

Synthesis and Characterization of the Ligand (S, S'-Bis (Benzo [d] Oxazol-2-yl) 2, 2'-((Methylenebis (4, 1 Phenylene)) Bis (Azanediyl)) Diethanethioate (BMPAE) and it's Complexes with Some Transition Metals Ions

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Abstract

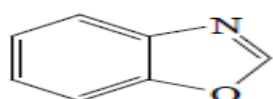
This study involved synthesis of ligand (S,S'-bis (benzo[d]oxazol-2-yl) 2,2'-((methylenebis(4,1-phenylene))bis(azanediyl))diethanethioate(BMPAE)by reaction in two steps. The first involved reaction between 2-Mercaptobenzoxazole with chloroacetyl chloride to get S-benzo[d]oxazol-2-yl 2-chloroethanethioate(compound-1).The second step reaction (compound-1) with 4,4'-Methylenedianiline to form S,S'-bis(benzo[d]oxazol-2-yl)2,2'-((methylenebis(4,1phenylene))bis(azanediyl))diethanethioate (BMPAE) .This ligand was characterized by melting point, FTIR,¹H NMR , ¹³C-NMR and elemental analysis. New chelating complexes were prepared from reaction ligand (BMPAE) with transition metal salts of Co (II), Cu (II), Cd (II), Ag (I), and Hg (II).The structures of these complexes were identified by FT-IR and UV-Vis spectra molar conductivity, melting points, elemental analysis, atomic absorption and magnetic susceptibility measurements. The FTIR spectra clearly show new bands, which were not found in ligand spectrum, while many other bands observed changes in shape, position and in intensity which are explained by the coordination with metal ions. All complexes showed tetrahedral geometry structures except Co (II), Cu (II) complexes are octahedral.

Keywords: *Heterocyclic, 2-Mercaptobenzoxazole, Benzoxazole complexes, Transition metal complexes.*

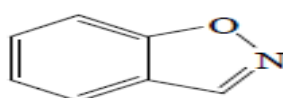
Introduction

Benzoxazoles are aromatic organic compounds, where benzene ring is fused with oxazole ring. These compounds include three isomers: Benzoxazole, 1,2-benzisoxazole and

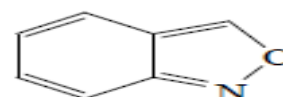
anthranil .Benzoxazoles derivatives found in natural products , and they have been used for synthesis another organic compounds [1,2] .



benzoxazole



1,2-benzisoxazole



anthranil

There are many methods for synthesis of these compounds including the reactions of acid chlorides, carboxylic acids and aldehydes with *o*-substituted amino aromatics [3].

Also they are found in the structures of drugs such as Flunoxapfen. Benzoxazole

derivatives are used in industry field which include their use as herbicides, such as Fenoxaprop [4]. These compounds show many pharmaceutical properties such as antibiotic, antiviral, antifungal, antibacterial, antitumor, antiulcer, anti-inflammatory, analgesic activities [5-9].

Benzoxazoles derivatives used as ligands to prepare some complexes by reacting with transition metal salts [10].

In this study include, ligand synthesis derived from Benzoxazole and its complexes with some transition metals [Co(II), Cu(II), Cd(II), Ag(II), and Hg(II)], and characterization by spectroscopic analysis and physical methods.

Experimental

Materials and Measurements

All chemical and solvents used in this study were supplied by BDH, Fluka, Sigma-Aldrich. The UV-Visible spectra were recorded by Shimadzu UV-Vis. model 1650PC at range (200-1000) nm at room temperature in ethanol as solvent. The FTIR spectra were obtained by using FTIR 8400S Shimadzu Spectrophotometer (Japan) by using potassium bromide (KBr) disc in the range (400-4000) cm^{-1} .

The $^1\text{H-NMR}$ spectrum of the ligand was recorded on Fourier transformation Bruker spectrometer, operating at (400MHz) with (DMSO-d_6), measurements were made at Department of chemistry, kashan university, Iran. Melting point were used to measure the melting point of all the prepared compounds by stuart melting point. The molar conductance measurements were carried out in ethanol solvent in concentration ($1 \times 10^{-3}\text{M}$)

at room temperature by conductivity meter ER 214. Magnetic susceptibility measurements for complexes were obtained at room temperature using Balances-Magnetic Susceptibility, Model MSB-Mk-1. The metal percentage in the complexes was obtained by using flame atomic absorption spectrophotometer, Shimadzu. AA-6300.. Elemental analyses were recorded on instrument type EA-99.mth.

Synthesis S-Benzo [d] Oxazol-2-yl 2-Chloroethanethioate (Compound-1)

An equimolar solution of 2-mercaptobenzoxazole (30g, 0.2mol) and chloroacetyl chloride (15.9mL, 0.2mol) in chloroform (100 mL), in the presence of anhydrous potassium carbonate (2g) under refluxing condition for about 5 hours. The product was drying under reducing pressure with recrystallization from absolute methanol. Yield 78%; mp 207-209 $^{\circ}\text{C}$ [12].

Synthesis of S, S'-Bis (Benzo[d] Oxazol-2-yl) 2, 2'-((Methylene Bis(4,1 Phenylene)) Bis (Azanediyl)) Diethanethioate (BMPAE)

A solution of 4, 4'-methylenedianiline (1.98g, 0.01 mol) in (20mL) ethanol was added to compound (1) (4.54g, 0.02mol) in ethanol. The reaction mixture was refluxed for 14 hours. The product (BMPAE) was formed and filtered then washed with water and recrystallized from ethanol [12].

