Synthesis and Charecterization of Metal Complexes of 2- [(1-methyl-1H-Tetrazole-5yl) thio]-N'-[(1E)-(4-fluoro phenyl) methylene] acetohydrazide

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Abstract

The ligand 2-[(1-methyl-1H-Tetrazole-5yl)thio]–N'-[(1E)-4-fluro Phenyl)methylene] acetohydrazide Was synthesized and the complex with Metal per chlorates of Cu(II) were synthesized and charecterized on the basis of IR, and H^1 NMR , UV-Visible molar conductivity, EPR ,Cyclic voltammetric analysis and Magnetic susceptibility Measurements. Spectral data reveal that ligands chealated with metal through Nitrogen-atoms. Magnetic susceptibility measurements favors octahedral co-ordination for Cu(II) metal complexes.

Key words: Transition metal complexes, Tetrazole-2-Thiol derivatives,Fluro benzene.

Introduction

Heterocyclic compounds containing five membered Tetrazole nucleus possess a diverse useful biological effects. In particular compounds bearing the Tetrazole nucleus are known to have anti-inflammatory and anti-oedema activities (1). Copper shows considerable bio-chemical actions as an essential trace metal or as a constituent of various exogenously consumed compounds in human beings.Present study in copper is arising from their varied use as antibacterial ,anti viral , fungicidal ,anti- helminthic activity,anti inflammatory,anti tumour agents,enzyme inhibitors and chemical nucleases[2-6] . Numerous complexes of copper and tetrazole derivatives are known and there is still enormously increasing interest in the copper complex of the tetrazole and its derivatives as ligands (7-10).Knowledge of the correct structure of these derivatives may throw light upon their biological, Physical and chemical properties and mechanisms of their mode of actions.

Materials and Methods All the chemicals and solvents used were of analar grade. All the reagents used for the preparation of Schiff bases were obtained from sigma Aldrich. These products were used with out further purification.

Instrumentation

The electronic spectra in Ethanol were recorded on perkin elmer lambda 35-2B-spectrometer. Molar conductance measurements were conducted by using 10^{-3}M solutions of the complexes in acetonitrile, on Elico 82-33 conductivity bridge at room temperature. Magnetic susceptibility measurements were carried out on a guoy balance at room temperature using mercuric thiocyanato cobaltate (II) as the calibrant. Dia-magnetic corrections were applied in compliance with Pascal`s constant. FT-IR spectra are recorded in KBr medium on a Perkin Elmer spectro photometer in wave Spectrometer number region 400cm^{-1}-4000 cm^{-1}, H^1 NMR spectra were recorded on Bruker spectrometer employing TMS as internal reference and DMSO – d6 as solvent.

Syntheses of 2-[(1-methyl-1H-Tetrazole-5-yl) thio]-N`-[(1E)-(4-Fluro-Phenyl) methylene] acetohydrazide

Anhydrous sodium carbonate (55 mmol) was added to a solution of [(1-methyl-5-mercapto-Tetrazole) Thiol] in acetone (50 ml). To the reaction mixture, ethyl bromo acetate (100 mmol) was added slowly at room temperature under stirring. The progress of the reaction was monitored by thin layer chromatography using a mixture of ethyl acetate and n-hexane (3:7) as eluent. The by product sodium bromide was removed by filtration. The mother liquor containing the products was concentrated under vacuum to remove acetone and residual acetone was removed using methanol to give its thio acetate derivative. The residue was used for next step as such.the residue thus collected was dissolved in methanol (30ml), to the clear solution Hydrazine hydrate (200 mmol) was added and refluxed. The progress of the reaction was monitored by thin-layer chromatography using a mixture of chloroform and methanol (9:1) as eluent. The reaction mass was cooled to 0 degree centigrade for crystallisation. On filtration and washing with chilled methanol acylated hydrazine derivative of heterocyclic compound was synthesised by the following procedure disclosed above, use of Fluro benzaldehyde yielded 2-[(4-Fluro phenyl)methylene] acetohydrazide.

