Synthesis and Characterization of Complexes Ions Co (II) and Ni(II) with new Ligand

Alaa J.Al-Khkany

Alaag.alkhany@uokufa.edu.iq

Pharmaceutical Chemistry department - Faculty of Pharmacy, Al-Najaf

Abstract

A ligand which from (2S,5R,6R)- 6-{[(2R)-2-amino- 2-(4-hydroxyphenyl)- acetyl]amino}- 3,3-dimethyl- 7-oxo- 4-thia- 1-azabicyclo[3.2.0]heptane- 2-carboxylic acid(Amoxicillin) with 1-naphthol-4- benzene was formulated in this study. The ligand preparation with Co (II)and Ni(II) metal ions was under optimal PH and concentration conditions. The consequences exposed that the complex concentrations were met the terms of Lambert- Beers rule. According to these results ,a mole ratio for the ligand complexes was evaluated as (metal :ligand) and equal to (1:2) . The ligand and its metal compound were characterized by UV- Visible spectrum and IR spectrum .

Keywords: Azo ligand, Idendetification , (Amoxicillin) , metal complexes .

Introduction

The creation of Cd(II), Zn(II), and Hg(II) compounds was investigated with dual new hetrocyclic azo ligands 2-[4-(1-sulfonaphthalene)azo]-L-Histidine (L1) and 2-[7-(1-hydroxy3-sulfonaphthalene)azo]-L-Histidine (L2) derived from coupling reacting of diazonium salt of naphthionic acid and 7-amino-1-naphthol-5-sulfonic acid with L-Histidine in an alkaline ethanolic solution. The fundamental structures of all new complexes have been described from their metal content, magnetic moment measurement, elemental analyses,, molar conductance and FT-IR, UV-Vis. and 1HNMR spectral investigations. Additionally, the composition of complexes was studied following the mole ratio method after setting the finest circumstances (pH and concentration).Beer's law was used over a concentration range (6×10-5 - 8×10-5M). All data explained that the complexes with (1:2) (M:L) metal to ligand, can be prepared as [M(L)2Cl2] and octahedral geometry, that L1 and L2 ligands represents N,N-bidentate chelating agents, corresponding to the azo nitrogen near naphthyl moiety and heterocyclic nitrogen in L-Histidine. The stability constant (β) and Gibbs free energy (ΔG) of the complexes had similarly been studied. Organic efficiency of ligands and their complexes were tested aginst Eschericha coli and Staphylococcus aureus.(1)The absolute necessity to fight some class of tumor is observed as critical health involvements. Consequently, the finding and expansion of operative anticancer agents are directly required. (E)-4-((2-hydroxyphenyl)diazenyl)-3-phenyl-1H-pyrazol-5(4H)-one, HL, and its Ni(II), Pd(II) plus Pt(II) compounds were produced. The organic activity has assessed for antitumor, antioxidant and antimicrobial activity along with DNA cleavage. Their structures have been consigned dependent on the elemental analysis, conductivity, magnetic moment, spectral measurements (IR, 1HNMR, mass and UV–Vis) and thermal analysis. 3D molecular modeling by means of DFT technique verified that the geometrical structures come to an agreement with the recommended experimental ones. The antitumor activity was evaluated against four different cell lines using MTT assay. The ligand HL displayed a potent cytotoxic activity compared with 5-fluorouracil as a reference drug. For metal complexes, the activity order was: Pd(II) > Ni(II) > Pt(II). A notable antioxidant activity for the ligand HL was documented. It was bigger than that of the metal complexes. Antimicrobial experiment results exposed that all compounds were moderate to highly active compared to carefully chosen bacterial strains but sluggish as antifungal except Pd(II) that exhibited an average antifungal activity. Gel electrophoresis presented unimportant nucleases activity for the ligand or its metal complexes even in the existence of H2O2 in case of DNA protection from damage. The antitumor activity of our complexes can be not owing to DNA cleavage but may be stated to a mechanism like that of 5-fluorouracil that restrict with DNA duplication. The current work proposes this ligand use in the design and expansion of new anticancer drugs.(2) Three new nanostructures of cobalt(II) compounds, $(CoL_1)\cdot 0.5DMF\cdot 1.5MeOH$ (**1**), [H_2L_1 = 5-(4-Carboxy phenyl azo) anthranilic acid], $(Co(L_2)_2)\cdot 1.5MeOH$ (**2**), [HL_2 = 5-(4-Carboxy phenyl azo) salicylaldehyde] and $(Co(L_3)_2)\cdot 0.5\,DMF\cdot 0.5MeOH$ (**3**), [HL_3 = 1-(4-Carboxy phenyl azo) 2-naphtol], were made by the reacting H_2L_1, HL_2 and HL_3 with $Co(OAc)_2\cdot 4H_2O$ throughout sonochemical method. Calcination of the nano-sized complexes **1**–**3** produce Co_3O_4 nanoparticles at 450 °C under air environment. The nanostructures have been distinguished by X-ray powder diffraction (XRD) and Scanning Electron Microscopy (SEM). Thermal stability of compounds **1**–**3** was considered by thermogravimetric (TG) and differential thermal analyses (DTA)(3) new azo-dyes, 3-phenyl azopentane-

