

Synthesis and Characterization of the Ligand Derivative from Benzothiazole [N-Benzothiazol-2-yl-N'-Naphthalen-1-yl-Ethane-1, 2-Diamine] and its Complexes with Some Transition Metal Ions

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Key words: Naphthalene, 2-Mercaptobenzothiazole, Benzothiazole complexes, medium, complexes, characterization

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Abstract: A new ligand N-Benzothiazol-2-yl-N'-Naphthalen-1-yl-Ethane-1,2-diamine (BTNEA) was synthesized from the reaction of 2-mercaptobenzothiazole with N-naphthalen-1-yl-ethane-1,2-diamine in absolute ethanol as reaction medium. Its complexes were prepared by reacting the ligand with metals salts of (Co(II), Cu(II), Zn(II), Cd(II) and Hg(II)). The structures of ligand and its complexes were confirmed by melting point, elemental analysis, FT-IR, ¹H-NMR and UV/visible spectra. In addition, to these characterization methods molar ratio (M:L), magnetic measurements, molar conductivity were used to characterize synthesized complexes. Flame atomic absorption spectroscopy was used to determine metal content (M%) of these complexes. The structures of the (Co(II), Cu(II)) complexes suggested as octahedral geometry while other complexes as tetrahedral geometry.

INTRODUCTION

Benzothiazole is one of heterocyclic compounds. The structure of benzothiazole consist bicycle ring benzene ring fused with 4,5-position of thiazole ring which includes sulphur and nitrogen atom in its structure^[1, 2]. It is a colorless and slightly viscous in nature and it has boiling point a (227-228 °C), the density and molar mass are 1.644 g mL⁻¹ and 139 g mol⁻¹, respectively^[3]. In 1887, 2-substituted benzothiazole was first synthesized by A.W. Hofmann where 2-mercaptobenzothiazole was synthesized from reaction o-aminophenol with carbon disulphide in presence of acetic anhydride as catalyst of reaction^[4] (Fig. 1).

2-mercaptobenzothiazole may be used as corrosion inhibitor and also used as antifreeze and cooling liquids^[5]. There are many compounds contain benzothiazoles ring and their derivative show biological activity which due to present the (-S-C=N-) in their structure (6), their

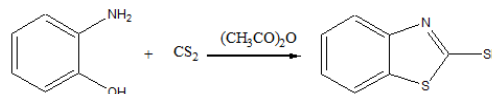


Fig. 1: ¹H-NMR spectrum of the (BTNEA) igand

biological activity such as anti-inflammatory, anticancer, analgesic, muscle-relaxant, antimicrobial, antiviral, antioxidant^[7-9] and plant growth regulatory activity^[10].

MATERIALS AND METHODS

Materials and Measurements: Chemicals and solvents in this research were supplied by Sigma-AI-drich , BDH, Fluka.

The FTIR spectra in the range (400-4000) cm⁻¹ were recorded as potassium bromide disc on FTIR 8400S Shimadzu Spectrophotometer (Japan). The UV-Visible spectra were measured in ethanol by using Shimadzu

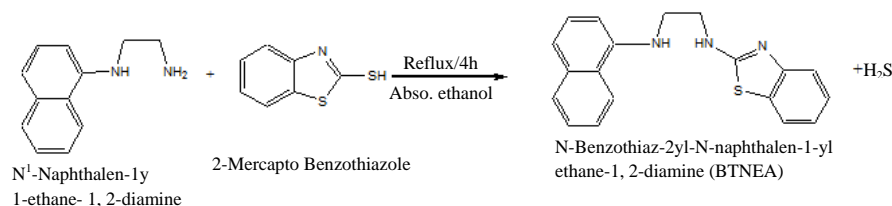


Fig. 2: The mechanism of ligand (BTNEA) synthesis

Table1: Elemental analysis and some physical properties of the ligand (BTNEA) and its complexes

