



Organic Amino Acids Chelates; Preparation, Spectroscopic Characterization and Applications as Foliar Fertilizers.

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Abstract

Cu(II) complexes of amino acid hydrolyzate soya protein isolate have been prepared. In order to study the mode of coordination in the above chelates and their effect as foliar fertilizers, Mn(II), Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) complexes of L-amino acids have been prepared and characterized by elemental, spectral analyses, (IR, UV-VIS, mass spectra and ESR), electrical conductance, magnetic moments and thermal analyses (DTA and TGA). ESR spectra of copper (II) complexes show isotropic and anisotropic types $d(x^2-y^2)$ with a covalent bond character. The amino acids chelates were evaluated as foliar fertilizers by treating plants with micronutrient, amino acid solutions and varying concentrations of micronutrient amino acids chelates. It was found that spraying plant with 2.5% micronutrient amino acids chelates gives the best results regarding: plant height, stem diameter, leaves area, number of flowers, number of branches per plants and total yield per plant.

Indexing terms/Keywords

L-amino acids; metal complexes; spectral and magnetic measurements, organic foliar fertilizers

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1. INTRODUCTION

Plant supplying with mineral nutrients effectively is a crucial factor for healthy leaf area on the trees and consequently effective photosynthesis. Deficiency of essential mineral nutrients especially micronutrients is of general occurrence during the past few decades, due to intensive cropping, extensive use of chemical fertilizers, loss of micronutrients by leaching, and decreased use of farm yard manure. Large area of agricultural land has been found to be deficient in one or other Micronutrients, It is realized that, productivity of crops is being adversely affected due to deficiencies of micronutrients [1]. Microelements are generally offered to plants by adding them to medium or spraying them on leaves. When they are applied as inorganic salts to the growing medium, they transform to insoluble forms, so their absorption by the plants decrease. Moreover, leaf fertilizers in form of inorganic mineral structure hardly diffuse from the leaf surface into the plant because of their high weight molecular structure [2]. In order to eliminate these negative effects leaf fertilizers with organic structure as synthetic chelates were developed [3,4,5]. It has been suggested that microelements as inorganic or organic complexes should be applied to the leaves instead of adding them to the growing medium in order to solve microelement requirements of the plants. Chelates obtained by the reaction of metallic salts with their synthetic or natural organic complexes save metal cations from undesirable reactions such as precipitation; they play a significant role in increasing solubility and availability of micronutrients [6,7]. For this reason, synthetic precursors which have the ability of making strong chelate is almost used in plant growing medium. From another point of view, these chelators are not phytotoxic to plants. They are able to make complexes especially with heavy metals and prevent them to uptake by plants in higher ratio [8]. The work in this research was directed to synthesis; spectral characterization of metal amino acid complexes derived from hydrolyzate of soya protein isolate and study their applications as foliar fertilizers. This process is considered as a low cost and a plant growth promoter novel technology.

2. EXPERIMENTAL

2.1. Materials and method

All chemicals used were of analytical reagent grade (AR) and of the highest purity available. C, H, N and Cl analyses were determined at the Analytical Unit of Cairo University, Egypt. A standard method was used to determine metal(II) ion. All metal complexes were dried under vacuum over P_2O_5 . The IR spectra were measured as KBr and CeBr pellets using a Perkin-Elmer 683 spectrophotometer ($4000-400\text{ cm}^{-1}$). Electronic spectra were recorded on a Perkin-Elmer 550 spectrophotometer. The conductance of 10^{-3} M solutions of the complexes in DMF was measured at 25°C with a Bibby conductimeter type MCI. Mass spectra were recorded using JEULJMS-AX-500 mass spectrometer provided with data system. Magnetic susceptibilities were measured at 25°C by the Gouy method using mercuric tetrathiocyanato cobalt(II) as the magnetic susceptibility standard. Diamagnetic corrections were estimated from Pascal's constant. The magnetic moments were calculated from the equation:

$$\mu_{\text{eff}} = 2.84 \sqrt{\chi_M^{\text{corr}} \cdot T}$$

The solid ESR spectra of the complexes were recorded with ELEXSYS E 500 Bruker spectrometer at room temperature. Diphenyl picrylhydrazide was used as a standard (DPPH) material. T. L. C was used to confirm the purity of prepared complexes.

2.2. Synthesis of complexes

2.2.1. Synthesis of metal complexes (1)-(16)

Complexes (1), (2), (3), (4), (6), (8), (9),(10) and (11): (0.02 mol) aqueous solution of L-lysine was added to (0.01 mol) aqueous solutions of the metal salt ($\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$, $\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}$, $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Co}(\text{OAc})_2$, $\text{Cd}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, $\text{Zn}(\text{OAc})_2$ and MgO) respectively ($2L_1H:1M$). Complex (5): aqueous solution of (0.01 mol) L-lysine was added to aqueous solution of (0.01 mol) of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ and this solution was added to (0.01mol) of $\text{CH}_4\text{N}_2\text{O}$ ($1L_1H: 1M: 1L_2$). Complex (7): aqueous solution of (0.01mol) of L-lysine and 0.01mol of L-histidine was added to aqueous solution of (0.02 mol) of $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, ($1L_1H:1L_4H:2M$), Complex (12): aqueous solution of (0.01 mol) of glutamic acid and (0.01 mol) of urea was added to aqueous solution of $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, ($1L_5H: 1L_2: 1M$) Complex (13): aqueous solution of (0.02 mol) of glutamic acid was added to $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$, ($2L_5H:1M$), Complex (14): aqueous solution of (0.02 mol) of cysteine was added to aqueous solution of (0.01 mol) $\text{Co}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ($2L_3H: 1M$), Complex (15): aqueous solution of (0.02 mol) of cysteine was added to aqueous solution of (0.01mol) of CuO , ($2L_3H:1M$). Complex (16): aqueous solution of mixture amino acids produced from hydrolysis of soy bean protein (0.02 mol) was added to aqueous solution of (0.01 mol) CuO . ($2L_2H: 1M$), the mixtures were refluxed with stirring for 2-4 hours depending on to nature of metal ion. The precipitates were filtered off, washed with ethanol several times, dried under vacuum in the presence of P_2O_5 . Analytical data are given in Table 1.

