

Preparation And Characterization Studies of Some Transition Metal Complexes With New azo ligand 5-[(6-Bromo-2-benzothiazolyl) azo]-4-hydroxy benzoic acid

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Abstract

New azo thiazole dye ligand 5-[(6-Bromo-2-benzothiazolyl)azo]-4-hydroxy benzoic acid(6-BrBTABA=LH₂), was prepared by coupling reaction between (6-Bromo-2- benzothiazole diazonium) chloride with 4-hydroxy benzoic acid in alkalin alcoholic solution .Six new chelat complexes of Cr(III),Co(II),Ni(II),Cu(II),Zn(II),Cd(II)and Ag(I) have been synthesized and characterized by element analysis ,molar conductance , magnetic susceptibility measurements at room temperature , infrared and electronic spectra . The analytical data show that the metal to ligand ratio (M:L)were 1:2 chelats with Cr(II) ,Co(II) and Ni(II) metal ions but 1:1 chelates with the Zn(II) ,Cd(II) and Ag(I) metal ions .

Keywords :- 5-[(6-Bromo-2-benzothiazolyl)azo]-4-hydroxy benzoic acid

(6-BrBTABA), complexes preparation ,characterization , spectrophotometry .

1-Introduction

The thiazolyl azo compounds and its derivatives as organic molecules highly conjugated with a high chromophore (K.Singh et al, 2006) (S.J.Naik and U.P.Halkar , 2005) (L.Qiu et al , 2004) .Thiazolyle compounds have attracted much attention as they are sensitive chromogenic reagents in addition to

being important complexing agents (E.Y.Hashem et al , 2003) (V.S.Lemos et al , 2002) (A.A.R-Jewad et al , 2005).They have been used for spectrophotometric and extraction photometric determination of many metal ions (S.Oszwaldowski and M.Jarosz , 1997) (M.J.Sanchez et al , 1988).Thiazolyl azo compounds are widely

used in the dye-stuffs industry (W.Lee et al , 2002) and also more recently in the field of non-linear optic (M.Matsui et al , 1998). The dyes give colored chelating complexes especially with some transition metal ions (A.M.Ali , 2006) (Khalid.J.Al-adely , 2004) (Khalid J.Al-adely , 2008) (Hari R.Maradiya and Vithal S.Patel , 2001). In this paper we describe preparation and characterization of new Thiazolylazo ligand(6-BrBTABA=LH₂) and the attempt to prepare and identify some transition metal complexes of this ligand .

2-Experimental

2.1- Materials and Measurements

All chemicals were of highest purity and used as supplied from BDH, Aldrich and Fluk except of 2-amino-6-bromo benzothiazole was prepared as described in the literature (A.G.Kuhait , 1984).

Elemental analysis were carried out by micro analytical unit 1108 C.H.N. elemental analyzer. Electronic absorption spectra in the visible and ultraviolet regions were measured with UV-visible spectrophotometer (shimadzu-UV-1650). using ethanol anhydrous as solvent . Infrared spectra were measured with test scan Shimaduz FTIR-8000 series, in the (4000-400) cm⁻¹ range using KBr discs . Magnetic susceptibilities were measured on powder samples using farady method ,blance magnetic susceptibility model MSB-MKI was employed for this purpose . pH measurement were carried out using pH

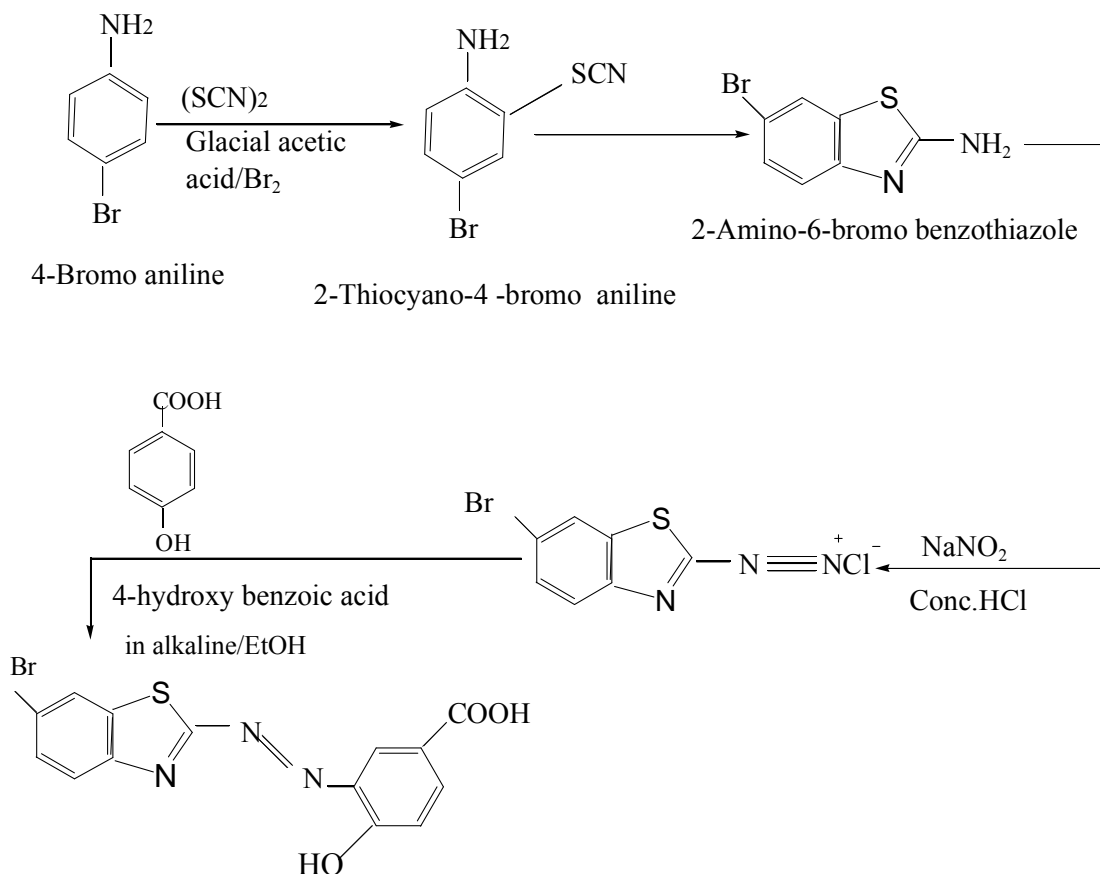
meter model pw 9421 (phlips). Electronic molar conductivity measurement were carried out at room temperature at concentration(10⁻³ M) in DMF using conductivity bridge model Ec 219. Melting point "P.D-303" Apel was used to measure the melting point of ligand and their complexes. The metal content of the complexes was measured by using atomic absorption /flame emission by shimadzu – AA-160.

