Synthesis and Spectrochemical Studies for Some Transition Divalent Metal Complexes with New Azo Ligand Derived from Pyrimidine ring

Ibtihal Kadhim Kareem and Ziena Mohammad Hatem
Chemistry Department/ Faculty of Education for girls/ University of Kufa/ Iraq
Ibtihal.dosh@uokufa.edu.iq

Abstract:-

The New Heterocyclic ligand 4-[(2,4,6-trioxohexahydropyrimidin-5-yl)diazenyl]benzoic acid (L) was prepared to give the final Didentate Heterocyclic compound with different donor atom system. The Prepared ligand was characterized using FTIR, ^{1}H-NMR, C.H.N. Elemental analysis and UV.-Vis. techniques.

Some chelating metal complexes were Prepared with Co (II), Ni(II) and Cu(II) ions and characterized by FTIR, UV.-Vis. ,Molar conductance, C.H.N. Elemental analysis and magnetic susceptibility. The Purity of azo dye ligand and prepare complexes were tested by Thin – Layer Chromatography (TLC) Technique . The complexes were found to have the general formula $[M(L)_2Cl_2]$ where M= Co (II), Ni(II) and Cu(II) . The FTIR results demonstrated that the coordination site were the azo Nitrogen atom and Oxygen atom of Carbonyl group of the azo ligand . The electronic spectral and magnetic measurement data indicated that the complexes exhibited octahedral geometry were suggested for there complexes, (M:L) ratio was (1:2) for all prepared complexes while the conductivity measurements shows non – electrical properties.

Keywords: New Heterocyclic azo ligand , Transition metal complexes , Pyrimidine ring.

Introduction

Heterocyclic azo compounds are a class of molecules that contain hetero atom in ortho position of azo group (-N=N-) (1) .The chemistry of Heterocyclic azo compounds had the subject of much investigation not only for their medicinal values and physiological significance but also for the fact that all Heterocyclic azo compounds with at least one hetero-atom (acting as bonding site) in their structures, can assist as potential azo ligands for complex formation mainly with transition metal ions(2). At present, the numbers of Heterocyclic azo compounds are used in analytical chemistry substantially(3). The application of these azo dyes in spectrophotometry is based on the color resulting from reaction with most of transition metals in order to form stable chelates (4). The simplest six-membered N-heterocyclic, Pyridine, has been attending for many years as a ligand with metal ions and the chemistry of coordination of the derivatives of pyridine is currently well-documented(5). The investigation of coordination behavior of azo compounds with heterocyclic having more than one hetero atom such as imidazole, pyrimidine and pyrazine (6). By complex formation with transition and non-transition metal ions in order to form chelate complexes containing heterocyclic azo compounds, the electrons on the hetero-atom actively participate in the formation of stable metal-ligand bonds(7).

The wide spectrua of Pyrimidine derivatives and their several chemical properties had led to their progressively extended use as originators for the preparation of many biologically active compounds.(8), and possess a wide spectrum of pharmaceutical properties and had study for activity against fungal,(9-11) and bacterial(12,13) infections .Therefore the antimicrobial activity determination of these type of azo ligands were already been performed by the diameter of zone of inhibition method as well antimicrobial activity(14).