2.3 Biological activity

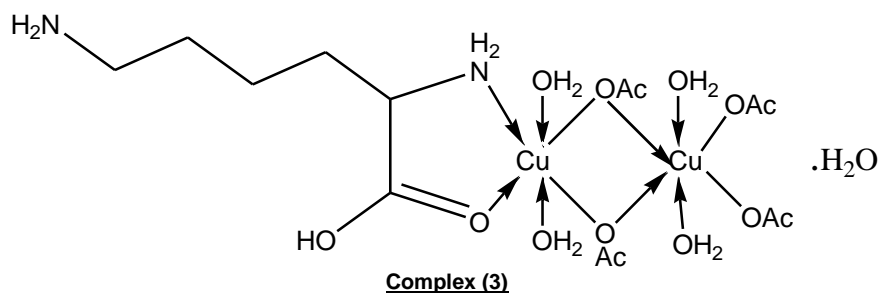
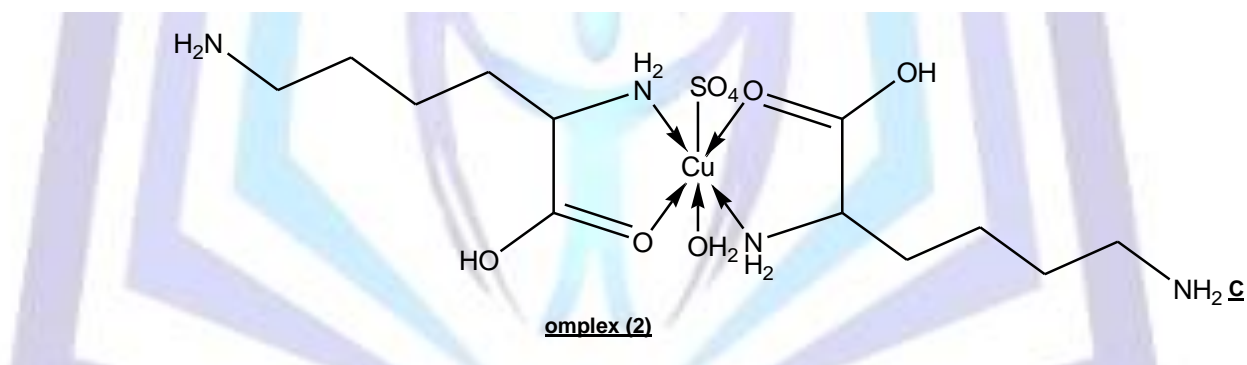
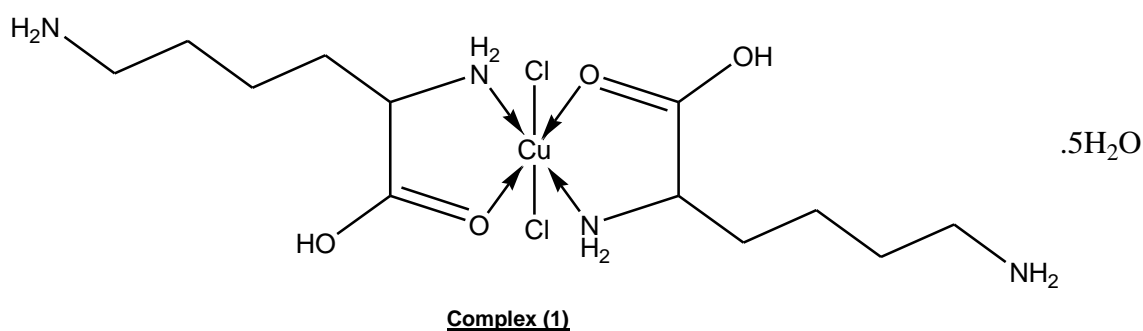
Evaluation of the growth promotion and productivity ability of the organically chelated metal nutrients on cucumber plant was conducted at Department of Technical Support in Delta Agro Chemical Company. The evaluation process was carried out in a green house with 400 m^2 area and a number of 10 lines containing 196 plants. Cucumber plant was divided into six groups: The first one "T₀" was sprayed only with water; and this group was considered the untreated control; the second group "T₁" was treated with 3% micronutrient solution (equivalent to 60 ppm of each micronutrient), "T₂" group was sprayed with 3 % amino acid solution, Groups four, five and six "T₃, T₄ and T₅" were treated with 2%, 2.5% and 3%T₃

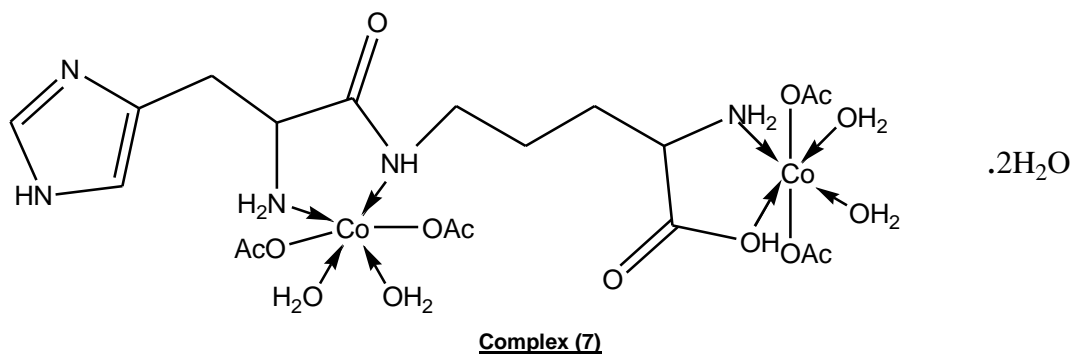
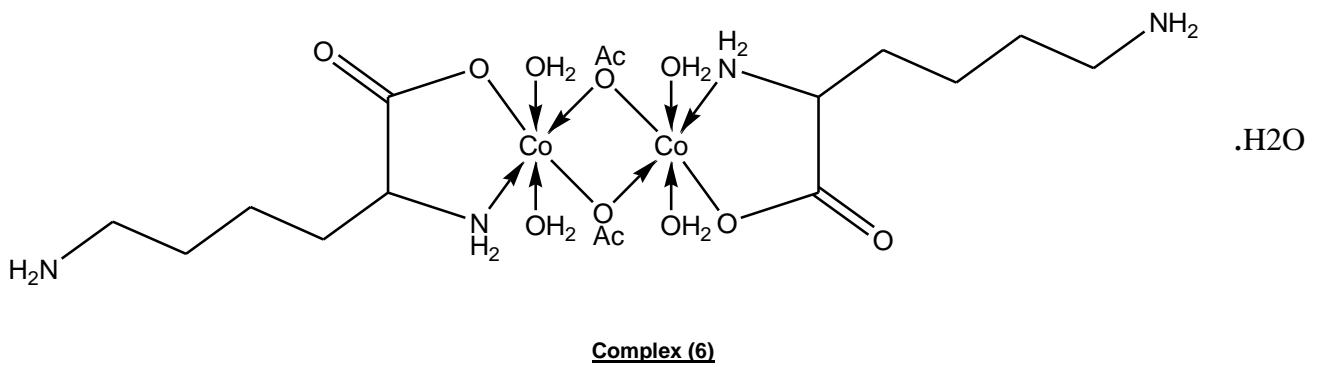
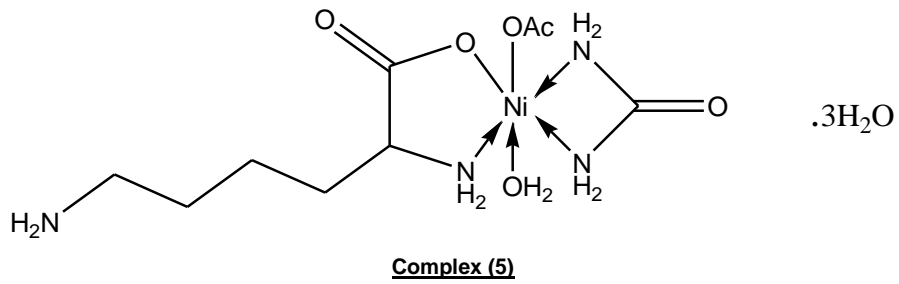
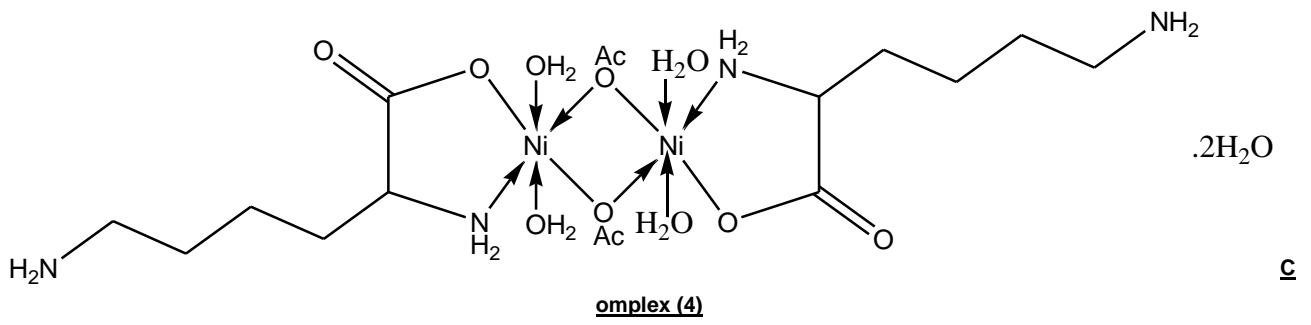


