– 1116	– –	– 792	– –	– –
$\text{Cd}(\text{H}_2\text{L}^1)\cdot 4\text{H}_2\text{O}$	3665 3340 –	–	1595 1554 –	–	–	636	– 791	– –	– –
$\text{UO}_2(\text{H}_2\text{L}^1)\cdot 2\text{H}_2\text{O}$	3398 – 2705	–	1615 1514 1431	1344 –	1260 1097	672	– –	– –	767



**Fig. 2.** The structures of the prepared gallic acid complexes.

### 3. Results and discussion

#### 3.1. Infrared, electronic spectra and magnetic susceptibility of gallic acid and its complexes

Table 3 collects the infrared spectra of gallic acid and its complexes. Three bands were detected at 3494, 3279 and 2669  $\text{cm}^{-1}$ , which are assigned to  $\nu_{\text{OH}}$ . In case of manganese, cobalt, nickel, zinc and cadmium complexes, the first two peaks shifted from their positions and the third disappeared, whereas phenolic hydroxyl groups participated in forming the complexes [21]. The  $\nu_{\text{C=O}}$  of the free legend is identified at 1666  $\text{cm}^{-1}$ . This band is absent in case of cobalt, nickel, copper, zinc, cadmium and uranyl complexes. In case of manganese complex, the  $\nu_{\text{C=O}}$  is shifted to lower frequency of about 27  $\text{cm}^{-1}$ . Such data are in favor of suggesting that the carbonyl group is strongly affected on coordination with transition [22].  $\text{H}_4\text{L}^1$  gave  $\delta_{\text{OH}}$ ,  $\gamma_{\text{OH}}$  and  $\nu_{\text{C=O}}$  modes of vibrations. Such data favored the carboxylate radical as possible oxidation of the

phenolic hydroxyl with the formation of quinone structure [23]. These bands are affected on coordination with metal ions, to pinpoint that the oxygen atom is a center for coordination with the metal ions, also  $\delta_{\text{C=O}}$  is a strong indicative that oxygen atom interact with metal ions. The different modes of vibrations of C–C, C=C and C–H are affected the complex, probably due to the aromaticity of the formed chelate is different from the legend [23]. The uranyl complex exhibits two bands at 942 and 825  $\text{cm}^{-1}$ , which are assigned to the asymmetric stretching frequency  $\nu_3$  and symmetric stretching frequency ( $\nu_1$ ), respectively, of the dioxouranium ion [24]. The  $\nu_3$  value is used for the calculation of the force constant ( $F$ ) [25] for the bonding sites of the O=U=O as follows:  $(\nu_3)^2 = (1307)^2 \times (F_{\text{U-O}})^{14.103}$ ,  $F_{\text{U-O}}$  value is found to be 7.3 m dyne  $\text{Å}^{-1}$  and  $R_{\text{U-O}} = 1.08 (F_{\text{U-O}})^{-1/3} + 1.17$ . Also, the U–O bond distance,  $R_{\text{U-O}}$  is calculated [26] and equals to 1.72 Å. The EAS of the black manganese-complex,  $[\text{Mn}(\text{H}_2\text{L}^1)_4\text{H}_2\text{O}]$ , gave four bands. The first two peaks were at 300 and 350 nm, which are assigned to  ${}^6\text{A}_{1g} \rightarrow {}^4\text{A}_{1g}$ , while the third at 450 nm and that is due to

**Table 4**  
Fundamental infrared bands ( $\text{cm}^{-1}$ ) of  $\text{H}_4\text{L}^2$ , and its complexes.

Compound	$\nu_{\text{OH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$ and $\nu_{\text{C-C}}$	$\nu_{\text{N=N}}$	$\delta_{\text{C=O}}$ and $\gamma_{\text{CO}}$	$\gamma_{\text{O-H}}$	H. bonding OH in COOH	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
$\text{H}_4\text{L}^2$	3452 3218 3033	1670	1595 1445	1493	690	835	750	–	–
$\text{Co}(\text{H}_3\text{L}^2)(\text{H}_4\text{L}^2)\text{Cl}\cdot 4\text{H}_2\text{O}$	3340 3060	–	1591 –	1506	692	833	744	513	609
$\text{Ni}(\text{H}_3\text{L}^2)(\text{H}_4\text{L}^2)\text{Cl}\cdot 4\text{H}_2\text{O}$	3352 3060	–	1587 –	1504	694	–	746	511	613
$\text{Cu}(\text{H}_4\text{L}^2)\text{Cl}_2\cdot 6\text{H}_2\text{O}$	3433 3344 3058	–	1589 –	1498	696	839	750	507	–
$\text{Ni Cu}(\text{H}_2\text{L}^2)_2(\text{H}_4\text{L}^2)\cdot 2\text{H}_2\text{O}$	3367 3056	–	1589 –	1498	694	–	756	478	621

