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Synthesis and characterization of a new ligand (E)-2-(4-((2-(2-((2-hydroxynaphthalen-1-yl) methylene) hydrazinyl) thiazol-4-yl) amino) phenyl) acetic acid, and its complexes

Nidhal. m. K[1*], Areej Ali Jarullah[1], and Taghreed M. Musa[2]

[1] Chemistry Department, College of Sciences, Diyala University

[2] Chemistry Department, College of Sciences, Mustansiriyah University

ndalmtb1981@gmail.com

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Abstract

In this research, a new heterocyclic compound (E)-2-(4-((2-(2-((2-hydroxynaphthalen-1-yl) methylene) hydrazinyl) thiazol-4-yl) amino) phenyl) acetic acid was synthesized from the reaction of 2-hydroxynaphthalene-1-carbaldehyde with 2-(4-((2-hydrazinylthiazol-4-yl)amino)phenyl)acetic acid. This compound was utilized as the ligand (HL) to synthesize series of complexes by its reaction with some metals elements salts (cobalt chloride hexahydrate, nickel chloride hexahydrate, copper chloride dihydrate and anhydrous zinc chloride). The ligand was characterized using different types of analytical techniques such as FT-IR, ^{1}H-NMR, mass spectrum and UV-Vis. Spectrum. The complexes were characterized by using UV-Vis- spectrum, LC.-MS. technique, FT-IR spectrophotometer, conductivity measurements, magnetic susceptibility and atomic absorption. The results of the analysis revealed that the final structures of the complexes are octahedral.

Key words: thiazol coordination compound, heterocyclic ligand, metals elements salts

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تحضير وتشخيص الليكاند الجديد (E)-2-(4-((2-(2-((2-hydroxynaphthalen-1-yl) methylene) hydrazinyl) thiazol-4-yl) amino) phenyl) acetic acid ومعقداته

نضال متعب خميس[1] و اريج علي جارالله[1] و تغريد محي الدين موسى[2]
قسم الكيمياء – كلية العلوم – جامعة ديالى

قسم الكيمياء – كلية العلوم – الجامعة المستنصرية

الخلاصة

في هذا البحث حضر المركب الحلقي غير المتجانس (E) -2- (4 - ((2- (2 - ((2-hydroxynaphthalen-1-yl) methylene) hydrazinyl) thiazol-4-yl) amino) phenyl) acetic acid من تفاعل 2-hydroxynaphthalene-1-carbaldehyde مع 2-(4-((2-hydrazinylthiazol-4-yl)amino)phenyl)acetic acid. تم استخدام هذا المركب كليكاند (HL) لتحضير سلسلة من المعقدات من خلال تفاعل الليكاند مع بعض أملاح العناصر الفلزية (كلوريد الكوبالت سداسي الماء و كلوريد النيكل سداسي الماء و كلوريد النحاس ثنائي الماء وكلوريد الزنك اللامائي). شخص الليكاند باستخدام أنواع مختلفة من التحليلات مثل FT-IR و ^{1}H-NMR والطيف الكتلي وطيف الأشعة فوق البنفسجية والمرئية. كما شخصت معقدات الكوبالت (II) والنيكل (II) والنحاس (II) والزنك (II) باستخدام طيف UV-Vis وتقنية LC-MS وطيف FT-IR وقياسات التوصيلية والحساسية المغناطيسية والامتصاص الذري. أعطت نتائج التحليل الهياكل المقترحة للمعقدات هي ثماني السطوح.

الكلمات المفتاحية : معقدات الثايزول ، ليكندات حلقية غير متجانسة ، املاح العناصر.

Introduction

The polydentate heterocyclic ligands which have nitrogen and sulfur atoms together have diverse coordination abilities toward transition metal; and accordingly, they have attracted large attention, especially in the synthesis and application of complexes bioactive. For example this kind of ligand (thiazole, thiadiazole and isothiazole derivatives assume exceptional prominence in the metal complexes construction from different types, especially in the organometallic compounds and functional materials[1, 2]. Thiazole ring contains an acidic proton at position C-2 , as a result, the ring of thiazole becomes extremely reactive compound to prepare a large number of new chemical compounds. Thiazole derivatives have piqued the attention of researchers, because of their different pharmacological, physical, and chemical properties [3];

thus, in the past years an assortment of new important curative potential compounds were synthesized like (anti-cancer, antioxidant, antibacterial, antifungal, anti-tubercular, diuretic, anti-inflammatory, antihypertension, anti-ulcerogenic, analgesic, and also controlling schizophrenia symptoms medications). A single nucleus of thiazole or fused ring is the main component of naturalist penicillin-like drugs that are known with antibiotics[4-9]. Schiff bases are a significant type of ligand that can react with ions of metals out of the nitrogen of azomethine and that is studied widely, due to their stability in different oxidative and reductive conditions, as well as that the ligands of imine are borderline between hard soft acid base[10,11].