2.2.Preparation and characterization of ligand (6-BrBTABA= LH₂)

The thiazolylazo ligand (6-BrBTABA)(see scheme 1)) was prepared by dissolving (2.29 gm,0.01 mol) 2-amino-6-bromo benzothiazole in 70ml of distilled water and 10ml of concentrated hydrochloric acid . The filtered solution was cooled at 5°C.To this mixture a solution of (0.75 gm,0.01 mol) of sodium nitrate in 30 ml of distilled water was added drop wise at 0-5°C and the mixture was stirred for 40 min .This diazonium chloride solution was added dropwise in 500ml beaker containing (1.38gm,0.01 mol) of 4-hydroxy benzoic acid dissolved in 200ml anhydrous ethanol. The mixture was stirred for an additional 2 hours, in an ice-bath allowed to stand over night and acidified with dilute hydrochloric acid until pH =6.0 was reached .The precipitate dye was filtered ,dried and recrystallized twice from ethanol then dried in the oven at 60 °C for several hours.The yield was 78% of brown powder

,melting at 188 °C .The solid ligand is stable in air at room temperature ,in soluble in water but completely soluble in most organic

solventes.The preparation of this ligand is shown in scheme (1).



Scheme(1):- Methods of preparation of the ligand 5-[(6-Bromo-2-benzothiazolyl)azo]-4-hydroxy benzoic acid(6-BrBTABA=LH₂).

2.3-Preparation and characterization of Complexes

The metal complexes were prepared by adding (0.756gm, 0.002 mol) ligand dissolved in hot ethanol 50 ml and added drop wise with stirring stoichiometric amount of(1:2) for $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ and (1:1) (0.378gm, 0.001 mol) of ligand for metal ions ZnCl_2 , $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ and AgNO_3 dissolved in 25ml hot buffer

solution (ammonium acetate) at optimal pH for each metal ions. The reaction mixture was heated to 60°C for 40 min. , then left overnight . The solid produced was filtered off, washed with 15 ml ethanol to remove the remaining un reacted substances and dried in a desiccators over anhydrous CaCl_2 .

The prepared complexes of this ligand are stable in air at room temperature and soluble in methanol ,ethanol ,acetone DMF and

DMSO but insoluble in water .The analytical and physical data for the prepared ligand and their metal complexes are listed in table (1).

Table(1):- Analytical and physical data of the thiazolylazo ligand and their complex .

No.	Compound	Color	m.P °C	Yield %	Molecular formula (Mol.Wt)	Found (Calc.)%			
						C	H	N	M
1	LH ₂ =Ligand	Brown	188	78	C ₁₄ H ₈ N ₃ O ₃ SBr (378.20)	44.56 (44.46)	2.23 (2.13)	11.27 (11.11)	—
2	[Cr(LH) ₂].Cl.H ₂ O	purple	227 d.	76	C ₂₈ H ₁₆ N ₆ O ₇ S ₂ Br ₂ ClCr (859.84)	39.25 (39.11)	1.96 (1.87)	9.56 (9.77)	6.29 (6.05)
3	[Co(LH) ₂].Cl.H ₂ O	Dark green	197	83	C ₂₈ H ₁₆ N ₆ O ₇ S ₂ Br ₂ ClC o (866.84)	38.71 (38.80)	1.74 (1.86)	9.86 (9.69)	7.04 (6.80)
4	[Ni(LH) ₂]. H ₂ O	Dark red	206	58	C ₂₈ H ₁₆ N ₆ O ₇ S ₂ Br ₂ Ni (831,08)	40.61 (40.47)	2.03 (1.94)	9.96 (10.11)	6.84 (7.06)
5	[Zn(LH)Cl].H ₂ O	Dark Purple	232 d.	80	C ₁₄ H ₉ N ₃ O ₄ SBrClZn (496.04)	33.76 (33.90)	1.92 (1.83)	8.34 (8.47)	13.39 (13.18)
6	[Cd(LH)Cl].H ₂ O	Purple	247 d.	69	C ₁₄ H ₉ N ₃ O ₄ SBrClCd (543.07)	31.12 (30.96)	1.59 (1.67)	7.91 (7.74)	—
7	[Ag(LH) H ₂ O]	Red	194	64	C ₁₄ H ₉ N ₃ O ₄ SBrAg (503.07)	33.57 (33.42)	1.89 (1.80)	8.52 (8.35)	21.67 921.44)