Synthesis of metal complexes

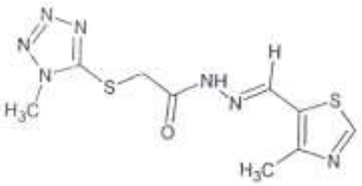
The metal complexes were prepared by mixing of (50ml) ethanolic solution of metal salt with the 50ml ethanolic solution of Schiff base in 1:6 (metal:ligand) ratio . The resulting mixture was refluxed on water bath for 5-9 hours. A coloured product appeared on standing and cooling the above solution. The precipitated complex was filtered and washed with ether and recrystallised with ethanol several times and dried over anhydrous $CaCl_2$ in a dessicator. Yield 70.5% IR (KBr pellets v,cm^{-1}) 3086 cm^{-1} , 1601 cm^{-1} ,1387 cm^{-1} , and 2017 cm^{-1} .

Results and discussion

Ligand

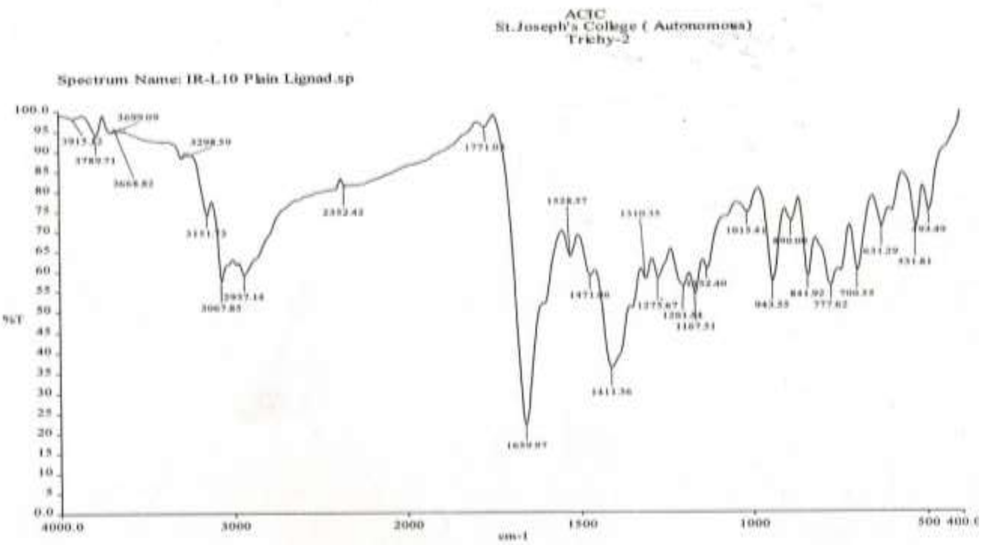
Melting point of the ligand is 185.2^{0}C and it is soluble in methanol , DMSO and in aceto nitrile.The structure of the ligand is given below.

changeto L2



IR spectral studies:

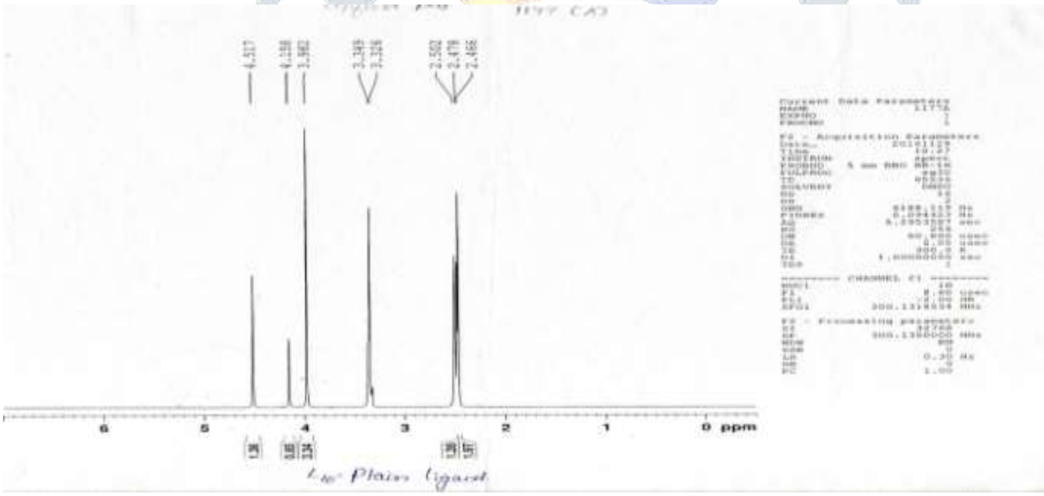
IR spectrum of the ligand exhibits sharp peak at 3401 cm^{-1} (NH-stretching), 765 cm^{-1} (NH wagging), 624 cm^{-1} (C-S), 2938cm^{-1} (aliphatic C-H), 1660 cm^{-1}(Amide (I) band), 1574cm^{-1}(C=N), 1203 cm^{-1}(C-N), 1037 cm^{-1} (N-N), 1478 cm^{-1} (aliphatic CH_3 deformation)