Experimental

Materials and method

The chemicals used in this study were equipped by a number of companies like (Aldrich and Fluka). Fusion degree measuring devices METLER TOLIDO 2013 Swiss and SMP30 were used for measuring the melting points. Infrared spectra were pointed by using the BROKER ALPHA II in the range (4000-400) cm^{-1}. The UV-Vis double beam spectrophotometer in the range 200–900nm was used and the concentration of each sample solution in (DMSO) 10^{-3} M. Molar conductivity of the complexes were recorded using a (BP3001) Professional Benchtop pH Meter. ^{1}H-NMR spectra were recorded using (Bucker Bio Spin GmbH, NMR spectrometer) frequency (400.13) with a Tetramethylsilane (TMS) as an internal standard. Mass spectra were recorded using a direct Injection Probe Shimadzu GCMS – QP 2010 Spectrometer. Magnetic Susceptibility were carried out using Faradays' method by (Balance Magnetic Susceptibility Model MSB-MKI). Atomic absorption flame for the complexes were obtained by using ((Analytika jena AA 350 NOV Germany 2012). LC-MS measurement for the complexes carried out by an Ic/ms_msab sciex model q_trap3200 made in the U.S.A.

Synthesis the ligand (HL)

Synthesis of 2-(4-(2-chloroacetamido)phenyl)acetic acid.

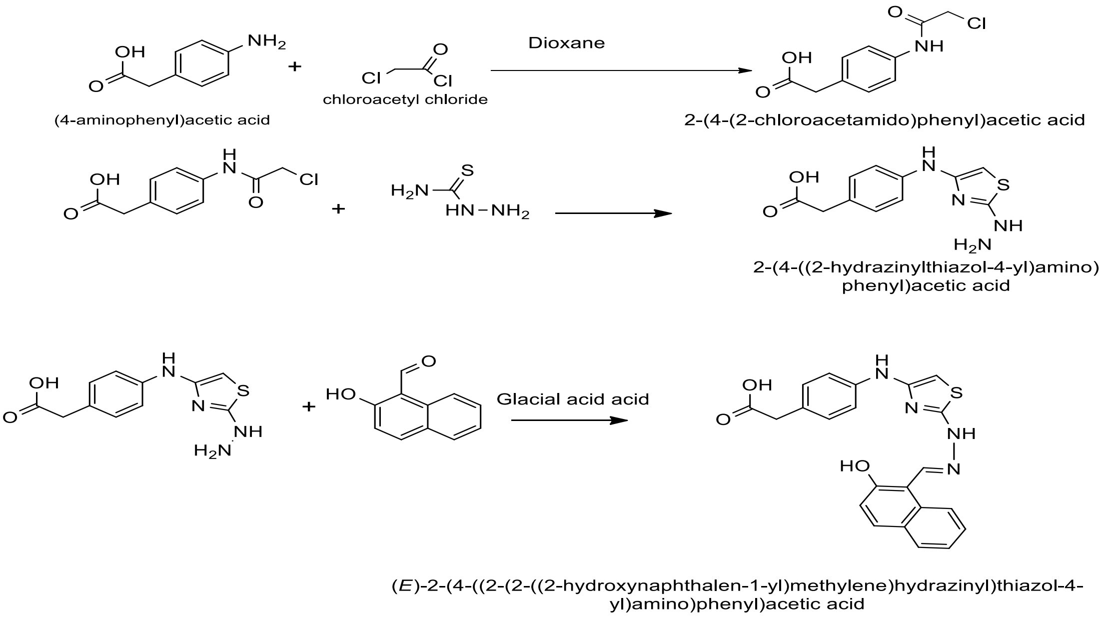
It was prepared by weighing (4 gm, 0.0264 mol) from 4-aminophenol acetic acid and (2.98 gm, 0.26 mol) from chloroacetyl chloride and, then they were mixed by dissolving in 1,4-dioxane after it purified for reflux 20 h . After heating the mixture under reflux for 24 h a precipitate formed. This precipitate is filtered and washed with ethanol and diethyl ether. The purity of the compounds was checked by TLC using (n-hexane:ethylacetacte) [12].

Synthesis of 2-(4-((2-hydrazinylthiazol-4-yl)amino)phenyl)acetic acid.

It was synthesized by the reaction of (0.04 gm , 0.00043mole) thiosemicarbazide with (0.1 gm, 0.00044mole) of 2-(4-(2-chloroacetamido)phenyl)acetic acid, where the mixture was dissolved in ethanol and placed in round bottom flask, followed by refluxing for 6 h [12].

Synthesis of the ligand (HL).