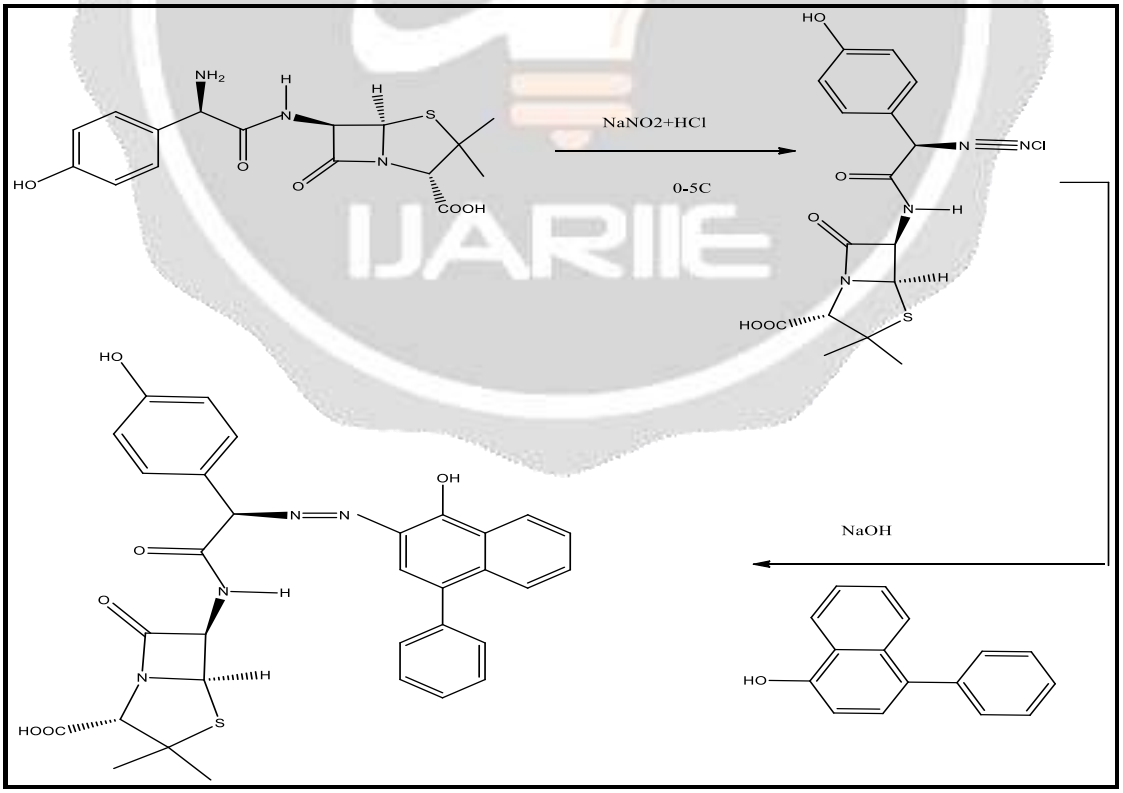
2,4-dion (LA), 3-(4-nitro phenyl azo)-pentane-2,4-dion (LP), 3-(2-nitro phenyl azo)-pentane-2,4-dion (LO) in addition to 4-(1-acetyle-2-oxo-propyl azo)-benzene sulfonate sodium (LS), were formulated from, aniline, 4-nitroaniline, 2-nitroaniline and sulfanilic acid with acetylacetone, respectively. Reacting these new dyes with acetate salts of copper(II), nickel(II) and cobalt(II) in molar ratios of 1:2 have been achieved to create azo metal (II) complexes with the common stoichiometry; CuL2, CoL2 and NiL3 in complexes. Structure of azo dyes was typified using FT-IR,1H NMR,13C NMR, UV-Visible and also the corresponding metal (II) complex have been distinguished by FT IR, UV-Visible and CHN and XRD analysis methods. Elemental analysis and spectral data specified that the dye as a ligand with dual teeth, N and O, represents a bidentate ligand. Changes in absorbance maxima of azo ligands against those resultant complexes have as well investigated. Correspondingly, in this work, singular value decomposition (SVD) as a chemometric method was used to conclude the Cu(II), Co(II) and Ni(II) compounds with the stated ligands in methanol by UV-Vis spectrophotometry. SVD method verified the realization of CuL_2, CoL_2 and NiL_3 compounds.[4]