of the amino acid micronutrient chelate solutions (equivalent to 40 ppm, 50ppm and 60ppm of each micronutrient) respectively. The solutions were applied in the form foliar sprays at two growth stages: on 15th and 30th days after transplantation. The growth characters like plant height, stem diameter, leaves area, number of flowers, number of branches per plants and total yield per plant was determined after last harvest.

3. RESULTS AND DISCUSSION

Acid hydrolysis of soy isolate protein produced L- amino acids which reacted with metal (II) ions (M (II)) to yield metal chelates. In order to study the structure of chelates and mode of coordination, M(II) chelates of some L-amino acids were prepared individually. These chelates were characterized by elemental and spectral analyses (IR, U.V-VIS, mass spectra and ESR), electrical conductances, magnetic measurements and thermal analyses (DTA and TGA). The prepared Metal(II) chelates were found to be stable at room temperature and non hydroscopic. The analytical and physical data (Table 2) and spectral data (Table 3) are compatible with the proposed structures, Figure 1. The molar conductances of the prepared complexes in 10^{-3} M DMF at 25C^o were in the range (1.2-19.1) Oh $m^{-1} cm^2 mol^{-1}$ Table 2, indicating non-electrolytic nature [9].





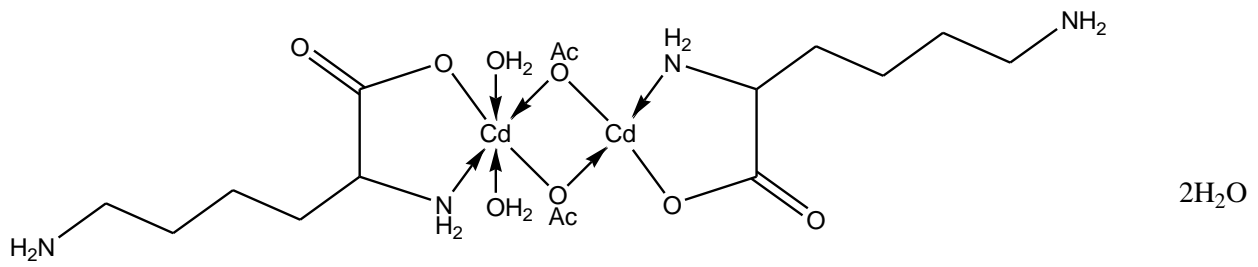
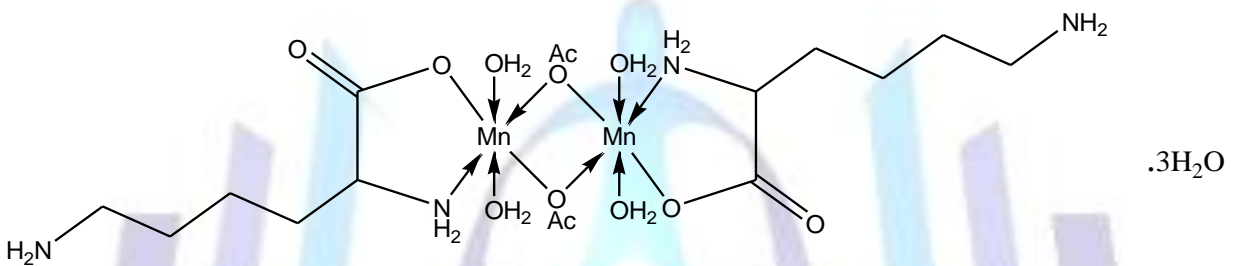
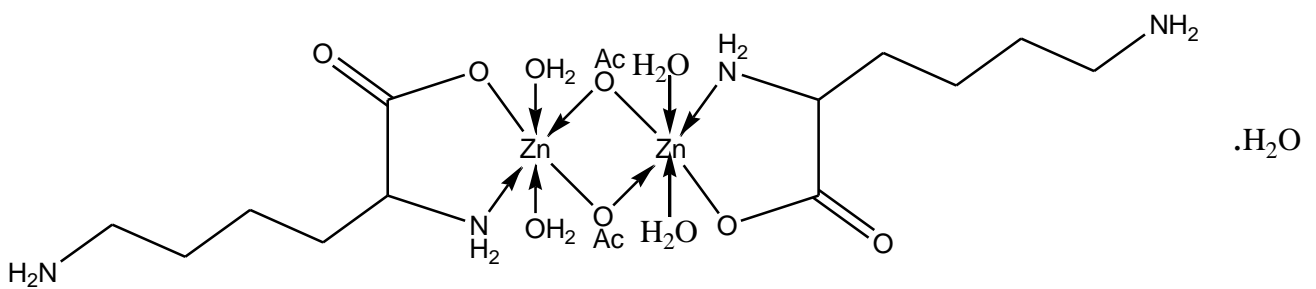
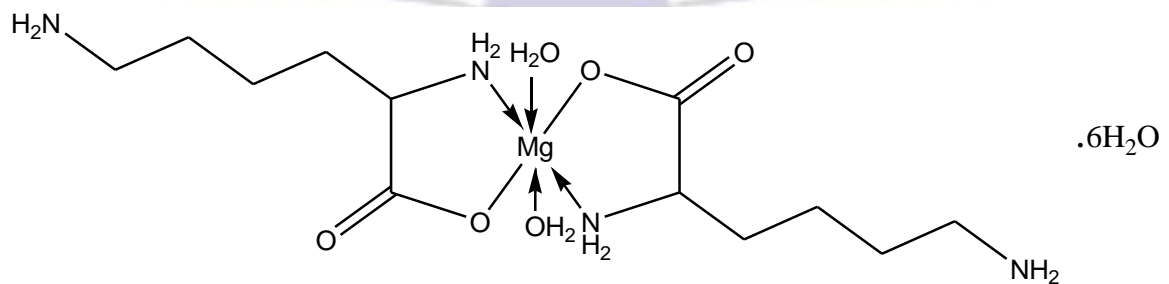
**Complex (8)****Complex (9)****Complex (10)****Complex (11)**