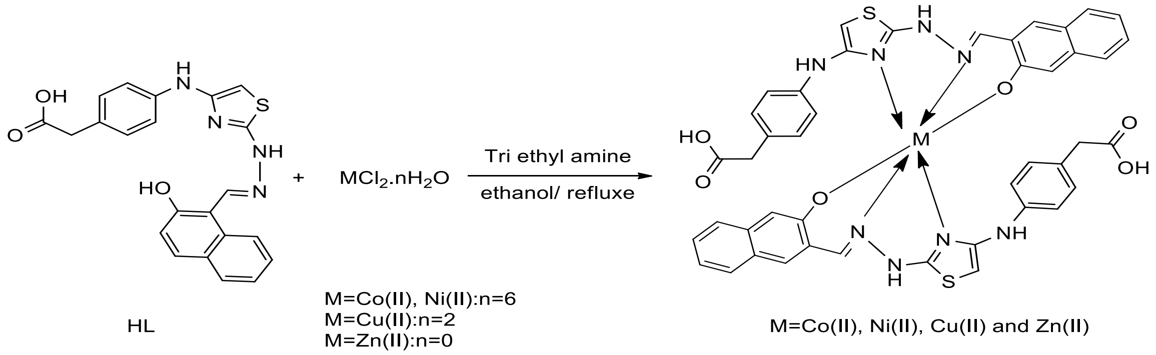
It was synthesized from the reaction between (0.498 gm, 0.0029mole) 2-hydroxynaphthalene-1-carbaldehyde and (0.771 gm, 0.0029 mol) of 2-(4-((2-hydrazinylthiazol-4-yl)amino)phenyl)acetic acid that have been dissolved in 50mL of ethanol where the mixture placed in round bottom flask with added two drop of glacial acetic acid. The mixture was refluxed for 6 h to produce the ligand (HL)[12]. Scheme (1) shows the steps involved in preparing the ligand.



Scheme 1: Steps of the ligand synthesis

Synthesis of complexes

Cobalt, Nickel, Copper and Zinc complexes were prepared by mixing a solution of ligand (0.46g, 0.001 mol) in (25 ml) ethanol with a solution of metal chlorides such as $CoCl_2.6H_2O$, $NiCl_2.6H_2O$, $CuCl_2.\ 2H_2O$ and $ZnCl_2$ (0.0005 mol) in (20 ml) ethanol [molar ratio(2:1, ligand: metal)]. Then, one drop of tri ethyl amine was added to the solution and the mixture was refluxed for 1 h, cooled at room temperature and the solid complex was washed with cold ethanol, filtered off, dried, weight and the product percentage was calculated. Scheme (2) shows the method followed to synthesize the complexes and the physical properties and atomic absorption data for the complexes was illustrated in Table (1)



Scheme 2: synthesis of $[M(C_{22}H_{17}N_4O_3S)_2]$complexes

Results and Discussion

Mass, ^{1}H-NMR and FT-IR Spectrum of (HL).

The mass spectrum of the ligand illustrated in Figure (1) showed a molecular weight peak at *m/z* = 418 g/mole which agrees well with the theoretical calculation of the M.wt formula of the ligand that is equal to the 418.47, which has the molecular formula ($C_{22}H_{18}N_4O_3S$). ^{1}H-NMR spectra Figure (2) was extracted the following data:11.40 (s,1H, COO$\underline{H}$), 10.81(s,1H, Ar-O$\underline{H}$), 10.53 (s,1H, thiozol-N$\underline{H}$-N=CH), 9.04 (s,1H,C$\underline{H}$=N), 8.54 (s,1H, Ar-N$\underline{H}$- thiozol), 8.22-7.20 (m,10 H, Ar-H), 4.38 (s,1H, CH, thiazol ring), 3.44(s, 2H, CH_2). The FT-IR spectra of ligand Figure (3) shows absorption bands at (3284 and 3201cm^{-1}) assigned to the stretching vibration of N –H. A bands were observed in the region 3445 and 3364 cm^{-1} due to the OH groups of the carboxylic and phenolic group respectively. The absorption bands at (1719cm^{-1}), (1623cm^{-1}), (1585 cm^{-1}) were attributed to the stretching vibrations of the C=O of carboxyl group, the azomethine group CH=N , and C=N group in the thiazol ring respectively. The band at (1255cm^{-1}) was evidence of stretching vibration of the (C-O) bond. (3033cm^{-1}) band was an indicative of the aromatic C-H , where is (2981-2935cm¹) band belongs to the aliphatic C-H, and (2907cm^{-1})to the C-H thiazol ring [12-15]as shown in table (2)..

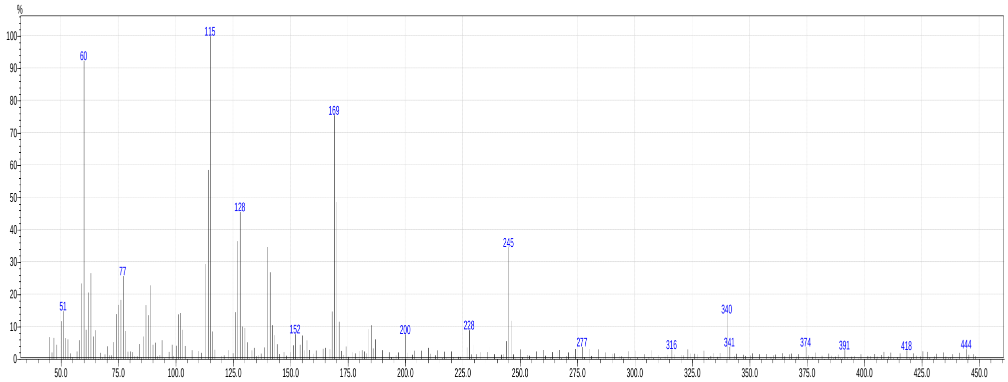


Figure 1: Mass spectrum of the ligand(HL)