Experimental

All chemicals were of highest purity within 4000 to 400 cm-1 range by means of KBr disc .Electronic spectrum has measured by Shimadzu UV-visible spectrophotometer UV-1600 A using ethanol solvent. The apparatus of Stuart melting level has been employed to determine the melting level of ligand and its compounds. Measured electrical molar conductivity has been accomplished at room temperature, at concentration of 10^{-3}M employing conductivity bride 31A version.

Formulation and depiction of ligand :-

A diazonium solution has been organized by dissolving [5] (3.6gm) of (Amoxicillin) in (30 cm3) of water and (3 cm3) of concerted hydrochloric acid. The categorized solution has refrigerated to zero C°, handled with (15 cm3) of aqueous (1.0 M) sodium nitrate drop by drop, and enthused for quarter hour. 1-naphthol-4- benzene (2.2gm) has been liquefied in (150 cm3) of ethanol , and 50 cm^3 of 10 % sodium hydroxide and 50 cm3 of 10 % sodium carbonate had been combined. The prepared diazonium solution has been at that point inserted drop by drop for coupling. After the combination was stimulated for sixty minutes at 0-5C°, it was converted to acid with 6 pH dilute hydrochloric acid. The precipitate has filtered off, and recrystallized two times from aqueous ethanol (70%), and at that time dried up in the oven at 70C° for some hours. The output was 69% of reddish brown powder. This ligand structure is depicted below..



2-amino [(2S,5R,6R)- 6-{[(2R) - 2-(4-hydroxyphenyl)- acetyl]amino}- 3,3-dimethyl- 7-oxo- 4-thia- 1-azabicyclo[3.2.0]heptane- 2-carboxylic acid azo]- . 1-naphthol-4- benzene*(APPA)*

Effect of pH

The influence of acidity of the absorbed magnitudes of the compounds has investigated in the 50% (v/v) ethanolic to water by varying the pH magnitude of the solution. The results are displayed in Figures 1-2, that revealed the finest absorbing of Co(II) and Ni(II)) structures are within 5 to 11 range. The substance shaped stable compounds with metal ions at similar pH.

