Preparation and Characterization and Biological Activities of Mixed Ligand Complexes of Co^{+2}, Ni^{+2} and Cu^{+2} with 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one and Glycine

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Abstract

A new ligand was synthesized and characterized by (FTIR) spectroscopy, Uv-vis and C.H.N. A speciation of mixed ligand complexes of Co(II), Ni(II) and Cu(II) with 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3] thiazin-(3H)- one and Glycine were prepare , isolated and characterized by (FTIR), Uv-vis spectra, atomic absorption , conductivity and magnetic susceptibility measurements. The biological activity for the prepared complexes was studied against selected kind of bacteria and fungus, for bacteria, gram negative as E coli and gram positive as staphylococcus aureus. The molecular structures of prepared complexes suggested according to the result of IR spectra, Uv-vis , magnetic susceptibility and molar conductance ,were octahedral for Co(II) and Ni(II) while square planner geometry for the Cu(II) complex .

Key words: Glycine, Transition metal complexes, spectroscopy

Introduction

There has been an increasing growth in the preparation, reactivity and structure of the Schiff bases because of their wide and potential applications in catalysis, ligand modeling, material chemistry and biological activity [1 -3]. Beside, Schiff bases were largely used as a ligands in coordination with metal ion due to their electron donor and chelating ability [4-8]. New Schiff base 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one has been prepared from the "condensation reaction" of 2-meroptobenzoic acid with acetophenone, "as well mix ligand complexes were synthesized by simple reaction of metal chloride" under basic medium.

Experimental

Materials and Methods

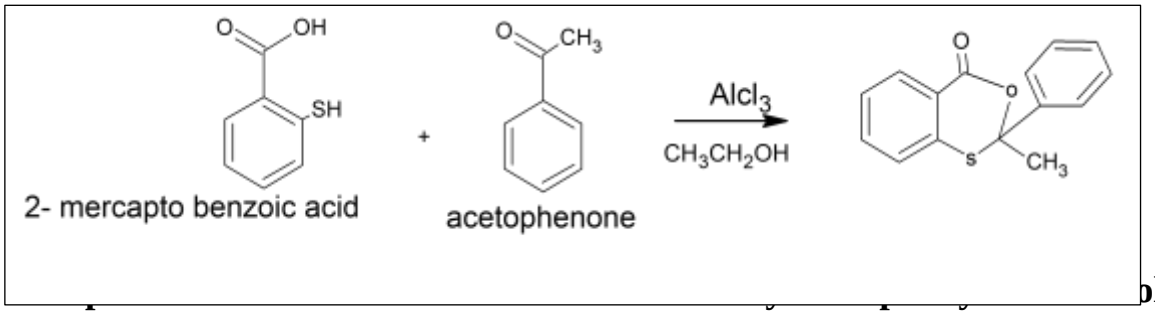
Chemicals that have been used in this research are: 2-meroptobenzoic acid (BDH), acetophenone (BDH), aluminum chloride (BDH), hydrazine hydrate (Fluka),, Cobalt (II) chloride hexahydrate (fluka) and Nickel(II) chloride hexahydrate (fluka) and Copper(II) chloride dihydrate (fluka) .

Physical measurements

The infrared spectra of the prepared compounds were recorded using FT-IR-8300-Shimadzu, in the wave length range of (4000-400) cm^{-1} . "The electronic spectra obtained using (UV-Vis-1650A) Shimadzu Spectrophotometer, in the range of wave-length (200- 1100 nm). Element analyses(C. H. N) were obtained using EA-034 mth". "For metal complexes". "Melting point apparatus of Gallen kamp M.F.B 600.01 was used to measure the melting points of all prepared compounds. Magnetic susceptibilities of samples in the solid state were measured using broker BM6 magnetic balance. Molar conductivity was measured using electrolytic conductivity measuring set model MC-1-Mark V.