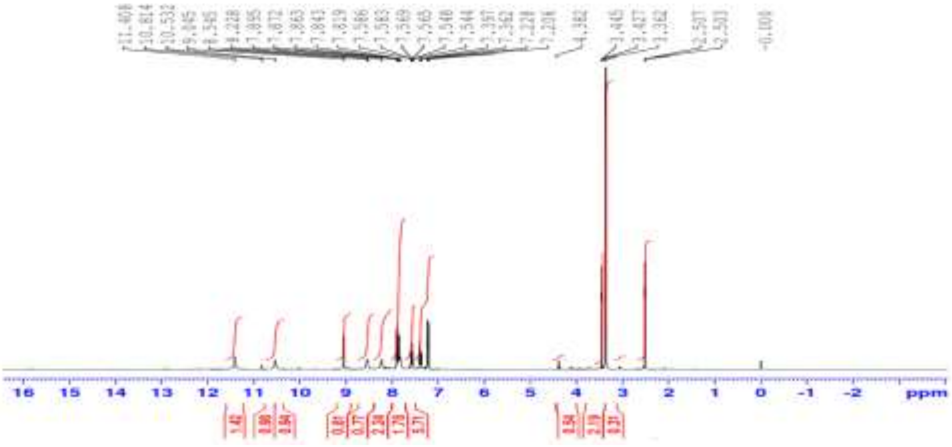


Figure 2 : ^{1}HNMR spectrum of the ligand (HL)

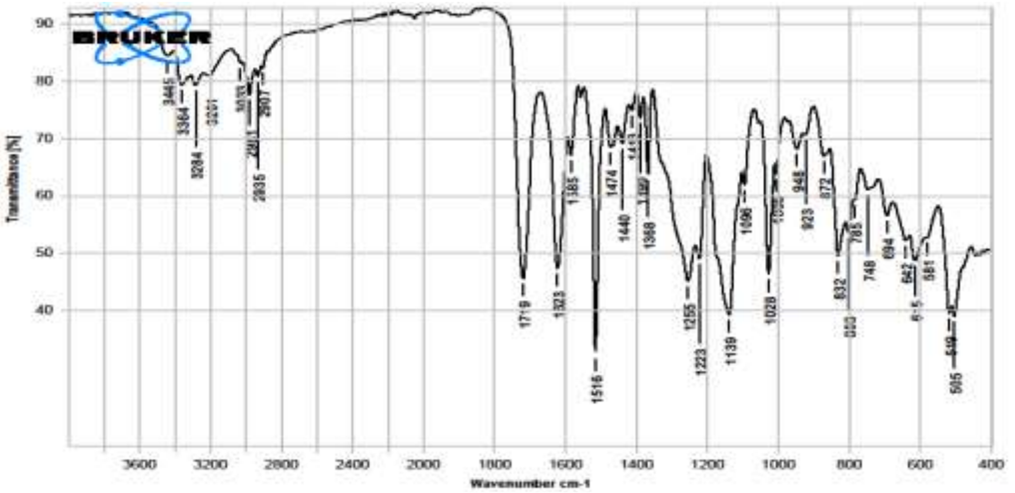


Figure 3: FT-IR spectrum of the ligand (HL)

FT-IR Spectra of complexes

The disappearance of the absorption peaks of O-H phenolic stretching frequency from the FT-IR spectrum of zinc, nickel, copper, and cobalt complexes compared to the spectrum of the free ligand and the occurrence of a displacement in the stretching vibration of C=N group in the thiazol ring and C=N for the azomethine group is considered a good indication of the coordination for the ligand to the metal ion through nitrogen atoms of an azomethine group, nitrogen atoms of thiazol ring and oxygen atoms for phenolic after deprotonation of protons of the hydroxyl group. In addition, new bands with weak intensity appeared at (562,554, 524, and 556) cm^{-1} due to stretching vibration stretching vibration of M-N, and at (422, 418, 460, and 420) cm^{-1} due to stretching vibration of M-O for Co(II), Cu(II), Ni(II), and Zn(II) complexes respectively[16,17]. Table (2) illustrated the FT-IR spectra results for ligand and its complexes.