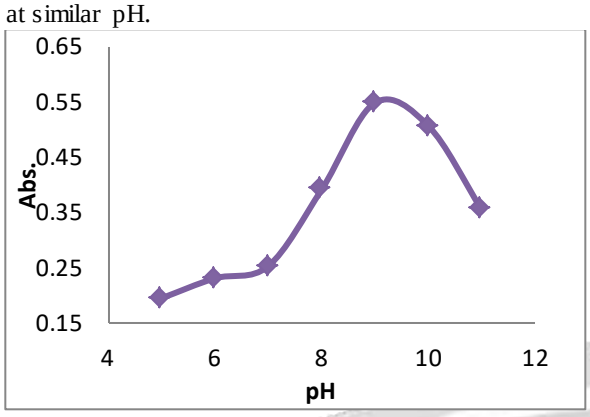


Figure 1:-The pH consequence on Co(II) compound

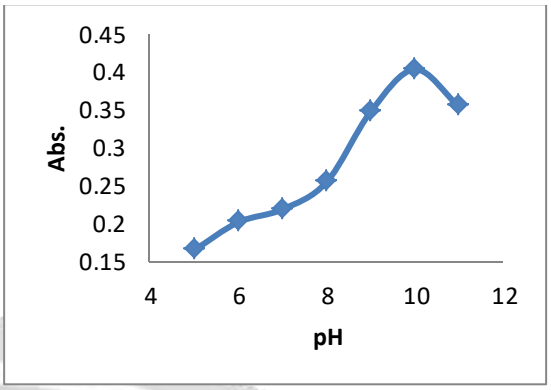


Figure 2:-The pH consequence on Ni(II) compound

Metal: Reagent ratio

The ratios of metal: reagent [6] of compounds has computed using molar ratio process at stable pH and concentration at greatest absorbance wavelengths. The consequences have specified in Table 1. The reagent has been realized to formulate (2: 1) chelates with completely metal ions.

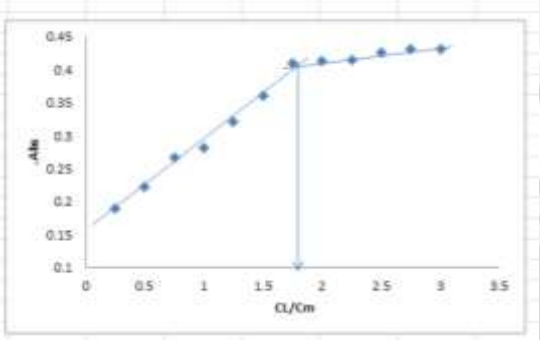


Figure 3:- The (M:L) mole ratio of Co(II) with (APPA)

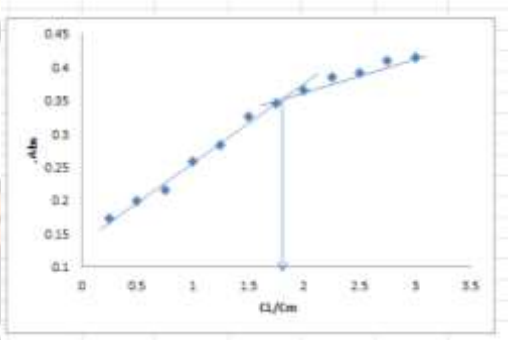


Figure 4:- The (M:L) mole ratio of Ni(II) with (APPA)

Formulation of complexes

All compounds had organized by inserting (2mmol) from ligand liquefied in heated ethanol (50 cm^3) and appended drop by drop with exciting astoiciometric amount of (1:2) for Co(II)and Ni(II) chloride salt softened in (10 cm^3) heated purified water. This combination has been warmed to 50C° for one hour. Then, it was kept in excess of night. The made solid item was filtered off, cleaned with distal water and desiccated by anhydrous $CaCl_2$.

Rudimentary analyses are compatible with ligand formula and its compounds are depicted in Table 1.

Table 1) Physical properties and analysis of ligand and its complexes

No.	Complex	Color	m.pC°
1	$C_{34}\ H_{34}\ N_4O_6S$	orang	256 – 257
2	$(C_{34}\ H_{34}\ N_4O_6S)_2\ Co$	green	301
3	$(C_{34}\ H_{34}\ N_4O_6S)_2\ Ni$	green	272

Absorbance spectra

U.V- visible Spectra:

Absorption spectra of the ligands in U.V. and visible region is (275 nm) that is attributed to $\pi \rightarrow \pi^*$ transition as a result of presence of conjugation in the ligand molecule. (472nm)[7] is related to $n \rightarrow \pi^*$. The peaks of absorption spectra ligand has gotten with the absorption maxima because of d-d transition. This transition is La-Porte prohibited transition, so it is weak in intensity. The location of ligand bands are shifted that may be due to interface of ligand with metal ion .The spectra of Co(II) compound absorbance band is gotten at λmax 648nm and Ni(II) complex absorption band is obtained at λmax 650nm. The band positions in the spectrum of metal compounds are according to the expected distorted octahedral in Table (2).