Experimental

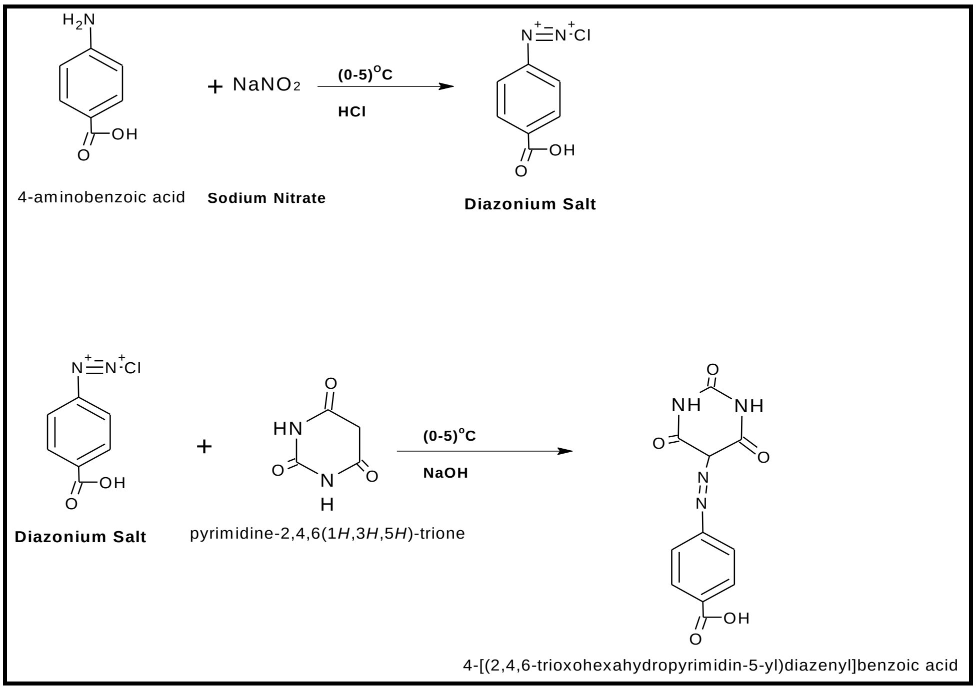
Materials and physical measurements

All chemicals used were of highest purity (BDH or Fluka) and used with out further purification.

Elemental analysis was carried out by means of micro analytical unit of (Euro2012, EA300A,Italy) C.H.N element analyzer .Absorption spectra were recorded using Shimadzu UV-Vis 1700 spectrophotometer, for solution of the complexes in aqueous ethanol at room temperature. Using 1cm quartz cell. IR spectra were recorded with FT-IR-8000 Shimadzu, in the range of (4000-400) cm^{-1} using KBr disc. Auto .Electrical conductivity measured by Digital conductivity Series Ino.Lab720 with solute concentration of 10^{-3}M in DMSO at room temperature.. ,the metal percentages were determined using atomic absorption technique by Shimadzu -AA-6300/Flame.

Synthesis of Heterocyclic azo ligand (4-[(2,4,6-trioxohexahydropyrimidin-5-yl)diazenyl] benzoic acid)

The ligand prepared by dissolving (1.37 g, 0.01 mol) of 4-aminobenzoic acid in 30 ml of distilled water and 5ml of concentrated hydrochloric acid, then the filtrated solution was cooled below 5 °C. To this mixture a solution of (0.75g, 0.01 mol) of sodium nitrate in 20 ml of distilled water was added drop wise at 0-5 °C. This diazonium solution was added drop wise to a 500 ml beaker containing (1.280 g, 0.01 mol) of pyrimidine-2,4,6(1H,3H,5H)-trione dissolved in 150 ml of alkaline ethanol. The mixture was allowed to stand over night and acidified with dilute hydrochloric acid to pH = 7.0. The crude dye was collected by filtration and recystallized twice from ethanol and then dried in the oven at 60 °C for two hrs (5). the melting point of the ligand was (210°C) and The structural formula of our ligand is shown in Scheme 1 .



Scheme 1: Preparation of the ligand(L)

Synthesis of complexes

The chelate complexes have been synthesized by dissolved (0.552 gm, 0.002 mol) of ligand (L) in 10 ml ethanol and then (0.001 mol) of metal chloride, M= Co(II), Ni(II), or Cu(II) dissolved and added drop wise with vigorous stirring to the ligand solution. The reaction mixture was left over night then the complexes were filtered off washed with distilled water, then with ethanol and dried in desiccators over anhydrous $CaCl_2$. Table.1 collects the some physical properties and analytical data for those complexes.

Table(1):- Some Physical properties and analytical data of the ligand (L) and its complexes.