Compounds	Color	Molecular Weigh (g/mol)	M.P (Co)	Yield (%)	Molecular formula	Found (Calc.) %			
						C	H	N	M
Ligand (BTNEA)	Brown	319.42	192-194	81	$C_{19}H_{17}N_3S$	71.73	5.22	12.94	-
$[Co(BTNEA)_2Cl_2].H_2O$	Pale Green	786.70	197-200	72	$C_{38}H_{36}Cl_2N_6OS_2 Co$	57.67 (58.02)	4.21 (4.61)	10.55 (10.68)	7.32 (7.49)
$[Cu(BTNEA)_2Cl_2].H_2O$	Pale Green	791.32	199-201	78	$C_{38}H_{36}Cl_2N_6OS_2 Cu$	57.26 (57.68)	4.31 (4.59)	10.15 (10.62)	7.59 (8.03)
$[Zn(BTNEA)Cl_2]$	Yellow	455.72	210-212	63	$C_{19}H_{17}Cl_2N_3SZn$	50.44 (50.08)	3.62 (3.76)	9.01 (9.22)	13.81 (14.35)
$[Cd(BTNEA)Cl_2].H_2O$	Yellow	520.76	235 (dec.)	79	$C_{19}H_{19}Cl_2N_3OSCd$	43.18 (43.82)	3.43 (3.68)	7.84 (8.07)	21.11 (21.59)
$[Hg (BTNEA)Cl_2]$	Yellow	590.92	273 (dec.)	83	$C_{19}H_{17}Cl_2N_3SHg$	38.07 (38.62)	2.71 (2.90)	6.98 (7.11)	- (33.95)

UV-Vis. model 1650 PC in the range (200-1000 nm) at room temperature. The 1H -NMR spectra recorded at Bruker model Ultrashild 300 MHz NMR. the solvent was DMSO- d_6 and the internal reference TMS. The Stuart melting point was used to measure the melting point of all compounds. At room temperature, Magnetic susceptibility measurement for complexes by using Balances-Magnetic Susceptibility, Model MSB-Mk-1. The molar conductance measurements were carried out in DMF solvent ($1 \times 10^{-3}M$) at room temperature by using conductivity mtere ER 214. The metal percentage in the complexes was measured by using flam atomic absorption spectrophotometer, Shimadzu. AA-6300. . Elemental analysis were recorded on instrument type EA-99.mth .

Preparation of the ligand (BTNEA): The new ligand N-Benzothiazol-2-yl-N'-naphthalen-1-yl-ethane-1,2-diamine (BTNEA) was synthesized from the reaction of 2-mercaptobenzothiazole with N-naphthalen-1-yl-ethane-1,2-diamine in absolute ethanol (Fig. 2).

A solution of (1.86 g, 10 mmol) N-naphthalen-1-yl-ethane-1,2-diamine dissolved in 25mL of absolute ethanol was added to 2-mercaptobenzothiazole solution (1.67 g, 10 mmol) dissolved in 25 mL of absolute ethanol with stirrer. The mixture refluxed for (4 h). The precipitate was collected and filtered after cooled at room temperature. The solid product was recrystallized from ethanol and dried (M.P= 192-194°C, yield% = 81%).

Preparation of the metal complexes: The metal complexes were prepared by the following general method.

A absolute ethanol solution of $CoCl_2.6H_2O$, $CuCl_2.2H_2O$ (2 mmol) while $ZnCl_2$, $CdCl_2.2H_2O$ and $HgCl_2$ (4 mmol) were added to ethanol solution of ligand (BTNEA) (4 mmol). The mixture was refluxed for 1 h. After that, the precipitate was formed, cooled and filtered. The solid product was washed and recrystallized by using ethanol, then dried. Table 1 reveals Elemental analysis also it shown the ligand physical properties and its complexes.