Table 2: The optimal pH values, concentration and wavelength (λ max) values of metal complexes

Metal ions	Optimal pH	Optimal wave length (λ_{max})nm
Co(II)	9	648
Ni(II)	8	650

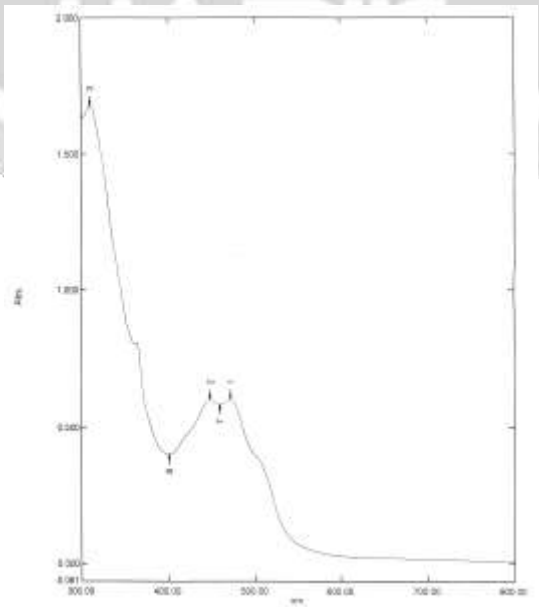


Figure 5:- UV.-Vis. Spectrum ligand

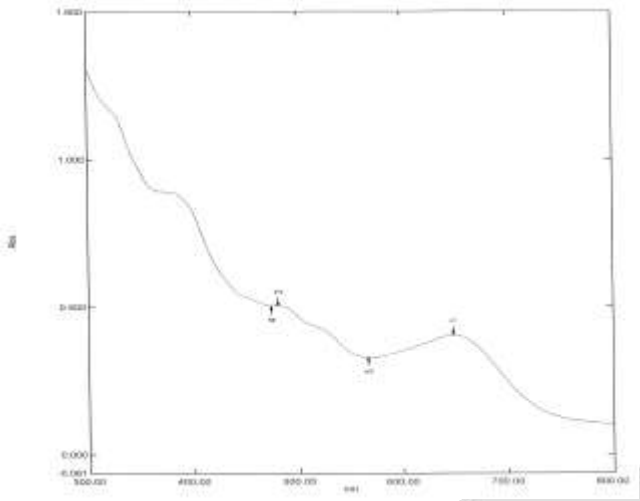


Figure 6:-UV.-Vis. Spectrum of Ni(II) complex with ligand (APPA)

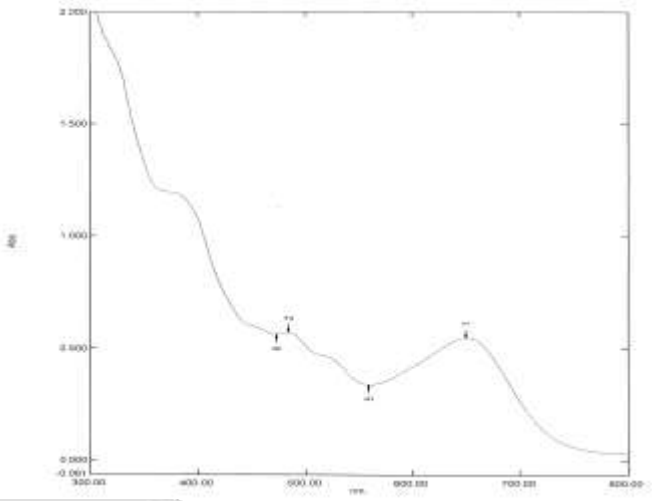


Figure 7:-UV.-Vis. Spectrum of Co(II) complex with ligand (APPA)