Table 1: Analytical and Physical Data of Metal Complexes.

No.	Complexes	Color	FW	M.P (°C)	Yield (%)	Analytical analysis found (Calc.)					Molar conductance $\Delta m (\Omega^{-1} \text{ cm}^2)$
						C	H	N	M	Cl	
(1)	[(L ₁ H)CuCl ₂].5H ₂ O C ₁₂ H ₃₆ N ₄ O ₉ Cu	Green	514.54	198	90	28.00 (27.98)	7.76 (6.99)	11.41 (10.88)	12.30 (12.34)	13.79	17.39
(2)	[(L ₁ H) Cu(SO ₄)].2H ₂ O C ₁₂ H ₂₈ N ₄ O ₈ CuS	Blue	451.54	220	85	33.20 (31.89)	4.14(6.20)	11.95 (12.40)	13.85 (14.07)	-	11.50
(3)	[(L ₁ H) Cu(OAc) ₄ (H ₂ O) ₄].H ₂ O C ₁₄ H ₃₆ N ₂ O ₁₅ Cu ₂	green	599.54	225	75	28.98 (28.02)	5.25 (6.00)	4.45 (4.67)	21.70 (21.19)	-	14.10
(4)	[(L ₁ H) Ni ₂ (OAc) ₂ (H ₂ O) ₄].2H ₂ O C ₁₆ H ₄₄ N ₄ O ₁₄ Ni ₂	Green	633	190	78	31.10 (30.33)	5.02 (6.95)	8.66 (8.84)	19.40 (18.54)	-	13.40
(5)	[(L ₁ HL ₂) Ni(OAc)(H ₂ O)].3H ₂ O C ₉ H ₂₈ N ₄ O ₉ Ni	Green	395	201	85	27.38 (27.34)	6.56 (7.08)	15.48(14.17)	14.32 (14.85)	-	11.32
(6)	[(L ₁ H) (Co) ₂ (OAc) ₂ (H ₂ O) ₄].H ₂ O C ₁₆ H ₄₂ N ₄ O ₁₃ Co ₂	violet	616	225	70	31.00 (31.16)	7.57 (6.81)	11.7 0 (9.09)	18.90 (19.13)	-	12.13
(7)	[(L ₁ HL ₄ H) Co(OAc) ₃ (H ₂ O) ₅].2H ₂ O C ₁₇ H ₄₀ N ₅ O ₁₆ Co ₂	Violet	688	220	85	30.42 (29.65)	7.63 (5.81)	12.15 (10.17)	17.00 (17.64)	-	19.10
(8)	[(L ₁ H)Cd ₂ (OAc) ₂ (H ₂ O) ₂].2H ₂ O C ₁₆ H ₃₆ N ₄ O ₁₂ Cd ₂	yellow	668	180	85	28.7 (28.74)	5.18 (5.38)	8.15 (8.38)	33.20 (33.65)	-	11.30
(9)	[(L ₁ H) Mn ₂ (OAc) ₂ (H ₂ O) ₄] C ₁₆ H ₄₆ N ₄ O ₁₅ Mn ₂	yellow	644	185	70	29.9 (29.81)	5.62 (7.14)	8.43 (8.69)	16.80 (17.05)	-	14.20
(10)	[(L ₁ H)Zn(OAc) ₂ (H ₂ O) ₂].H ₂ O C ₁₆ H ₄₂ N ₄ O ₁₃ Zn ₂	yellow	628	>300	80	32.05 (30.57)	4.45 (6.68)	8.71 (8.91)	21.60 (20.82)	-	12.30
(11)	[(L ₁ H) MgO(H ₂ O)].6H ₂ O C ₁₂ H ₄₂ N ₄ O ₁₆ Mg	Yellow	458	230	80	31.6 (31.44)	7.81 (9.17)	12.64 (12.22)	5.00 (5.30)	-	13.40
(12)	[(L ₂ L ₅ H) Ni(OAc) ₂].H ₂ O C ₁₁ H ₂₀ N ₅ O ₁₀ Ni	Green	424	190	75	31.87(31.13)	6.56 (4.71)	16.4 (16.50)	13.4 (13.84)	-	11.8
(13)	[L ₅ H) Co(OAc)(H ₂ O)].H ₂ O C ₁₂ H ₂₃ N ₂ O ₁₂ Co	Violet	446	260	80	33.9(32.28)	5.35(6.50)	7.09(6.27)	13.50(13.21)	-	10.2
(14)	[(L ₃ H) Co(OAc) ₂ (H ₂ O)].5H ₂ O C ₆ H ₁₆ N ₂ S ₂ O ₆ Co	violet	425	250	90	16.55 (16.94)	3.61 (3.76)	6.71 (6.58)	13.3 (13.86)	-	13.1
(15)	[(L ₃ H)Cu] C ₃ H ₆ NO ₂ SCu	green	184	190	90	20.4(19.56)	3.71(3.26)	7.2(7.60)	34.1(34.53)	-	10.2
(16)	[(L ₆ H) CuO _n (H ₂ O)].nH ₂ O	Green	-	-	-	-	-	-	-	-	11.1

L₁H= Lysine , L₂=Urea, L₃H= Cysteine, L₄H=Histidine and L₅H=Glutamic acid L₆H=amino acid hydrolyzed