Preparation of compound (I)

A mixture of (3.72g, 0.025 mole) 2-meroptobenzoic acid and (6.75g , 0.05 mole) acetophenone in 100ml of ethanol was stirred magnetically, and (2.7g , 20mmole) of aluminum chloride was gradually added , then stir the mixture for 5 hours at 25 ^{0}c , then 200ml of distilled water was slowly add, until
precipitate formed which re- crystallized from absolute ethanol and dried.



[e][1,3]thiazin-(3H)- one

A mixture of (2.85g, 0.01 mole) of compound (1) in 60ml of absolute ethanol and 45ml of 98% hydrated hydrazine was stirred at room temperature and refluxed for 6houre the crystals were collected . After evaporate of the solvent then filtration, and dried in vacuum.

Synthesis of complexes

Ethanolic solution of ($CoCl_2.6H_2O$) (0.26g, 0.001 mole) , ($NiCl_2.6H_2O$) (0.23g, 0.001 mole) and ($CuCl_2.2H_2O$) (0.13g, 0.001 mole) mixed with ethanolic solution of (0.23g, 0.001 mole) of 3- amino-2- methyl 3-amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one and (0.22g, 0.001 mole) of Glycine followed by the gradual addition of saturated solution of sodium bicarbonate ($NaHCO_3$) was added to mixture, the mixture was refluxed for 1hour. After cooling the resulting precipitate was filtered washed with water, and ethanol, then dried which resulted in the formation of their respective metal complexes. "The physical properties and analytical data of these complexes are shown in **Table 1**"