RESULTS AND DISCUSSION

The new ligand N-Benzothiazol-2-yl-N'-naphthalen-1-yl-ethane-1,2-diamine (BTNEA) was synthesized from the reaction of 2-mercaptobenzothiazole with N-naphthalen-1-yl-ethane-1,2-diamine in absolute ethanol, this reaction occurs in the following mechanism^[11]: Fig. 2: The mechanism of ligand (BTNEA)synthesis ligand (BTNEA) structure and its synthesized complexes were confirmed by different measurements: FTIR, electronic and 1H -NMR spectra, magnetic susceptibility measurements, molar ratio, flame atomic absorption spectroscopy, molar conductivity, melting point and elemental analysis. The ligand and its complexes appear good solubility in some of polar organic solvents such as ethanol, DMSO, THF and DMF.

The molar ratio method for the synthesized complexes were used to determine the metal to ligand ratio and using ethanol as solvent at room temperature. These methods showed that the metal to ligand ratio is (1:2) for Co (II) and Cu (II) complexes while in case Zn(II) , Cd (II) and Hg (II) complexes are (1:1) (Fig. 3).

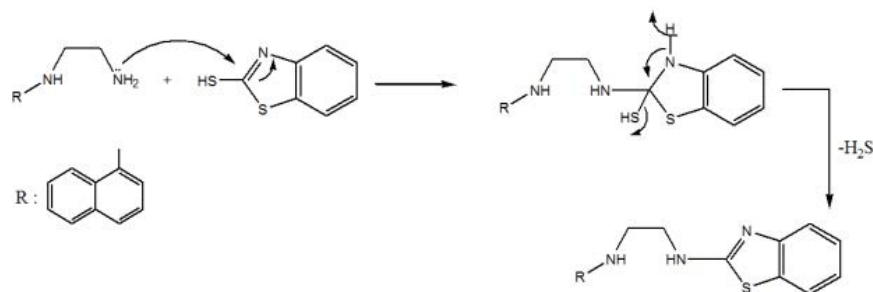


Fig. 3: Infrared spectrum of $[\text{Co}(\text{BTNEA})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ complex

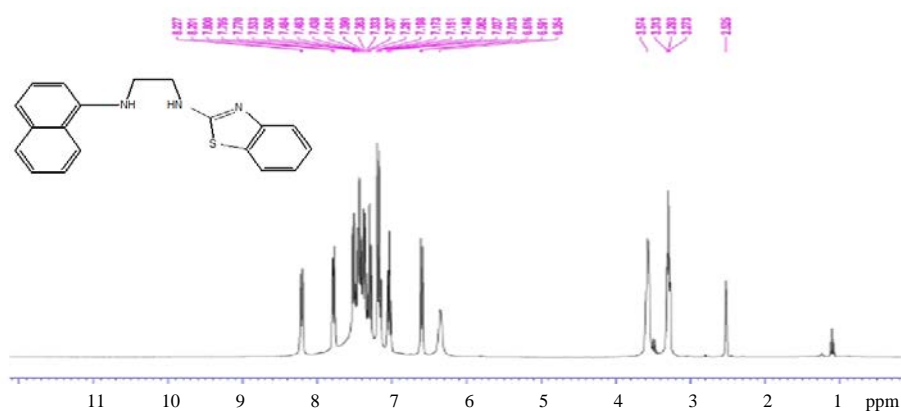


Fig. 4: Infrared spectrum of $[\text{Cu}(\text{BTNEA})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$ complex

Table 2: The important infrared spectral bands for the synthesized complexes and ligand (BTNEA)

Compounds	$\nu(\text{O-H})$	$\nu(\text{N-H})$	$\nu(\text{C-H})$ aromatic	$\nu(\text{C-H})$ aliphatic	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{C})$ aromatic	$\nu(\text{C-N})$	$\nu(\text{C-S})$	$\nu(\text{M-N})$
Ligand (BTNEA)	-	3340	3039	2962		1581	1527	1080	-
$[\text{Co}(\text{BTNEA})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$	3548	3431	3039	2962		1581	1527	1060	466
$[\text{Cu}(\text{BTNEA})_2\text{Cl}_2]\cdot\text{H}_2\text{O}$	3502	3386	3039	2962			1496	671	
$[\text{Zn}(\text{BTNEA})\text{Cl}_2]$	-	3402	3062	2970		1581	1527	1059	476
$[\text{Cd}(\text{BTNEA})\text{Cl}_2]\cdot\text{H}_2\text{O}$	3533	3428	3132	2970			1527	1069	
$[\text{Hg}(\text{BTNEA})\text{Cl}_2]$	-	3425	3132	2947		1581	1481	640	455
				2900			1527	1058	
						1581	1481	686	468