**Table 5**  
Fundamental infrared bands ( $\text{cm}^{-1}$ ) of  $\text{H}_5\text{L}^3$  and its complexes.

Compound	$\nu_{\text{OH}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$ and $\nu_{\text{C-C}}$	$\nu_{\text{N=N}}$	$\delta_{\text{C=O}}$ and $\gamma_{\text{CO}}$	$\gamma_{\text{O-H}}$	H. bonding OH in COOH	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
$\text{H}_5\text{L}^3$	3312	1681	1606 1518	1452 –	663	818	753	–	–
$\text{Co}(\text{H}_5\text{L}^3)\text{Cl}_2\cdot 6\text{H}_2\text{O}$	3344	1654	1604 –	1451	668	–	756	592	640
$\text{Ni}(\text{H}_3\text{L}^4)\cdot 4\text{H}_2\text{O}$	3340	–	1597 1568	1383	1114	680	761	445	541
$\text{Cu}(\text{H}_3\text{L}^4)\cdot 6\text{H}_2\text{O}$	3342	1599 1446	–	1383	1117	696	764	446	534

**Table 6**  
Fundamental infrared bands ( $\text{cm}^{-1}$ ) of  $\text{H}_5\text{L}^4$  and its complexes.

Compound	$\nu_{\text{OH}}$	$\nu_{\text{C=C}}$ and $\nu_{\text{C-C}}$	$\nu_{\text{N=N}}$	$\nu_{\text{C-OH}}$ and $\delta_{\text{OH}}$	$\delta_{\text{C=O}}$ and $\gamma_{\text{CO}}$	$\gamma_{\text{O-H}}$	H. bonding OH in COOH	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$
$\text{H}_5\text{L}^4$	3367 3203 3072	1710	1601 1452	1491	688	879	758	–	–
$\text{Co}(\text{H}_3\text{L}^4)\cdot 5\text{H}_2\text{O}$	3321 3224 3217	–	1575 –	–	687	–	759	445	503
$\text{Ni}(\text{H}_3\text{L}^4)\cdot 4\text{H}_2\text{O}$	3340	1597 1568	– 1383	–	680	–	761	445	541
$\text{Cu}(\text{H}_3\text{L}^4)\cdot 6\text{H}_2\text{O}$	3342 –	1599 1446	– 1383	–	696	839	764	446	534
$\text{Cd}(\text{H}_3\text{L}^4)\cdot 2\text{H}_2\text{O}$	3406 –	1579	– 1388	–	684	–	759	437	511

${}^6A_{1g} \rightarrow {}^4T_{2g}$  transition, and the last band was at 510 nm, which is assigned to  ${}^6A_{1g} \rightarrow {}^4T_{1g}$  transition [27,28]. Their room temperature

$\mu_{\text{eff}}$  value of 5.4 B.M typified the existence of Octahedral configuration. The black cobalt-complex,  $[\text{Co}(\text{H}_2\text{L}^1)\cdot 2\text{H}_2\text{O}]$  gave three bands