3.1. General characterization

3.1.1 Mass spectra

The mass spectra of Ni(II) complex (**5**) shows peak (m/z) at 395 a.m.u consistent with the molecular weight of the complex (395 a.m.u). Furthermore, the fragments observed at $m/z = 59, 75, 85, 92, 117, 133, 138, 150, 163, 177, 198, 217, 233, 281, 304$ and 395 a.m.u are corresponding to $C_2H_3O_2$, $C_2H_5NO_2$, $C_3H_3NO_2$, $C_3H_{10}NO_2$, $C_4H_7NO_3$, $C_4H_9N_2O_3$, $C_4H_{14}N_2O_3$, $C_5H_{14}N_2O_3$, $C_6H_{15}N_2O_3$, $C_7H_{16}N_2O_3$, $C_7H_{21}NO_4$, $C_7H_{24}NO_5$, $C_7H_{24}NO_6$, $C_7H_{24}NO_8$, $C_7H_{24}NO_9$ and $C_9H_{28}N_4O_9Ni$ moieties respectively. The mass spectra of Ni(II) complex (**12**) shows peak (m/z) at 424 a.m.u consistent with the molecular weight of the complex (309 a.m.u). Furthermore, the fragments observed at $m/z = 59, 62, 76, 102, 115, 128, 142, 153, 169, 185, 187, 211, 242, 244, 263, 283, 312$ and 224 correspond to $C_2H_3O_2$, $C_2H_6O_2$, $C_2H_6NO_2$, $C_3H_6N_2O_2$, $C_4H_7N_2O_2$, $C_5H_4N_3O$, $C_6H_7N_3O_2$, $C_6H_7N_3O_3$, $C_6H_7N_3O_4$, $C_6H_9N_3O_4$, $C_8H_9N_3O_4$, $C_9H_{12}N_3O_5$, $C_9H_{14}N_3O_5$, $C_9H_{17}N_3O_6$, $C_8H_{17}N_4O_8$, $C_8H_{16}N_5O_9$ and $C_9H_{20}N_5O_9Ni$ moieties respectively. The mass spectra of Co(II) complex (**13**) shows peak (m/z) at 428 a.m.u consistent with the molecular weight of the complex (428 a.m.u). Furthermore, the fragments observed at $m/z = 56, 65, 87, 102, 129, 140, 148, 165, 195, 213, 244, 248, 310$ and 428 correspond to C_2O_2 , $C_2H_9O_2$, $C_3H_5NO_2$, $C_4H_6NO_2$, $C_4H_5N_2O_3$, $C_5H_4N_2O_3$, $C_4H_8N_2O_4$, $C_5H_3N_2O_4$, $C_6H_5N_2O_5$, $C_6H_7N_2O_5$, $C_6H_{10}N_2O_7$, $C_7H_{14}N_2O_8$, $C_7H_{16}N_2O_9$, and $C_{11}H_{21}N_2O_{11}Co$ moieties respectively.

3.1.2. IR spectra

The IR spectral data of the copper(II) complexes indicate that, the ligand behaved as a neutral bidentate (complexes **1, 2, 3**). The bands characteristic to $\nu(NH_2)$ appear at (3292-3244) and (2940-2850) cm^{-1} range and $\nu(C=O)$ observed at (1660-1630) and (1585-1570) cm^{-1} range [9,10]. This suggests that the complexes are ketonic in their nature. The spectra show bands in the (3454- 3423) cm^{-1} range due to $\nu(OH)$ [11,12]. Complexes show bands in the (1281-1258) cm^{-1} range this is corresponding to $\nu(C-O)$. Also complexes show bands in the (1560-1524) and (1395-1380) cm^{-1} ranges corresponding to $\nu(OAc)$ group, the strong broad bands in the (3530-3245) and (3240-2950) cm^{-1} ranges, confirm the presence of hydrated and coordinated water molecules [9,13], the intra and intermolecular hydrogen bondings in the copper(II) complexes (**1**), (**2**) and (**3**) appear in the (3650-2900) and (3300-2650) cm^{-1} range respectively [11,14,15]. the bonding of copper(II) ion to the ligand through the nitrogen and oxygen atoms in further supported by the presence of new bands in the 590-498 cm^{-1} and 648-573 cm^{-1} range, due to $\nu(Cu-N)$ and $\nu(Cu-O)$ respectively [12,14]. The bonding of the copper(II) ion to the chloride group in further supported by the presence of new bands in the 431 cm^{-1} and 618 cm^{-1} due to $\nu(Cu-Cl)$ and sulfate group in further supported by the presence of new bands in the 1125, 1075, 738 and 618 cm^{-1} respectively due to $\nu(Cu-SO_4)$ [14]. The IR spectral data are presented in (Table 2) indicate that, the ligand behaved either neutral bidentate (complex 13), or monobasic bidentate (complexes **6, 7, and 14**). $\nu(NH_2)$ appear in the ranges (3390-3061) (2990-2900) cm^{-1} and $\nu(C=O)$ observed at (1660-1620) and (1605-1585) cm^{-1} ranges [16]. This suggests that, the complexes are ketonic in their nature. Complex (13) show band at 3420 cm^{-1} due to $\nu(OH)$ group [17]. complexes (**6, 7, 13**) spectra show bands in the ranges (1545-1407) and (1414-1385) cm^{-1} corresponding $\nu(OAc)$, complexes (6, 7 and 14) show bands in the 1263-1183 cm^{-1} range, this is due to $\nu(C-O)$. Complex (13) shows band at the 1257 cm^{-1} corresponds to $\nu(C-OH)$, The strong broad bands in the (3530-3200) and (3100-2500) cm^{-1} range are due to hydrated and coordinated water molecules, the intra-and intermolecular hydrogen bondings in the metal complexes appear in the (3650-3260) and (3150-2580) cm^{-1} ranges respectively. The presence of new bands in the 505-426 and 578-550 cm^{-1} range are corresponding to $\nu(M-N)$ and $\nu(M-O)$ respectively [14,18]. Complex (**14**) shows band at 2371-2344 cm^{-1} due to $\nu(SH)$. The IR data (Table 2) indicate that, the ligand behaved either neutral bidentate (**12**), or monobasic bidentate. Complexes (**4**) and (**5**) show bands in the (3279-3250) and (3000-2935) cm^{-1} range assigned to $\nu(NH_2)$ whereas the $\nu(C=O)$ bands appear in the ranges (1662-1620) and (1620-1585) cm^{-1} . These findings confirmed that, the ligand coordinated to the metal ion in ketonic form. Complexes show band in the (1560-1507) and (1410-1407) cm^{-1} ranges corresponded to $\nu(OAc)$, the bands appearing in the (1235-1157) cm^{-1} range, corresponds to $\nu(C-O)$, The strong broad bands appeared in the (3550-3500) and (3250-2850) cm^{-1} range confirmed the presence of hydrated and coordinated water molecules, the intra-and intermolecular hydrogen bondings in the metal complexes appear in the (3650-3600) and (3300-2750) cm^{-1} range respectively. The presence of new bands in the 480-420 and 552-537 cm^{-1} range are corresponding to $\nu(M-N)$ and $\nu(M-O)$ respectively, The IR data (Table 2) indicate that, the ligand behaved as monobasic bidentate (complexes 8, 9, 10 and 11). The observed bands in the (3443-2941) and (2940-2285) cm^{-1} range are due to $\nu(NH_2)$ and while the bands appearing in the ranges in the (1614-1610) and (1584-1581) cm^{-1} are to due to $\nu(C=O)$ appears range, confirming that, the ligand coordinated to the metal ion in ketonic form. Complexes show bands in the (1509-1508) and (1409-1348) cm^{-1} ranges corresponding to $\nu(OAc)$. Complexes show bands in the 1223-1182 cm^{-1} and 1258 cm^{-1} range, this is due to $\nu(C-O)$. The strong broad bands observed in the (3550-3000) and (3350-2500) cm^{-1} ranges confirmed the presence of hydrated and coordinated water molecules, the intra-and intermolecular hydrogen bondings in the metal complexes appear in the (3650-3400) and (3390-2500) cm^{-1} range respectively. The presence of new bands in the 480-431 and 553-548 cm^{-1} range are corresponding to $\nu(M-N)$ and $\nu(M-O)$ respectively. The IR data (Table 2) indicate that, observed bands in the (3240-2965) cm^{-1} range assigned $\nu(NH_2)$ while the band appearing in the range (1622-1600 cm^{-1}) range is due to $\nu(C=O)$. These findings confirmed that, the ligand coordinated to the metal ion in ketonic form. Complexes show band at 3446 cm^{-1} due to $\nu(OH)$, while the bands appearing in the 1117-1046 cm^{-1} range is corresponding to $\nu(C-O)$. The strong broad bands in the (3500-3200) and (3300-3000) cm^{-1} ranges confirm the presence of hydrated and coordinated water molecules. The intra-and intermolecular hydrogen bondings in the metal complexes appear in the (3650-3350) and (3250-2950) cm^{-1} ranges respectively. The presence of new bands in the 431 and 566 cm^{-1} ranges corresponding to $\nu(M-N)$ and $\nu(M-O)$ respectively.