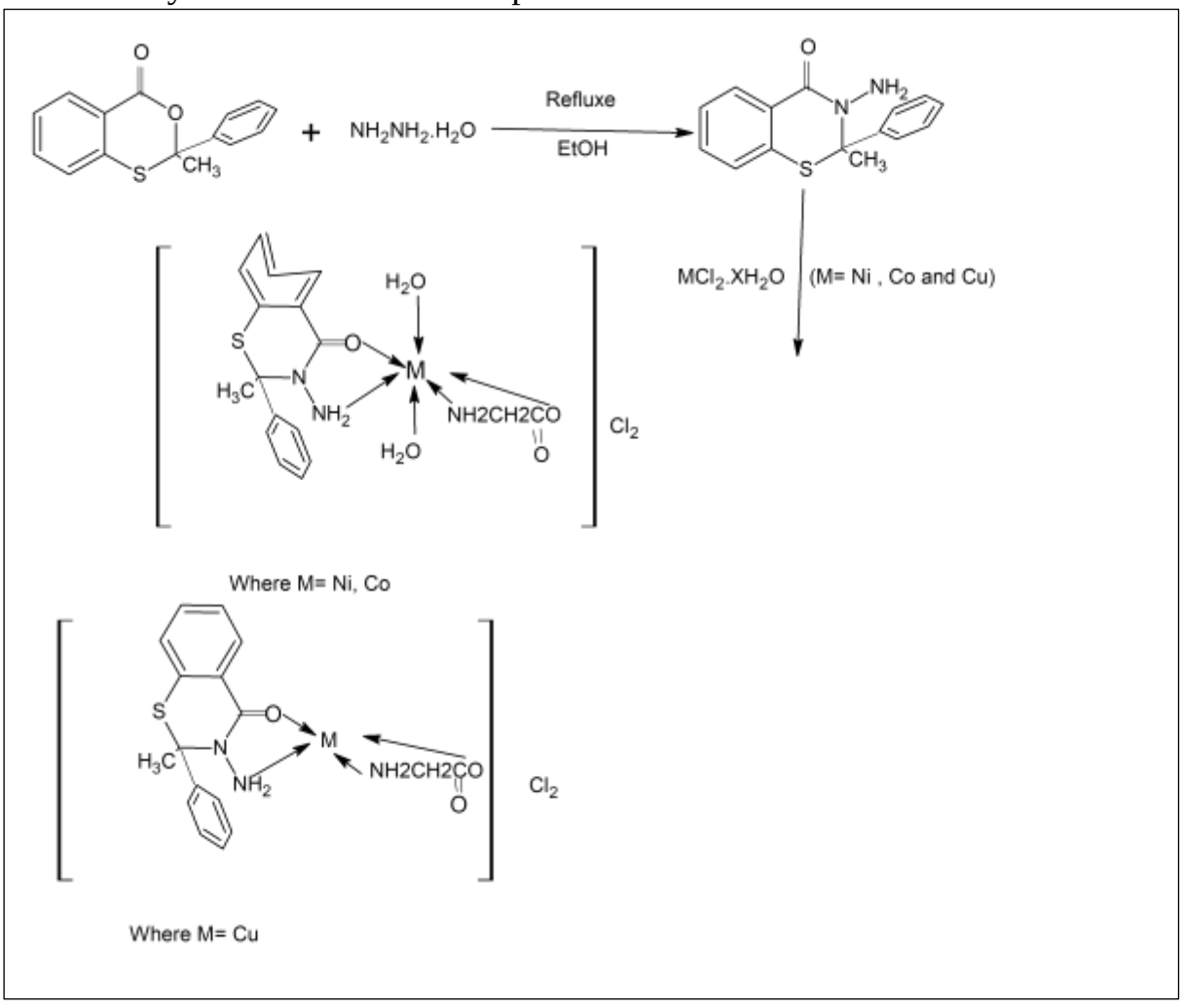


Fig. 2 preparation of 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one] and there complexes.

Table 1: "physical properties of the synthesized compounds"

"Compound"	color	"Yield%"	M.P ^{0}C	"Found" (calcu.)%			
				M%	C%	H%	N%
$C_{15}H_{14}N_2OS$	whit	63	280-282		66.40 (66.66)	4.61 (5.18)	10.03 (10.37)
$[Co(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$	Brown	71	254-256	12.42 (11.99)	41.05 (41.46)	4.00 (4.26)	8.86 (8.53)
$[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$	red	54	238-240	11.37 (11.94)	41.07 (41.44)	4.01 (4.26)	8.87 (8.53)
$[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]Cl_2$	green	75	248-250	13.54 (13.36)	42.93 (42.58)	3.86 (3.96)	8.10 (8.76)

Result and Discussion

Synthetic Comments

In this work the mix ligand complexes have been prepared by simple reaction of $MCl_2.XH_2O$. under basic medium.

Analytical data of ligand and their mix ligand complex

Analysis of the ligand and mix Ligand complexes are reported in Table1. The elemental analysis data agree well with the proposed formula for the complexes were studied in various solvent. The complexes were soluble in DMSO , DMF , ether and chloroform.

Infra red Spectroscopic Study

The FTIR spectrum of the3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one] show band at 3322 cm^{-1} which may be to NH_2 group and the stretching frequency at 1640 cm^{-1} can be attributed to carbonyl group of the heterocyclic ring , these two bands moved to lower frequency in all mixed ligand complexes as compared to 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one] which indicate the coordination to metal ion and appear band in rang (502-545)cm^{-1} reveal the formation of metal nitrogen linkage (M-N)[9-10], as well as the red shift of (C=O) group supports the linkage of oxygen of carbonyl group to metal ion, this concedes the behavior of the ligand as bidentate ligand forming five-member ring system which is thermodynamically stable. The spectra of mixed ligand complexes show evidence that supports participate of carboxylate (COO^-) and amino group in coordination, in comparison with free ligand glycine. These band moved to lower frequency in spectra of mix ligand complexes. The IR spectra of Co (II) and Ni (II) complexes exhibited broad bands at 3482 $cm^{-1}$and 3421 cm^{-1} respectively, this band assigned to the OH stretching vibration of the coordinated water molecules[11-13].