IR spectrum analysis:

The prepared ligands and their Co (II) and Ni (II)-azo compound gave good yield. Many spectral studies carried out such as :

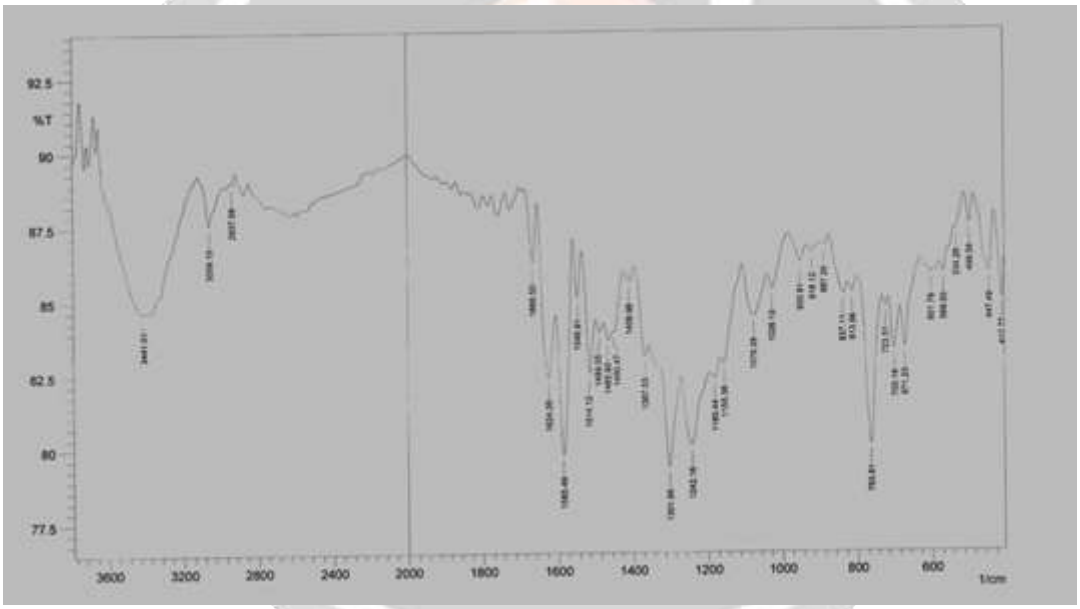


Figure 8: FT-IR bands of (APPA)

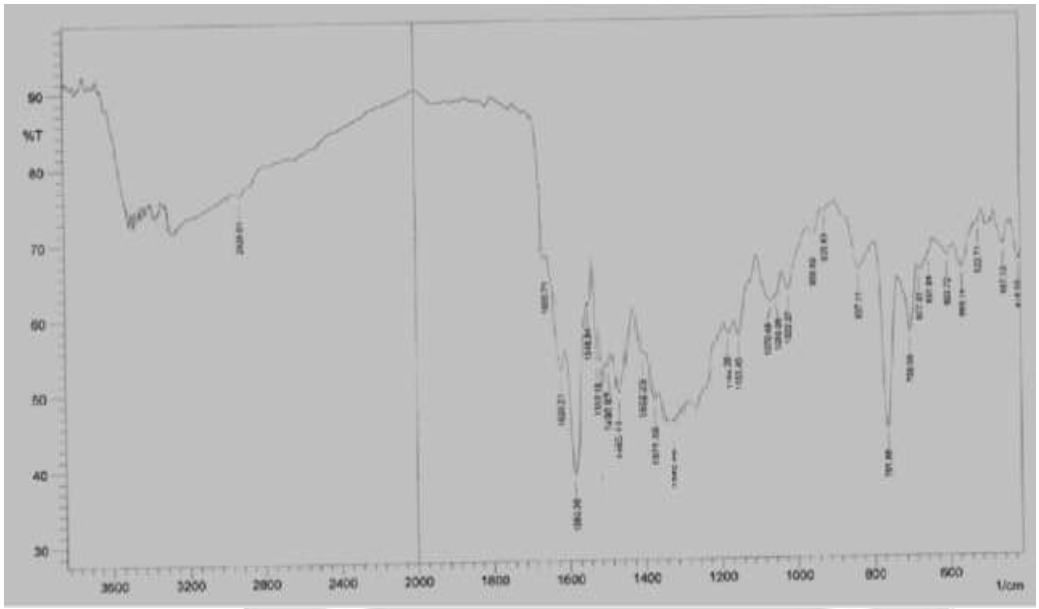


Figure 9: FT-IR bands of ion compound of Co (II) with (APPA)