LH₂=(6-BrBTABA); d =Complex melt with decompose

3-Result and Discussion

3.1-Absorption spectra

The absorption spectra of the free ligand (6-BrBTABA=LH₂) and their metal complexes with Cr(III),Co(II),Ni(II),Zn(II),Cd(II)and Ag(I) ions in aqueous ethanolic solution were recorded with in wavelength (515-630)nm. The

wavelength for the maximum absorption (λ_{max}) of the ligand was found at 416 nm. The prepared metal complexes showed abthochromic shift ranging between (99-214)nm depending on the metal ion .The absorption spectra of the chelat complexes are shown in figures.(1)and (2).

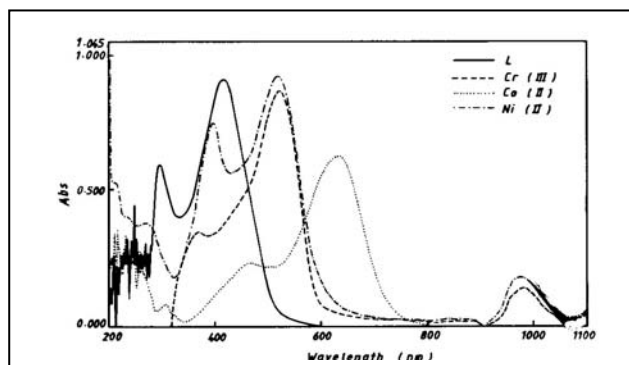


Fig (1):- The absorption spectra of free ligand(LH₂) free and their complexes in a suitable pH;Conc.

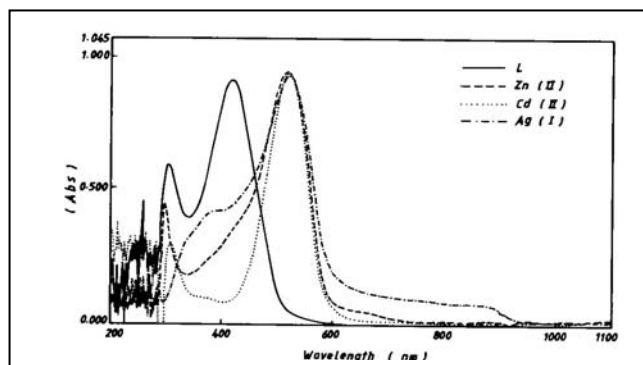


Fig (2):- The absorption spectra of ligand (LH₂) and their complexes in a $=(1.5 \times 10^{-5} \text{M})$ in aqueous ethanolic suitable H;Conc. $= (1.25 \times 10^{-5} \text{M})$ in aqueous solution 50% (V/V); ethanolic solution 50% (V/V);

3.2- Infrared spectra

The FT-IR spectra of azo dye ligand(6-BrBTABA) and some complexes are shown in figures.(3),(4),(5) and(6) .The most important IR assignments of ligand and their complexes (KBr disc)are listed in table (2).The characteristic broad band around(3325) cm^{-1} indicates the $\nu(\text{OH})$ stretching in the spectrum of ligand suggests a strong intermolecular hydrogen bonding (F.A.Snavely and C.H.Yodcer , 1968) (A.G.Catchpok et al , 1962).The spectrum of Ag(I) complex show medium sharp band at (835) cm^{-1} which attributed to the coordination of water molecule (A.A.El-Bindary ,

1996).But the spectra of remaining complexes show broad medium and weak bands around (3480-3360) cm^{-1} indicate the presence of water in these complexes (A.Z.El-sonbati , 1991) . The strong band observed at1600 cm^{-1} indicate stretching vibration of the $\nu(\text{C}=\text{O})$ in both ligand and their complexes .The fixed position of these bands in all complexes means that the carboxyl group (COOH) does not participate in coordination (K.Nakamoto , 1970). The weak band at 3120 cm^{-1} in the spectrum of the ligand is due to $\nu(\text{C}-\text{H})$ aromatic. This band is stable in position as well as in intensity for both ligand and chelat

complexes. The spectrum of ligand show absorption band at 1595 cm^{-1} due to $\nu(\text{C}=\text{N})$ of thiazole ring (Khalid J.Al-adely , 2000). This band is shifted to lower frequencies at $(1565\text{-}1520)\text{ cm}^{-1}$ in the spectra of metal complexes. These differences in shape and intensity suggest linkage of metal ions with the nitrogen atom in thiazole ring . The azo group $\nu(\text{N}=\text{N})$ at 1520 cm^{-1} and 1480 cm^{-1} are due to ν_s and ν_{as} respectively in spectrum of ligand while in complexes spectra these bands are shifted to lower frequencies at $(1510\text{-}1480)\text{ cm}^{-1}$ and $(1465\text{-}1449)\text{ cm}^{-1}$ with different in shape and decreased in intensity due to complex formation indicates could be attributed to the metal –azo group back bonding (L.Mangsup et al , 2003) (R.T.Mehdi and A.M.Ali , 2005).