The infrared spectra: The (FTIR) spectrum of free ligand (BTNEA) showed many bands at (3440, 1581 and 663) cm^{-1} which due to $\nu(\text{N-H})$ secondary amine, $\nu(\text{C}=\text{N})$, $\nu(\text{C-S})$, respectively. The bands at (1527, 1496), (3039) and (2962, 2893 cm^{-1}) were assigned to $\nu(\text{C}=\text{C})$, $\nu(\text{C-H})$ aromatic and $\nu(\text{C-H})$ aliphatic, respectively^[1, 12-15].

The (FTIR) spectra of the synthesized complexes exhibited the secondary amine frequency of the ligand at 3440 cm^{-1} which shifted to lower frequencies after complexation about (9-56 cm^{-1}), the shifts of secondary amine frequency in complexes spectra indicated to coordination of ligand to metal atom by the nitrogen of amine group^[13]. The $\nu(\text{C}=\text{N})$ band does not suffer

shifted in complexes spectra which means that the azomethine of benzothiazole unshared in coordination. The new bands at (466, 476, 457, 455 and 468 cm^{-1}) are due to the $\nu(\text{M-N})$ for complexes Co(II), Cu(II), Zn(II), Cd(II) and Hg(II), respectively while the new bands at (3548, 3502 and 3533) cm^{-1} are due to the $\nu(\text{O-H})$ of water molecules for complexes Co(II), Cu(II) and Cd(II) respectively^[17]. The important infrared spectral bands for the synthesized ligand and its complexes are given in Table 2 and Fig. 4.

¹H-NMR spectrum of the Ligand (BTNEA): The ¹H-NMR spectrum of the ligand (BTNEA) was measured by using DMSO- d_6 and TMS as internal reference. This