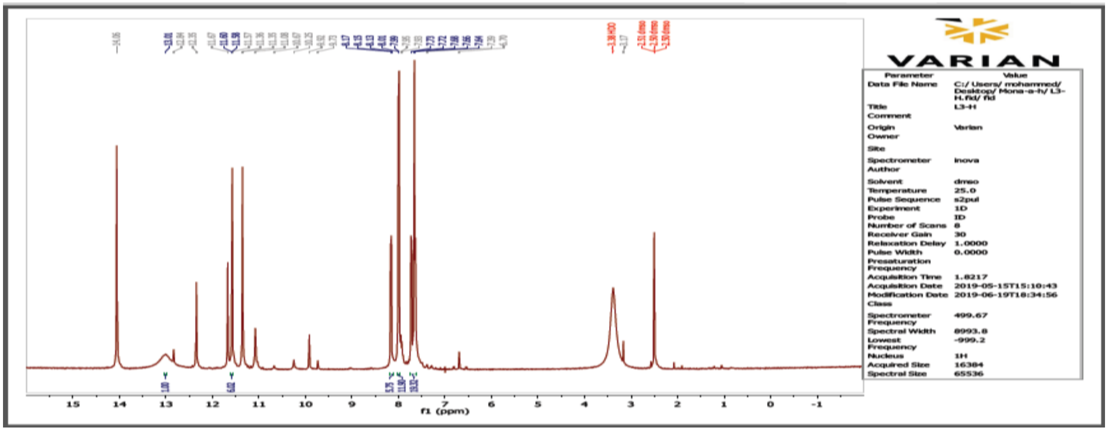
No.	Compound	Color	m.p C°	Found (Calc.)%			
				C	H	N	M
1	$C_{11}H_8N_4O_5$	Light Yellow	210	47.283 (47.826)	2.179 (2.89)	19.780 (20.028)	—
2	$[Co(C_{11}H_8N_4O_5)_2Cl_2]$	Reddish Brawn	290	38.299 (38.695)	1.965 (2.345)	15.891 (16.416)	8.188 (8.638)
3	$[Ni(C_{11}H_8N_4O_5)_2Cl_2]$	Reddish Brawn	300<	38.301 (38.709)	1.767 (2.346)	16.054 (16.422)	8.311 (8.605)
4	$[Cu(C_{11}H_8N_4O_5)_2Cl_2]$	Yellow	285	37.900 (38.435)	1.679 (2.329	15.878 (16.306)	8.949 (9.251)

Results and discussion

The metal complexes are insoluble in water and soluble in methanol ,ethanol, DMF, DMSO, acetone and $CHCl_3$.

^{1}H-NMR Spectrum of the Ligand (L)

The H^1-NMR Spectrum of the ligand was recorded in DMSO-d6 . The H^1-NMR spectrum of the ligand shows the following signals :δ 6.70-7.66 (m,4$H_{\text{benzene ring}}$) , δ3.12(m,1$H_{\text{pyrimidine ring}}$),12.84 (s,1H,O=C-OH $_{\text{Carboxylic acid}}$), δ 11.08-11.35(d,2H,$NH_{\text{barbituric acid}}$). As showed in(Fig1)(15,16).



Parameter	Value
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Author	
Solvent	dmso
Temperature	25.0
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Experiment	1D
Probe	ID
Number of Scans	8
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Modification Date	2019-06-19T18:34:56
Class	
Spectrometer Frequency	499.67
Spectral Width	8993.8
Lowest Frequency	-999.2
Nucleus	1H
Acquired Size	16384
Spectral Size	65536

(Fig.1):- 1H-NMR Spectrum for Ligand

Electronic spectra and Magnetic susceptibilities

The Electronic spectra of the ligand (L) (Fig.2) and its metal complexes were studied and the spectral data were listed in table (2) . The UV-Vis spectra of the Heterocyclic azo ligand was characterized mainly by three absorption peaks at (203 and 236) nm assigned to($\pi \longrightarrow \pi$ *) and at (310)nm assigned to (n $\longrightarrow$ π^*) these electronic transition were shifted towards higher or lower frequency in the electronic spectra of the prepared complexes , confirming the coordination of the ligand with metal ions .

The electronic spectrum of Co (II) complex in (Fig.3) showed three absorption peaks , at (15243 , 17301 and 25947)cm^{-1} , There are assigned to **($^4T_1g(F)$ $\longrightarrow$ $^4T_1g(F)(V1)$, $^4T_1g(F)$ $\longrightarrow$ $^4T_1g(P)(V3)$** and Charge Transfer (C.T.)

respectively. This suggests that the complex octahedral (17). The magnetic moment of Co (II)complex(4.37 B.M) suggest a high – spin octahedral configuration .The high values of (Meff) may be due to orbital contribution.