The spectrum of free ligand show two absorption bands at 1275 cm^{-1} and 825 cm^{-1} due to $\nu(\text{C}-\text{S})$ of hetro cyclic thiazole ring (Khalid J.Al-adely , 2000) (K.C.Satpathy, and H.P.Mishra , 1981). These bands are stable in

position and intensity in both ligand and their metal complexes means that the sulphur atom of the hetero cyclic ring does not participate in coordination (Khalid J.Al-adely , 2000) (L.Mangsup et al , 2003) (A.M.Ali et al , 2006). New weak bands appeared in the region of $(575\text{-}420)\text{ cm}^{-1}$ in the complexes spectra , which are not present in the spectrum of the free ligand may be attributed to $\nu(\text{M}-\text{O})$, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{Cl})$ bands (Khalid.J.Al-adely ,2004) (Khalid J.Al-adely , 2008) (Khalid J.Al-adely , 2000) (A.M.Ali et al , 2006) (Y.Saito et al , 1973).

Thus the above IR spectra data lead to suggest that ligand behaves as tridentate chelating agent coordinating through the positions of hydroxyl oxygen , nitrogen atom of azo group nearest to aphenyl ring and thiazole ring nitrogen to give one or two five-membered chelat ring (mole ratio 1:1 or 1:2). Figures (3),(4),(5) and (6) shows the spectra of ligand $(6\text{-BrBTABA}=\text{LH}_2)$, $[\text{Cr}(\text{LH})_2]\text{Cl}\cdot\text{H}_2\text{O}$, $[\text{Ni}(\text{LH})_2]\cdot\text{H}_2\text{O}$, and $[\text{Ag}(\text{LH})\text{H}_2\text{O}]$.