FT-IR Spectrum of plain ligand

^{1}H-NMR spectrum data (Change to plain l10 NMR) Pl.check the values

Plain ligand

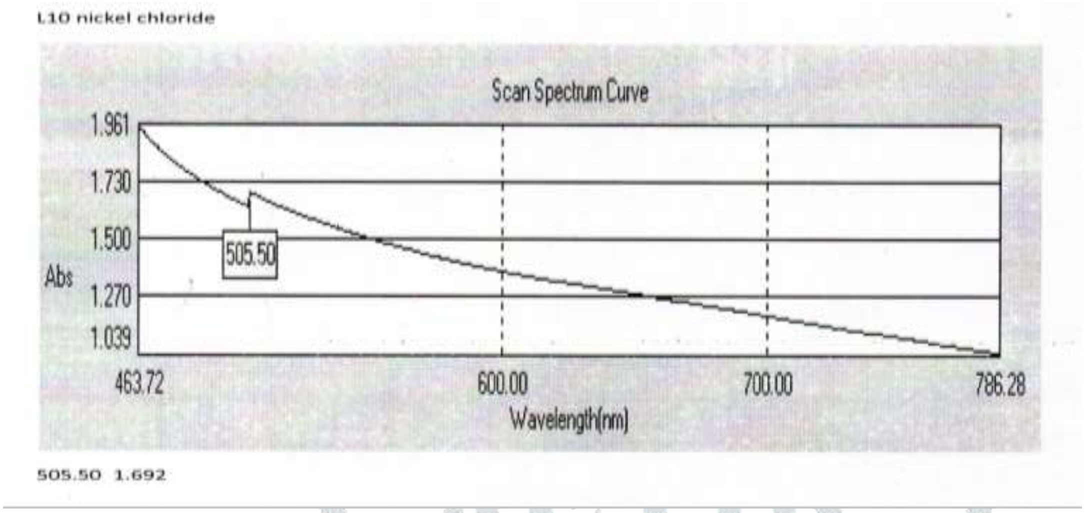


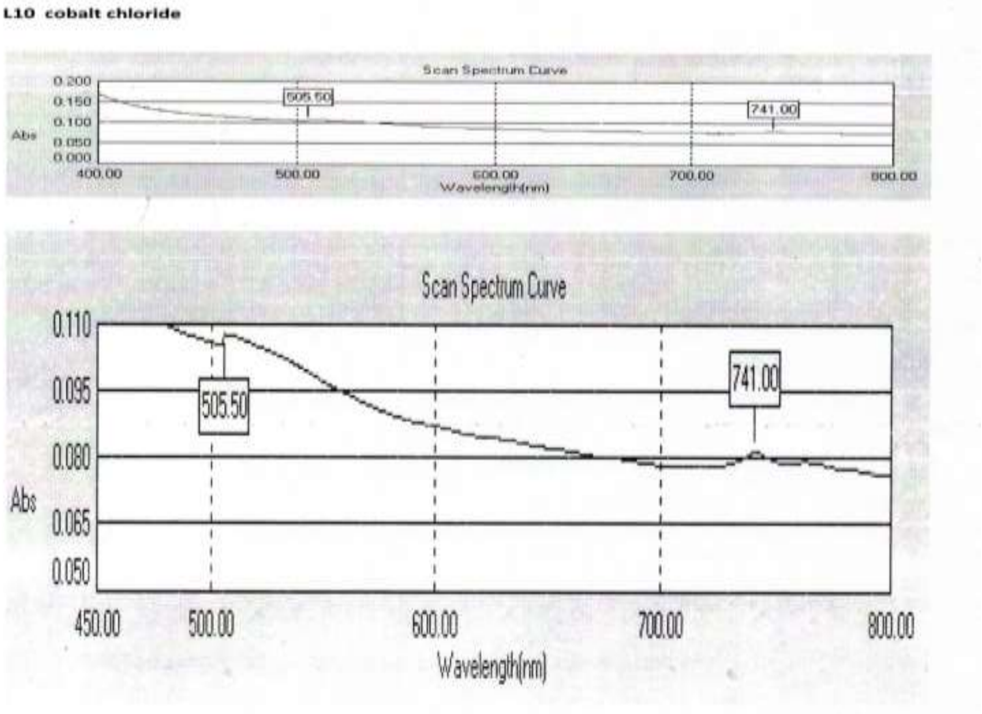
NMR spectrum of the plain ligand showed ^{1}H-NMR 4.56 (2H,SCH2), and 7.54-7.62 (2H,d), 8.48(1H,S,Tetrazole)