The electronic spectrum of Ni (II) complex in (Fig.4) showed one absorption peak at ((25316 cm^{-1}) assigned to ligand to metal charge transfer (LMCT) Transition(18),Suggesting an octahedral geometry around Ni(II) complex. The magnetic moment value of Ni(II) complex(3.32 B.M) suggesting an octahedral environment.

The electronic spectrum of Cu (II) complex in (Fig.5) showed one absorption peak at (25974 cm^{-1}) assigned to charge transfer spectrum. This peak was a good agreement of Octahedral geometry, The magnetic moment value (1.70B.M) suggesting an octahedral environment. (19).

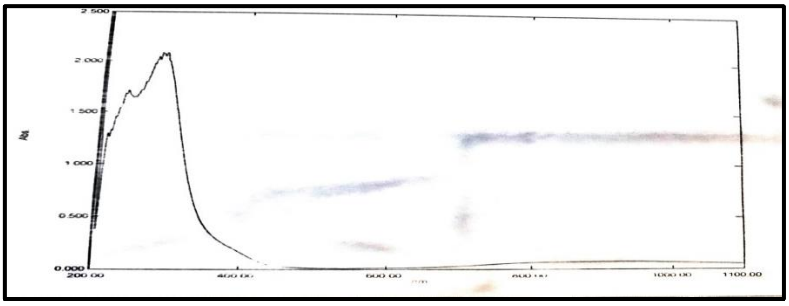
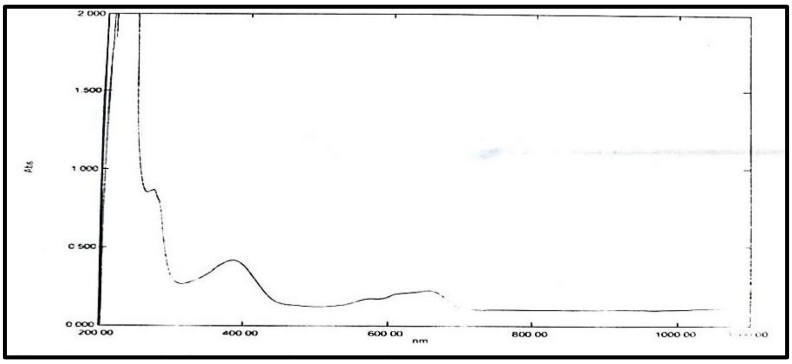
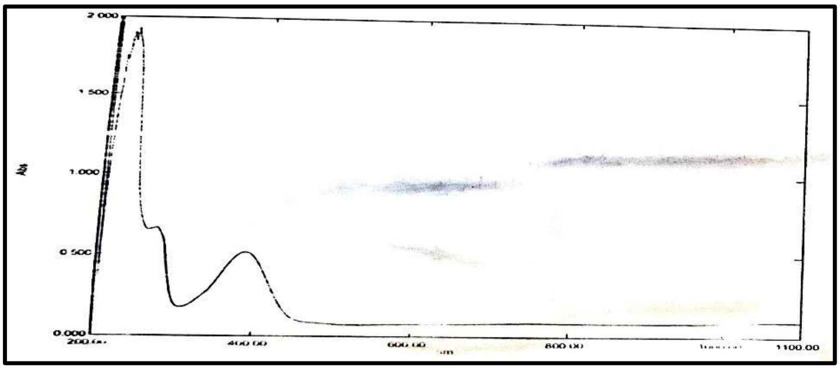


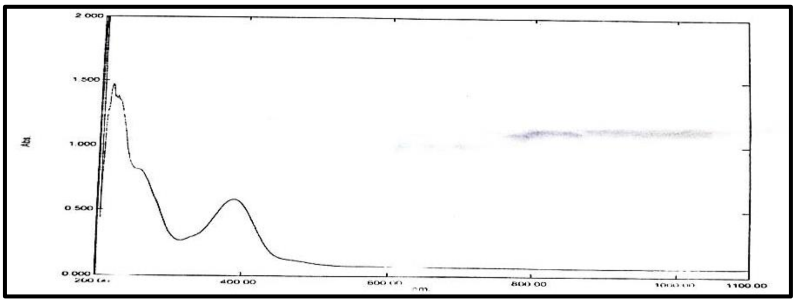
Fig. (2):- Absorbance spectrum of ligand (L_1)



Figure(3):- Absorbance spectra of Co(II) complex



Figure(4):- Absorbance spectra of Ni(II) complex



Figure(5):- Absorbance spectra of Cu(II) complex .