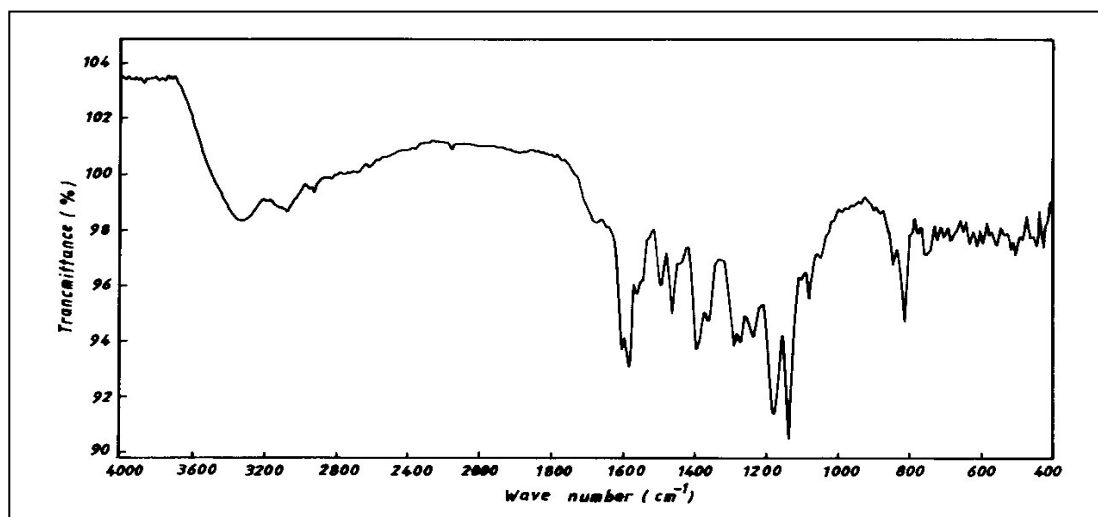


Fig.(3):- IR spectrum of the free ligand $(6\text{-BrBTABA}=\text{LH}_2)$

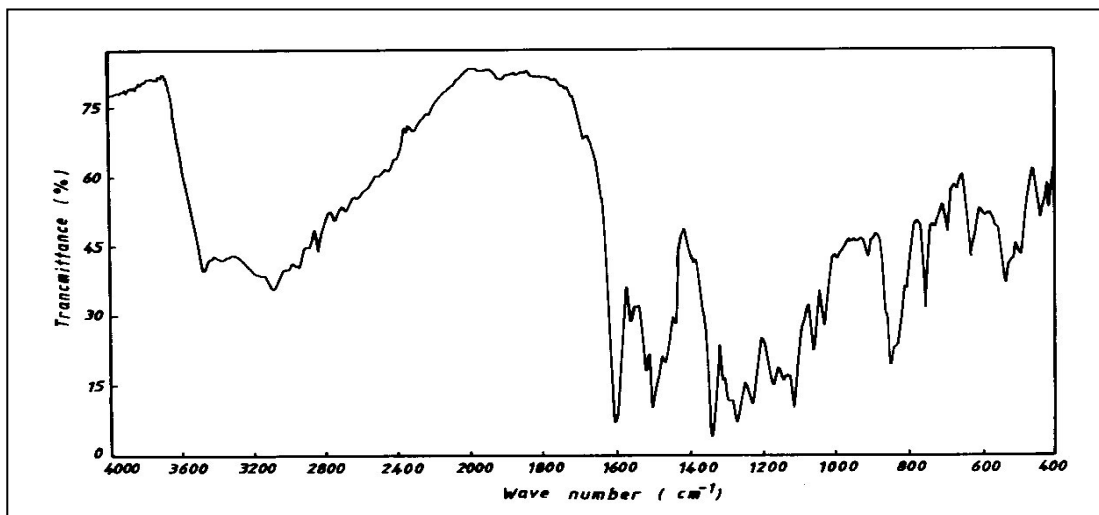
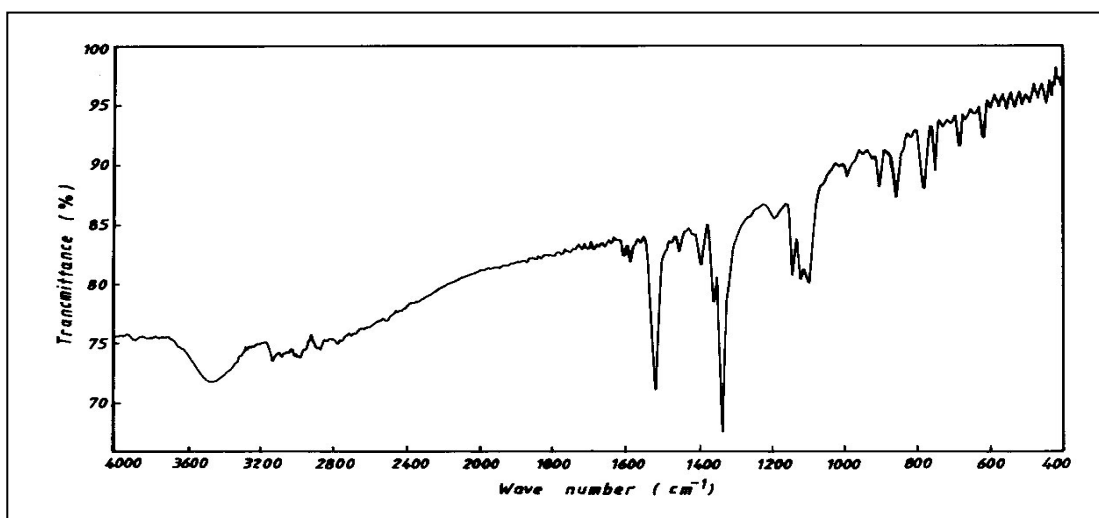
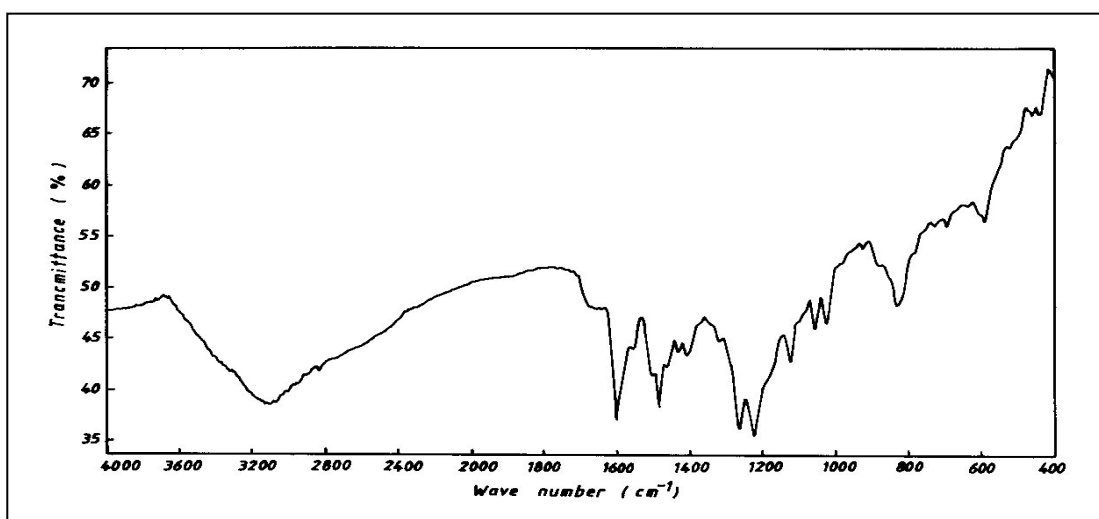
Fig.(4):- IR spectrum of the complex $[\text{Cr}(\text{LH})_2]\text{Cl}\cdot\text{H}_2\text{O}$ Fig.(5):- IR spectrum of the complex $[\text{Ni}(\text{LH})_2]\cdot\text{H}_2\text{O}$ Fig.(6):- IR spectrum of the complex $[\text{Ag}(\text{LH})\text{H}_2\text{O}]$

Table (2) :- Characterisation data for IR absorption bands of the ligand and their complexes in cm^{-1} units (KBr disc).