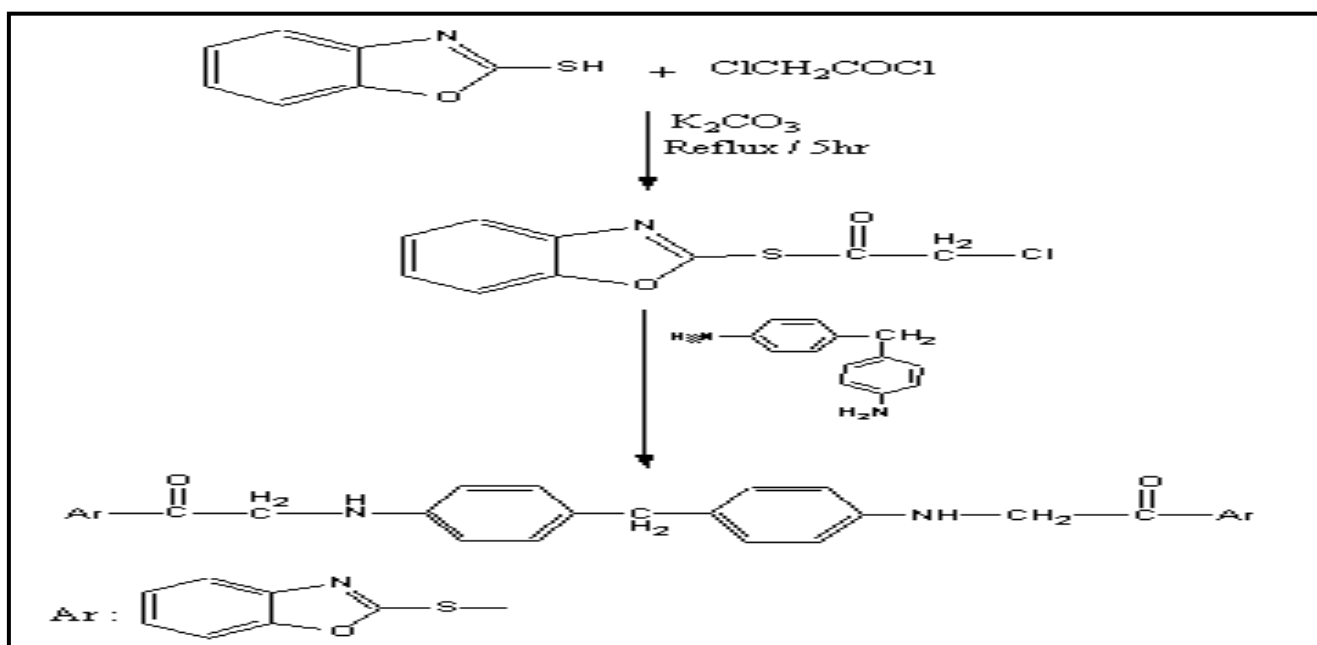


Fig. 1: Synthesis of the ligand (BMPAE)

Synthesis of the [Co (II), Cu (II), Cd (II), Ag (II), and Hg (II)] Complexes

A solution (0.58g, 0.001 mol) of ligand (BMPAE) which prepared by dissolving in 20 ml ethanol ether 1:1 ratio as solvent. A solution of (0.001mol) of the transition metal salts [Co (II), Cu (II), Cd (II), Ag (II), and Hg (II)] in 20 ml ethanol, with continuous stirring at room temperature for completely dissolving then Reflux for 1hour. Direct precipitates of complexes were formed. Work up of the of the complexes such as filtered, washed and recrystallized from ethanol and ethyl acetate under specific condition [13] .

Results and Discussion

A new ligand S, S'-bis (benzo[d]oxazol-2-yl)-2, 2'-((methylenebis (4, 1 phenylene)) bis (azanediyl)) diethanethioate (BMPAE) was prepared by reacting 2-mercaptobenzoxazole and chloroacetyl chloride, then the product reacted with 4, 4'-methylenedianiline. The complexes for this ligand were prepared with metals chlorides of [Co (II), Cu (II), Cd (II), Ag (I), and Hg (II)] in ethanol. The ligand and its complexes are soluble in some solvents, such as ethanol and DMF. The molar ratio method was equivalent to determine the metal to ligand ratio. This method showed that the metal to ligand ratio is (1:1). The physical properties and elemental analyses are shown in Table (1).

¹H and ¹³C-NMR Spectra of the Ligand (BMPAE)

The ¹H-NMR(DMSO-d₆) spectrum of ligand, figure(2) showed many signals at the range (m, δ:6.6-7.3ppm 16H), which due to aromatic protons, while the signal at (s, δ:5.2ppm, 2H) indicated to protons of amine groups, also the signals at (s, δ:3.7ppm, 2H), (s, 2.8ppm, 4H) referred to protons of m ethylene groups[11-14] .

The ¹³C-NMR(DMSO-d₆) spectrum of ligand, figure(3) appeared signals at (δ:15.61ppm (C1) , 173.0ppm (C17) 17.62ppm (C16) ,49.98ppm (C8) ,114.83ppm (C15) , 127.37-159.78ppm (aromatic ring carbon)[15-17].

The Infra-red Spectra

The Infra-red Spectrum of the Ligand (BMPAE)

The FTIR spectrum of the ligand (BMPAE),, figure(4) appeared absorption bands at

(3278,3058) and (1504 , 1450) cm⁻¹, which due to stretching vibrations of(N-H),(C-H) and (C=C) aromatic, respectively, and showed new band at (2923, 2854)cm⁻¹ which attributed to stretching vibration of (C-H) m ethylene groups .

The band sat (1724, 1357) cm⁻¹ attributed to stretching vibrations of(C=O) and (C-S) groups ⁽¹⁷⁾.The FTIR spectrum of ligand showed two bands at (1620, 1195) cm⁻¹, which due to the presence of ν(C=N) and (C-O) groups of Benzoxazole ring [14, 17-21].

The Infra-red Spectra of the Complexes

The FTIR spectra of the synthesized complexes appeared bands at the range(1688-1698) cm⁻¹, which indicated to stretching vibrations of(C=O).The carbonyl group in the free ligand showed at (1724) cm⁻¹, which shifted to lower wave number after complexation [15,21].