Table (2):-The electronic spectra of the ligand and its chelate complexes.

Compounds	$\lambda_{\text{Max.}}$ nm(cm^{-1})	Transition	Magnetic susceptibilities
$C_{11}H_8N_4O_5$	203nm (49261 cm^{-1}) 236nm (42.372 cm^{-1}) 310nm (32258 cm^{-1})	$\pi \longrightarrow \pi^*$ $\pi \longrightarrow \pi^*$ $n \longrightarrow \pi^*$	
$[Co\,(C_{11}H_8N_4O_5)_2Cl_2]$	385 nm (25974 cm^{-1}) 578nm (17301 cm^{-1}) 656nm (15243 cm^{-1})	C.T $^4T_1g(F) \longrightarrow {}^4T_1g(P)$ $^4T_1g(F) \longrightarrow {}^4T_2g(F)$	4.37
$[Ni\,(C_{11}H_8N_4O_5)_2Cl_2]$	395nm (25316 cm^{-1})	C.T	3.32
$[Cu\,(C_{11}H_8N_4O_5)_2Cl_2]$	385nm (25974 cm^{-1})	C.T	1.70

Infrared spectra

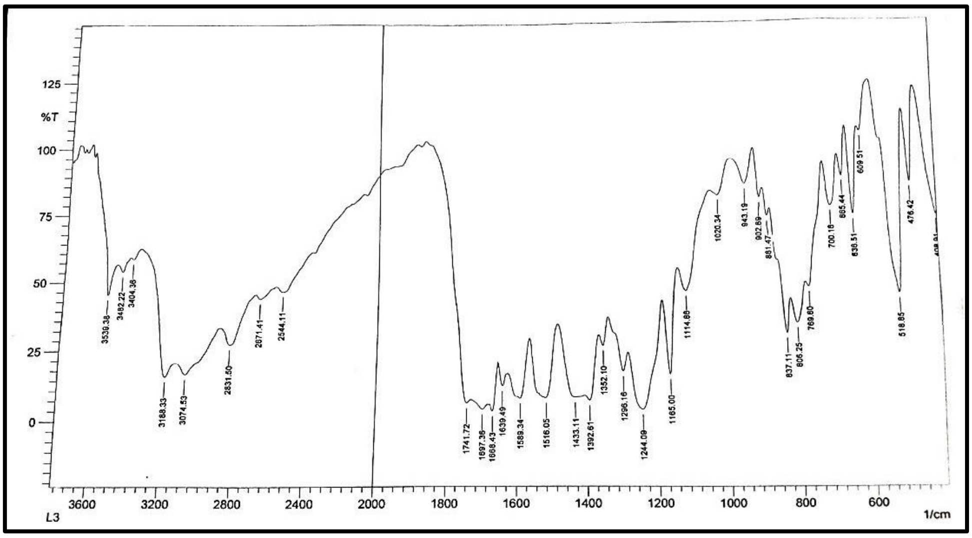
The infrared spectra of the free ligand (L) and its complexes with Co (II),Ni (II) and Cu(II) are given in Table.3. These spectra are complicated owing to the extensive overlap of number of bands arising from υ(C═O), υ(N═N) and other bands due to the pyrimidine ring which appeared in the region below 1700 cm^{-1}. The comparison between the IR spectral data of the free ligand with that of its complexes are illustrated as follow:-

The Band in IR spectrum of free ligand at (1741 and 1697) cm^{-1}, assignable to stretching vibration υ (C=O) groups of pyrimidine ring respectively these bands are in stable positions in the ligand and its complexes (5,20). The band at (1668) cm^{-1} in IR spectrum of free ligand can be attributed to the stretching vibration of Carbonyl group υ (C=O)in pyrimidine ring, which was shifted to higher or lower frequency in the IR spectra of the complexes. These shifting indicated the coordination of the ligand with metal ion via oxygen atom (21) The appearance of a new non-ligand band around (432- 420) cm^{-1} in IR spectra of complexes with L_1 due to υ (M-O) substantiates (13) This is further substantiated by the presence of a new band around (557-516) cm^{-1} respectively assignable to υ(M-N)(15). It is concluded that the ligand behaves as a didentate ligand coordinated to the metal ions via oxygen atom of carbonyl group of pyrimidine ring and nitrogen atoms of azo group (N=N) as showed in Figuer (5,6,7 and 8).