No.	Compound	$\nu(\text{O-H})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu(\text{N=N})$	$\nu(\text{C-S})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
1	$\text{LH}_2=\text{Ligand}$	3325 w.br.	1600 m	1595 s.	1520 m. 1480 s.	1275 m. 825 s.	—	—	—
2	$[\text{Cr}(\text{LH})_2]\text{Cl}\cdot\text{H}_2\text{O}$	3480 w.br.	1600 s.	1560 m.	1510 w. 1465 s.	1270 m. 830 m.sh	565 m.	440 w.	425 w.
3	$[\text{Co}(\text{LH})_2]\text{Cl}\cdot\text{H}_2\text{O}$	3450 w.br.	1600 m.	1520 S.	1500 m. 1455 m.	1270 m. 825 m.	540 w.	465 w.	430 w.
4	$[\text{Ni}(\text{LH})_2]\cdot\text{H}_2\text{O}$	3440 m.br	1605 m.	1545 s.	1510 s. 1460 m.	1275 s. 835 m.	575 w.	460 w.	420 w.
5	$[\text{Zn}(\text{LH})\text{Cl}]\cdot\text{H}_2\text{O}$	3435 w.br	1600 s.	1565 m.	1495 w. 1450 m.	1275 m. 820 m.	560 w.	455 w.	430 w.
6	$[\text{Cd}(\text{LH})\text{Cl}]\cdot\text{H}_2\text{O}$	3420 w.br.	1600 m.	1560 s.	1480 m. 1465 m.	1275 m. 830 s.	570 w.	445 w.	435 w.
7	$[\text{Ag}(\text{LH})\text{H}_2\text{O}]$	3360 w.br.	1600 s.	1540 m. sh.	1485 s. 1440 w.	1275 m. 845 w.	535 w.	465 w.	440 w.

$\text{LH}_2=\text{ligand}(6\text{-BrBTABA})$, W=weak , S=strange ,m= medium , br=broad , sh= shoulder .

3.3- Calculation of the metal complexes stability constant (β)

Stability constant are determined spectrophotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength (λ_{max}), pH values and concentration. The degree of formation of the chelat complexes are calculated based on the relationship (W.C.Vosburgh and G.R.Cooper, 1941), $\beta=(1-\alpha)/(\alpha^2c)$ for (1:1) metal complexes(M:L) and $\beta=(1-\alpha)/4\alpha^3c^2$, for 1:2 metal complexes (M:L), and $\alpha=(A_m - A_s)/A_m$, where A_s and A_m are the absorbance of the partially and fully formed complex respectively at optimum concentration.

The calculated β and $\log \beta$ values for the prepared complexes are given in table (3). The stability constants follows the sequence ; $Co(II) > Cr(III) > Ni(II) > Zn(II) > Ag(I) > Cd(II)$; the the sequence of metal ions of first row transition metal agree with Irving-williams series of stability constant (F.A.Catton and G.Willkinson, 1980).

3.4-Magnetic properties and electronic spectra

The electronic absorption spectral and magnetic moment data of solid state complexes at room temperature are reported in table (3). The magnetic moment of the $Cr(III)$ complex gave a little higher value ($\mu_{eff} = 4.16 B.M$) which suggest a low spin octahedral geometry ($t_2^3 g^0 e g$)⁽²⁹⁾. The

electronic spectrum of this complex showed two bands at 980 nm ($10204 cm^{-1}$) $v_1[{}^4A_2 g(F) \longrightarrow T_2^4 g(F)]$ and 526 nm ($19011 cm^{-1}$) $v_2[{}^4A_2 g(F) \longrightarrow T_1^4 g(F)]$. The value of magnetic moment of the cobalt(II) complex has been found to be diamagnetic ($\mu_{eff} = 0.0 B.M$) which suggest a low spin octahedral geometry ($t_2^6 g^0 e g$) because of this complex indicates that $Co(II)$ is oxidized to $Co(III)$ during complexation. The change of the oxidation state due to the aqueous solution of $Co(II)$ salts are spontaneously oxidized to $Co(III)$ in the presence of strong ligand such as thiazolylazo compounds (A.M.Ali et al, 2006) (W.C.Vosburgh and G.R.Cooper, 1941). The $Co(III)$ complex showed two absorption bands at 630 nm ($15873 cm^{-1}$) and 487 nm ($20534 cm^{-1}$) attributed to $v_1[{}^1A_1 g \longrightarrow T_1^1 g]$ and $v_2[{}^1A_1 g \longrightarrow T_2^1 g]$ transitions respectively. Nickel(II) complex evaluate magnetic moment of $\mu_{eff} = 2.97 B.M$ which suggest a high spin octahedral geometry ($t_2^6 g^2 e g$) (P.Venkateswar et al, 1986). The d-d transition in the spectrum of this complex showed three bands were observed as 967nm ($10431 cm^{-1}$), 514 nm ($19455 cm^{-1}$) and 407 nm ($24570 cm^{-1}$) attributed to $v_1[{}^3A_2 g \longrightarrow T_2^3 g(F)]$, $v_2[{}^3A_2 g \longrightarrow T_1^3 g(F)]$ and $v_3[{}^3A_2 g \longrightarrow T_1^3 g(p)]$ transitions respectively. Magnetic susceptibility for $Zn(II)$, $Cd(II)$ and $Ag(I)$

complexes are diamagnetic ($\mu_{\text{eff}} = 0.0$ B.M) due to the electronic configuration $d^{10}(t_2^6 e^4 g)$ and the electronic spectra of these complexes exhibit high intense charge transfer transition in the visible region (515-543) nm, which are assigned as metal to ligand charge transition (MLCT) (Ayman H.Ahmed et al, 2006). The electronic spectral of the prepared ligand (6-BrBTABA), three absorption bands were detected, first one located at 416nm (24038) cm^{-1} for $(n \rightarrow \pi^*)$ of the azo group (N=N) while the second was at 296 nm (33784) cm^{-1} for $\pi \rightarrow \pi^*$ of the two interact

(C=C) groups of aromatic and thiazole rings (T.Shimonouchi and I.Nakagawa, 1962) and the third one located at 235 nm (42553) cm^{-1} for $n \rightarrow \sigma^*$ of the hydroxyl group(OH).