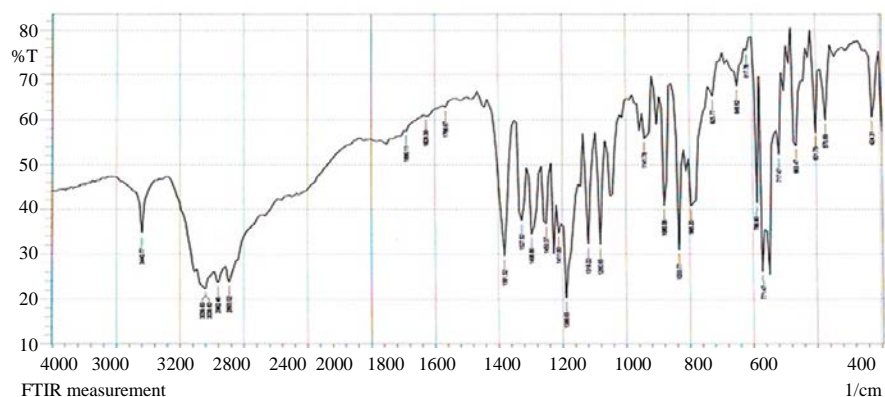


Fig. 5: Infrared spectrum of $[Zn(BTNEA)Cl_2]$ complex

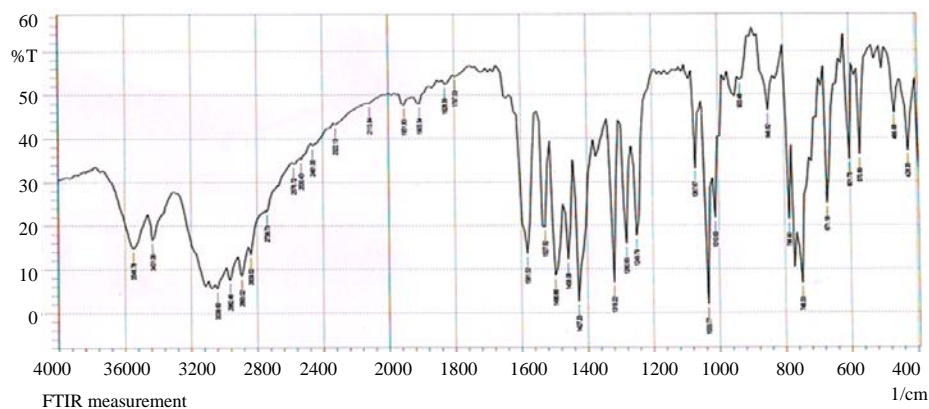


Fig. 6: Infrared spectrum of $[Cd(BTNEA)Cl_2] \cdot H_2O$ complex

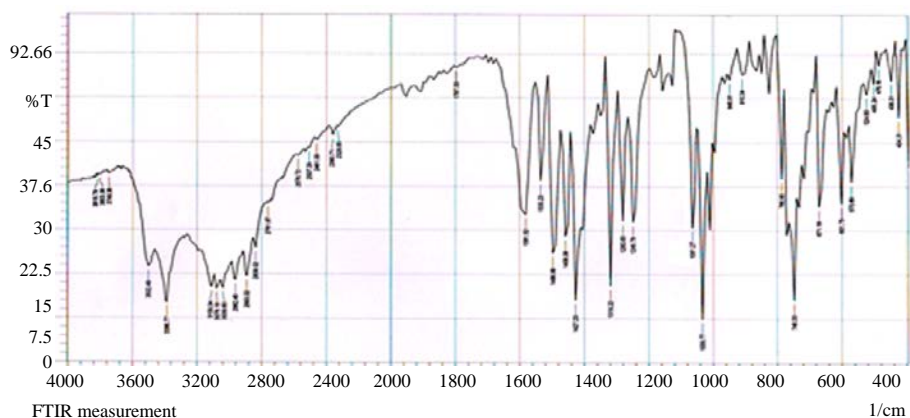


Fig. 7: Infrared spectrum of $[Hg(BTNEA)Cl_2]$ complex

spectrum, (Fig. 5 and 6), showed many signals at (M, 7H, 7.013-7.508 ppm) and (M, 4H, 7.533-8.227 ppm) due to aromatic protons of naphthalene and benzothiazole rings, respectively^[17]. The two signals at (S, 2H, 6.354, 6.616 ppm) which due to protons of (N-H) secondary amine and signals concentrated at the range (4H, 2.525-3.313 ppm) were attributed to methylene groups^[18, 11., 19].

The magnetic measurements and electronic spectrum:

The electronic spectrum of free ligand (BTNEA) in absolute ethanol at ($10^{-5}M$), (Fig. 7 and 8), showed two peaks at 239 and 286 nm which assigned to $\pi-\pi^*$ and $n-\pi^*$ electronic transitions^[20]. The electronic spectrum of green Co(II) complex, (Fig. 8) exhibited three bands, the first peak at 445 nm which may be assigned to the $^4T_{1g}$