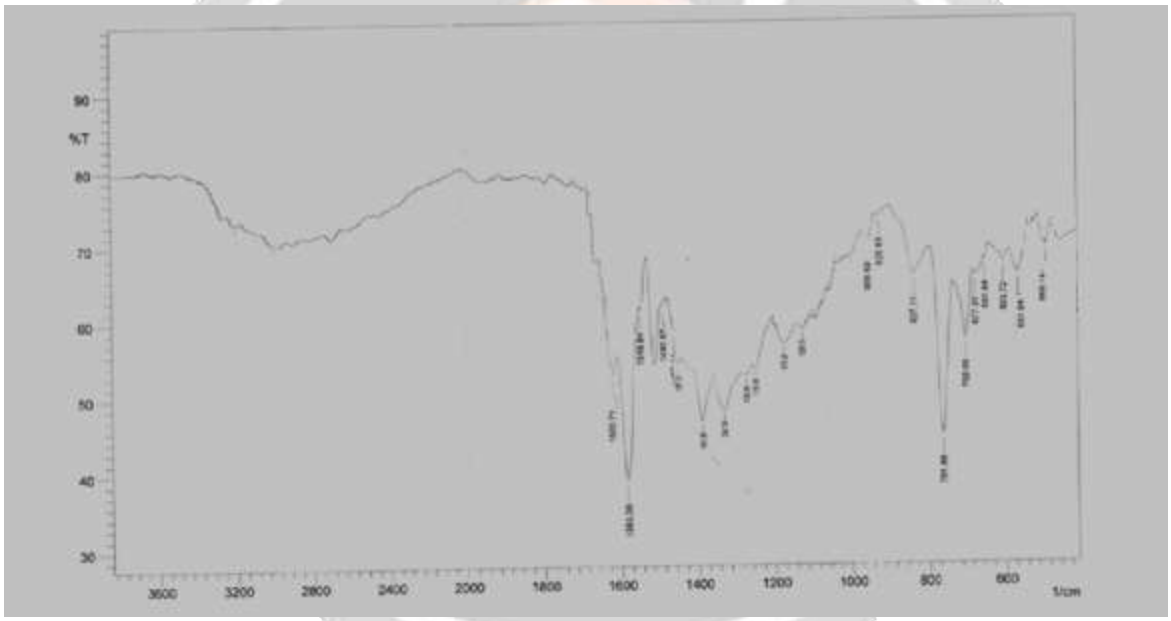


Figure 10: FT-IR bands of ion compound of Ni (II) with (APPA)

Table 3:- Characteristic IR absorbance spectra of APPA spectra besides its compounds in cm^{-1} [8,9].

Complex	υ(O─H)	υ(C═N)	υ(N═N)	υ(M─N)
$C_{19}H_{17}N_7O_5S$	3441.01	*1624.21*	*1512.19*	-
$(C_{19}H_{17}N_7O_5S)_2Co$	-	*1620.21*	1371.39	475.13
$(C_{19}H_{17}N_7O_5S)_2Ni$	-	1619.71	1400	498.10

Conductivity measurements

The compounds illustrate the measured conductivity magnitudes of 11.1 to 12.9 $S.cm^2. mol^{-1}$ in ethanol solution. These magnitudes are signifying nonionic arrangement of these compounds [10]. The conductivity magnitudes are recorded in Table 4.

