Bull. Chem. Soc. Ethiop. **2025**, 39(8), 1549-1558.
DOI: https://dx.doi.org/10.4314/bcse.v39i8.8

ISSN 1011-3924
Printed in Ethiopia
Online ISSN 1726-801X

MIXED LIGANDS OF (E)-1-(3-(((1H-1,2,4-TRIAZOL-3-YL)IMINO)METHYL)-4-HYDROXY-5-METHOXYPHENYL)ETHAN-1-ONE AND CHLOROANILIC ACID: SYNTHESIS, CHARACTERIZATION AND THERMAL STABILITY STUDY

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(Received March 13, 2025; Revised March 28, 2025; Accepted March 31, 2025)

ABSTRACT. The present work involved the synthesis, characterization and thermal study of metal complexes of Co(II), Cu(II), Ni(II) and Zn(II) derived from mixed ligands;HL^1: (E)-1-(3-(((1H-1,2,4-triazol-3-yl)imino)methyl)-4-hydroxy-5-methoxyphenyl)ethan-1-one and H_2L^2: 2,3-dichloro-5,6-dihydroxycyclohexa-2,5-diene-1,4-dione. The new ligands and their metal complexes were fully identified on the basis of FT-IR, EI-MS, NMR, UV-Visible spectroscopy, molar conductivity and magnetic susceptibility measurements. The new metal complexes were prepared in their solutions in ethanol and in solid state with respect 1:1:1 mole ratio of $M:L^1:HL^2$. As well as the elemental microanalysis was carried out to confirm the skeletal structure of the metal complexes. The physicochemical properties such as melting point, magnetic susceptibility and molar conductivity at room temperature were determined. The spectral data of IR, UV-Visible spectra and magnetic moments revealed the formation of octahedral environment around Co(II), Ni(II), Cu(II) and Zn(II) ions. As well as the TG-DTA measurements confirmed the thermal stability due to the cleavage of weak points in the skeletal structures of metal complexes.

KEY WORDS: (E)-1-(3-(((1H-1,2,4-triazol-3-yl)imino)methyl)-4-hydroxy-5-methoxyphenyl)ethan-1-one, Thermal stability of apocynin, Thermal stability of mixed ligands

INTRODUCTION

The mixed ligands of isoniazid and its derivatives have attracted great attention in the last decade due to their unique properties [1] and their metal complexes are extensively studied with wide applications of LED industry, trace analyses of toxic metals [2-4]. A number of functionalized compounds conducted with 2,3-dichloro-5,6-dihydroxycyclohexa-2,5-diene-1,4-dione are readily accessible, so they are promising rich and versatile coordination chemistry and they have heterocyclic π-conjugated systems with good co-ordination abilities to metal centers and own the capability to exhibit luminescence [6-10]. The mixed ligands of chloroanilic acid and 1,2,4-triazole Schiff bases have investigated with the field of coordination chemistry and their applications in the green-analytical chemistry [11, 12], biological activity [13] and nano chemistry applications [14, 15]. However, the update literatures that focused on the preparation and characterization and TG-DSC stability has been creating us to start the development new route for the synthesis, spectroscopic and TG-DTA studying.

EXPERIMENTAL

Material and methods

The starting materials and solvents were purchased from Merck company used as received without further purification like apocynin, 3-amino-1*H*-1,2,4-triazole and chloroanilic acid. Melting points were recorded by a Stuart melting point (digital) SMP30 apparatus. FT- IR spectrum was