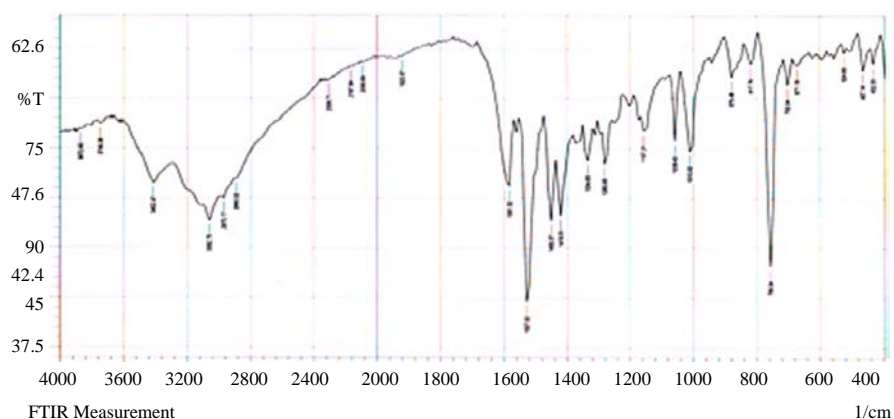


Fig. 8: Infrared spectrum of $[Zn(BTNEA)Cl_2]$ complex

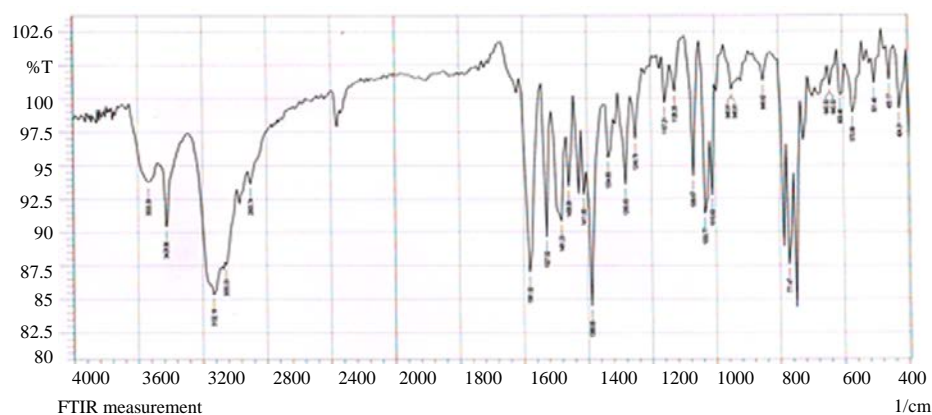


Fig. 9: Infrared spectrum of $[Cd(BTNEA)Cl_2]H_2O$ complex

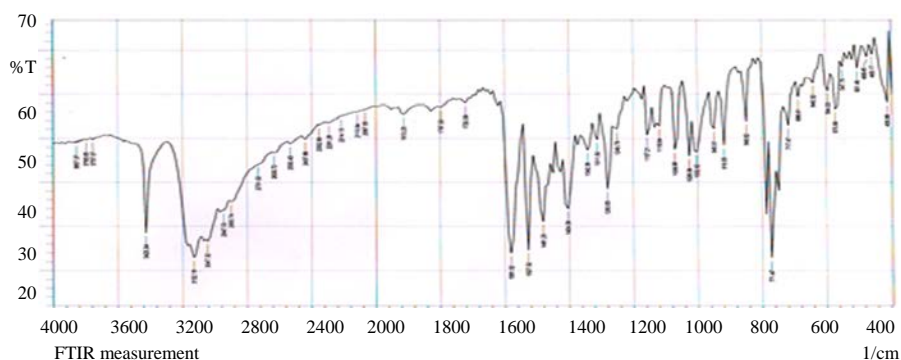


Fig. 10: Infrared spectrum of $[Hg(BTNEA)Cl_2]$ complex

$\rightarrow^4A_2g(F)$ while the other peaks at 509 and 691 nm due to $^4T_{1g} \rightarrow ^4T_{1g}(P)$ and $^4T_{1g} \rightarrow ^4T_{2g}(F)$. The magnetic moment of this complex is ($\mu_{eff} = 3.82$ B.M.) which suggest octahedral geometry around cobalt ion^[21, 22]. The electronic spectrum of paler green Cu(II) complex (Fig. 9) showed two peaks, the first peak at 431 nm which represents the charge transfer while second peak located at 704 nm due to $^2E_g \rightarrow ^2T_{2g}$. The magnetic moment of this complex is ($\mu_{eff} = 1.74$ B.M.) which suggest octahedral geometry around copper ion^[23, 24].