Table 2: IR Frequencies Metal Complexes and their Assignments.

No.	$\nu(\text{H}_2\text{O}/\text{OH})$	$\nu(\text{Hbonding})$	$\nu(\text{NH}_2)$	$\nu(\text{C}=\text{O})$	$\nu(\text{C-O})/$ (C-OH)	$\nu[(\text{OAc})/\text{SO}_4/$ $\text{Cl}/\text{SH}]$	$\nu(\text{M-O})$	$\nu(\text{M-N})$
(1)	3423, 3530-3250	3650-3264, 3250-2700	3292-2850	1660-1580	1258	431	573	498
(2)	3454 3530-3250 3240-3000	3650-2900 3100-3000	3244-3290	1630-1585	1281	1125, 1075 738, 618	574	500
(3)	3445 3500-3200 3245-2950	3650-3310 3300-2650	3260-2940	1660-1570	1280	1560,1395 1524,1380	648	590
(4)	3500-3250 3200-2850	3650-3300 3200-2750	3279-2935	1620-1589	1235	1507,1407	552	431
(5)	3550-3190 3170-2950	3600-3150, 3130-2750	3250-3000	1662-1623	1157	1560,1410	541	480
(6)	3500- 3200 2700-2500	3550-3300 2750-2600	3377-2936	1620,1585	1263	1509,1405	550	476
(7)	3530-3360 3100-2800	3600-3350 3050-2900	3300-2940	1640 -1585	1183	1545,1405 1407,1385	552	505
(8)	3550-2500	3600-2500	443-2939	1610-1581	1182	1508,1348	550	431
(9)	3500-3350 3000-2900	3650-3700	3410-2940	1610-1582	1221-1184	1509,1409	548	477
(10)	3500-3350	3600-2500	2939	1610-1584	1223-1182	1509,1404	553	480
(11)	3414 3500-3380 3350-3100	3650-3390 3400-3150	2941-2285	1614-1584	1223	-	549	475
(12)	3438	3500-3200	3009-2900	1660-1639	1258	1512-1407	537	420
(13)	3500	3550-2990	3061-2900	1640 -1590	1257	1511-1414	578	464
(14)	3520-3225 3100-3050	3650-3260 3150-2580	3390-2990	1660-1605	1218	2371-2344	560	426
(15)	3446	3650-3000 2980-2450	1590	1730	-	-	-	475
(16)	3446 3550-3300 3200-3000	3650-3250 3350-2950	3240-2965	1622-1600	1117-1046	-	566	431

3.1.3. Electronic spectra

The electronic spectral data of copper(II) complexes (**1**, **2** and **3**) are shown in Table 3. The complexes showed bands in the 272-270, 370-368, 509-408, 577-457 and 620-610 nm ranges. The first two bands are assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions within the ligand and the other bands are due to ${}^2B_{1g} \rightarrow {}^2A_{1g} \rightarrow {}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2B_{2g}$ transitions respectively, indicating that, the copper(II) complexes have distorted octahedral geometry [19]. The electronic spectral data for nickel(II) complexes (**4**, **5** and **12**) and cobalt(II) complexes (**6**, **7**, **13** and **14**) are shown in Table 3. Nickel(II) and cobalt(II) complexes showed bands in the 271-265, 374-368 and 445-421 nm ranges, these bands are due to intraligand transitions within the ligand. Nickel(II) complexes (**4**, **5** and **12**) show bands in the 634-630, 578-529 and 454-445 nm



ranges, corresponding to ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F) \nu_1$, ${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(\nu_2)$ and ${}^3A_{2g}(F) \rightarrow {}^3T_{1g}(P) \nu_3$ transitions, indicating octahedral nickel(II) complexes [9,20]. The ν_2/ν_1 ratio is 1.2, 1.15 and 1.20 which are less than the usual range of 1.5-1.75, indicating distorted octahedral Nickel(II) complex [9,19]. Cobalt(II) complexes (6, 7, 13 and 14) show bands in the 632-581 and 578-532 nm ranges, which are assigned to ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F) \nu_1$, ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}(F) \nu_2$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(P) \nu_3$ transitions respectively. The lower value of ν_2/ν_1 (1.42) in complex (11), 1.14 for complex (12), 1.11 for complex (13) and 1.18 for complex (14), may be due to distortion of the octahedral structures [9,21]. The electronic spectral data for complexes (8, 9, 10 and 11) complexes are presented in Table 3. The complexes displays bands in the 275-263 and 374-369 nm ranges, corresponding to intraligand transitions within the ligand [13,22]. Complex (9) show sbands at 481, 560 and 631 nm, these bands are corresponding to ${}^6A_{1g} \rightarrow {}^4E_g$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and ${}^6A_{1g} \rightarrow {}^4T_{1g}$ transitions which are compatible to an octahedral structure for manganese(II) complex [23,24]. The bands displayed by Zinc(II) complex (10) and cadmium(II) complex (8) and magnesium(II) complex (11) are due to interligand transitions within the ligand Table 3.

Table 3: Electronic Spectra (nm) and Magnetic Moments (B.M) for the Complexes.