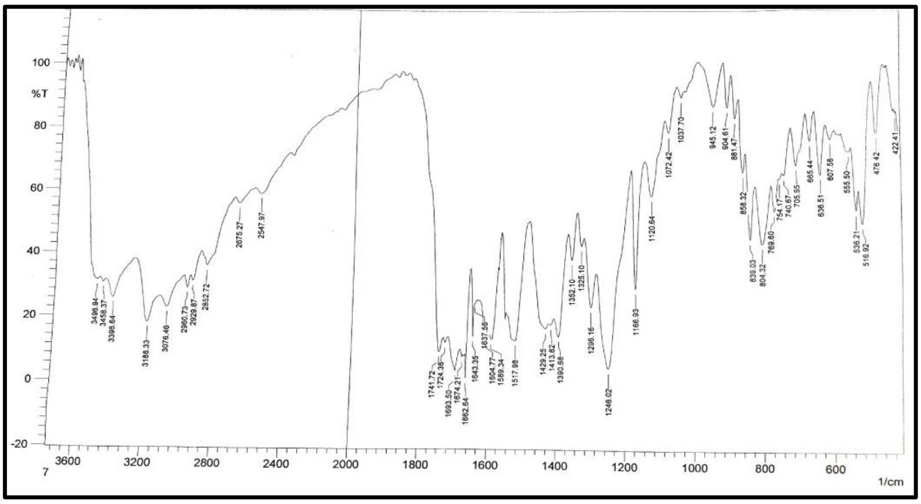
Table (3):- Characteristic IR absorption bands of the ligands L_1 and its complexes in cm^{-1} units.

Compound	**(O-H) carboxylic**	**υ(N-H-)**	**(C-H) aroma.**	**N=N**	**υ(HO-C=O) carboxylic and υ(C=O) Pyrimidine Ring**	**υ(C=O)**	**υ(M─N)**	**υ(M─O)**
$C_{11}H_8N_4O_5$	2544-3539	3188	3074	1516	1741& 1697	1668	---	---

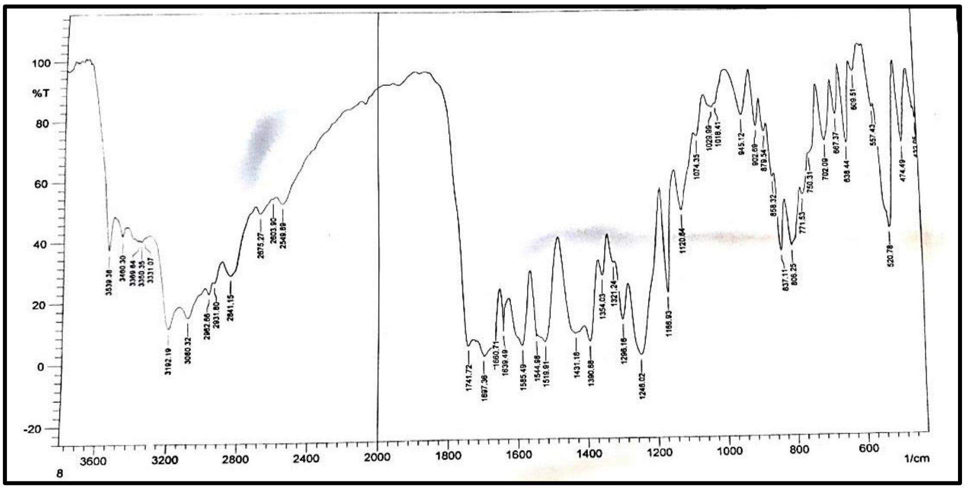
[Co ($C_{11}H_8N_4O_5)_2Cl_2$]	2547-3496	3188	3076	1517	1741& 1697	1674	536	422
[Ni ($C_{11}H_8N_4O_5)_2Cl_2$]	2549-3539	3192	3080	1519	1741& 1697	1660 .	557	432
[Cu ($C_{11}H_8N_4O_5)_2Cl_2$]	2553-3489	3186	3078	1521	1739& 1693	1641.	516 .	420