The sharp medium band at 3278 cm⁻¹ is attributed to ν (N–H) stretching vibrations. This band is shifted to lower wave numbers in the spectra of complexes the range (3224-3265) cm⁻¹, which indicates the coordination of the amine group nitrogen[15,22].

The new bands which appeared in the range (447-483) and (524-586) cm⁻¹ may be assigned ν(M–O) and (M–N), respectively [25].

The shifting of the wave number of carbonyl and amine groups in synthesized complexes comparing with free ligand and the appearance a new bands in the complexes spectra are evidences on coordination between the ligand and metals ions.

Electronic Spectra

The electronic spectra of the ligand and its complexes were recorded in ethanol as solvent at room temperature which summarized in Table (4).

The electronic spectrum the ligand observed the existence of three absorption peaks at (214,246) and (297) nm, which are assigned to the π → π* and n → π* transitions, respectively [26].

The Co(II) complex spectrum included four peaks at(386 , 525,565 and 668) nm , the first

peak which can be assigned to charge transfer transition, the other peaks are assigned to (${}^4T_{1g} \rightarrow {}^4A_{2g}$ (F), ${}^4T_{1g} \rightarrow {}^4T_{1g}$ (P) and ${}^4T_{1g} \rightarrow {}^4T_{2g}$ (F)) transitions, respectively, these peaks due to octahedral geometry [27].

The electronic spectrum of the Cu (II) complex include speak at (442) nm, which assigned to charge transfer transition, while the peak at (689) nm which due to ${}^2E_g \rightarrow {}^2T_{2g}$ transition, these transitions is correspond to octahedral complexes [28].

The UV-Vis spectra of the cd (II), Ag (II) and Hg (II) complexes did not show any peaks due to (d-d) transitions, because the (d) orbital's are completely occupied the peaks at (393,387 and 363) nm may be attributed to charge transitions [27, 30].

Magnetic Moment Measurements

Magnetic moments of metal complexes were measured at room temperature by using Hg [Co (SCN)] as the calibrate. The effective magnetic (MEFF) values of the complexes are showed in Table (4).

The magnetic moment of the Co (II) complex is 3.73B.M, which corresponds to octahedral geometry, also the magnetic moment of Cu(II) complex is 1.71B.M, which corresponds to octahedral geometry around Cu (II) ion, while the Cd (II), Ag (I) and Hg (II) complexes are Diamagnetic [29-31].

Molar Conductance Measurements

The molar conductance of the metal complexes were measured by using ethanol as solvent at room temperature in ($1 \times 10^{-3}M$) the values of molar conductance for these complexes were found at the range (16.2-84.1ohm⁻¹ cm² mole⁻¹)for complexes, which refer to Co (II) and Cu (II) complexes are non-electrolyte nature, Ag (I) complex is electrolyte in [1:1] ratio, while cd (II) and Hg (II) complexes are found electrolytes in [1:2] ratio [32].

Conclusion

In this paper, the new ligand (BMPAE) was prepared by reacting 2-mercaptobenzoxazole and chloroacetyl chloride and then the product reacted with 4, 4'-methylenedianiline.

The complexes for this ligand were prepared with metals chlorides of [Co (II), Cu (II), Cd (II), Ag (I), and Hg (II)] in ethanol. The ligand and its complexes were characterized by spectral methods (FTIR, UV-VIS, ¹H-NMR, ¹³C-NMR), elemental analysis, melting points, molar conductivity and magnetic measurements.

The ligand coordinates with transition metal ions through the nitrogen of the amine group and the oxygen of the carbonyl group.

Based on these results, octahedral structures for Co(II) and Cu(II) complexes, while the structure of Cd(II), Ag(I), and Hg (II) are tetrahedral, Figure (16).

Table 1: Elemental analysis and some physical properties of the ligand (BMPAE) and its complexes

No	Compounds	Color	Molecular Weigh (g/mol)	M.P (C°)	Yield %	Molecular Formula	Found (Calc.)%			
							C	H	N	M
1	L(BMPAE)	Brown	580.677	212-214	82	C ₃₁ H ₂₄ N ₄ O ₄ S ₂	64.12 (64.32)	4.43 (4.33)	9.65 (9.87)	-
2	[Co(L)Cl ₂]	Green	710.52	234-236	71	C ₃₁ H ₂₄ Cl ₂ N ₄ O ₄	52.12 (52.40)	3.51 (3.40)	7.41 (7.89)	8.63 (8.29)
3	[Cu(L)Cl ₂]	Pale Green	715.13	241-243	79	C ₃₁ H ₂₄ Cl ₂ N ₄ O ₄	52.32 (52.06)	3.23 (3.38)	7.72 (7.83)	8.98 (8.89)
4	[Cd(L) Cl ₂]	Pale Brown	764.00	265-267	69	C ₃₁ H ₂₄ Cl ₂ N ₄ O ₄	48.93 (48.73)	3.02 (3.17)	7.12 (7.33)	14.97 (14.71)
5	[Ag(L) (NO ₃)	Pale Brown	750.55	287 (dec.)	73	C ₃₁ H ₂₄ N ₅ O ₇ S ₂	49.39 (49.61)	3.34 (3.22)	9.17 (9.33)	14.78 (14.37)
6	[Hg(L) Cl ₂]	Pale Brown	852.17	299 (dec.)	78	C ₃₁ H ₂₄ Cl ₂ N ₄ O ₄	43.35 (43.69)	2.92 (2.84)	6.29 (6.57)	23.94 (23.54)

Table 2: The $^1\text{H-NMR}$ and $^{13}\text{C-NMR}$ spectral data of the synthesized ligands (BMPAE)

Ligand	$^1\text{H-NMR}$	$^{13}\text{C-NMR}$
L(BMPAE)	-m, δ :6.6-7.3ppm 16H : aromatic protons -s, δ :5.2ppm, 2H : amine group protons -(s , δ :3.7ppm , 2H), (s , 2.8ppm , 4H) : methylene groups protons	δ :15.61ppm (C1) 173.0 ppm (C17) 17.62 ppm (C16) 49.98 ppm (C8) 114.83 ppm (C15) 127.37-159.78 ppm (aromatic ring carbon)