Comp. No.	λ_{\max} (nm)	μ_{eff} (BM)
(1)	271, 368, 413, 509, 576, 610	1.71
(2)	272, 368, 465, 570, 615	1.73
(3)	270, 370, 408, 457, 574, 620	1.62
(4)	271, 368, 421, 454, 570, 634	2.66
(5)	266, 374, 445, 529, 632	2.96
(6)	275, 369, 577, 629	2.32
(7)	274, 532, 581, 622	3.203
(8)	266, 374, 403	Diamagnetic
(9)	263, 369, 481, 560, 631	4.43
(10)	275, 370, 400	Diamagnetic
(11)	267, 370, 405	Diamagnetic
(12)	270, 368, 578, 630	3.12
(13)	265, 275, 368, 578, 615	4.9
(14)	274, 371, 573, 620	4.72

3.1.4. Magnetic moments

The magnetic moments for nickel(II) complexes (4, 5 and 12) and cobalt(II) complexes (6, 7, 13 and 14) are shown in (Table 3). Nickel(II) complexes (4, 5 and 12) recorded 2.66, 2.96 and 3.12 B.M respectively, indicating octahedral structure around nickel(II) ion [9,25,26]. Cobalt(II) complexes (7 and 13) show recorded 3.2 and 4.9 B.M indicating high-spin octahedral geometry around cobalt (II) ion [27]. Copper(II) complexes (1, 2 and 3) show values 1.71, 1.73, and 1.62 B.M respectively indicating octahedral structure around the metal ion [22], whereas manganese(II) complexes (9), shows value 4.43 B.M indicating High spin octahedral structure around Mn(II) ion [9,21]. Zinc(II) complex (10), cadmium(II) complexes (8) and magnesium(II) complex (11) are found to be diamagnetic.

3.1.5. Electron Spin Resonance

The ESR spectral data, (Table 4) at room temperature for solid copper(II) complexes (1), (2), (3), (6), (9), (12), (13) and (14) showed axial and isotropic types which are characteristic of a monomer or dimer structure. configuration with



a $d(x^2-y^2)$ ground state, which is the most common with copper(II) complexes (1) and (2) showed spectra characteristic of a monomer for copper(II) complexes (3) [12], shows broad signal in the low field region, indicating spin-exchange interactions take place between the copper(II) ions [9,12,24,26]. Complexes (1) and (2) showed $g_{\parallel} > g_{\perp} > 2.04$, indicating a tetragonal distortion [9,27,28], corresponding to elongation along the fold symmetry axis Z. The g-values are related by the expression $G = (g_{\parallel}-2) / (g_{\perp}-2)$ [22]. If $G > 4.0$, then, the local tetragonal axes are aligned parallel or only slightly misaligned, if $G < 4.0$, the significant exchange coupling is present. The complexes (1), and (2) showed G value > 4.0 , indicating tetragonal axes are present. Also, these complexes showed $g_{\parallel} \geq 2.3$, suggesting considerable covalent bond character around the copper (II) ion [29]. Also, the in-plane σ -covalence parameter, $\alpha^2(\text{Cu})$ was calculated by:

$$\alpha^2(\text{Cu}) = (A_{\parallel}/0.036) + (g_{\parallel}-2.002) + 3/7(g_{\perp} - 2.002) + 0.04 \dots \dots \dots (1)$$

The calculated values for (1) and (2) are 0.69 and 0.77, (Table 4), suggesting covalent bond character [9,28,30]. The $g_{\parallel}/A_{\parallel}$ is taken as an indication for the stereochemistry of the copper(II) complexes. Addison has suggested that, this ratio may be an empirical indication of the stereochemistry of copper(II) complex [31]. The value $g_{\parallel}/A_{\parallel}$ quotient in the (105-135) cm^{-1} range is expected for copper(II) complexes within perfectly square based geometry and those higher than this value for tetragonally distorted complexes. The values for copper(II) complexes (1) and (2) are associated with a tetragonally distorted field around copper(II) centers [26,29]. For copper(II) complexes with 2B_1 ground state, the g-values can be related to the parallel (K_{\parallel}) and perpendicular (K_{\perp}) components of the orbital reduction factor (K_{\perp}) as follows [30]:-

$$K_{\parallel}^2 = (g_{\parallel} - 2.0023)\Delta E_{xz} / 8\lambda_o \dots \dots \dots (2)$$

$$K_{\perp}^2 = (g_{\perp} - 2.0023)\Delta E_{xy} / 2\lambda_o \dots \dots \dots (3)$$

$$K^2 = (k_{\parallel}^2 + 2k_{\perp}^2) / 3 \dots \dots \dots (4)$$

Where λ_o is the spine orbit coupling of free copper ion (-828 cm^{-1}) and ΔE_{xy} and ΔE_{xz} are the electronic transition energies of ${}^2B_1 \rightarrow {}^2B_2$ and ${}^2B_1 \rightarrow {}^2E$ respectively. For the purpose of calculation, it was assumed that, the maximum in the band corresponds to ΔE_{xy} and ΔE_{xz} can be taken from the wavelength of these bands. From the above relations, the orbital reduction factors (K_{\parallel} , K_{\perp} and K) which are a measure of covalence can be calculated. For an ionic environment, $K = 1$ and for a covalent environment $K < 1$; the lower the value of K, the greater is the covalent character. The values of K for (1) and (2) (Table 4) showed considerable covalent bond character. The in- plane and out-of-plane π -bonding coefficients (β_1^2 and β^2) respectively are dependent upon to values of ΔE_{xy} and ΔE_{xz} in the following equations [31]:-

$$\alpha^2\beta^2 = (g_{\perp} - 2.002)\Delta E_{xy} / 2\lambda_o \dots \dots \dots (5)$$

$$\alpha^2\beta_1^2 = (g_{\parallel} - 2.002)\Delta E_{xz} / 8\lambda_o \dots \dots \dots (6)$$

In this work, the complexes (1) and (2) showed β_1^2 values 1.2 and 1.05, indicating a moderate degree of ionic character in the in-plane π -bonding, while β^2 are 0.88 and 1.44, indicating covalent and ionic character in the out-of-plane π -bonding [32,33]. The ESR spectra of cobalt(II) complexes (6), (13) and (14) show isotropic type with $g_{\text{iso}} = 2.07$, 2.06 and 2.08, respectively indicating octahedral geometry around cobalt(II) ion [34]. The ESR spectrum for manganese(II) complex (19) shows an isotropic type with $g_{\text{iso}} = 2.05$, indicating tetrahedral geometry around manganese(II) ion [34]. However, The Ni(II) complex (12) shows $g_{\parallel} = 2.2$ and $g_{\perp} = 2.05$ with $g_{\text{iso}} = 2.1$, also The spectrum shows $g_{\parallel} > g_{\perp} > 2.03$, indicating octahedral structure.