The electronic spectra for Zn(II) Cd(II) and Hg(II) complexes (Fig. 10-12) appeared bands concentrated at 368, 322 and 302 nm which may be attributed to charge transfer, the spectra for these complexes did not appear any (d-d) transition. The complexes of Zn(II) Cd(II) and Hg(II) are diamagnetic. These results indicated to tetrahedral geometry^[23, 25, 26]. Table 3 showed the Magnetic moments and electronic spectra of the ligand (BTNEA) and its complexes.

Table 3: Conductivity of the ligand (BTNEA) and its complexes, electronic spectra and magnetic moments

Compounds	λ (nm)	ν (cm ⁻¹)	Transitions	μ_{eff} (B.M)	Conductivity ohm ⁻¹ .cm ² .mole ⁻¹	Geometry
Ligand (BTNEA)	239	41841	π - π^*	-	-	-
	286	34965	n - π^*	-	-	-
[Co(BTNEA) ₂ Cl ₂].H ₂ O	398	25125	Charge transfer	3.82	14.7	octahedral
	445	22471	$^4T_{1g} \rightarrow ^4A_{2g}$ (F)			
	509	19646	$^4T_{1g} \rightarrow ^4T_{1g}$ (P)			
	691	14471	$^4T_{1g} \rightarrow ^4T_{2g}$ (F)			
[Cu(BTNEA) ₂ Cl ₂].H ₂ O	431	23201	Charge transfer	1.74	12.6	octahedral
	704	12204	$^2E_g \rightarrow ^2T_{2g}$			
[Zn(BTNEA)Cl ₂]	368	27173	Charge transfer	dia.	13.1	tetrahedral
[Cd(BTNEA)Cl ₂].H ₂ O	322	31055	Charge transfer	dia.	16.3	tetrahedral
[Hg(BTNEA)Cl ₂]	302	33112	Charge transfer	dia.	19.2	tetrahedral

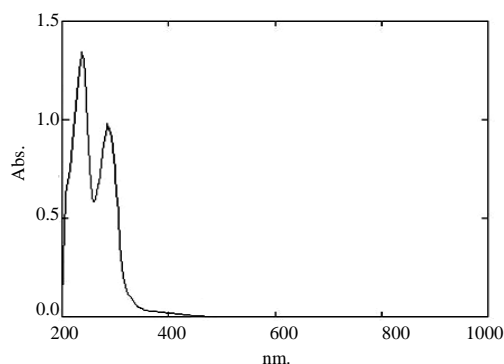


Fig. 11: Electronic spectrum of the free ligand (BTNEA)