Table 3: The important infrared spectral bands for the synthesized ligand (BMPAE) and its complexes

Compounds	$\nu(\text{N-H})$	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C=O})$ $\nu(\text{C=N})$ Benzoxazole	$\nu(\text{C=C})$ aromatic	$\nu(\text{C-S})$	$\nu(\text{M-N})$	$\nu(\text{M-O})$
L(BMPAE)	3278	3058	2923 2854	1724 1620	1504 1450	1357	-	-
[Co(L)Cl ₂]	3240	3039	2923 2854	1688 1589	1504 1442	1264	477	566
[Cu(L)Cl ₂]	3255	3066	2923 2854	1702 1604	1521 1481	1249	483	586
[Cd(L)] Cl ₂	3247	3031	2923 2854	1698 1620	1504 1473	1280	478	540
[Ag(L)] (NO ₃)	3265	3024	2923 2854	1695 1620	1512 1473	1365	447	570
[Hg(L)] Cl ₂	3224	3047	2923 2854	1688 1612	1504 1442	1280	478	570

Table 4: Electronic spectra, Magnetic Moments and Molar conductivity of the ligand (BMPAE) and its complexes

No	compounds	$\lambda(\text{nm})$	$\nu(\text{cm}^{-1})$	Transitions	μ_{eff} (B.M)	Conductivity $\text{ohm}^{-1}.\text{cm}^2.\text{mole}^{-1}$	Geometry
1	L(BMPAE)	214 246 297	46728 40650 33670	$\pi-\pi^*$ $\pi-\pi^*$ $n-\pi^*$	-	-	-
2	[Co(L)Cl ₂]	386 525 565 668	25906 19047 17699 14970	Charge transfer $^4\text{T}_{1g} \rightarrow ^4\text{A}_{2g}$ (F) $^4\text{T}_{1g} \rightarrow ^4\text{T}_{1g}$ (P) $^4\text{T}_{1g} \rightarrow ^4\text{T}_{2g}$ (F)	3.73	16.2	octahedral
3	[Cu(L)Cl ₂]	442 689	22624 14523	Charge transfer $^2\text{E}_g \rightarrow ^2\text{T}_{2g}$	1.71	18.2	octahedral
4	[Cd(L)] Cl ₂	393	25445	Charge transfer	dia.	84.1	tetrahedral
5	[Ag(L)] (NO ₃)	387	25839	Charge transfer	dia.	37.6	tetrahedral
6	[Hg(L)] Cl ₂	363	27548	Charge transfer	dia.	72.3	tetrahedral

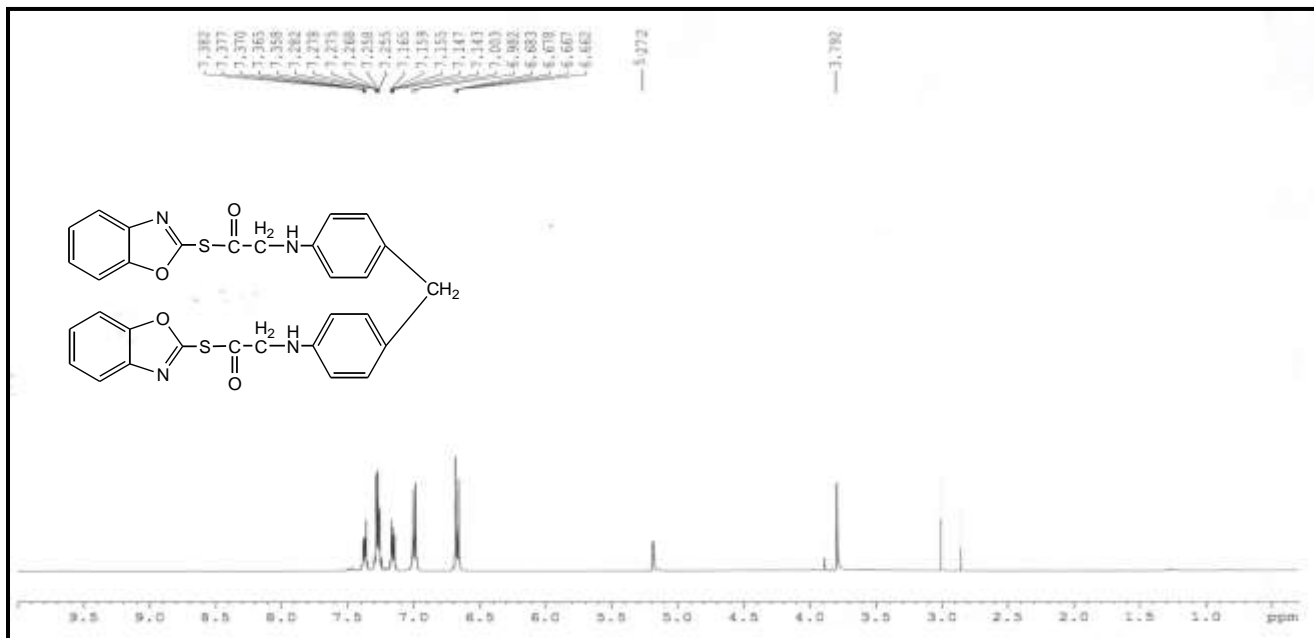


Fig 2: ¹H-NMR Spectrum of the synthesized ligand (BMPAE)

