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PREPARATION AND IDENTIFICATION OF COMPLEXES IONS CO(II), CU(II) LIGAND 2- (BENZOTHIOZOLYL AZO-4- BENZYL PHENOL

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ABSTRACT

In this paper, chelate compounds of Co(II) and Cu(II) as a result of making reactions for those ions with the ligand 2-(Benzothiozolyl azo-4- benzyl phenol has been presented. The preparing procedure for compounds has been performed by setting up the optimal concentration and pH conditions. UV-Vis investigation of the compound solutions have been examined for various pH and concentration magnitudes based on the rule of Lampert-Beers. The compound geometries can be figured out in relation to mole ratio technique that can be found by the spectroscopy identification of the compound solutions. The gotten ratios of metal: ligand has been (1:2) for every compound. Ligand detection has been done via UV-Vis and IR measurements. The measured conductivity consequences prove that the ligand has been tridentate. Furthermore, the anticipated complexes structures of Co(II) and Cu(II) ions were octahedral.

KEYWORDS: Spectral studies, Thiazolyl, coblute, copper.

INTRODUCTION

A derived ligand from 4,5-diphenyl imidazole was equipped, this ligand has been prepared from Co (II),Ni(II),Cu(II), Zn(II),Cd(II) metal ions within optimal concentration and PH conditions. The results of these complex concentrations are agreed with Lambert Beers rule. In view of that, a mole ratio was determined for the mentioned ligand complexes as (metal:ligand) ratio of (1:2). The ligand plus its metal compounds have been characterized using UV-Vis and IR spectroscopy investigations, the H1 NMR was depicted a coordination with compound preparations and the magnetic sensitivity results of metal compound ions was

shown the octahedral figure for them.[1] The pyrimidine based azo-linked Schiff base ligand, 5-benzoyl-1-((E)-(2-hydroxy-3-methoxy-5-((E)phenyldiazenyl)benzylidene)amino)-4-phenylpyrimidin-2(1H)-one (HL), and its transition metal (II) compounds have been produced and described by means of ^{1}H-NMR, ^{13}C-NMR. FT-IR, fundamental analysis, MS, UV-Vis, magnetic susceptibility, molar conductance and thermal analysis methods. The obtained conductance data indicate that all metal compounds comprise non-electrolytic behavior. Square pyramidal structure for Pd(II) and octahedral structure regarding all other synthesized compounds has been deduced from the electronic absorbance spectrum and magnetic susceptibility measurements of the compounds. A test of the important IR bands of the effective ligand groups and the solid compounds explains that HL has been synchronized based on ONO metal ions tridentate mode. Besides, the absorbance and emission features of the azo-azomethine based ligand and its compounds have been studied. The acquired results of ligand fluorescence emissions plus its metal (II) compounds rely on the transition metal ions category. Their derivatives have shown reasonable Stokes' shift magnitudes within 44 and 107 nm range. Every complex has displayed excellent photostability results. additionally, antioxidant, antimicrobial and pBR322 plasmid DNA cleavage behavior have been studied. Each complex has exhibited high-quality DPPH• (1,1-diphenyl-2-picrylhydrazyl) major scavenging action and $[MnL_2]•H_2O$ and $[NiL_2]•H_2O$ complexes have shown outstanding metal chelating nature. The entire complexes have investigated dual strand DNA cleavage natures.[2] Azo naphthol 1-[(4-Antipyril)azo]-2-naphthol (4-AAP-2-N) ligand has organized with three chelate complexes by creating reaction this ligand with Co (II),Ni(II) and Cu(II) metal ions. The preparing procedure was carried out by setting up the required concentration circumstances of U.V- visible spectrum of the complex solutions that were tested for assorted concentrations and pH. The complex structures have been realized in accordance with mole ratio process that have gotten from the spectroscopy investigation of the compound solutions. The acquired metal: ligand ratios are (1:2) for each complex ion. (UV-Vis) absorbing spectrum of ethanolic complex solution depicted bath-chromic shift, unlike the free ligand. The tested IR spectrum of the chelating complexes may be a sign of that an organization among the metal ions and the organized ligand turns out efficiently. The conductivity and the metal ions percentage of the complexes have been measured. As well, the structural complexes arrangements of Cu (II) and Co(II). ions are proposed to be as octahedral.[3] The preparation and spectral identification of metal compounds for Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions with new heterocyclic azo dye as ligand 2-[2^{-}- (1- Hydroxy - 4- Chloro phenyl) azo]-