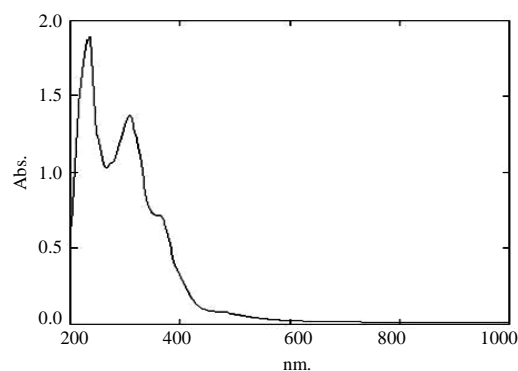


Fig. 14: Electronic spectrum of [Zn(BTNEA)Cl₂]. H₂O complex

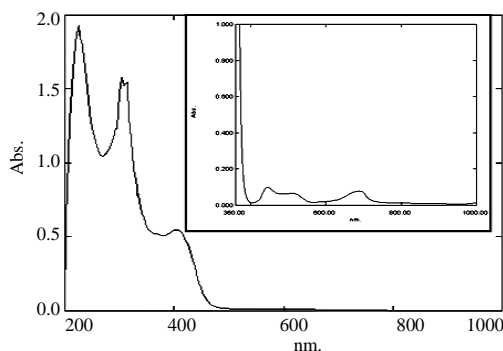


Fig. 12: Electronic spectrum of the complex [Ce(BTNEA)₂Cl₂]. H₂O

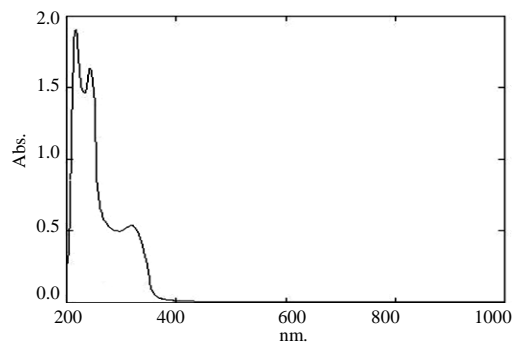


Fig. 15: Electronic spectrum of [Cd(BTNEA)Cl₂]. H₂O complex

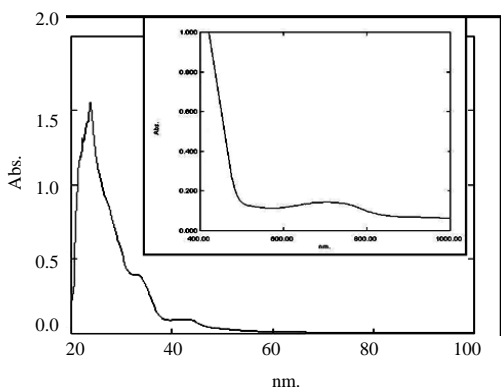


Fig. 13: Electronic spectrum of [Cu(BTNEA)₂Cl₂]. H₂O complex

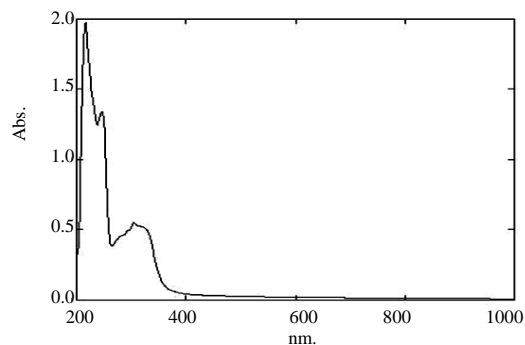


Fig. 16: Electronic spectrum of [Hg(BTNEA)Cl₂] complex

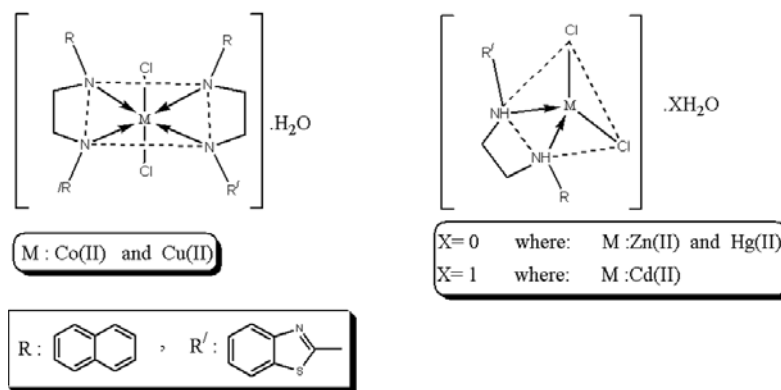


Fig. 17: The proposed chemical structure formula of the complexes

Molar conductivity measurements: The molar conductance of the synthesized complexes were recorded at 25°C, 10^{-3}M in absolute ethanol as solvent, the values of molar conductance are in the range (12.6-19.2 $\text{ohm}^{-1}\text{cm}^2\text{mole}^{-1}$) which indicate to the non-electrolyte nature of these complexes^[27], Table 3 showed the Magnetic moments, electronic spectra of the ligand and its complexes and the molar conductance values of the complexes.

CONCLUSION

From the spectroscopy methods, elemental analysis, magnetic measurements, flame atomic absorption spectroscopy, molar ratio and molar conductivity which suggest tetrahedral geometry for all complexes, except Co(II) and Cu(II) complexes are octahedral geometry. The ligand behaves as bidentate ligand which coordinates to the Co(II), Cu(II), Zn(II), Cd(II) and Hg(II) ions by nitrogen atoms of secondary amine. The structures of the synthesized complexes.

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