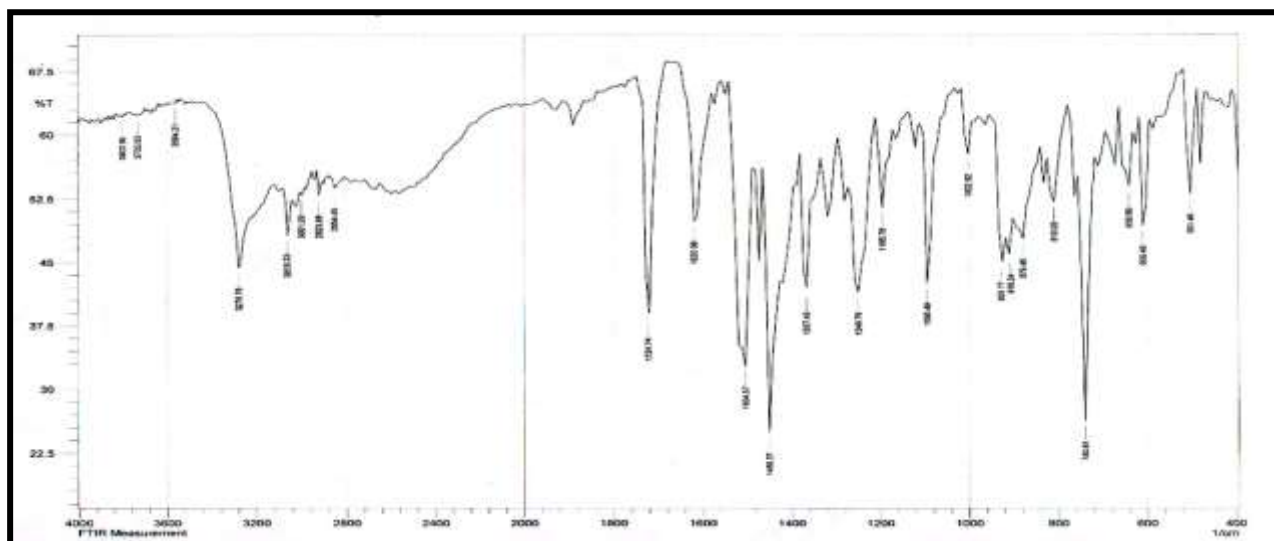


Fig 3: ¹³C-NMR Spectrum of the synthesized ligand (BMPAE)

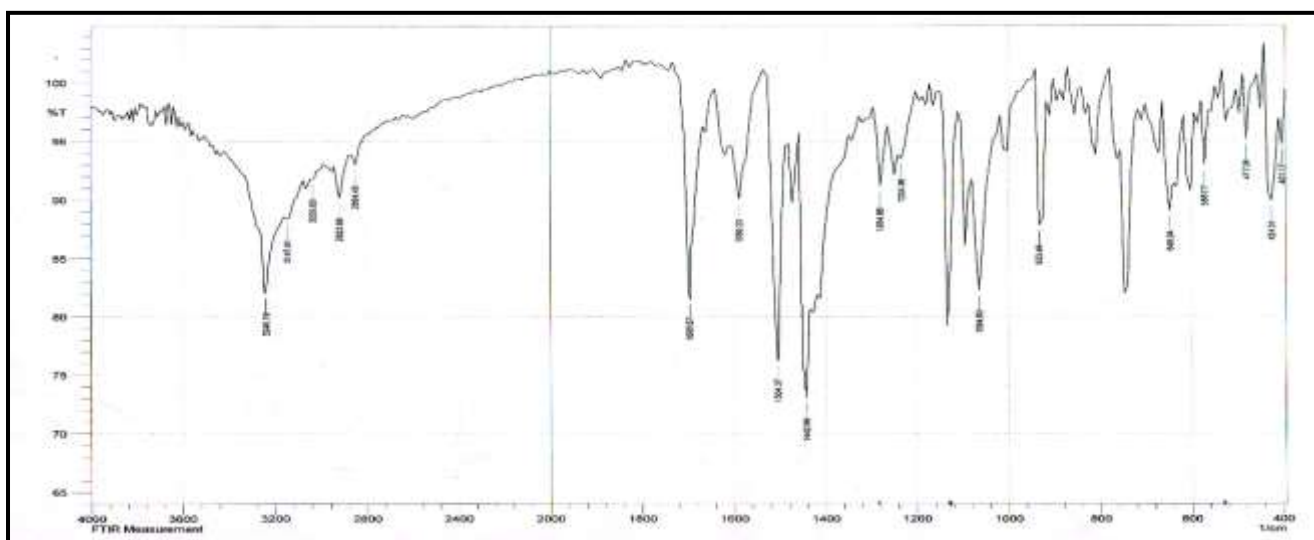


Fig 4: FTIR Spectrum of the synthesized ligand (BMPAE)