LC-MS Spectra of metal complexes

The (LC-MS) of the complexes at Figures (4 -7) showed peaks (m/z = 894.2, 895 ,899.7and 900.3) gm/mole assigning to the molecular complexes of [Co $(C_{22}H_{17}N_4O_3)_2$], [Ni $(C_{22}H_{17}N_4O_3)_2$], [Cu $(C_{22}H_{17}N_4O_3)_2$], and [Zn $(C_{22}H_{17}N_4O_3)_2$] respectively, and confirms the suggested structure were identical to the theoretical calculation that equal to 893.857 gm/mole for Co-complex and Ni-complexes is 893.617 gm/mole while the Cu-complex 898.47 gm/mole and 900.304 gm/mole for Zn-complex approximately.

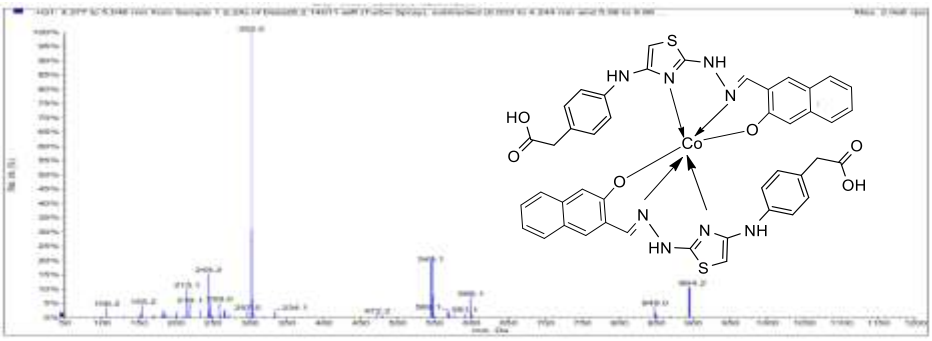


Figure 4: Mass spectrum for $[Co(C_{22}H_{17}N_4O_3S)_2]$ complex

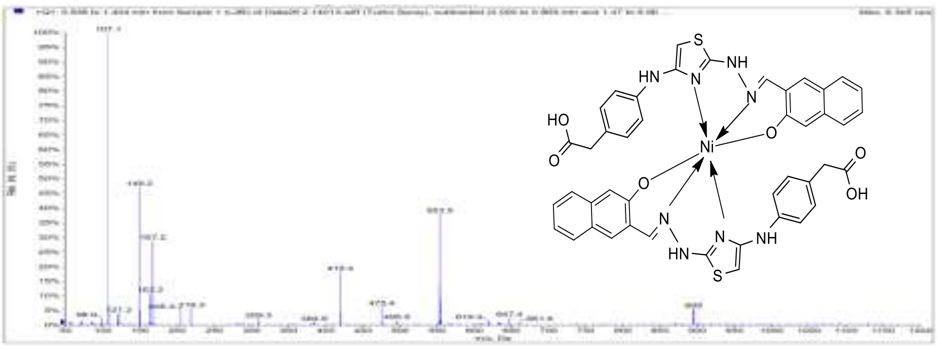


Figure 5: Mass spectrum for $[Ni(C_{22}H_{17}N_4O_3S)_2]$ complex

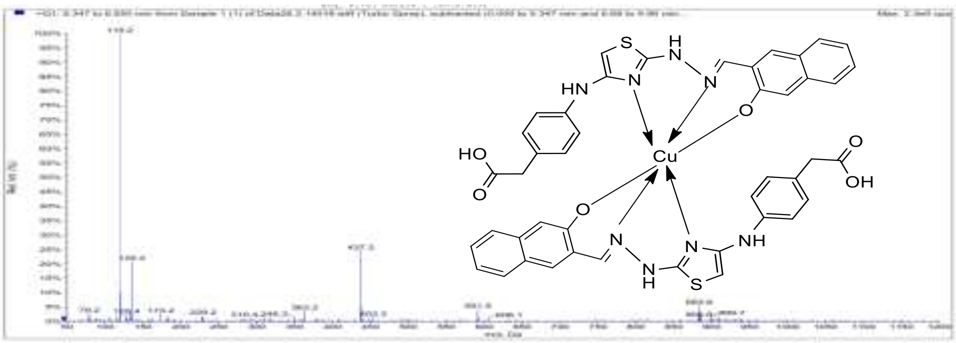


Figure 6: Mass spectrum for $[Cu(C_{22}H_{17}N_4O_3S)_2]$ complex

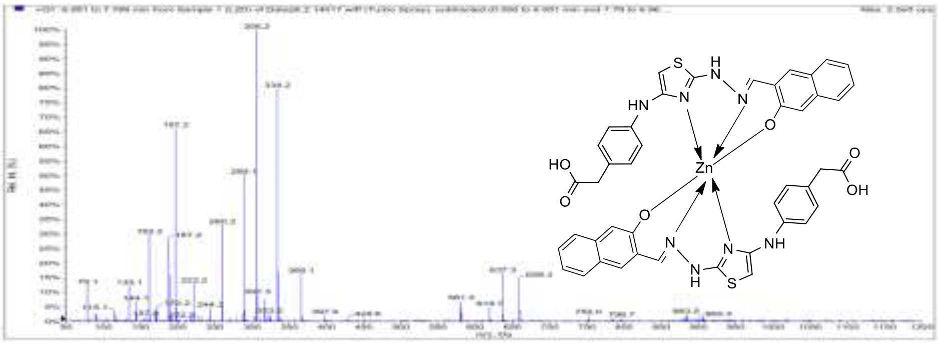


Figure 7: Mass spectrum for $[Zn(C_{22}H_{17}N_4O_3S)_2]$ complex

UV-Vis, magnetic properties and molar conductance