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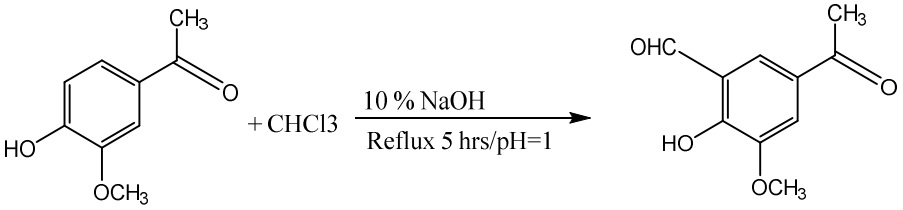
recorded by a Shimadzu (FT-IR) model 4800 s spectrophotometer in the range (4000-400) cm^{-1}. The electronic spectra of the ligands and their complexes were recorded by Shimadzu UV-Vis 160 ultraviolet spectrophotometer at 25 ℃ using 1cm quartz cell and examined at the range at (200-1100) nm at (10^{-3}) M in chloroform and DMSO solvents. The content of nickel, palladium and platinum in their complexes were estimated by flame atomic absorption (FAAS) technique has been measured using a Shimadzu AA680G atomic absorption spectrophotometer at the laboratories of Ibn-Sinaa Company. Elemental analysis for the primary ligand, L^1 and secondary one, HL^2 and their complexes were determined by (C, H, N) calibration Linear Regression Euro EA elemental analysis. The suggested molecular weight of the two ligands and their complexes were measured by electron ionization mass spectroscopy on GC-MS (DIRECT PROBE) via ES technique. ^1H, ^{13}C-NMR spectrum of primary ligand, L^1 and metal complexes were recorded on Bruker DMX- 500 spectrophotometer (400 MH_Z), by using DMSO-d_6. The molar conductance of complexes solutions in DMSO solvent was determined at 298 ℃ using an Inolab Muli 740, WTW 82362-Germany. Magnetic susceptibility of prepared complexes was determined at 310 ℃ by Auto magnetic susceptibility Balance in Mustansiriyah University, College of Science, Chemistry Department.

Synthesis of 5-acetyl-2-hydroxy-3-methoxybenzaldehyde, S

This derivative was prepared according to the modified procedure established in literature [18]. To apocynin (2.5 g, 16 mmol) and (3 mL) of triethylamine in 50 mL) absolute ethanol, was added a solution of 10% NaOH rapidly. The mixture was heated under reflux for 3 hours, then (25 g, 150 mmol) of chloroform was added with stirring. After cooling the mixture reaction to room temperature, 5 mL of HCl was added to get the target derivative with 78% yield, as a yellow powder, mp: 160-162 ºC. ^1H NMR ($CDCl_3$, 400 MHz): 11.47 (s, 1H, OH), 10.00 (s, 1H, CHO), 7.83 (d, 1H, J¼ 1.6 Hz, ArH), 7.74e7.73 (d, 1H, J¼ 1.6 Hz, ArH), 3.98 (s, 3H, OCH_3), 2.62 (s, 3H, CH_3CO). MS (ESI) m/z 193[M+ H], 195 [M + 2H]. Analysis calculated for $C_{10}H_{10}O_4$, Scheme 1.

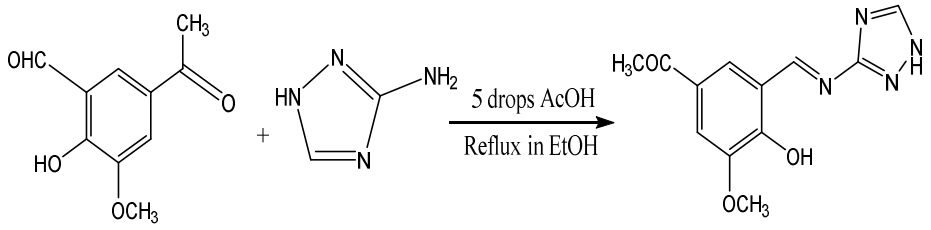


Scheme 1. Preparation of S derivative.

Synthesis of (E)-1-(3-(((1H-1,2,4-triazol-3-yl)imino)methyl)-4-hydroxy-5-methoxyphenyl)ethan-1-one, HL^1:

To the solution of 3-amino-4H-1,2,4-triazole (1.68 g., 20 mmol) in 22 mL of ethanol, 5-acetyl-2-hydroxy-3-methoxybenzaldehyde S, (3.851 g 20 mmol) in 35 mL ethanol was added. The mixture was refluxed for 3 hours after acidification the medium of reaction with 2-3 drops of hydrochloric acid 36.5% HCl, then and it was allowed to cool down at room temperature for three hours and a yellow crude was separated out, filtered, washed with ethanol and diethyl ether, dried and re-crystallized from hot ethanol to give compound HL^1; Scheme 2; m.p. 155-158 °C; color yellow crystal; yield 75%; FT-IR υ (cm^{-1}): 3640 (phenolic -OH), 3100 (NH_2, sym.) , 1650 (C=O, amide),

1280 (C-O phenolic); R_f ($CHCl_3$: methanol; 1:2), ^{1}H NMR (400 MHz DMSO-d_6), 12.70 (s, 1H, OH), 9.70 (s, 1H, CH=N-), 7.78 (d, 2H, CH=CH-triazole), 7.55 (d, 1H, CH=CH-Ar), 4.22 (s, 3H, -OCH_3).