Table 4: Conductivity measurements of complexes in Ethanol

Complex	Λm ($S.mol^{-1}.cm^2$)in Ethanol
[Co L_2 Cl_2]	11.1
[Ni L_2 Cl_2]	12.9

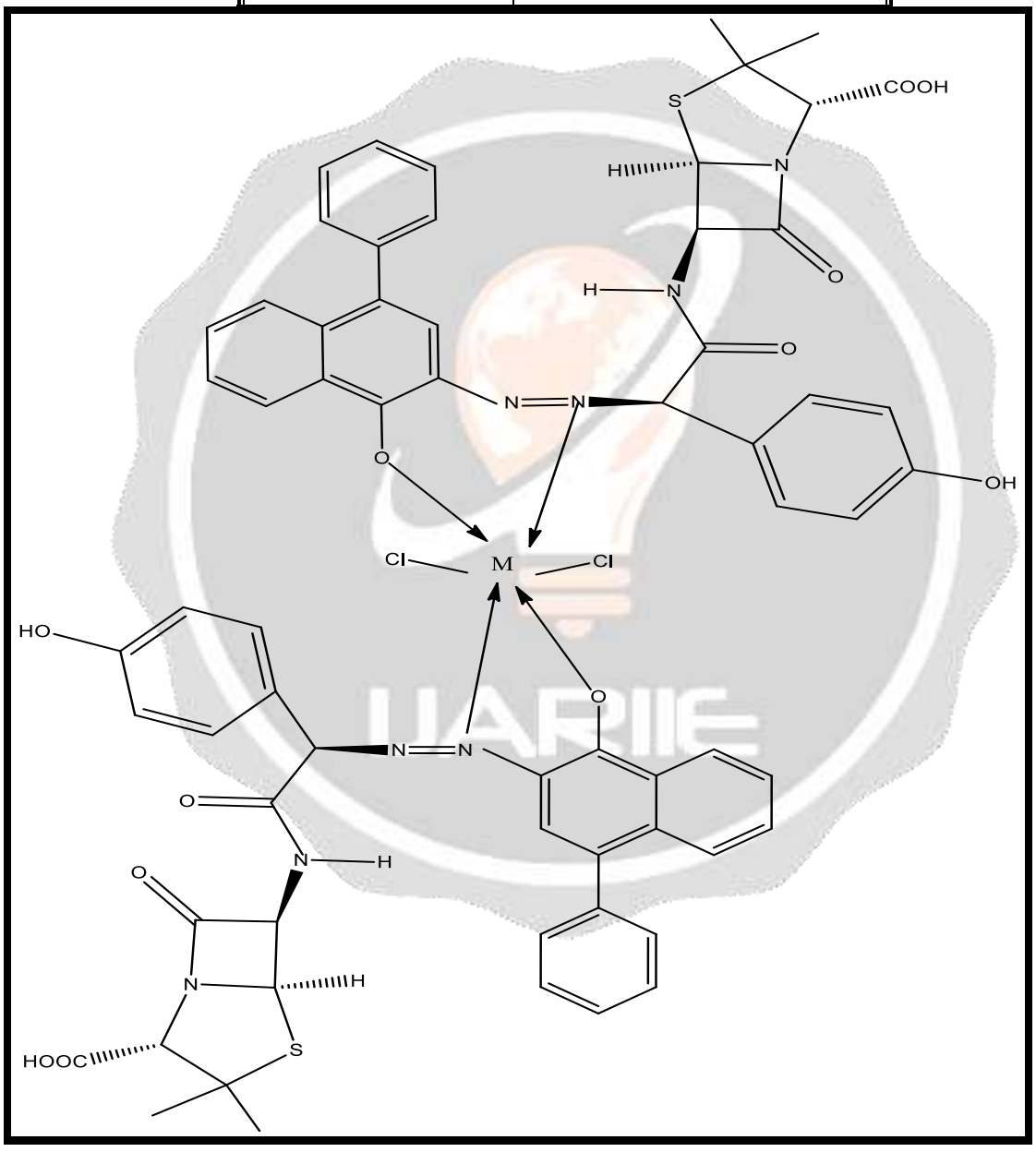


Figure11:-The structural formula of complex Ni(II) and Co(II)

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