3.5- conductivity measurements

The molar conductivity were measured for all complexes by using dimethyl formamide DMF as a solvent with the concentration of 10^{-3} M at room temperature. Most complexes showed very weak conductance which means non ionic nature (D.A.Skoog, 1988) while the Cr(III) complex and Co(II) complex to be a good electrolyte 1:1 with ionic nature (Khalid.J.Al-adely, 2007) (table3).

Table (3):- Electronic spectra, conductivity measurements and magnetic moment.

No.	Complexes	Absorption bands $\nu \text{ cm}^{-1}$	Transition	Conductivity $\text{S.mol}^{-1}.\text{cm}^2$	μ_{eff} (B.M)
1	[Cr(LH) ₂]Cl.H ₂ O	10204	${}^4A_2 g \xrightarrow{\nu_1} T_2 g(F)$	85.31	1.83
		19011	${}^4A_2 g \xrightarrow{\nu_2} T_1 g(F)$		
2	[Co(LH) ₂]Cl.H ₂ O	15873	${}^1A_1 g \xrightarrow{\nu_1} T_1 g$	79.53	(0.00)dia
		20534	${}^1A_1 g \xrightarrow{\nu_2} T_2 g$		
3	[Ni(LH) ₂].H ₂ O	10341	${}^3A_2 g \xrightarrow{\nu_1} T_2 g(F)$	9.25	2.97
		19455	${}^3A_2 g \xrightarrow{\nu_2} T_1 g(F)$		
		24570	${}^3A_2 g \xrightarrow{\nu_3} T_1 g(P)$		
4	[Zn(LH)Cl].H ₂ O	—	—	8.51	(0.00)dia
5	[Cd(LH)Cl].H ₂ O	—	—	10.83	(0.00)dia
6	[Ag(LH)H ₂ O]	—	—	12.47	(0.00)dia

3.6-Effect of pH and time

To study of pH effect we found that the absorbance of complex solution was effected with change pH values. The absorption of chelat complexes solution were studied in the 50% (V/V) ethanolic solution at pH(5.0-8.5).This results are agree with literature

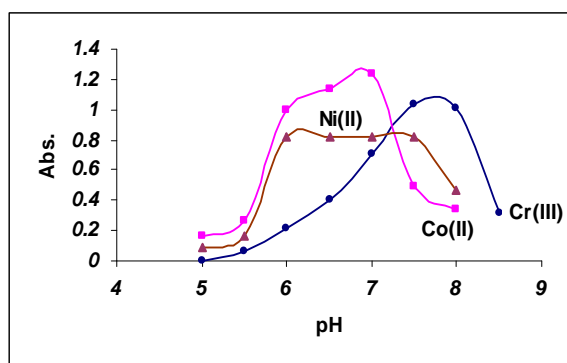


Fig (7):- Effect of pH on the absorbance of (6-BrBTABA) –metal chelats;ligand Conc. =(1.25x10⁻⁵M); metal ions Conc.=(1.75-2.25)

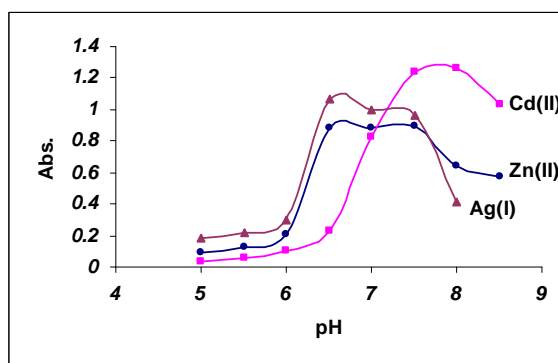


Fig (8):- Effect of pH on the absorbance of (6-BrBTABA) –metal chelats;ligand Conc.=(1.25x10⁻⁵M); metal ions Conc. x10⁻⁵M =(1.25-1.75)x10⁻⁵M.

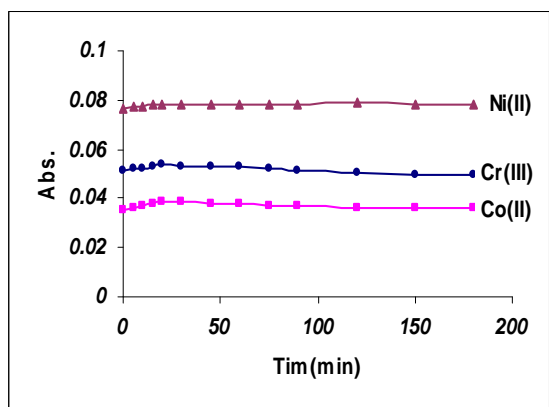


Fig (9):-Effect of time on the absorbance of metal complexes ;M=Cr(III),Co(II) and Ni(II)

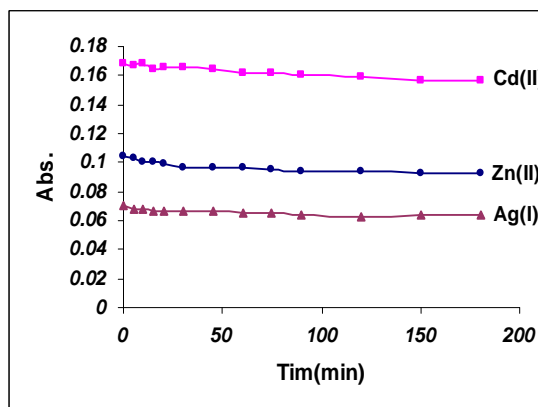


Fig (10):- Effect of time on the absorbance of metal complexes; M=Zn(II),Cd(II) and Ag(I)