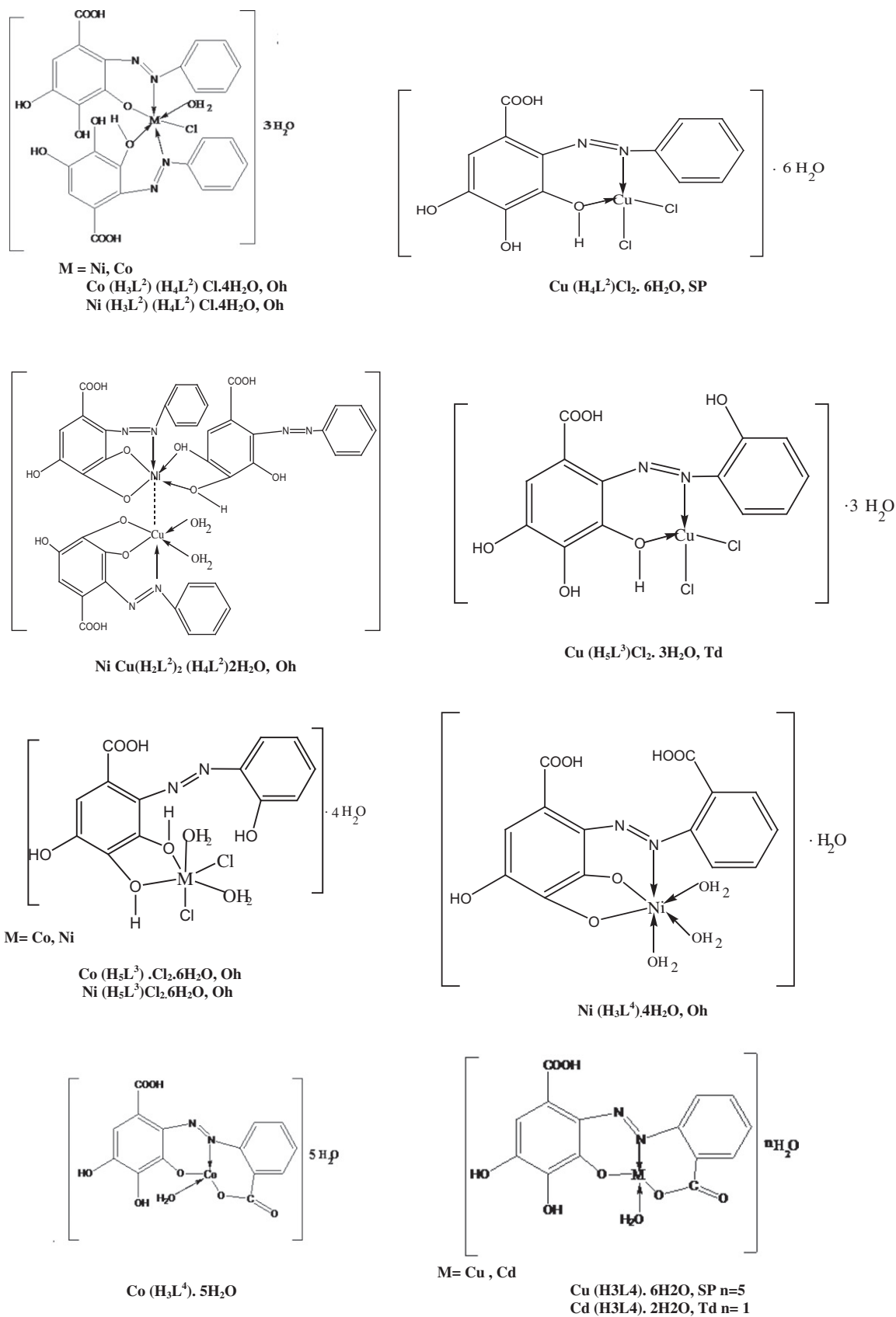


Fig. 3. The structures of the prepared azo gallic acid complexes.

at 300, 389 and 675 nm (broad in nature),  $^4A_2 \rightarrow ^4T_1$  (P) transition of  $T_d$  structure [29]. Their room temperature  $\mu_{\text{eff}}$  value of 4.6 B.M. verified such geometry. The black nickel-complex,  $[\text{Ni}(\text{H}_2\text{L}^1)(\text{H}_4\text{L}^1)\cdot 4\text{H}_2\text{O}]$  gave five bands at 286, 314, 320, 460 and 510 nm and their  $\mu_{\text{eff}}$  value, which equals 3.8 B.M. of Octahedral structure [30]. The black copper-complex,  $[\text{Cu}(\text{H}_2\text{L}^1)\cdot 4\text{H}_2\text{O}]$  gave four bands at 400, 485, 510 and 565 nm, typified the presence of Square Planar stereochemistry mainly of  $^2B_{1g} \rightarrow ^2B_{2g}$  electronic transition in  $D_{4h}$  symmetry [31]. The room temperature magnetic moment value,  $\mu_{\text{eff}}$ , is 1.73 B.M. The black zinc and cadmium complexes,  $[\text{Zn}(\text{H}_2\text{L}^1)\cdot 3\text{H}_2\text{O}]$ ,  $[\text{Cd}(\text{H}_2\text{L}^1)\cdot 4\text{H}_2\text{O}]$ , respectively, gave four bands at 300, 382, 486 and 564 nm for zinc complex and three bands at 260, 450 and 470 nm for cadmium complex. Both complexes are diamagnetic. The EAS of the brown uranyl-complex,  $[\text{UO}_2(\text{H}_2\text{L}^1)\cdot 2\text{H}_2\text{O}]$  gave three bands, the first two peaks were at 300 and 400 of charge transfer, probably ligand  $\rightarrow O_{\text{dbnd}}\text{U}=\text{O}$ , while the last band at 500 nm can be definitely assigned to the  $^1\Sigma_g^+ \rightarrow ^2\pi_4$  transition [32].

From the analytical data, and the foregoing spectral and magnetic moment results, gallic acid is of bidentate attachment through two oxygen atoms in the hydroxyl group on the reaction with transition metal salts of Mn (II), Co (II), Ni (II), Cu (II), Zn (II), Cd (II),  $\text{UO}_2$  (II) and so the structures are suggested as in Fig. 2.