imidazole (HClPAI) have been synthesized by making reaction for adizonium chloride salt solution of 2-amino -4- chloro phenol with imidazole in alkaline ethanolic solution. Azo dye ligand and their metal complexes were identified as a result of analytical data, ^{1}H NMR, Mass spectrum, IR, Electronic spectral data, XRD, SEM, thermal analysis (TG-DSC-DTG), magnetic susceptibility and molar conductance. The elemental analysis of the metal compounds confirm the stoichiometry of the type $[M(L)_2]$ Cl in the case of M = Cr(III), Fe(III), Co(II) and $[M(L)_2]$ in the case of M = Mn(II), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) and L = azo dye ligand. Measured Molar conductance for arranged metal compounds demonstrated 1:1 electrolyte for Cr(III), Fe(III) and Co(III) ions and non-electrolyte for other metal compounds. The resultant data explain that the azo dye ligand acts as tridentate and coordinates to the metal ion via nitrogen atom of azo group that stands for the utmost imidazole molecule, nitrogen atom of azomethine group of heterocyclic imidazole ring and phenolic oxygen. Octahedral setting was proposed for every one of metal compounds as in.[4] This work presents synthesis, characterization, and application of several metal (II) compounds with (E)-2-hydroxy-N/-((thiophen-2-yl)methylene)benzohydrazide (H2L). Prepared compounds have recognized by elemental, thermal, FT-IR, UV–Vis, 1H NMR, and XRD analysis, in addition to molar conductivity and magnetic moment tests. Changes in FT-IR and 1H NMR spectra of hydrazone ligand upon coordination indicated that the ligand acts in the same way as a monoanonic ligand with ONS contributor positions. Kinetic values have been evaluated for all thermal degradation stages of the ligand and its compounds using ‘Coats–Redfern’ method. All results confirm that all prepared compounds have 1:2 metal-to-ligand stoichiometry except Zn(II) complex, which has 1:1 metal-to-ligand stoichiometry. The antimicrobial activity for compounds was investigated. The antimicrobial activity results revealed that Zn(II) complex (1) has a high-quality potency in opposition to gram positive (E. coli) and gram negative bacteria (P. vulgaris) in comparision with doxymycin standard. At B3LYP/6-311G (d,p) level, Density Functional Theorem (DFT) records has achieved to examine the optimized structure of both, the ligand and the compounds. Overall energy, HOMO energy, and LUMO as well as Mullikan atomic charges have been determined. Dipole moment, orientation, and structure activity relationship were performed and discussed. DFT calculations, moreover, confirmed practical antimicrobial results.[5]

Experimental

Materials and physical measurements

First of all, each used material or item in this study was absolutely pure in the case of BDH or Fluka. Absorption spectrum has measured by UV-Vis 1650 spectrophotometer for complexes solution in aqueous ethanol by means of 1cm quartz cell at room temperature. IR spectrum had been determined with FT-IR-8000 Shimadzu, in (4000-400) cm-1 range by means of KBr disc. Measured Electrical conductivity using digital conductivity meter under Alpha – 800 and solute concentration of 10^{-3}M in ethanol at room temperature. pH measurements had been conducted by (PH– meter), 720, WTW 82362.

Synthesis and characterization of azo ligand

In accordance with the method proposed by (Gusev)[6] and et.al in the preparation of this type of ligand by dissolving 2.29 gm of (2-Amino-6-bromobenzothiazole) in a mixture of 4mL concentration HCl acid and 25mL of distilled water and cooling the mixture to 0 0C. After that, sodium nitrite solution will be added that is prepared from the solved 1.4g in 10mL distilled water to the solution of thiazole derivative and avoid high temperature wise at 00C. Then, the solution will be left to be stable for a period of 15 minutes to complete, then drop by drop add salt diazonium with regular stirring to a solution having 2.224g naphthol-4-sulfonic and 1.2g sodium hydroxide solved in 150mL of ethanol without cooling to higher than 00C. Observe red bold color for the mixture, then leave the complex for two hours to reach to stability condition. After that, add 150mL of distilled cold water for getting stable ligand by modifying the pH solution to 6. Then, leave the precipitate for 24 hours and wash it a number of times with distilled water. Lastly, after drying process, calculate the output percentage and the degree of melting point.