Scheme 2. Synthesis of primary ligand, HL^1

Metals complexes synthesis

To a solution of the metal salts in ethanol, where the salts of ($CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.2H_2O$ or $ZnCl_2$) was added to the primary ligand (2.18 g, 10 mmol) and after stirring the solution on water bath for 30 min, a remarkable change in color turned from green in case of CuL complex to dark green, the solution of secondary ligand, (2.07 g, 10 mmol) H_2L^2 was added in 22 mL methanol then refluxed the mixture for 1-3 hours. After keeping the mixture for several hours at room temperature, a colored precipitated was form, green complex of **C1**, olive complex of **C2** and dark yellow complexes of **C3** and **C4**. The color melting point, yield, metal analysis and solubility of the ligand and its complexes are given in Table 1.

Table 1. Physical properties and elemental analyses of the prepared compounds.

Symbol compd.	Color	M.P.	M.wt.	Elemental analysis % Found (cal.)			Metal M% Found (cal.)	Suggest formula
				C%	H%	N%		
HL^1	Yellow	155-158	263.1	55.38 (55.04)	4.66 (4.62)	21.53 (20.68)	-	$C_{12}H_{12}N_4O_3$
H_2L^2	Orange	> 300	208.09	36.11 (40.0)	3.00 (3.33)	12.26 (14.0)	-	$C_6H_2Cl_2O_4$
C1	Green	280-282	398.2	29.11 (30.22)	2.07 (1.99)	7.64 (8.50)	19.22 (18.95)	$C_{18}H_{16}Cl_2N_4CoO_8$
C2	Olive	290 d	445.97	45.1 (32.4)	3.10 (2.97)	10.72 (18.93)	25.77 (24.39)	$C_{18}H_{16}Cl_2N_4NiO_8$
C3	Dark yellow	315 d	641.99	27.76 (26.66)	2.19 (2.44)	15,30 (15.55)	34.02 (33.17)	$C_{18}H_{16}Cl_2N_4CuO_8$
C4	Pale yellow	277 d		55.88 (54.20)	4.22 (4.88)	17.88 (16.99)	22.22 (21.88)	$C_{18}H_{12}N_4ZnO_6$

RESULTS AND DISCUSSION

Spectroscopic characterization

The NMR spectrum of HL^1 in DMSO exhibited weak signal at 12.5 ppm assigned to de shielded –NH proton attached to amide group. As well as the multiple absorption at (6.88-7.9) and (7.92-

8.11) ppm are attributed to s pin-spin coupling of aromatic ring and furan rings, respectively [11]. Furthermore, the singlet peak at 8.97 ppm is strong evidence for the nuclear spin of immine –CH=N- formed up on condensation of H-C=O moiety of apocynin precursor and amino group of 3-amino-4H-1,2,4-triazole. As well as the data of ^{13}C NMR spectrum of HL^1 was presented in table (2). The resonance of carbon atoms of triazole –C=N- and immine –CH=N- were resonated at 170.55 and 155.80 ppm, respectively, which are good support for condensation reaction of HL^1. Furthermore, the ^{1}H NMR is main spectroscopic method to show the comparison of chemical shifts between the mono or bi basic chelating ligands with metal chelates, here the shift in the –CH=N- to lowering absorption at 8.18 ppm is assigned to binding of nitrogen atom to the empty orbitals of zinc(II) ion. As well as the disappearance of hydrogen atoms in the enol form of HL^1 ligand in the NMR spectrum of Zn(II) complex revealed the participation of phenolic -OH moiety via de protonation and –C=N- of triazole ring. As well as, the singlet peaks at 9.16 and 8.90 ppm in the spectrum of complex is good evidence for the secondary ligand involving aromatic protons of 1,4-benzoquinine ring [12,15].