Table 4: ESR data for the metal (II) complexes

No.	g_{\parallel}	g_{\perp}	g_{iso}	A_{\parallel} (G)	A_{\perp} (G)	A_{iso} A_b (G)	G^c	$ E_{xy} $ (cm^{-1})	E_{xz} (cm^{-1})	K_{\perp}^2	K_{\parallel}^2	K	$g_{\parallel}/A_{\parallel}$ (cm^{-1})	\square^{\square}	\square^{\square}	\square^{\square}
(1)	2.3 3	2.0 8	2.1 6	120 G	30 G	60G	4. 7	1626 0	2352 9	1.1 1	0.8	1.0	179. 2	0.7 7	1.4 4	1.0 5
(2)	2.2 6	2.0 6	2.1 3	160	20	66.7	4. 3	1754 3	2150 5	0.6 1	0.8 4	0.8 3	141. 3	0.6 9	0.8 8	1.2
(6)	-	-	2.0 7	-	-	-	-	-	-	-	-	-	-	-	-	-
(9)	-	-	2.0 5	-	-	-	-	-	-	-	-	-	-	-	-	-
(12)	2.2)	2.0 5	2.1	-	-	-	-	-	-	-	-	-	-	-	-	-
(13)	-)	-	2.0 6	-	-	-	-	-	-	-	-	-	-	-	-	-
(14)	-)	-	2.0 8	-	-	-	-	-	-	-	-	-	-	-	-	-

- a) $3g_{\text{iso}} = (g_{\parallel} + 2g_{\perp})$
 b) $3A_{\text{iso}} = (A_{\parallel} + 2A_{\perp})$
 c) $G = (g_{\parallel} - 2)/(g_{\perp} - 2)$

3.1.6. Thermal Analyses (DTA and TGA)

Since The IR spectra indicate the presence of water molecules, thermal analyses, were carried out to ascertain their nature. The DTA and TGA curves in the temperature 25-600 °C range for complexes (1) (3) and (13) show that, these complexes are thermally stable up to 60 °C. The results show also that, the complexes lose hydrated water molecules in the 60-90 °C range; this process is accompanied by an endothermic peak. The coordinated water molecules were eliminated at relativity higher temperature than those of the hydrated water molecules 120-180 °C, (Table 5), which are accompanied by an endothermic peak. These results are compatible with TGA data [9,24,33]. The removal of an CH_3COOH molecule accompanied by endothermic peaks for complexes (3) and (13) respectively in the (265-310)°C and (120-198)°C ranges. Loss of an HCL molecule accompanied by an exothermic peak was observed for complex (1) at the temperature range 259-310°C, DTA results are compatible with the TGA data. The complexes show an endothermic peak within 198-260 °C range with no weight loss (TGA), due to melting points of the complexes. The complexes show exothermic peaks within 259-550 °C range, (Table 5), corresponding to oxidative thermal decomposition, which proceeds slowly with a final residue, leaving metal oxides [24]. The observations were confirmed by TGA weight losses. The thermal decomposition of complex (2) can be represented as follow:


Table 5: Thermal analyses for metal(II) complexes.

Comp. No.	Temp. (°C)	DTA (peak)		TGA (Wt.loss %)		Assignments
		Endo	Exo	Calc.	Found	
(1)	60	Endo	-	3.49	3.1	Loss of hydrated 1H ₂ O
	85	Endo	-	3.6	3.53	Loss of hydrated 1H ₂ O
	100	Endo	-	3.7	3.62	Loss of hydrated 1H ₂ O
	160	Endo	-	7.82	7.9	Loss of hydrated 2H ₂ O
	198	Endo	-	-	-	Melting point
	259	-	exo	8.36	8.84	Loss of coordinated Cl
	310	-	exo	9.1	9.2	Loss of coordinated Cl
	380	-	exo	-	-	
	450	-	exo	-	-	
	520	-	exo	17.96	17.7	Decomposition process with the formation of CuO
(3)	80	Endo	-	3	2.67	Loss of hydrated 1H ₂ O
	120	Endo	-	6.38	6.8	Loss of coordinated 2H ₂ O
	180	Endo	-	6.7	6.2	Loss of coordinated 2H ₂ O
	250	Endo	-	-	-	Melting point
	265	Endo	-	24.66	24.6	Loss of coordinated 2OAC
	310	Endo	-	30.1	29.46	Loss of coordinated 2OAC
	365	-	exo	-	-	
	390	-	exo	-	-	
	475	-	exo	-	-	
	520	-	exo	29.1	28.57	Decomposition process with the formation of CuO
(13)	65	Endo	-	4.03	3.57	Loss of hydrated 1H ₂ O
	120	Endo	-	4.2	4.01	Loss of coordinated 1H ₂ O
	198	Endo	-	14.39	14.28	Loss of coordinated 1OAC
	260	Endo	-	-	-	Melting point
	390	-	exo	-	-	
	415	-	exo	-	-	
	435	-	exo	-	-	
	550	-	exo	16.8	16.5	Decomposition process with the formation of CoO

3.2. Biological activity

The synthesized metal chelates were evaluated as plant growth promoter. Results indicated that the growth criteria like plant height and number of branches per plant were improved by increasing dose of the organically chelated amino acid metal nutrient to a concentration of 2.5%. At this concentration the plants recorded the maximum height (110 cm), while plant recorded lower height (97.7 cm) when the micronutrient chelate was foliarly applied the plant at 2.0 % concentration. Treating plants with micronutrient solution 3% produced plants with 86.4 cm while amino acid solution 3% produced plants with 89.2 cm height. The least plant height (78.3) cm was recorded upon treating the plant with the control. The number of branches per plant was maximum (9.1) using 2.5% amino acid chelate as a foliar spray. It was followed by 2% foliar spray of amino acid chelate with 8.1 branches per plant. Whereas foliar spray of unchelated metal nutrient solution at 3% produced 5.4 branches per plant and the amino acid solution at concentration 3% showed 6.2 branches per plant. The least number of branches per plant (2.9) was recorded using the control. (Table 6). Growth characters like stem diameter of plants and leave area of plants were increased significantly with application of increased



dose of amino acid chelated metal nutrients. Among the different treatments of chelated metal nutrients treatments, spraying plants with 2.5% of the organically chelated amino acid metal nutrient showed better results than the other treatments through improved characters of number of flowers per plant. The maximum number of flowers per plant 4.3 and 4.4 flower/plant was recorded at 3% and 2.5 % treatment respectively while the control recorded 2.2 (flower/plant). The yield per plant was maximum (112 gm) with the spray of 2.5 % of chelated amino acid metal nutrients.

Table 6: Effect of foliar application of untreated control T₀, 3 % micronutrient solution T₁, 3% amino acid solution T₂, 2% amino acid micronutrient T₃, 2.5% amino acid micronutrient T₄ and 3 % amino acid micronutrient T₅.

Treatment	Average of					
	Plant height (cm)	Stem diameter (mm)	Second Leave area (mm)	Yield per plant (gm)	Branches Number	Number of flowers
T ₀	78.3	5	112.7	33	2.9	2.2
T ₁	86.4	6.2	135.2	53	5.4	3
T ₂	89.2	6.5	147.6	75	6.2	3.6
T ₃	97.7	7.4	167.4	90	8.1	3.9
T ₄	110	8.7	171.2	112	9.1	4.4
T ₅	108.5	9	171.6	110	9	4.3

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