### 3.2. Infrared, electronic spectra and magnetic studies of azo gallic acid complexes

The fundamental bands of azo gallic acid compounds and their complexes are given in Tables 4–6. By comparing the infrared spectra of the complexes with that of the free legend, it should be possible to determine the binding sites. The vibration frequencies of coordinated functional groups (e.g.  $\nu_{\text{OH}}$ ,  $\nu_{\text{C}=\text{O}}$ ,  $\delta_{\text{O}-\text{H}}$ ,  $\text{N}=\text{N}, \dots$ ) were affected with different degrees. In case of  $\text{H}_4\text{L}^2$  and  $\text{H}_5\text{L}^4$ , three bands appeared at 3452, 3218, 3033  $\text{cm}^{-1}$  and 3367, 3203, 3072  $\text{cm}^{-1}$ , respectively. While  $\text{H}_5\text{L}^3$  legend gave a broad band at 3312  $\text{cm}^{-1}$ , which is assigned to  $\nu_{\text{OH}}$ , [33–35] (Tables 4 and 5). Some changes occurred on the complex, the data in such region are related either to the  $-\text{OH}$  group which affected the coordination or to the existence of water molecule. Hydrogen bonded structures were expected due to intra-molecular H-bonding between the azo group and the o-carboxy H-bonding of the type  $\text{O}-\text{H} \cdots \text{N}$  between the  $-\text{OH}$  or  $-\text{COOH}$  substituent and the  $\text{N}=\text{N}$  group [36–39]. The  $\nu_{\text{C}=\text{O}}$  of  $\text{H}_4\text{L}^2$ ,  $\text{H}_5\text{L}^3$  and  $\text{H}_5\text{L}^4$  legends are at 1670, 1681 and 1710  $\text{cm}^{-1}$ , respectively [22]. This peak was absent in all complexes, suggesting that the carbonyl group is strongly affect the coordination with transition metal ions either by direct interaction between the lone pair of electrons of the carbonyl group with metal ion or through tautomerization. Also,  $\delta_{\text{C}=\text{O}}$  vibration band led to the same conclusion.  $\text{H}_4\text{L}^2$ ,  $\text{H}_5\text{L}^3$  and  $\text{H}_5\text{L}^4$  compounds gave bands at 1493, 1452 and 1491  $\text{cm}^{-1}$ , respectively, which identified the azo vibration [36–38]. The shift of this band in all complexes indicated that the azo group is involved in coordination. The presence of  $\gamma_{\text{C}=\text{O}}$ ,  $\nu_{\text{C}=\text{O}}$  modes of vibrations in the metal complexes, suggests that the oxygen atom is also a center of coordination [23]. New bands appeared in all azo gallic acid complexes in the frequency ranges 437–592  $\text{cm}^{-1}$  and 503–640  $\text{cm}^{-1}$ , which are attributed to  $\nu_{\text{M}-\text{N}}$  and  $\nu_{\text{M}-\text{O}}$ , respectively. Table 1 illustrates the spectral, electronic transitions and magnetic properties of the complexes. The data indicated the existence of most complexes in Octahedral and Tetrahedral geometries [29,31,40], except the copper complexes which is Square Planar. From the analytical data, electronic spectra and magnetic moment results, the structures are suggested as in Fig. 3.

### 3.3. ESR of copper complexes

The room temperature polycrystalline X-band ESR spectra of  $[\text{Cu}(\text{H}_2\text{L}^1)\cdot 4\text{H}_2\text{O}]$ ,  $[\text{Cu}(\text{H}_4\text{L}^2)\text{Cl}_2\cdot 6\text{H}_2\text{O}]$ ,  $[\text{Cu}(\text{H}_5\text{L}^3)\text{Cl}_2\cdot 3\text{H}_2\text{O}]$  and  $[\text{Cu}(\text{H}_5\text{L}^4)\cdot 6\text{H}_2\text{O}]$  complexes gave similar spectral patterns, Fig. 4. All complexes are isotropic in nature with  $g_s$  values at 2.14, 2.48, 2.09 and 2.11 and (A) values at 280, 200, 210 and 300, respectively. The spectra show broad signals, which might be due to the polymeric nature of these complexes. These data resulted due to isotropic spectral feature [41,42].