Metal complexes: Pl check transitions

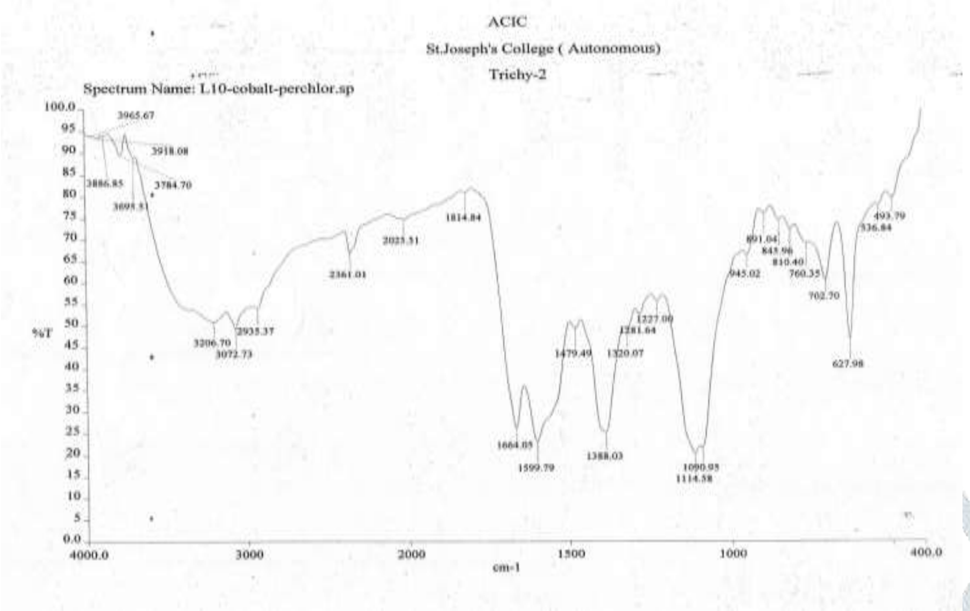
Conductance studies shows that the chloride complex of Cu (II) is non electrolyte. The magnetic moment of the complex is in consistent with the expected values for the given geometry of complexe The bluishgreen colour of copper chlorate complex and strong absorption at 27,322 cm^{-1} suggests 4T1g(F) -> 4T1(g)(P) transition of octahedral geometry. The copper complex of the ligand shows three Transition bands at 23,923 cm^{-1}, 19802 cm^{-1} , 16286 cm^{-1} Corresponding to the following Transitions……. The magnetic moment of 2.8 BM confirms the above geometry.