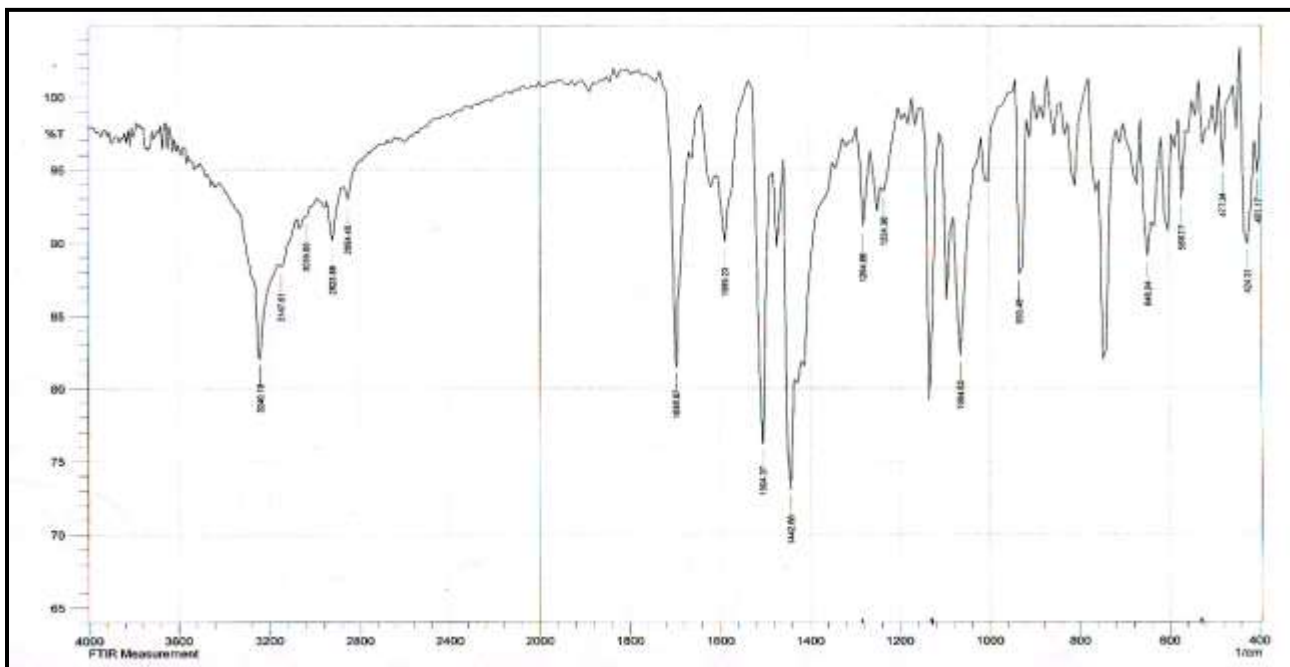


Fig. 5: FTIR Spectrum of the [Co (L)Cl₂] complex

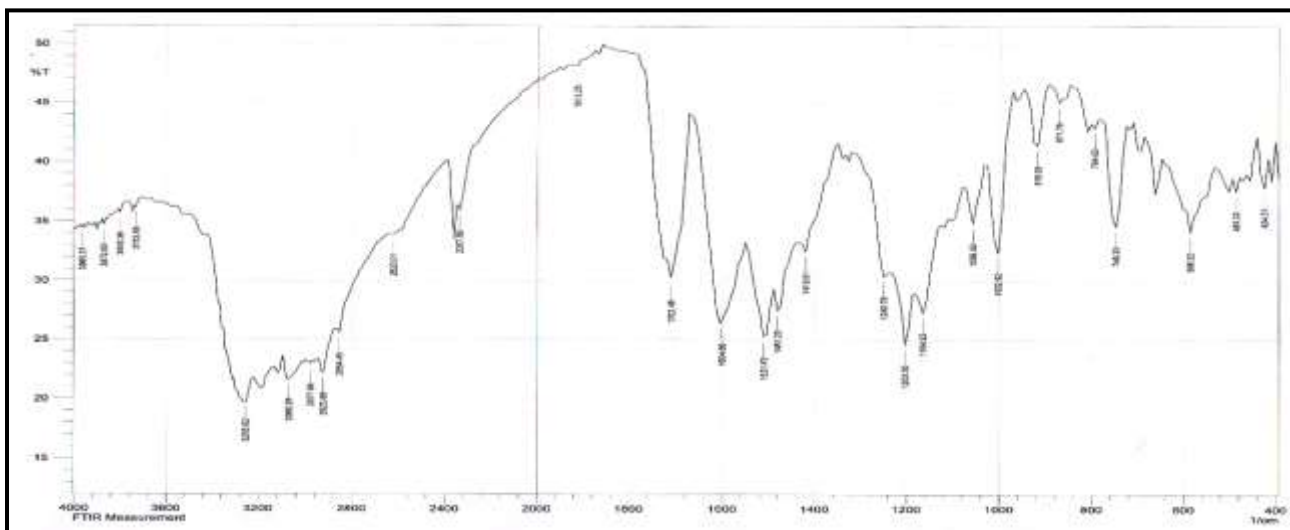


Fig. 6: FTIR Spectrum of the [Cu (L) Cl₂] complex

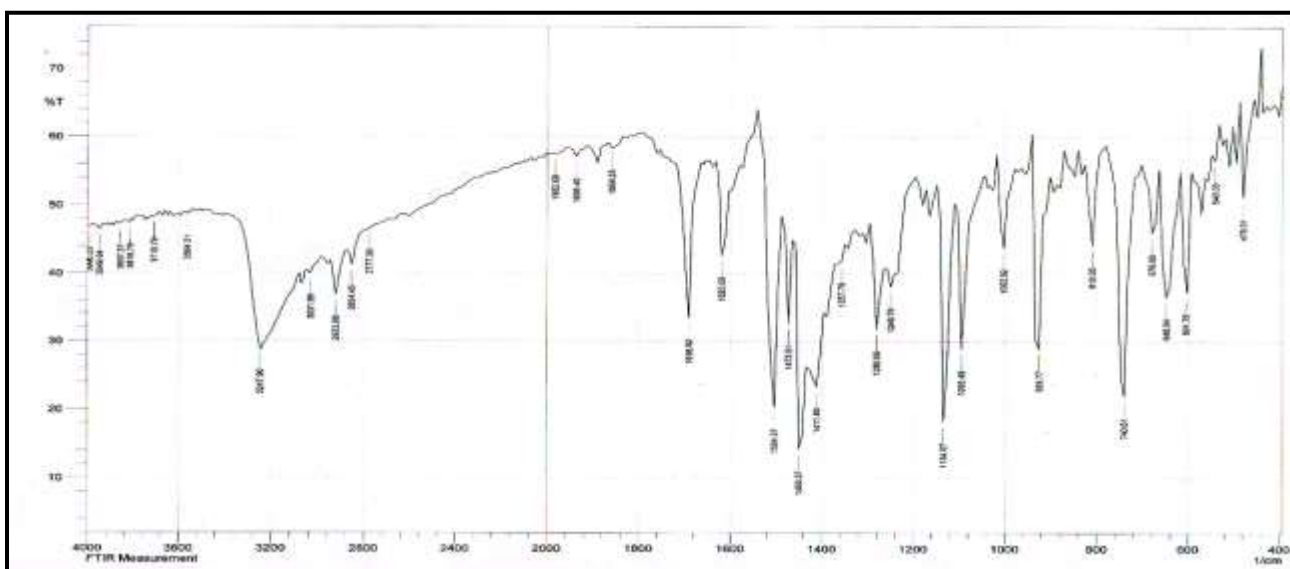


Fig. 7: FTIR Spectrum of the [Cd (L) Cl₂] complex

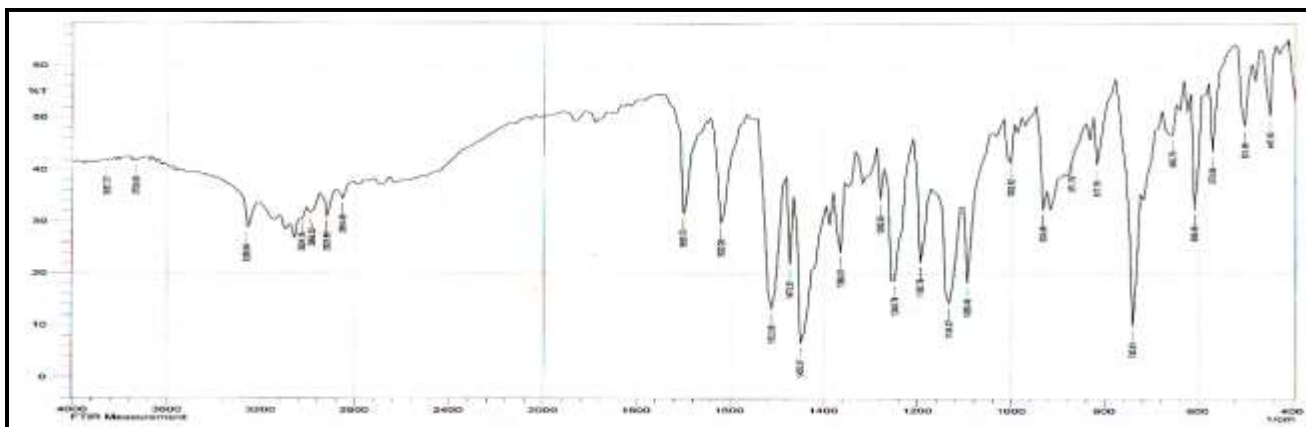