### 3.4. Thermal analysis

The (DTA) for  $\text{H}_4\text{L}^1$ ,  $\text{H}_4\text{L}^2$ ,  $\text{H}_5\text{L}^3$  and  $\text{H}_5\text{L}^4$  compounds and their complexes are presented in Table 7. The change of entropy,  $\Delta S^\ddagger$ , values for all complexes, are nearly of the same magnitude and lie within the range of (–0.27 to –0.32)  $\text{kJ K}^{-1} \text{mole}^{-1}$ . So, the transition states are more ordered, the fraction appeared in the calculated order of the thermal reaction,  $n$ , confirmed the reactions proceeded in the complicated mechanisms. The calculated values of the collision parameters,  $Z$ , showed a direct relation to  $E_a$  [43]. The values of the decomposed substance fraction ( $\alpha_m$ ), at maximum development of the reaction were calculated. It is nearly with the same magnitude and lies within the range 0.5–0.8. Based on least square calculations, the  $\ln \Delta T$  versus  $1000/T$  plots for all complexes gave straight lines from which, the activation energies were calculated [44].

DSC is a technique used to study the thermal transitions of a compound, such as glass transitions, crystallization and melting.

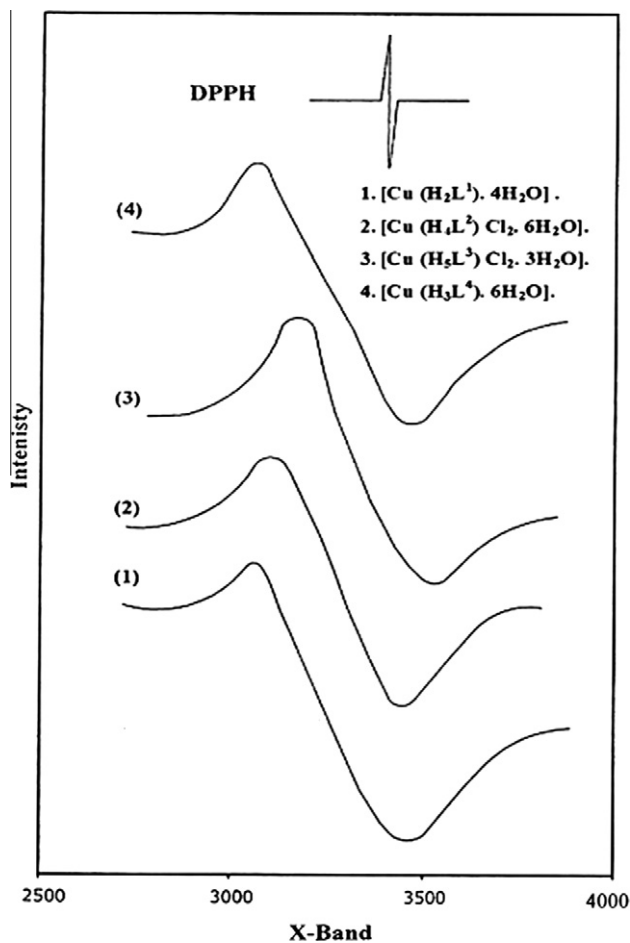


Fig. 4. X-Band ESR spectra of copper complexes.