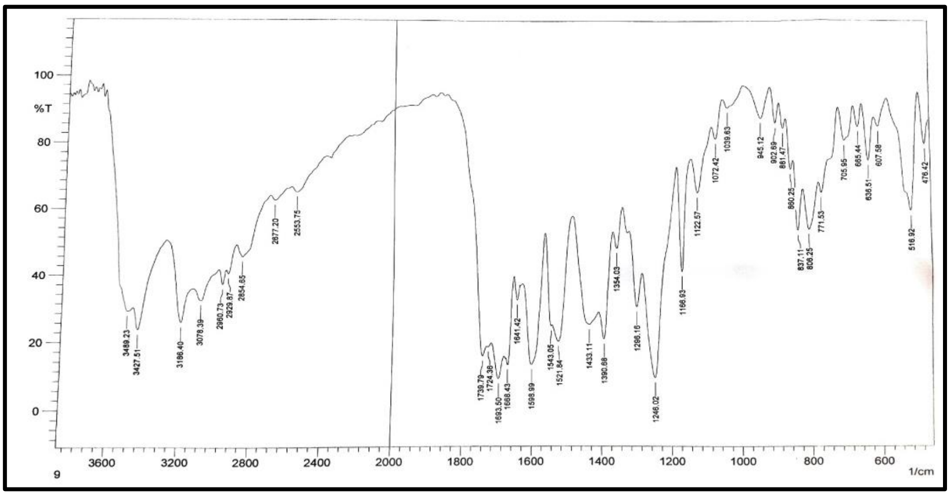
Figure(5):- IR spectrum of the ligand (L)



Figure(6):- IR spectrum of ion complex of Co(II) with the ligand (L)



Figure(7):- IR spectrum of ion complex of Ni(II) with the ligand (L)



Figure(8):- IR spectrum of ion complex of Cu(II) with the ligand (L)

Conductivity measurements

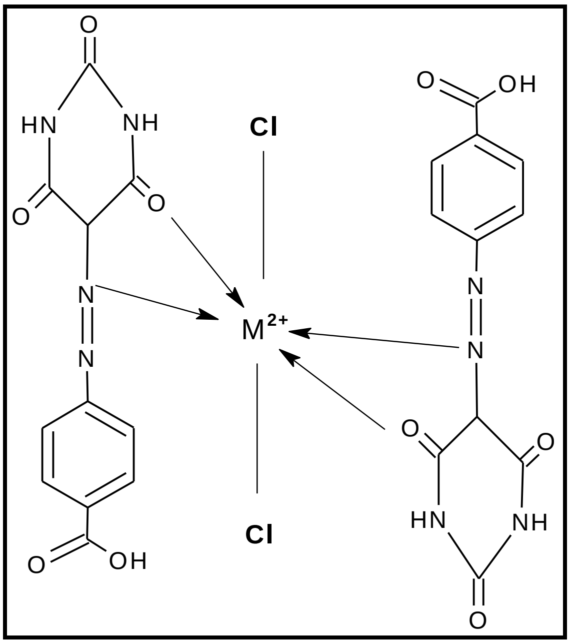
All complexes showed the conductivity measurement values ranging between (9.67 – 11.74) S.cm^2. mol^{-1}in DMSO at room temperature, these values indicating Nonionic structure of these complexes (22).The conductivity values are listed in table 4.

Table(4):- Conductivity measurements of complexes

Complex	Conductivity S.cm^2.mol^{-1}
[Co ($C_{11}H_7N_4O_5)_2Cl_2$]	9.67
[Ni ($C_{11}H_7N_4O_5)_2Cl_2$]	10.32

[Cu ($C_{11}H_7N_4O_5)_2Cl_2$]	11.74

According to the results the coordination number of all metal ions is found to be six with bonding through the Nitrogen atom of azo group and the Oxygen atom of carbonyl group of heterocyclic pyrimidine ring. The structural formula of prepared complexes is most probably octahedral geometry shown in fig.9.



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

Figure(9):- The proposed structural formula of Co (II), Ni(II) and Cu (II) with the ligand (L)

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