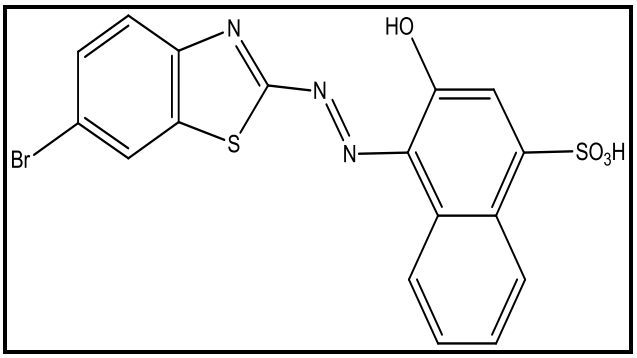


Figure (1): Structure of the ligand.

Complexes Synthesis

The chelat compounds have been produced at optimal pH values by dissolving (0.0464 gm), 0.01 mol of ligand in 10 ml ethanol. After that, 0.01 mol of metal chloride, M = Co (II), Cu (II) liquefied in 10 ml distilled water that is gradually inserted with dynamic stirring to the ligand solution. The reaction mixture has been left more than one night. Then, the complexes will be refined and washed with distilled water. Table.1 presents several physical features and investigative data for these compounds.

Table (1): Physical characteristics and investigative details of the ligand L_2 and its compounds.

No.	Complex	Color	M.pC°
1	$[C_{17}H_{10}BrN_3S_2O_4]$	Brown	98-99
2	$[Co\ (C_{17}H_{10}BrN_3S_2O_4)_2]$	Dark brown	162
3	$[Cu\ (C_{17}H_{10}BrN_3S_2O_4)_2]$	Red	250

RESULTS AND DISCUSSION

pH Effect

To investigate the effect of pH, appropriate pH magnitudes for metal compound solutions have applied within 5 to 10 range. To estimate the most advantageous pH magnitudes of metal compound solutions. The pH effect on the absorbance was investigated and discussed based on Figs. 2-3.

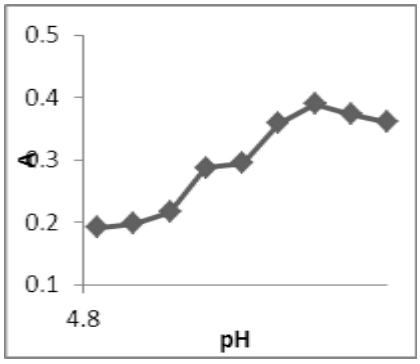
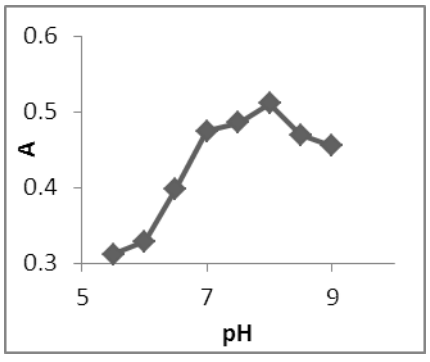