**Table 7**  
DTA analysis of gallic acid and its azo complexes:

Compound	Type	$T_m$ (K)	$\Delta E$ (kJ mol <sup>-1</sup> )	$n$	$\alpha_m$	$\Delta S^*$ (kJ K <sup>-1</sup> mol <sup>-1</sup> )	$\Delta H^*$ (kJ mol <sup>-1</sup> )	$10^3$ (Z s <sup>-1</sup> )
H <sub>4</sub> L <sup>1</sup>	Endo	397.5	109.1	1.441	0.6	-0.29	-117.2	0.033
	Endo	540.6	439.8	1.206	0.6	-0.29	-156	0.098
	Exo	721.8	50.74	0.501	0.7	-0.31	-225	0.008
Co (H <sub>2</sub> L <sup>1</sup> )-H <sub>2</sub> O	Endo	377.3	55.27	1.491	0.6	-0.3	-113	0.018
	Exo	625	10.3.70	0.864	0.7	-0.3	-189	0.02
	Exo	676.3	225.5	1.029	0.6	-0.3	-201	0.04
	Exo	697	58.92	1.676	0.5	-0.31	-216	0.01
Ni (H <sub>3</sub> L <sup>1</sup> ) <sub>2</sub> -4H <sub>2</sub> O	Endo	383.4	37.41	1.385	0.6	-0.3	-116.2	0.012
	Exo	613	101.6	0.616	0.7	-0.3	-185.4	0.02
	Exo	664.1	169.5	2.02	0.5	-0.3	-199	0.031
Cu(H <sub>2</sub> L <sup>1</sup> )-4H <sub>2</sub> O	Endo	372.5	18.7	1.627	0.5	-0.31	-115	0.006
	Exo	645.5	193.1	1.61	0.5	-0.3	-192	0.036
H <sub>4</sub> L <sup>2</sup>	Exo	383	203.9	1.496	0.6	-0.29	-111	0.064
	Exo	833.3	14.37.00	0.492	0.8	-0.32	-270	0.002
	Exo	873	143	2.3	0.5	-0.31	-267	0.02
Co(H <sub>3</sub> L <sup>2</sup> ) (H <sub>4</sub> L <sup>2</sup> )Cl-4H <sub>2</sub> O	Exo	373	18.7	1.465	0.6	-0.3	-115	0.006
	Exo	658.7	1873	0.957	0.6	-0.31	-209	0.003
Ni (H <sub>3</sub> L <sup>2</sup> ) (H <sub>4</sub> L <sup>2</sup> ) Cl-4H <sub>2</sub> O	Exo	623.6	459.9	0.658	0.7	-0.29	-181	0.089
	Exo	663	925.3	1.353	0.6	-0.29	-189	0.168
	Exo	723	464.6	1.206	0.6	-0.29	-212	0.077
Cu(H <sub>4</sub> L <sup>2</sup> )Cl <sub>2</sub> -6H <sub>2</sub> O	Exo	373	20.33	1.543	0.6	-0.31	-115	0.007
	Exo	605	480.9	0.949	0.6	-0.29	-175	0.096
	Exo	678	144	0.912	0.6	-0.3	-204	0.026
Ni Cu(H <sub>2</sub> L <sup>2</sup> ) <sub>2</sub> (H <sub>4</sub> L <sup>2</sup> ):2H <sub>2</sub> O	Exo	373	352.8	1.393	0.6	-0.28	-106	0.114
	Exo	583	82.78	1.373	0.6	-0.3	-177	0.017
	Exo	623	166.1	1.156	0.6	-0.3	-186	0.032
	Exo	663.2	25.73	1.186	0.6	-0.32	-209	0.005
H <sub>5</sub> L <sup>3</sup>	Exo	373	196	0.55	0.7	-0.29	-108	0.063
	Exo	658.9	4230	1.57	0.5	-0.27	-180	0.771
	Exo	888	1605	1.54	0.6	-0.29	-254	0.217
	Exo	903	24.71	1.69	0.5	-0.32	-290	0.003
Co(H <sub>5</sub> L <sup>3</sup> ) Cl <sub>2</sub> -6H <sub>2</sub> O	Exo	373	95.5	1.94	0.5	-0.29	-110	0.031
	Exo	612.5	179.1	0.85	0.7	-0.3	-182	0.035
Ni (H <sub>5</sub> L <sup>3</sup> ) Cl <sub>2</sub> -6H <sub>2</sub> O	Exo	383	24.4	1.7	0.5	-0.3	117.4	0.008
	Exo	611.4	117.1	0.7	0.7	-0.3	-184.2	0.023
	Exo	693	436.1	1.2	0.6	-0.29	-202.7	0.076
Cu(H <sub>5</sub> L <sup>3</sup> )Cl <sub>2</sub> -3H <sub>2</sub> O	Exo	546.7	179.1	1.6	0.5	-0.29	-161.8	0.039
	Exo	373	20.5	1.9	0.5	-0.3	-114.7	0.007
H <sub>5</sub> L <sup>4</sup>	Exo	705	79.2	0.83	0.7	-0.3	-216.4	0.014
	Exo	853.7	383.2	0.86	0.7	-0.29	-253.6	0.054
	Exo	383	39.53	1.608	0.5	-0.3	-116	0.012
Co (H <sub>3</sub> L <sup>4</sup> ):5H <sub>2</sub> O	Exo	682.2	68.23	1.182	0.6	-0.31	-210	0.012
	Exo	652.6	68.2	0.891	0.7	-0.3	-200.3	0.01
Ni (H <sub>3</sub> L <sup>4</sup> ):4H <sub>2</sub> O	Exo	555.5	23.86	0.97	0.6	-0.31	-173.8	0.005
	Exo	573	395.5	1.08	0.6	-0.29	166.2	0.083
Cu (H <sub>3</sub> L <sup>4</sup> ):6H <sub>2</sub> O	Exo	404.4	30.44	1.163	0.6	-0.31	-124	0.009
	Exo	623	76.28	0.859	0.7	-0.31	-190	0.015
	Exo	738.8	399.9	1.136	0.6	-0.29	-217	0.065