Table 2. NMR data of HL^1 and its **C4** complex.

Compound	Chemical shift values in ^{1}H NMR and ^{13}C NMR (ppm) with assignment
HL^1	^{1}H NMR (400 MHz, DMSO-d_6) δ: 12.50 (s, phenolic -OH), δ: 6.95-7.50 (triazole-CH=CH), 7.92-8.11 (m, 3H, furan-H), 8.88 (s, 1H, -CH=N-NH), 2.50 -3.321 (s, DMSO solvent). ^{13}C NMR (500 MHz, DMSO-d_6) δ: 39.32-40.57 (C-DMSO-solvent), 120.40, 129.26 (Py-CH=CH-),127.10 (furan-r-CH=CH-), 129.87, 139.85, 133.69 (C-O phenolic), 136.91,165.25 (-C-N- traizole), 195.50 (HN-C=N).
C4	^{1}H NMR (400 MHz, DMSO-d_6) δ: 11.70 (s, OH-benzoquinone), δ: 6.66-7.43 (pyridine-CH=CH), 7.90-8.09 (m, 3H, furan-H), 8.50 (s, 1H, -CH=N-NH), 2.50 -3.321 (s, DMSO solvent). ^{13}C NMR (500 MHz, DMSO-d_6) δ: 31.81 (CH_3-NH), 39.32-40.57 (C-DMSO), 124.48 (HC=CH-furan), 125.11-125.04 (2C.C=C=Ar), 127.01 (-C=C-benzoquinone), 125.90 (CH=CH-benzoquinone), 130.66 (C=C-furane), 132.21 (C-O phenolic), 145.79 (C=N-immine), 154.12 (-C=N-trazole), 190.42 (1-C=O, quinone), 210 (3-C=O, quinone

Mass spectral analysis

The exact molecular weights of the free primary ligand of isoniazid and its metal complexes formed beside the secondary ligand of benzoquinone, H_2L^2 were depicted through the measurement of electron-spray ionization mass spectroscopy. The MS spectrum of HL^1 exhibited high intensity peak at m/z = 263 assigned to its expected chemical formula; $C_{12}H_{12}N_4O_3$. As well as the other variable peaks at 252 and 235 may be attributed to the effect of isotopes and gas phase ionization of methyl and hydroxyl groups respectively. However, the MS spectra of **C1**, **C2** and **C3** complexes showed their molecular ions in the mass spectra at 398, 447 and 630 respectively [18, 19]. These base peaks are good evidence for the isotopes of chlorine-37 and Cl-35 isotopes, (Figures 1 and 2).

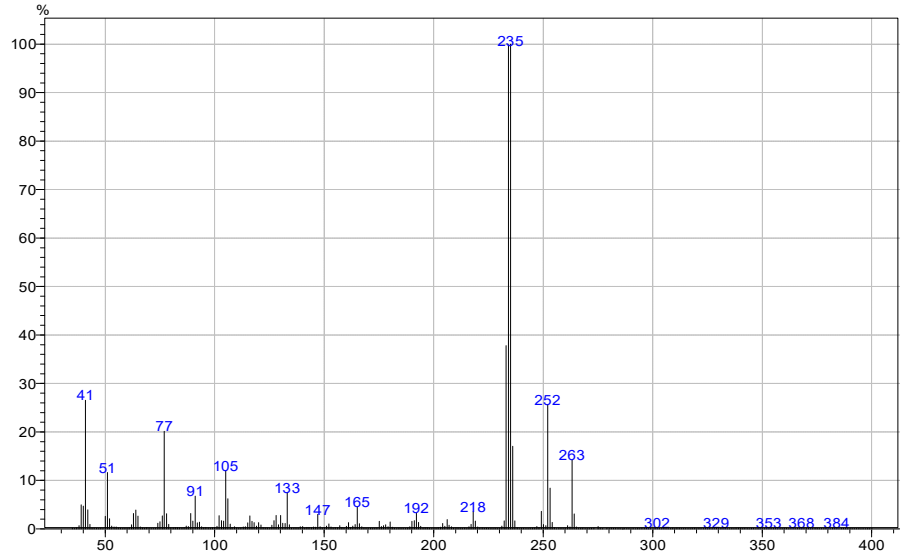


Figure 1. EIS-MS spectrum of HL^1.