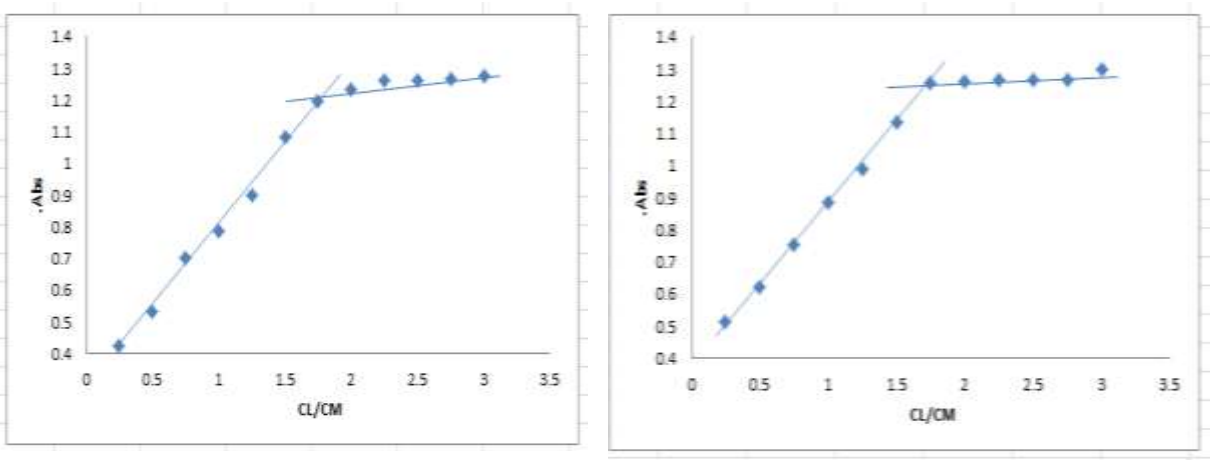
Figure (2): pH of Co complexe



Figure(3): pH of Cu complexe

Metal: ligand ratios

The complex (metal: ligand) ratios have calculated using molar ratio technique at constant concentrations and pH at wavelengths of utmost absorbance. The ligand has formed within (2: 1) chelates ratio for each metal ion. These results have good conformity with the reported magnitudes for several thiazolyl compounds.

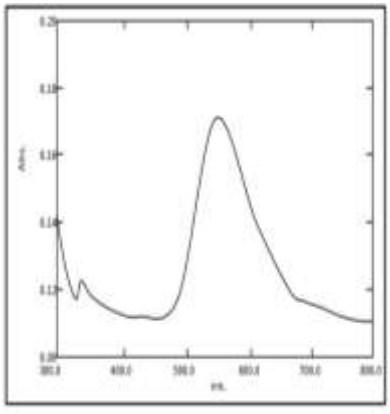


Figure(4):- The molar ratio (M:L) was (2:1) for all ions.

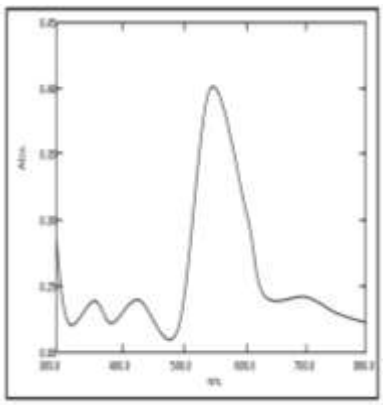
M=Cu,Co

Absorption spectra

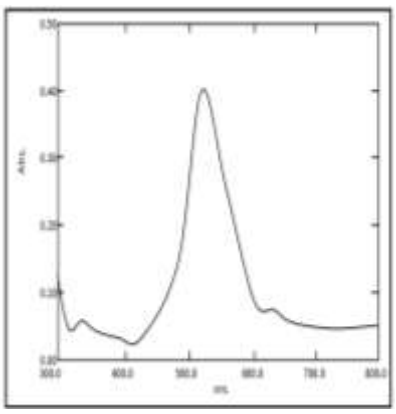
The shown results of UV spectrum of the ligand in ethanole have the highest peak in the absorption at a wave length (478nm) and with metal ions under study were observed to change color from reddish brown to dark green for the solutions of platinum and palladium ions bilateral.[11]



Figure(5):- UV.-Vis. band of ligand Co complex with ligand.



Figure(6):- UV.-Vis. band of Cu complex with ligand



Figure(7):- UV.-Vis. band of ligand

Table (2): The optimized pH values, optimized molar concentration and wavelength (λ_{max}) metal ions.

Metal Ions	Optimized pH	Optimized molar conc. X 10^{-4} M	Optimized wave length (λ_{max}) nm
Cu(II)	8	5	550
Co(II)	8	5	544

Infrared (IR) Spectrum

The IR band of the free ligand and its compounds with Co (II),Cu (II) ions are given in Table.3.