Table 2: FT-IR spectra of (3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one and glycine) and their complexes

Compound	υNH_2	υ C=O	υ COO^- asy. sym	υ M-N	υ M-O
$C_2H_5NO_2$	3343	1769	1662 1415	-	-
$C_{15}H_{14}N_2OS$	3322	1640	1655 1415	545	436
$[Co(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$	3302	1637	1625 1411	513	462
$[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$	3318	1598	1620 1415	502	492
$[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]Cl_2$	3309	1635	1582 1414	522	422

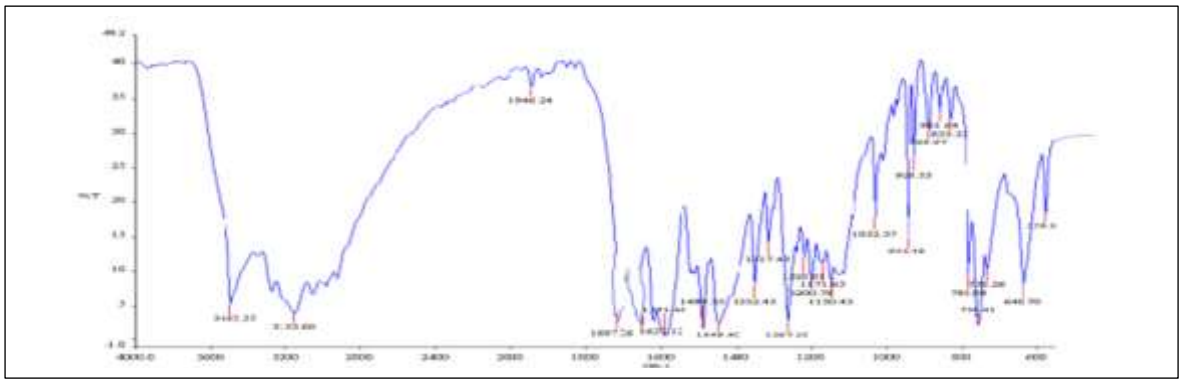


Figure 4: IR spectra of $[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$complexes.

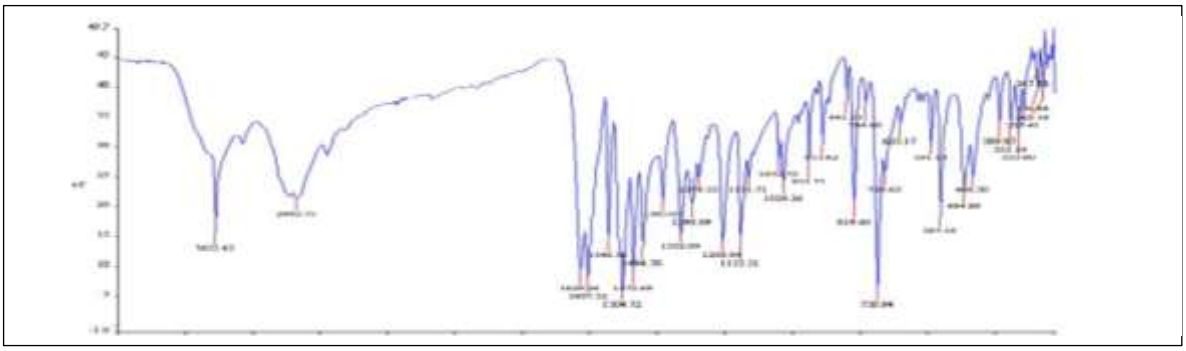


Figure 5: IR spectra of $[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]Cl_2$

Magnetic Susceptibility and Molar Conductivity Measurement

The magnetic susceptibility measurements of the metal complexes at room temperature are paramagnetic complexes. The molar conductivity of mixed ligands complexes with the mentioned metal ions were measured using 10^{-3}M DMSO solvent at room temperature Table 3 . The obtained data indicate that the synthesized mix ligand complexes have electrolytic.

Table 3: Magnetic moment and molar conductivity

Compound	μeff.	λ_M ($ohm^{-1}cm^2mole^{-1}$)
$[Co(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]\ Cl_2$	4.73	72
$[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2]\ Cl_2$	3.14	80
$[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]\ Cl_2$	1.86	78

UV / Visible Analyses

The electronic spectra of the free ligand and glycine were recorded ,the spectra of 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one shows band in 42119 cm^{-1} is attribute to π- π * and band at 26881 due to n-π * .