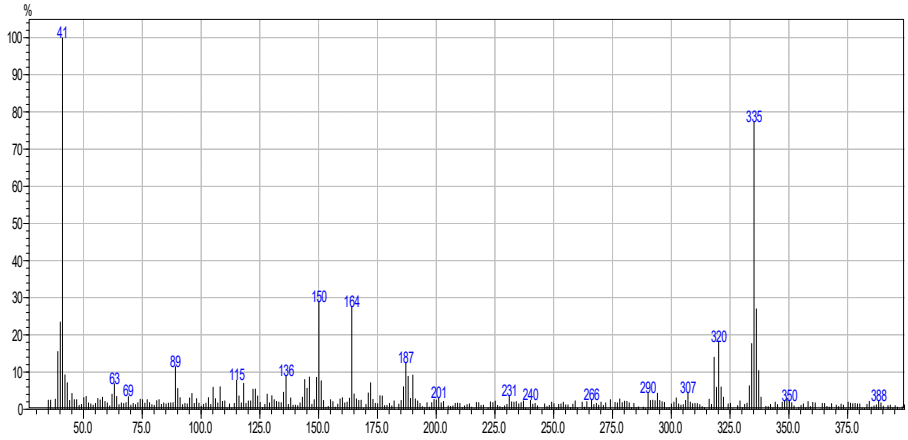


Figure 2. EIS-MS spectrum of **C4**.

FT-IR spectrum of ligand and its complexes

The main bands of FT-IR spectrum of ligand and its complexes are presented in the following discussion. The free ligand shows strong bands at 1280 and 1620 cm^{-1} assigning to the vibrations of thioamide –C=O and –C=N- of triazole and benzoquinone ring. The chelation of cobalt(II), nickel(II), copper(II) and zinc(II) ions to the active sites –C=O and –N=CH groups have been observed from the lowering in their absorptions to the regions (1680-1600) and (1390-1260) cm^{-1}. As well as the weak to medium bands at around (560-500) and (450-410) cm^{-1} are associated

with the coordination bonds of (M-N) and (M-O), respectively [18, 19]. As well as the broad bands at (3400-3500) cm^{-1} is assigned to stretching frequency of phenolic O-H moiety that was overlapped with –OH of coordinated water molecules in **C1-C3** complexes. However, the other bands located in the (2962-3025) cm^{-1} and (110-1265) cm^{-1} are remarkably assigned to the stretching frequencies of aliphatic C-H, aromatic C-H and (C-O) bonds in the mixed ligands of Schiff base-base isoniazid and chloroanilic acid, respectively [21].

Electronic spectra and magnetic susceptibility of complexes

The UV-Vis absorption spectrum of Schiff base of triazole, HL^1 in ethanol exhibited three absorption bands. Two bands at (350 nm, 27100 cm^{-1}) and (250 nm, 40000 cm^{-1}) transitions [19], Figure 3. The solutions of **C1**, **C2** and **C3** complexes in methanol (10^{-3} M) displayed weak absorptions at (400-1100) nm assigning to d-d spectra and LMCT bands. The octahedral complexes of nickel(II) and cobalt(II) exhibited weak bands at (510-390) and (350-288) nm which are mainly attributed to $^3A_2g \rightarrow {}^3T_2g$, $^3A_2g \rightarrow {}^3T_1g(F)$ and $^2Eg \rightarrow {}^2T_2g(D)$ transitions, respectively. The observed data could be led to the splitting energies of 10Dq of C1,C2 and C3 that are 15500, 20800 and 19700 cm^{-1} by plotting Tanabe-Sugano diagrams [22] with respect to the parameters of Racah at 862 and 1080 cm^{-1} for the free ions of $Co^{2+}$and Ni^{2+}, respectively. All the solid metal complexes showed expected effective magnetic moments at 4.50, 2.90 and 1.77 BM due to the orbital contribution in cobalt(II) high spin state with d^7 configuration, whereas the nickel(II) complex was agree with two odd electrons in its outer shell. The broadening in the d-d spectrum of **C3** complex besides the increasing in magnetic susceptibility of $3d^9$ configuration is the basic concept of Jahn-Teller z-out distortion [24-26], Figure 4. However, the pale yellow solution of zinc(II) complex showed two intense bands at 364 nm, 27473 cm^{-1} and 278 nm, 35972 cm^{-1} which are associated with LMCT and ligand field of HL^1 and benzoquinone secondary ligand,H_2L^2, respectively.