DSC curves are obtained for H<sub>4</sub>L<sup>1</sup> and its Ni-complex, Fig. 5, which are done under a flow of N<sub>2</sub> at heating rate 10 °C/min in the temperature range 25–500 °C. It is clear that there are no glass transition temperatures ( $T_g$ ) for both H<sub>4</sub>L<sup>1</sup> and its Ni-complex, where the crystallization temperatures ( $T_c$ ) for both systems were at 124, 110.7 °C, respectively. The melting temperatures ( $T_m$ ) are at 449 and 392.6 °C, respectively. The heat capacity can be determined by dividing the heat flow by the heating rate. The variation of  $C_p$  versus  $T$  can be represented using Debye model as the following relations [45,46]:

$$C_p = \alpha T^3 + \gamma T, \quad \frac{C_p}{T} = \alpha T^2 + \gamma \quad (1)$$

where ( $a$ ) is the slope of the line and  $b$  is the intersection of the line with  $y$ -axis ( $C_p$  axis),  $C_p$  is the specific heat at constant volume,  $\gamma$  is constant equals  $10^{-4}$  cal/g. mole.

According to Debye model [46]:

$$\alpha = \frac{234R}{\theta_D^3}, \quad \theta_D = \sqrt[3]{\frac{234R}{\alpha}}$$

$R$  is the universal gas constant equals 8.3 J/mole/K and  $\theta_D$  is Debye temperature, which defined as the separate temperature between different temperature. By plotting  $\frac{C_p}{T}$  as  $y$ -axis and  $T^2$  as  $x$ -axis, a straight line is obtained with a slope equals  $\alpha$ , also the intersection with  $y$ -axis gives the coefficient ( $\gamma$ ), Table 8.

### 3.5. Biological activity study

In this study, four microorganisms representing different microbial categories, Gram-positive (*Staphylococcus aureus*), Gram-negative (*Escherichia coli*, *Pseudomonas aeruginosa*) and one Yeast

**Table 8**  
The slopes and intercept for DSC curves of gallic acid and its Ni-complex.

Compound	$C_p = aT + b$		$\frac{C_p}{T} = \alpha T^2 + \gamma$	
	$a$	$B$	$\gamma$	$A$
H <sub>4</sub> L <sup>1</sup>	0.01	-0.54	-0.225	$2 \times 10^{-6}$
[Ni (H <sub>3</sub> L <sup>1</sup> ) <sub>2</sub> -4H <sub>2</sub> O]	0.03	-8.47	-0.012	$2 \times 10^{-7}$