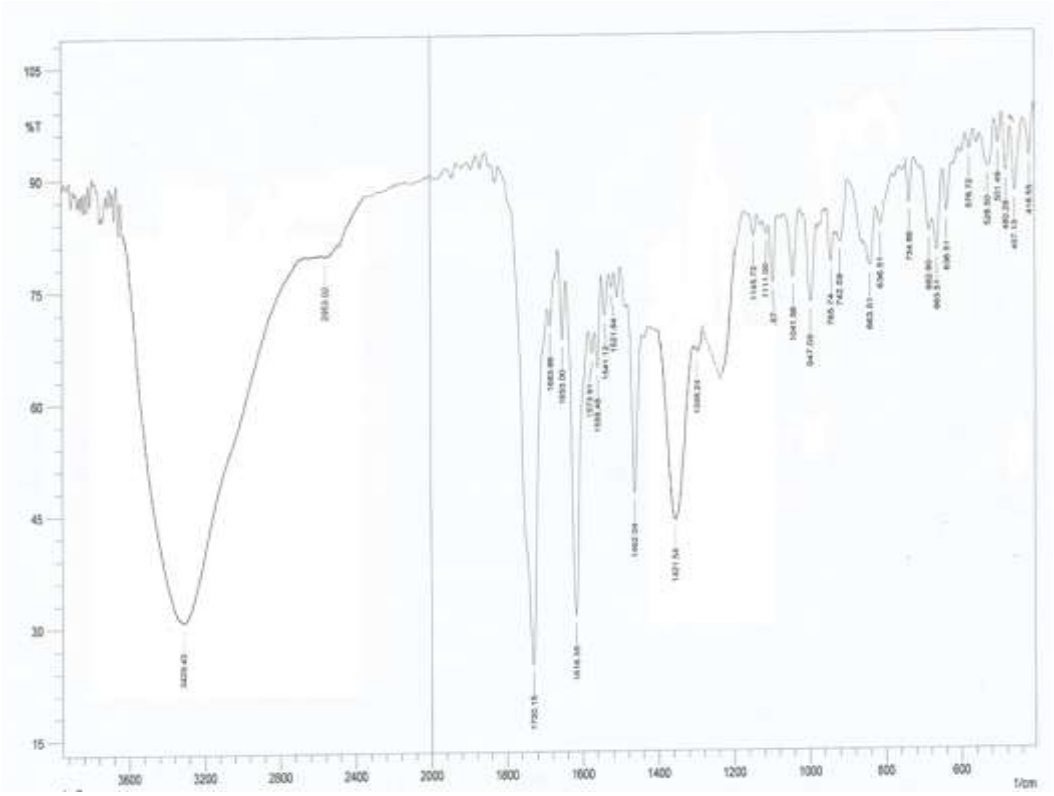


Figure (8):-IR band of ligand L.

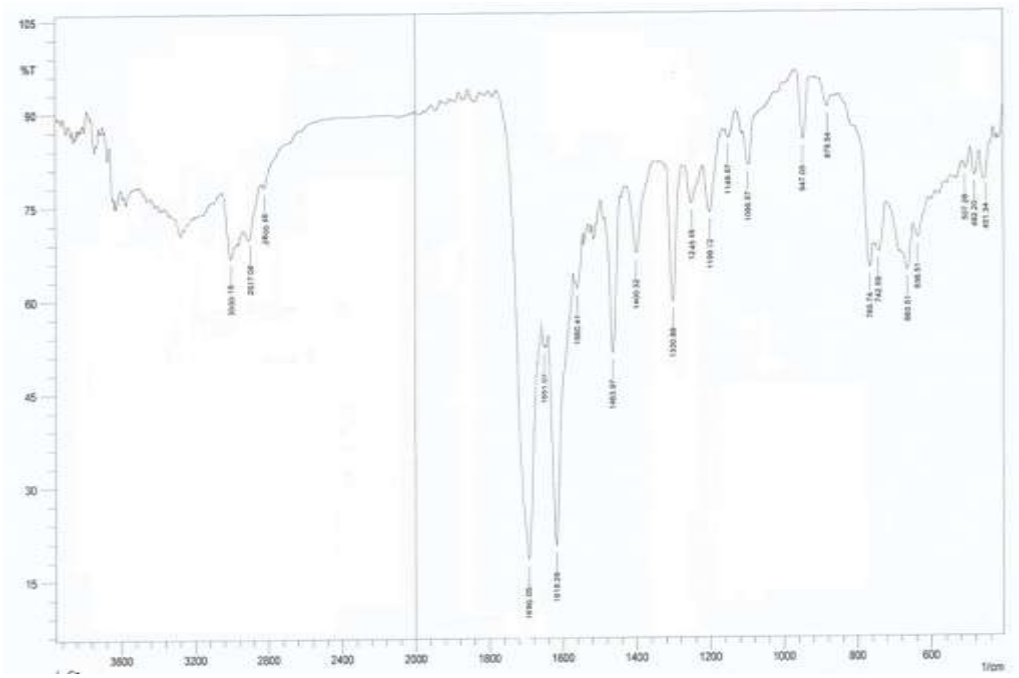


Figure (9): IR band of Cu complex with the ligand.