The electronic spectra of the mix Co(II) complex show there bands at(91457 , 14340 and 17254)cm^{-1} assigned $^4T_1g^F \rightarrow {}^4T_2g^F$ (v_1), $^4T_1g^F \rightarrow {}^4A_2g^F$ (v_2) and $^4T_1g^F \rightarrow {}^4T_1g^p$ (v_3).

The spectra of the mix $[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]\ Cl_2$ displayed there bands at(10882 , 14340 and 22530)cm^{-1}, these transitions assigned to $^3A_2g^F \rightarrow {}^3T_2g^F$ (v_1), $^3A_2g^F \rightarrow {}^3T_1g^F$ (v_2) and $^3A_1g^F \rightarrow {}^3T_1g^p$ (v_3) transition respectively . Octahedral geometry is proposed for Co (II) and Ni (II) complexes by electronic Spectral studies electronic Spectral studies and Magnetic measurements

The spectra of the mix $[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]Cl_2$ complex shows bands in (27.750 and 24096)cm^{-1} these bands corresponded to $^2B_1g \rightarrow {}^2Eg$ and $^2B_1g \rightarrow {}^2A_1g$, the location of these bands together with magnetic moment value (1.86 BM) gave "the square planer geometry around copper [14-16]

Table 4: UV /Visible analysis data

Compound	Wave number (cm^{-1})	assignment	structure
$[Co(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$	91457 14340 17254	$^4T_1g^F \rightarrow {}^4T_2g^F$ (v_1) $^4T_1g^F \rightarrow {}^4A_2g^F$ (v_2) $^4T_1g^F \rightarrow {}^4T_1g^p$ (v_3)	Octahedral
$[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]Cl_2$	10882 14340 22530	$^3A_2g^F \rightarrow {}^3T_2g^F$ (v_1), $^3A_2g^F \rightarrow {}^3T_1g^F$ (v_2) $^3A_1g^F \rightarrow {}^3T_1g^p$ (v_3)	Octahedral
$[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]Cl_2$	27.750 24096	$^2B_1g \rightarrow {}^2Eg$ $^2B_1g \rightarrow {}^2A_1g$	Square Planer