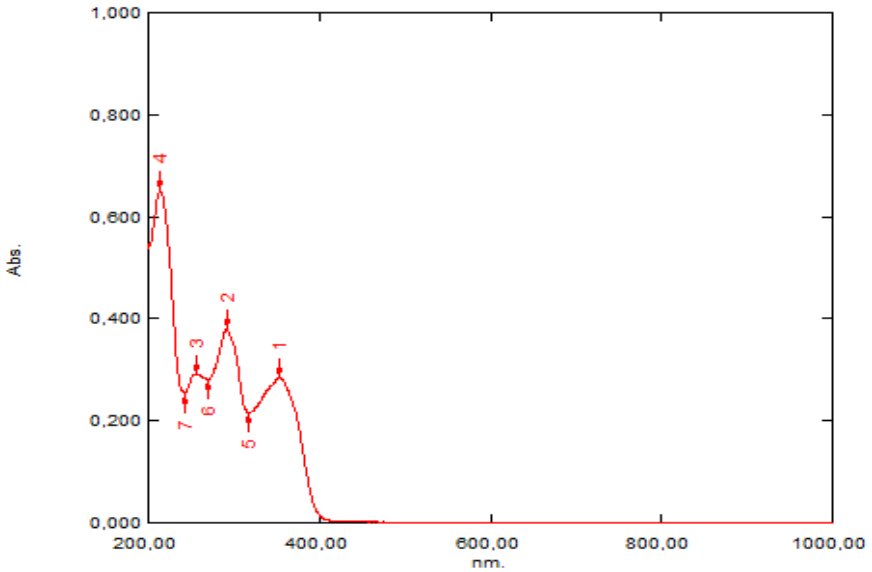


Figure 3. UV-Visible spectrum of HL^1 in methanol (0.001 M).

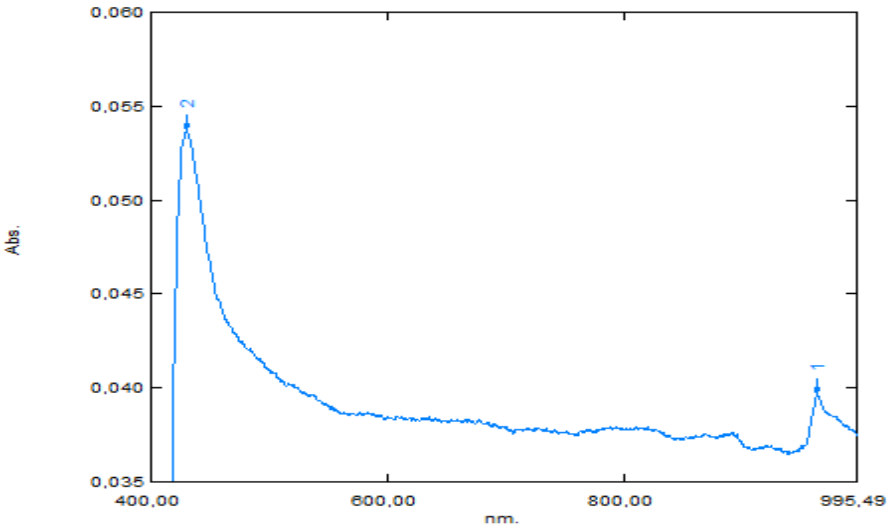


Figure 4. UV-Visible spectrum of $[CuL^1(HL^2)]$ in ethanol (0.001 M).

Molar conductance for synthesized complexes:

The solutions of all metal complexes were prepared in 10^{-3} M concentration in DMF solvent for the measuring of molar conductance, which fall in the region (14.22-9.88) ohm^{-1} cm^2 mol^{-1} confirming the neutral behavior of all complexes, this is consistent with the proposed chemical formula and their structures since the two reagents of 1,2,4-triazole; HL^1 and 1,4-benzoquinone; H_2L^2 secondary ligand behaved as monobasic bi dentate ligands and no counter ions are present in their structures [22, 25].