The electronic spectrum of ligand and its complexes were measured in DMSO as illustrated in Figures(8-12). The UV-Vis spectrum of the ligands in Figure (8) showed four maximum absorption bands: the first absorption band appeared at (421.2 nm, 23741cm^{-1}) was belonged to intra ligand charge transfer (ILCT), the second and the third high intensity peaks appeared in the UV region at (362.8 nm, 27563 cm^{-1}) and (327.6 nm, 30525cm^{-1}) were assigned to (n→π*) transitions, while the fourth absorption band appeared at (259.6 nm, 38520 cm^{-1}) due to (π →π*) [18] . Electronic transitions with their assignments for ligand and all complexes are summarized in Table (3) [19, 20].

The observed value of magnetic moment for cobalt(II), nickel(II), and copper(II) complexes exhibit (μ_{eff}=3.57, 2.8 , 1.78) B.M respectively, indicating paramagnetic nature and characteristic of high spin octahedral complexes. But the prepared Zn(II) complex was diamagnetic which was prospective for d^{10} ion[21].

The molar conductance of the all synthesized complexes was measured in dimethyl sulfoxide solvent at room temperature, and the data obtained from that indicates that the synthesized complexes were non-ionic. Magnetic susceptibility, and molar conductance values of all synthesized complexes were listed in Table (3).

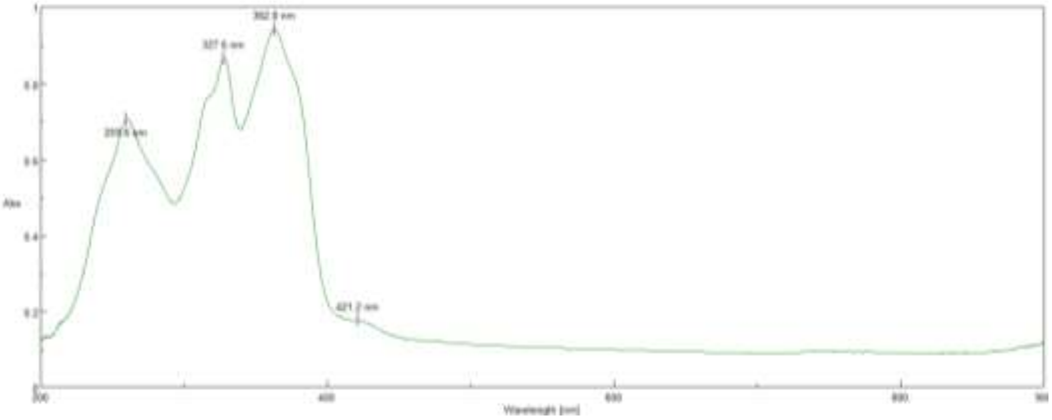


Figure 8: UV-Vis spectrum for ($C_{22}H_{18}$ N_4 O_3S)