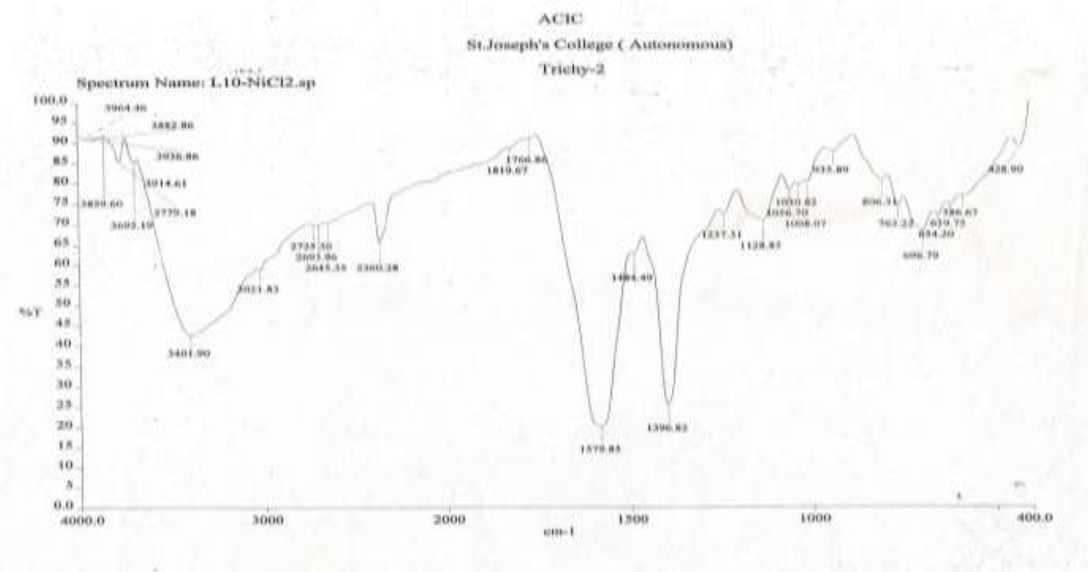
Elecronic spectra of metal complex

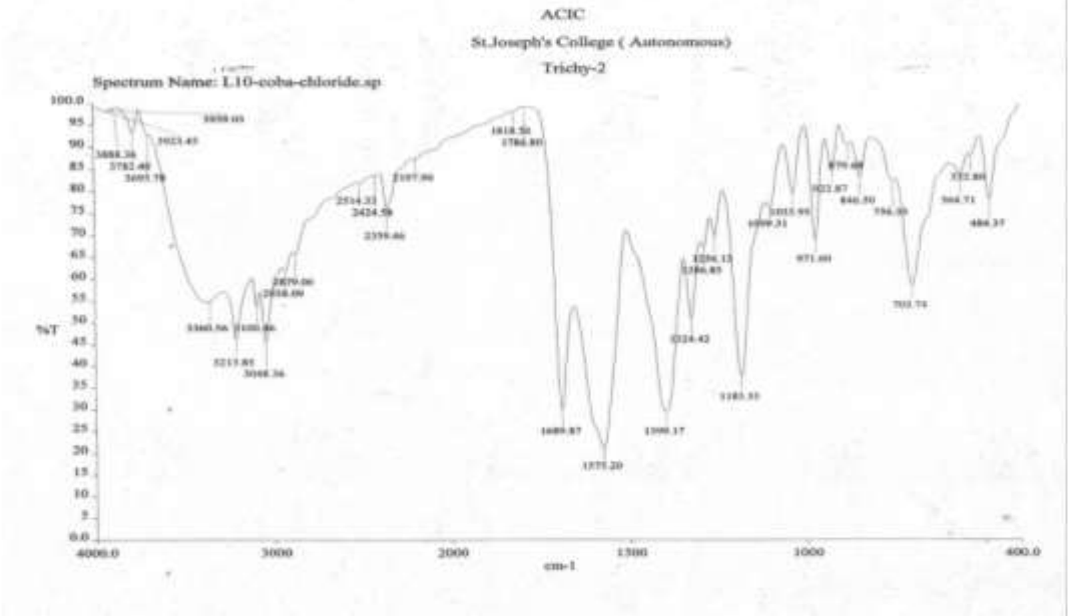




IR Spectra of Metal Complexes :