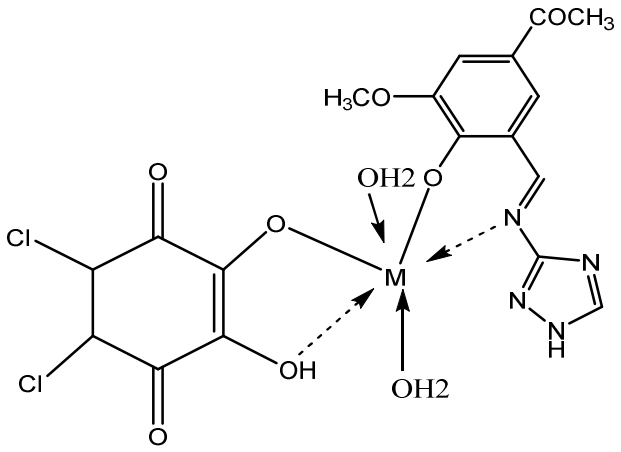
Thermal stability studying of HL^1 and its mixed complexes

Thermo gravimetric analyses were performed under helium inert gas with the average rate of heating at 10 °C per 1 minute. The thermal stability of Schiff base derived from apocynin and 3-amino-1,2,4-triazole, HL^1 and chloroanilic acid H_2L^2 were confirmed beside their chemical formula elucidation. The TG-DTA of HL^1 exhibits exothermic fragmentation at 288 °C with % weigh loss 6.77 and the differential DTA cure was optimized at 265 °C. As well as the second and third steps of thermal analysis was observed at 350 °C and 455 °C with % weight losses at around (4.2-5.99) respectively [28, 29]. These fragmentations can be attributed to the breakdown of the weak points in the structure of ligands such as cleavage of chloro, hydroxyl and phenyl group respectively. However, the DTA curve at maximum temperature T_{max} = 590 °C confirms the thermal stability of the ligand through the immine –C=N-, hydrogen bonded phenolic –OH and HC=N- moieties respectively. The TG-DTA of C1 and C2 complexes in helium atmosphere show endothermic processes curves in their TG-DSC thermo gravimetric analyses at (190-220) and (175-229) °C with loss weight percent about 13.5 to 10% assigning to cleavage the coordinated water molecules in the inner-sphere of complex [27,30]. The second step of TG were observed at (300-320) and (310-477) °C ranged with loss weight = 8.5-13.22 %, this step is so important due to breaking down ascribed to break down of weak points of complex like $–OCH_3$ and degradation of triazole ring [27, 28]. As well as the TG curve observed at (395-445) °C are assigned to break down of chlorine and HC-N- moiety with stable phase of $CoN+Co_2O_3$ and NiO with 55% and

48% weight values respectively. The TG-DSC curves obtained for almost prepared complexes with exothermic processes at the second and final steps of analyses confirmed the high stability of mixed ligand complexes with respect to literatures [26, 27].

CONCLUSION

According to the data observed from elemental analyses and spectroscopic analyses, the octahedral geometry around cobalt(II), nickel(II) and copper(II) ions were adopted, Scheme 3. As well as, the intra-ligand charge transfer is the distinct property of 1,4-benzoquinine ligand which is observed in the UV spectra of all prepared metal complexes. As well as the TG-DSC of all the complexes at inert gases of helium and argon showed high stability due to the elevation in the wide temperature of decomposition in the region (250-380) ^{o}C and the observed maximum isothermal processes of decomposition afforded that **C1**, **C3** and **C4** were formed in high yield of the two mixed ligands with strong points of M-O and M-N coordination and covalent bonds. Furthermore, the zinc(II) complex was adopted as square pyramid geometry with penta coordination number in the chemical formula; $[Zn(L^1)(HL^2)(H_2O)]$.



M(II)=Co,Ni or Cu(II)

Scheme 3. Octahedral structure of metal complex with mixed HL^1-HL^2.

ACKNOWLEDGEMENTS

The authors are grateful to Chemistry Department, College of Science, Mustansiriyah University for measurement of molar conductivity and magnetic susceptibility of metal complexes. The authors also appreciate the efforts of Ibn-Cina Center for Researches, Ministry of Industry, Baghdad, Iraq.

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