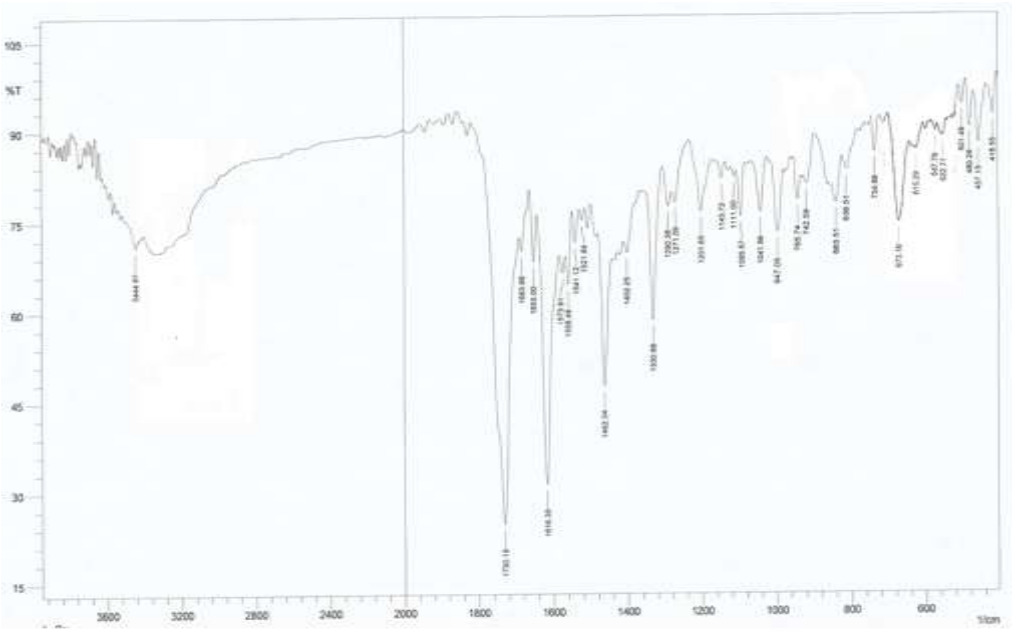


Figure (10): IR Band of Co complex with the ligand.

Table (3): Characteristic IR absorbance bands of the ligand and its compounds in cm^{-1} units.

Cluster	Ligand	Co (II)	Cu (II)
(OH)	3250	-	-
(N=N)	1494	1509	1485
(C – S)	12501	1222	1210
(M – O)	–	512	510
(M – N)	–	454	479

The measurements of Conductivity

The entire compounds illustrate the measured conductivity magnitudes ranged from 12.7 to 14.5 $S.cm^2. mol^{-1}$in DMSO at room temperature. These values confirm nonionic structure of these complexes.[12] The conductivity measurements have been shown in Table 4.

Table (4): Conductivity measurements of complexes.

Complex	Conductivity $S.cm^2.mol^{-1}$
$[Co(C_{17}H_{10}BrN_3S_2O_4)_2]$	13.9
$[Cu(C_{17}H_{10}BrN_3S_2O_4)_2]$	16.6

Along with the resultant measurements, the number of coordination of each metal ion is six with bonding through the N azo cluster and the O of phenol cluster of heterocyclic thiozolyl ring. The geometrical formula of equipped compounds is almost certainly octahydral as depicted in Fig.11.

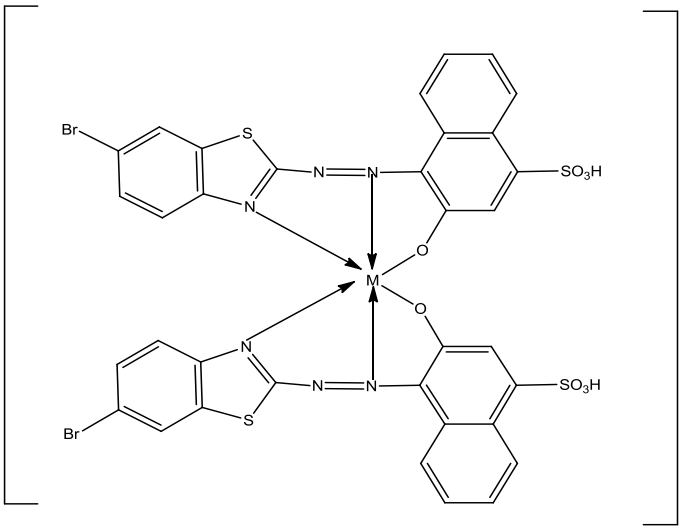


Figure (11):- The Most probable compound structures of Co (II),Cu(II) with the ligand (BTBP).

M= Co (II),Cu(II).

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