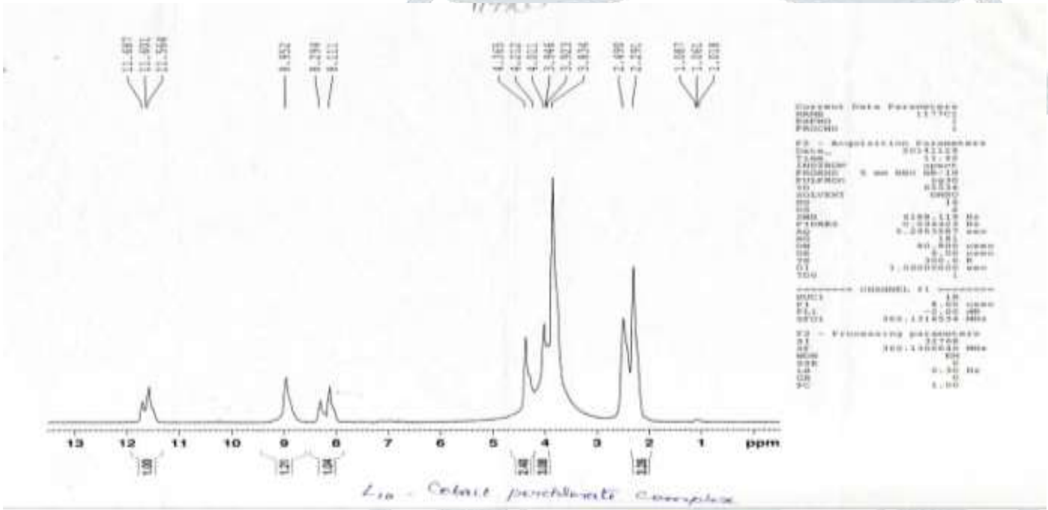


IR spectra

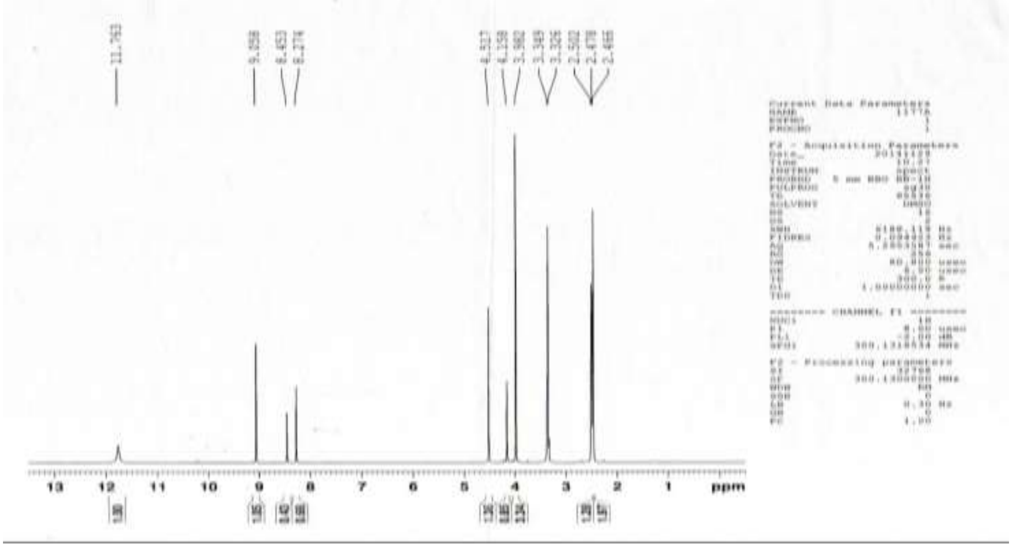
Comparison of the IR spectrum of the ligand with IR spectra of the copper complex suggest that the co-ordination of the, peptide linkage N-with metal ion. The positive shift of amide (I) band (-NH stretch) suggest the co-ordination of the peptide linkage` N` with the metal ion and the oxygen of the peptide linkage is not involved in the co-ordination. The negative shift of the ligand in the form of feeble vibration in NH bending 1532 Cm^{-1} and the negative shift of C-N stretch at 1203 Cm^{-1}-1228 Cm^{-1} confirms the co-ordination of peptide linkage N- with the metal ion. The stretch in between 535 cm^{-1} - 540cm^{-1} which is found only in the IR spectra Of Complex is assigned to M-N stretch.The other stretches are not very much affected in the spectra of complex in comparison with that of ligand .