Fig 8: FTIR Spectrum of the [Ag (L)] NO₃ complex

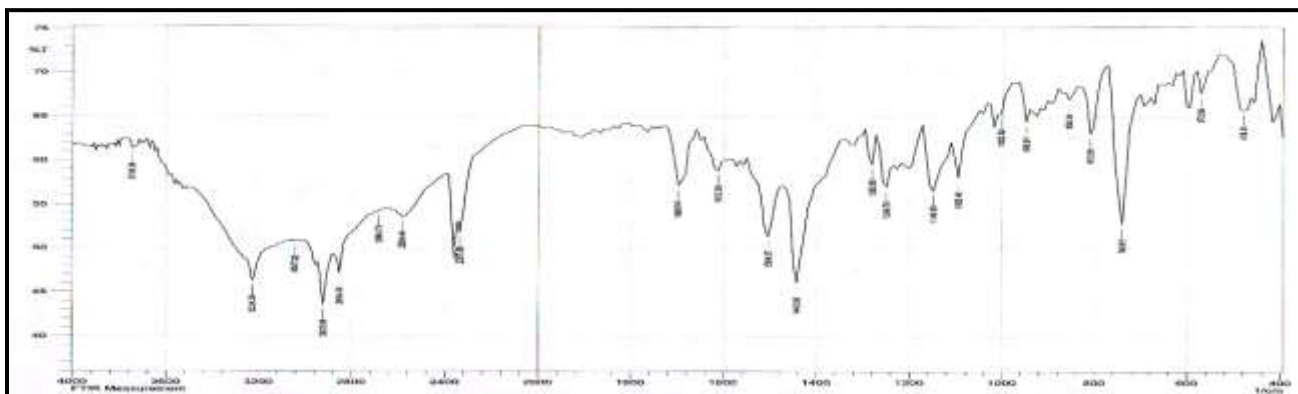


Fig 9: FTIR Spectrum of the [Hg (L)] Cl₂ complex

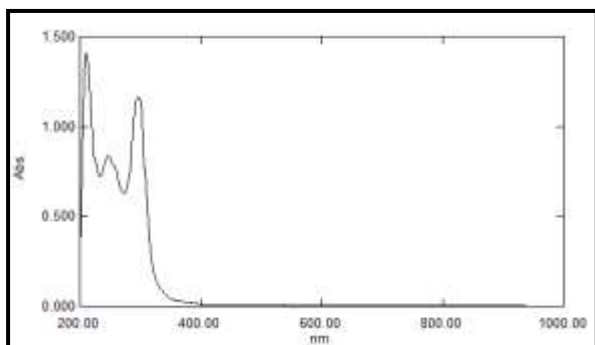


Fig 10: UV-Vis. Spectrum of the synthesized ligand (BMPAE)

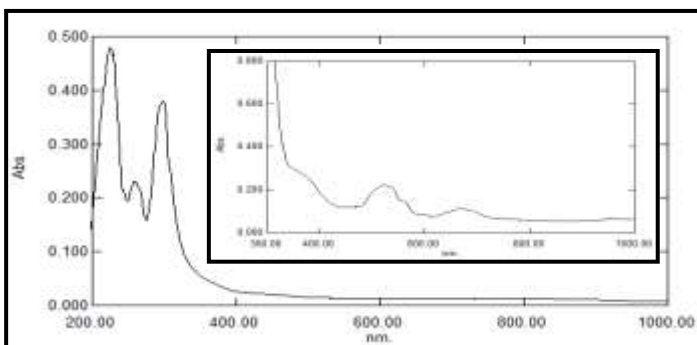


Fig 11: UV-Vis. Spectrum of the [Co (L) Cl₂] complex.