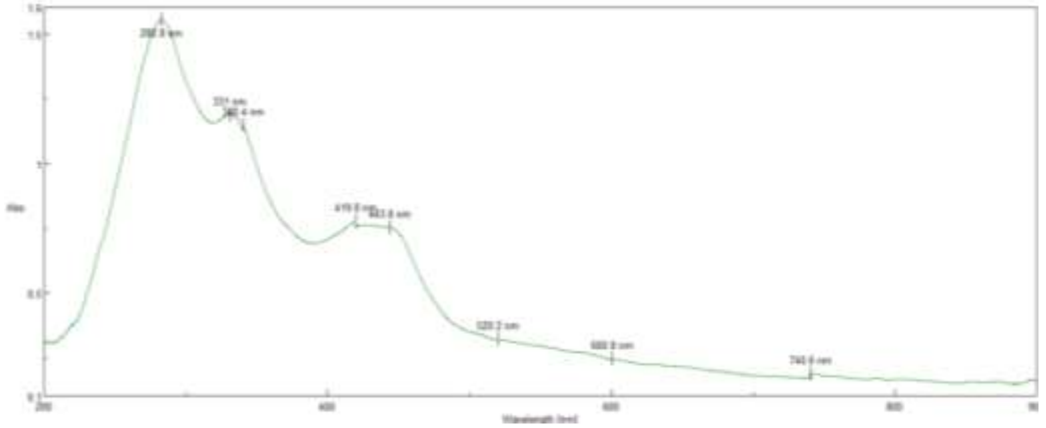


Figure 9: UV-Vis spectrum for [Co ($C_{22}H_{17}$ N_4 O_3S)$_2$] complex

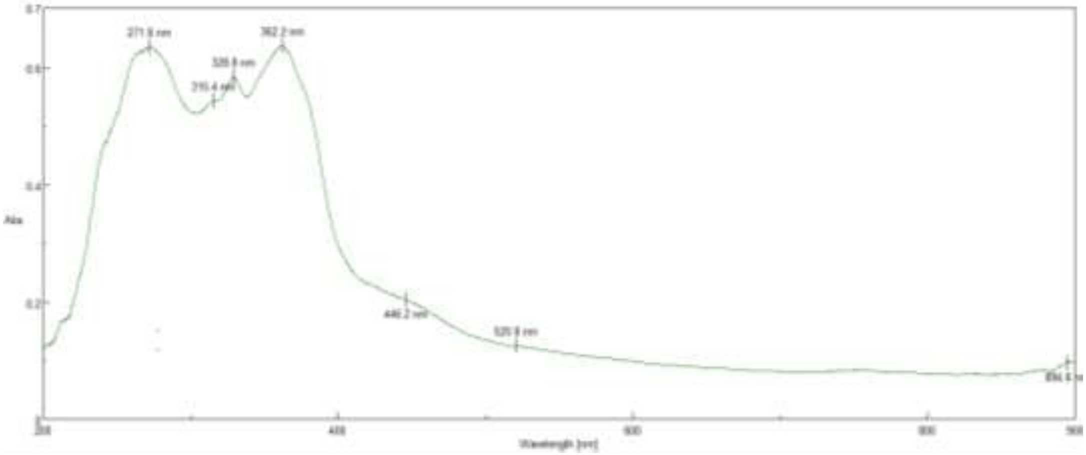


Figure 10: UV-Vis spectrum for [Ni ($C_{22}H_{17}N_4O_3S$)$_2$]complex

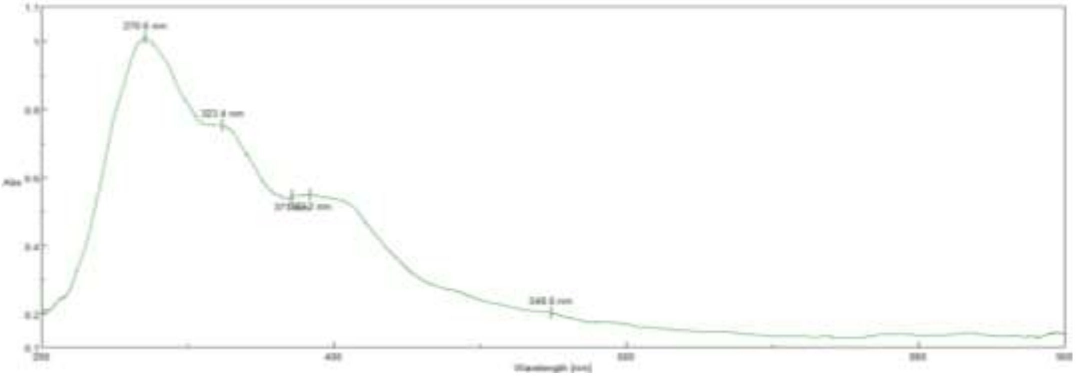


Figure 11: UV-Vis spectrum for $[Cu(C_{22}H_{17}N_4O_3S)_2]$ complex

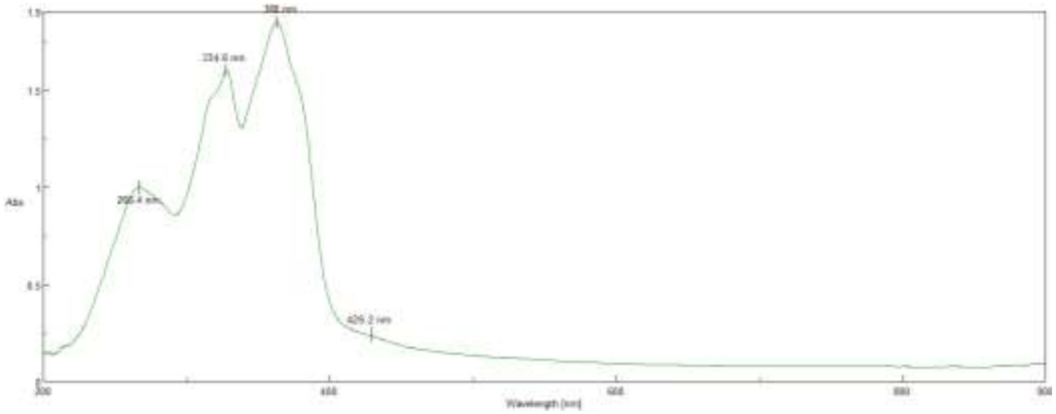


Figure 12: UV-Vis spectrum for $[Zn(C_{22}H_{17}N_4O_3S)_2]$ complex

Table1: Physical properties and atomic absorption data

COMPOUND	COLOR	YIELD %	M.WT. GM/MOLE	M.P. °C	METAL PERCENTAGE% IN COMPLEX FOUND (CALC.)
$C_{22}H_{18}N_4O_3S$	Orange	86	418	293	-
$[Co(C_{22}H_{17}N_4O_3S)_2]$	green	87.8	893.857	350d	6.49 (6.59)
$[Ni(C_{22}H_{17}N_4O_3S)_2]$	Shine brown	88.2	893.617	350d	6.83 (6.56)
$[Cu(C_{22}H_{17}N_4O_3S)_2]$	Shine brown	90.8	898.47	350d	7.83 (7.07)
$[Zn(C_{22}H_{17}N_4O_3S)_2]$	Red	86.6	900.304	350d	7.25 (7.26)