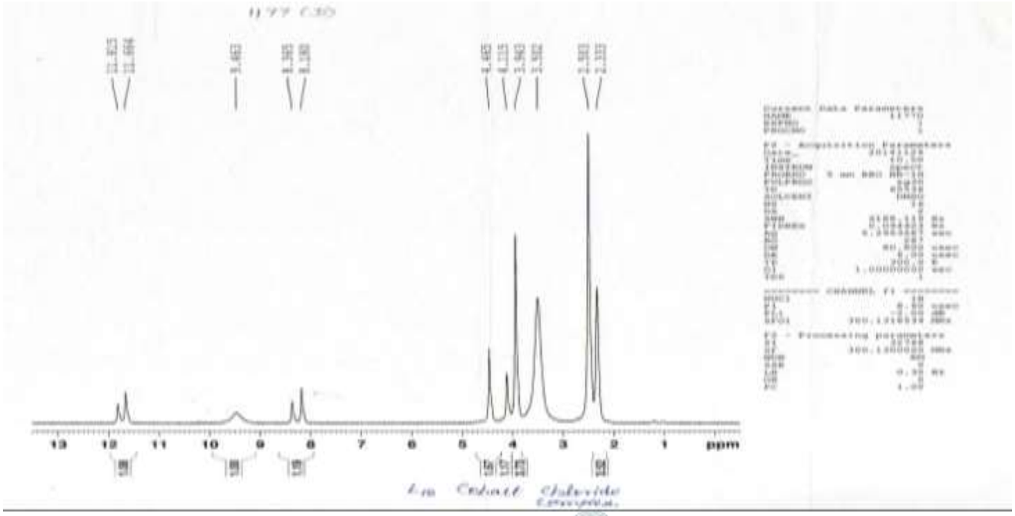
^{1}H NMR spectra

^{1}H NMR spectra of copper (II) complex



Pl. Change the dia to l 10 cu ii

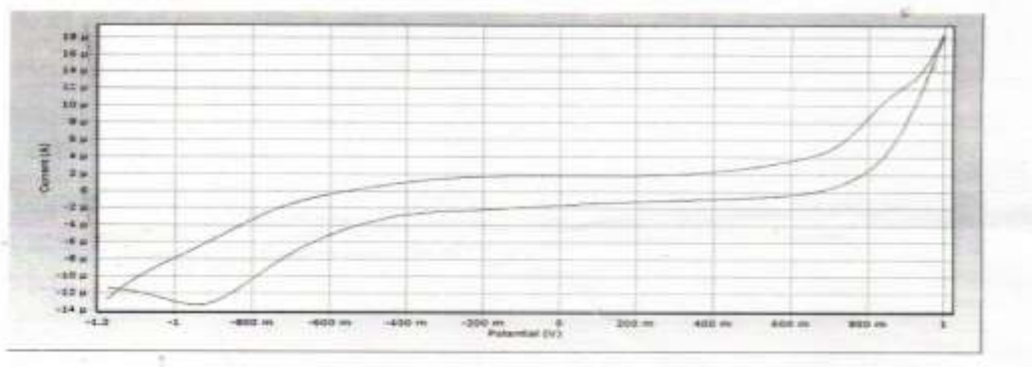




The complex exhibited ~H NMR signals besides the signals of aromatic Protons 7.5 -7.997 ppm and Tetrazole protons 9.04 - 9.26 ppm.The downfield shifts of 11.771 to 11.939 in the case of copper per chlorate confirms –NH Co- ordination.

Cyclic voltammetry:

yclic voltammogram of cobalt chloride



The cyclic voltammogram recorded for the ligand cobalt chloride complex shows an oxidation peak at 630mv and a reduction peak at 1100mv. The presence of single peak indicates the electron transfer , and as the difference between oxidation and reduction peaks are very small it is confirmed that one electron transfer is involved and it is reversible.

Conclusion

The formation of these complexes were confirmed by analytical, IR, UV-Visible, H NMR spectral data, Magnetic moments and cyclic voltammetry analyses . The probable geometries for Co (II), Ni(II) are octahedral and in the formation of Cobalt Chloride complex one electron transfer is involved and it is reversible.

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