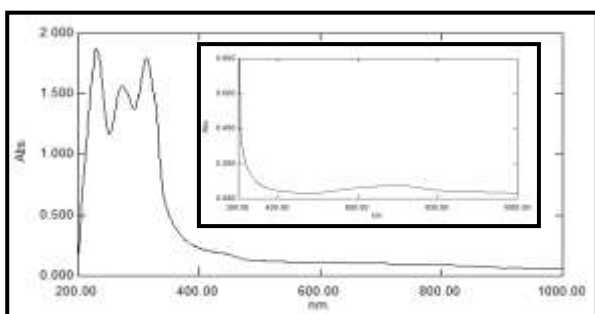


Fig 12: UV-Vis. Spectrum of the [Cu (L) Cl₂] complex

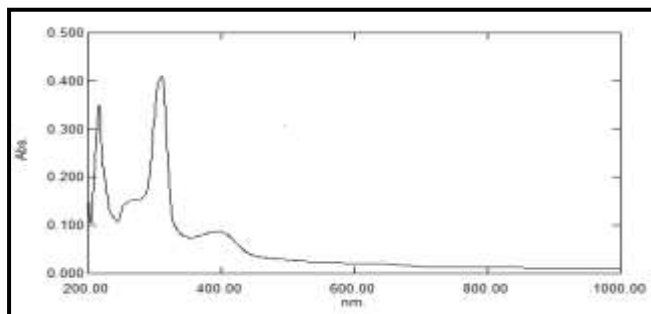


Fig 13: UV-Vis. Spectrum of the [Cd (L) Cl₂] complex

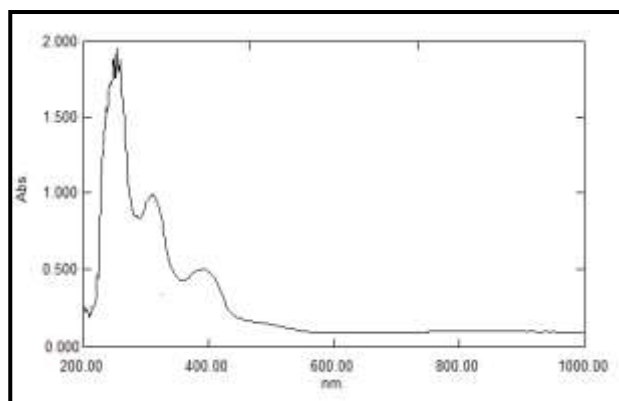


Fig 14: UV-Vis. Spectrum of the [Ag (L)] NO₃ complex

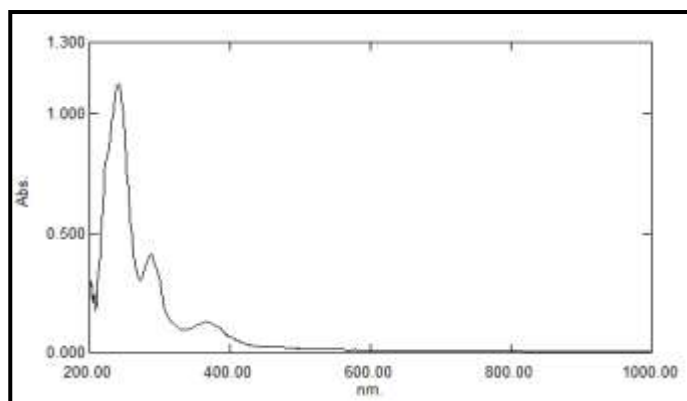


Fig 15: UV-Vis. Spectrum of the [Hg (L)] Cl₂ complex

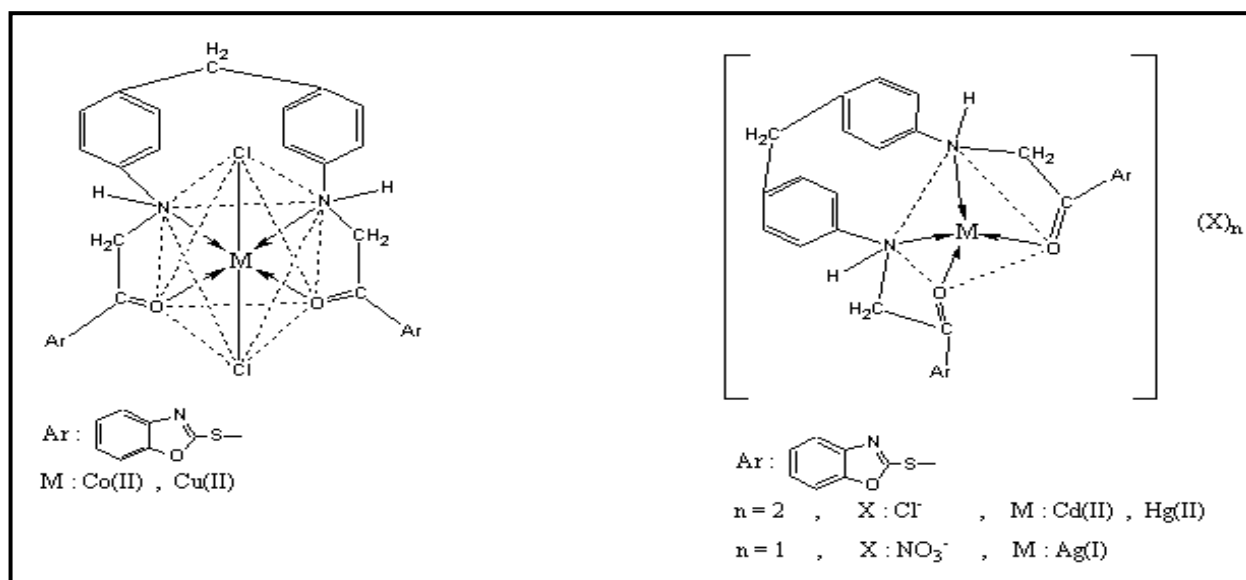


Fig. 16: The structural formula of the synthesized complexes

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