Table 2: FT-IR spectra data in (cm^{-1})

COMPOUND	υ (OH)	υ (NH)	υ (C=N)	Y(C-O)	Y(C-S)	υ (M-N)	υ (M-O)
$C_{22}H_{18}$ N_4 O_3S	3445 3364	3284 3201	1623 1585	1255	748		
$[Co(C_{22}H_{17}N_4O_3S)_2]$	3373	3283 3240	1613 1596	1246	746	562	422
$[Ni(C_{22}H_{17}N_4O_3S)_2]$	3396	3333 3248	1597 1573	1247	750	554	418
$[Cu(C_{22}H_{17}$ $N_4O_3S)_2]$	3435	3255	1617 1598	1248	739	524	460
$[Zn(C_{22}H_{17}N_4O_3S)_2]$	3413	3246 3169	1612 1572	1240	744	556	420

Table 3: Electronic spectra, molar conductivity, and magnetic moment (B.M) data

Compound Symbol	Λ NM	Y CM^{-1}	ASSIGNMENT	$M_{EFF.}$ B.M	MOLAR CONDUCTANCE ΛM.S.CM^2.MOLE^{-1}	SUGGESTED GEOMETRY COMPLEXES
$C_{22}H_{18}$ N_4 O_3S	259.6 327.6 362.8 421.2	38520 30525 27563 23741	π→π* n→π* n→π* ILCT			
$[Co(C_{22}H_{17}N_4O_3S)_2]$	282.8 331 340.4 419.8 443.6 520.2 600.8 740.6	35360.6 30211.4 29377.2 23820.8 22542.8 19223.3 16644.4 13502.5	π→π* n→π* n→ π* (M→L) C.T $^4T_1g \rightarrow {}^4T_1g._{(p)}$ $^4T_1g \rightarrow {}^4A_2g._{(F)}$ $^4T_1g \rightarrow {}^4T_2g._{(F)}$	**3.57**	**19.2**	Oh

[Ni($C_{22}H_{17}N_4O_3S)_2$]	271.8	36791.7	$\pi\rightarrow\pi^*$	**2.8**	**4.44**	Oh
	315.4	31705.7	$\pi\rightarrow\pi^*$			
	328.8	30413.6	$n\rightarrow\pi^*$			
	362.2	27609.0	$n\rightarrow\pi^*$			
	446.2	22411.4	(M→L) C.T			
	520.8	19201.2	$^3A_2g \rightarrow {}^3T_1g_{(p)}$ $^3A_2g \rightarrow {}^3T_1g_{(F)}$			
	894.8	11175.6				
[Cu($C_{22}H_{17}$ $N_4O_3S)_2$]	270.6	36954.9	$\pi\rightarrow\pi^*$	**1.78**	**9.30**	Oh
	323.4	30921.4	$\pi\rightarrow\pi^*$			
	371	26954.1	$\pi\rightarrow\pi^*$			
	382.2	26164.3	C.T			
	548.6	18228.2	$^2Eg \rightarrow {}^2T_2g$			
[Zn($C_{22}H_{17}N_4O_3S)_2$]	266.4	37537.5	$\pi\rightarrow\pi^*$	0	**3.6**	Oh
	334.6	29886.4	$n\rightarrow\pi^*$			
	368.8	27114.9	$n\rightarrow\pi^*$			
	426.2	23463.1	(M→L) C.T			

Conclusion

In this paper, new series of complexes were synthesized and characterized using different techniques. The metal ions utilized in this work were coordinated to ligand (HL) by the oxygen of the methoxy group, the nitrogen atom of the azomethane group, and the nitrogen atoms of a thiazol ring. The complexes of Co(II), Cu(II), and Ni(II), compared with the free ligand showed new low-intensity bands assigned to (d-d) transition in the visible region, an indication of the occurrence of coordination between the ligand and the metal, while the Zn-complex shows no absorption bands in the visible region, which indicates that no electronic transition happened type (d-d) in the system of d10 but the proportional change in the band location compared with the free ligand, guide of the occurrence of coordination between Zn and ligand. The conductivity measurements appeared that all complexes were non-ionic. The LC-MS of the complexes confirms the suggested structures were identical to the theoretical calculation. According to the obtained data, the proposed structures for complexes were octahedral geometry.

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