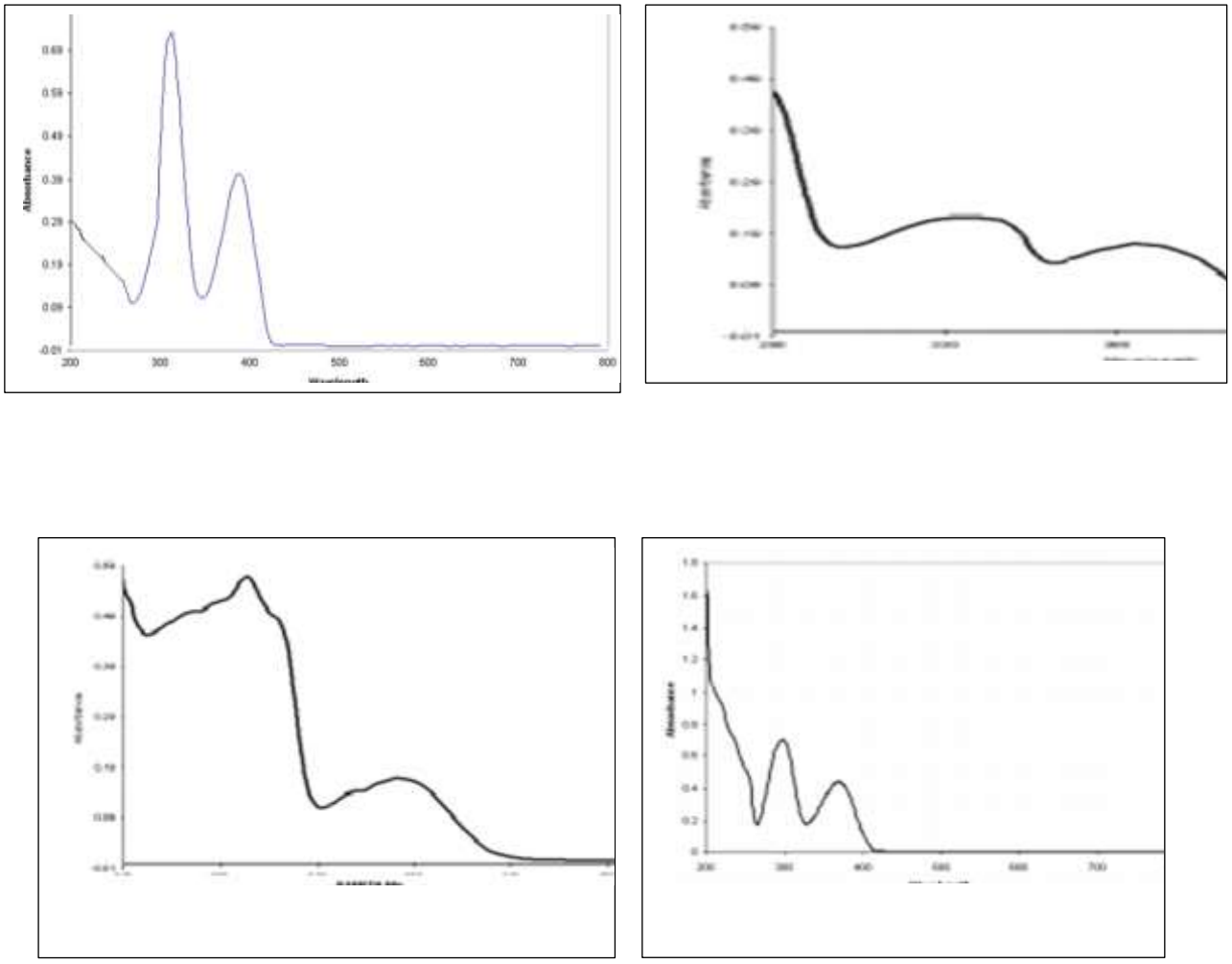


Fig 6: Electronic Spectral data of 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3]thiazin-(3H)- one and its mixed ligands complexes

Biological Activity

The free ligand (L) and its the mix ligand metal complexes were studied against selected types of bacteria and fungus, for bacteria, gram negative as E coli and gram positive as staphylococcus aureus . Table shows anti fungal activity and antibacterial activity of all the prepared compound:-

Table 5 : A ntifungal activity and antibacterial activity of all the prepared compound

Compound	Trichophyton rubrum	Eschriachia-coli	Staph
$C_{15}H_{14}N_2OS$	-	-	-
$[Co(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]\ Cl_2$	++	++	+
$[Ni(C_{15}H_{14}N_2OS)(C_2H_5NO_2)(H_2O)_2]\ Cl_2$	+++	+	
$[Cu(C_{15}H_{14}N_2OS)(C_2H_5NO_2]Cl_2$	++	-	++

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الخلاصة

يتضمن البحث تحضير وتشخيص ليكند جديد باستخدام التحليل الطيفي (FTIR) و Uv-vis و C.H.N. وكذلك تم تحضير معقدات الكوبلت Co(II) والنيكل Ni(II) والنحاس Cu(II) مع مزيج من ليكندات 3- amino-2- methyl -2-phenyl-2H-benzol [e][1,3] thiazin-(3H)- one و Glycine

تم عزل المعقدات المحضره ودراستها باستخدام الطرق الطيفيه FTIR و Uv-vis والامتصاص الذري اللهبي والتوصيليه الكهربائيه المولاريه والحساسيه المغناطيسيه . تمت دراسة الفعاليه البيولوجيه للمعقدات المحضره ضد نوع معين من البكتريا والفطريات ، للبكتيريا ، gram negativeمثل E coli و gram positive مثل a staphylococcus aureus . اضهرت اطياف الاشعه المرئيه وفوق البنفسجيه وقياسات الحساسيه المغناطيسيه والتوصيليه الكهربائيه المولاريه ان الشكل الهندسي للمعقد Co(II) , Ni(II) ثماني السطوح بينما الشكل الهندسي لمعقد Cu(II) مربع مستوي .