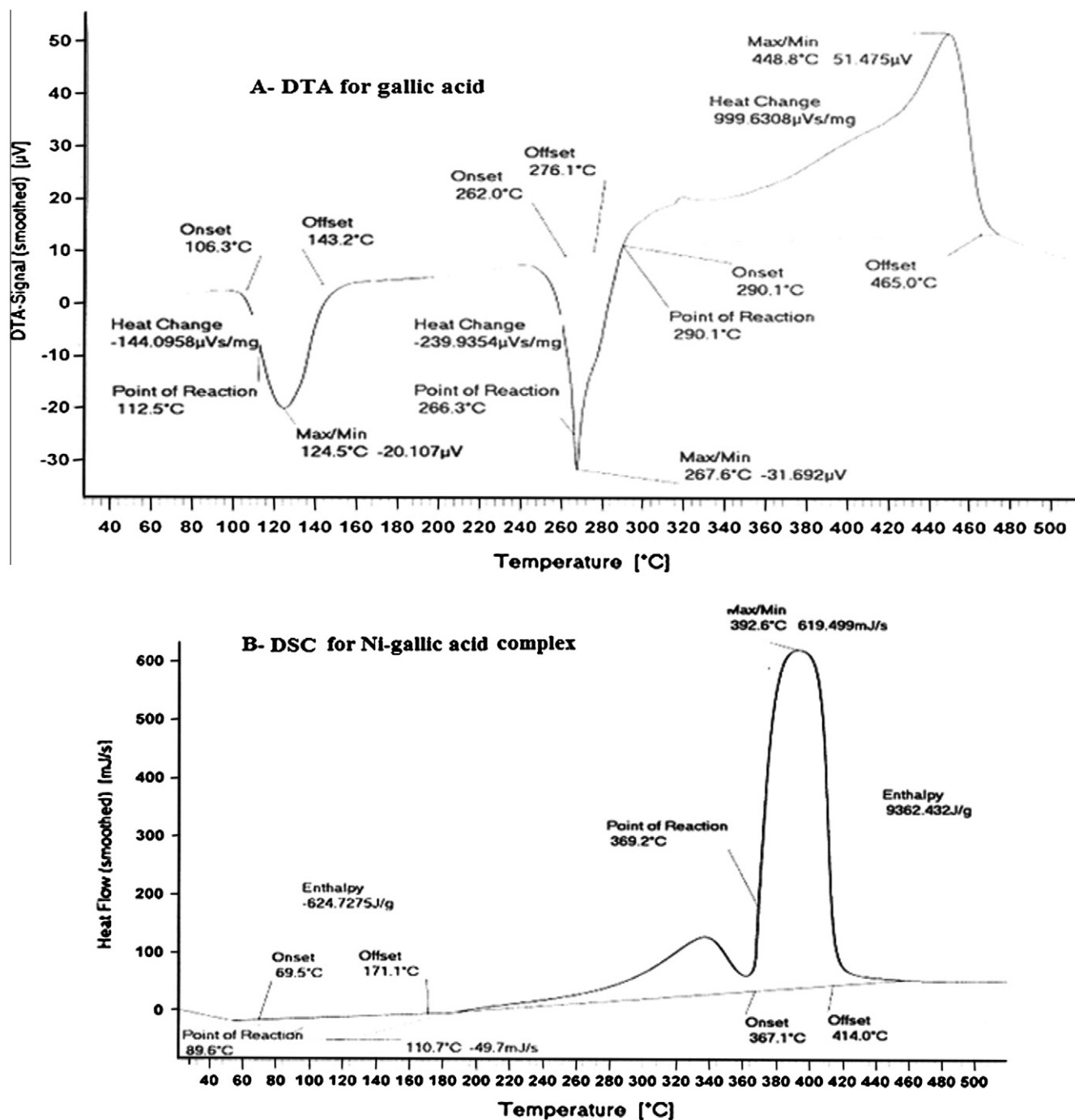


Fig. 5. DTA and DSC curves for gallic acid and its Ni-complex.

Table 9

Biological activities of some selected ligands and their metal complexes.

Compound	G+ bacteria	G- bacteria		Yeast
	<i>Staphylococcus aureus</i>	<i>Escherichia coli</i>	<i>Pseudomonas aeruginosa</i>	<i>Candida albicans</i>
$\text{UO}_2(\text{H}_2\text{L}^1)\cdot 2\text{H}_2\text{O}$	+	+	+	+
$\text{H}_4\text{L}^2$	+	-	+	-
$\text{Ni Cu}(\text{H}_2\text{L}^2)_2(\text{H}_4\text{L}^2)\cdot 2\text{H}_2\text{O}$	-	-	+	-
$\text{H}_5\text{L}^3$	+	-	+	-
$\text{Co}(\text{H}_5\text{L}^3)\text{Cl}_2\cdot 6\text{H}_2\text{O}$	-	-	+	-
$\text{Cu}(\text{H}_3\text{L}^4)\cdot 6\text{H}_2\text{O}$	-	+	+	-

(*Candida albicans*) were used. The study included six compounds, two legends ( $\text{H}_4\text{L}^2$  and  $\text{H}_5\text{L}^3$ ) and four complexes of different metal

ions (Co, Ni Cu mixed metal, Cu and  $\text{UO}_2$ ). The minimum inhibition concentrations (MIC) for the tested compounds were determined



via the double dilution technique [47]. All compounds were dissolved in DMSO. Five concentrations were prepared for each compound (2, 4, 8, 16 and 32 µg/ml). The bacteria were incubated at 37 °C for 24 h in nutrient broth medium, however, the yeast was incubated in malt extract broth for 48 h. MIC was considered at the lowest concentration causing full inhibition of the test organism growth. MIC values for tested compounds for different microorganisms are given in Table 9. The data allow the following observations and conclusions:

- (a) *C. albicans* was found to be resistant for all investigated compounds.
- (b) It seems that the free legend  $H_5L^4$  is inactive, but its copper complex is of highest activity. So, the copper plays a major role in activity. Compounds with noticeable activity may be considered a start point for development of some new antimicrobial agents.
- (c) It is observed that uranyl complex has higher activity [47]. Such increased activity of the metal chelates could be explained on the basis of overtone's concept and chelating theory [47–49]. On chelating, the polarity of the metal ion is reduced to a greater extent due to the overlap of the legend orbital and partial sharing of the positive charge of metal ion with the donor groups. Further, it increases the delocalization of p- and d- electrons over the whole chelate and enhances the lipophilicity of the complex. The increased lipophilicity enhances the penetration of the complexes into lipid membranes and blocking of metal binding sites on the enzymes of the microorganism.

#### 4. Conclusion

Gallic acid and its azo derivatives were of distinctive behavior. This is because the variety of the geometry of their formed complexes. This was reflected in various studies, such as thermal analysis and biological activity. Due to the lack of publishing about these complexes, we recommend to do intensive studies of the current work subject to explore all the characteristics of such complexes and the possibility of applied use.

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