3.7- Metal :Ligand Ratios

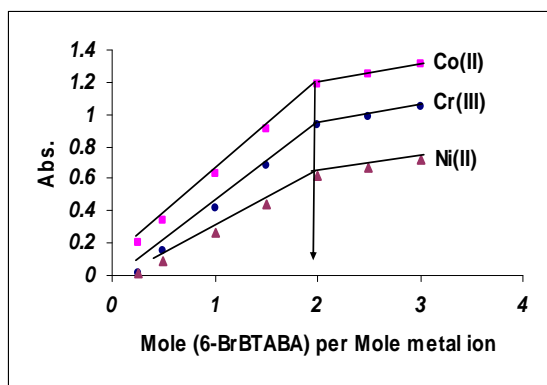
The metal:ligand ratios(M:L) of chelat complexes were determined by the

(Havard R.Hovind , 1975). In the figures (7)and(8) shows the effect of pH .Also we absorbed the reaction are complete in 10 min at room temperature and remains stable for at least 24 hr. .This shows that ligand (6-BrBTABA) demonstrats strong coordination with all our metal ions (figurs. 9&10).

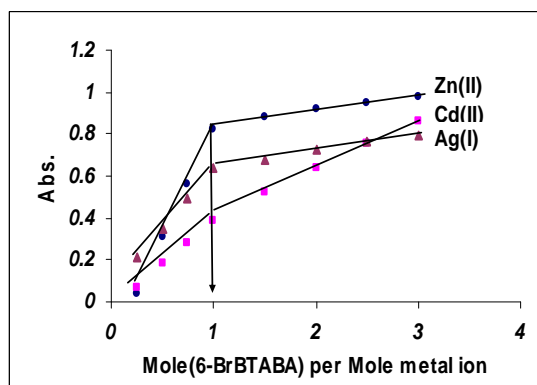
spectrophotometric method of molar ratio at fixed molar concentration ,optimal pH and wavelengths of maximum absorption(λ_{max}) in

aqueous ethanolic solution 50% (V/V). The ligand was found to form 1:1(L:M) complexes with Zn(II), Cd(II) and Ag(I) metal ions and 1:2 (M:L) chelate complexes with Cr(III), Co(II) and Ni(II) metal ions. The results of this study are shown in figures (11) and

(12). The optimal pH, optimal concentration, mole ratios (M:L), stability constants (β and $\log\beta$) and maximum absorption wavelengths (λ_{max}) with molar absorptivity (ϵ) of these complexes are listed in table (4).



**Fig.(11):-Molar ratio method (M:L)
(6-BrBTABA)-metal chelates
M=Cr(III),Co(II) and Ni(II)**

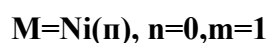
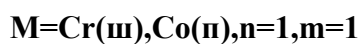
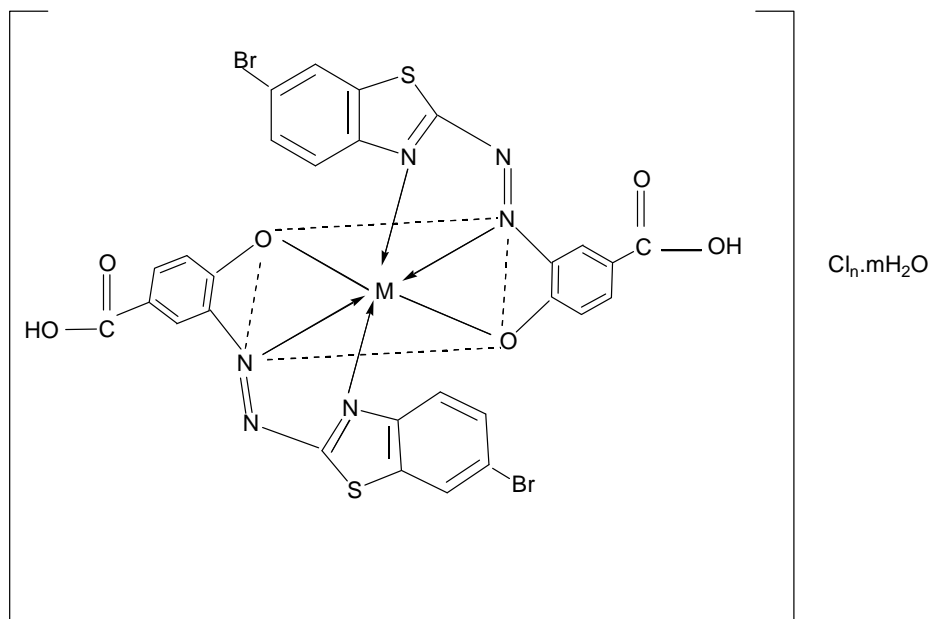


**Fig.(12):- Molar ratio method (M:L)
(6-BrBTABA) -metal chelates
M=Zn(II),Cd(II) and Ag(I).**

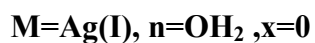
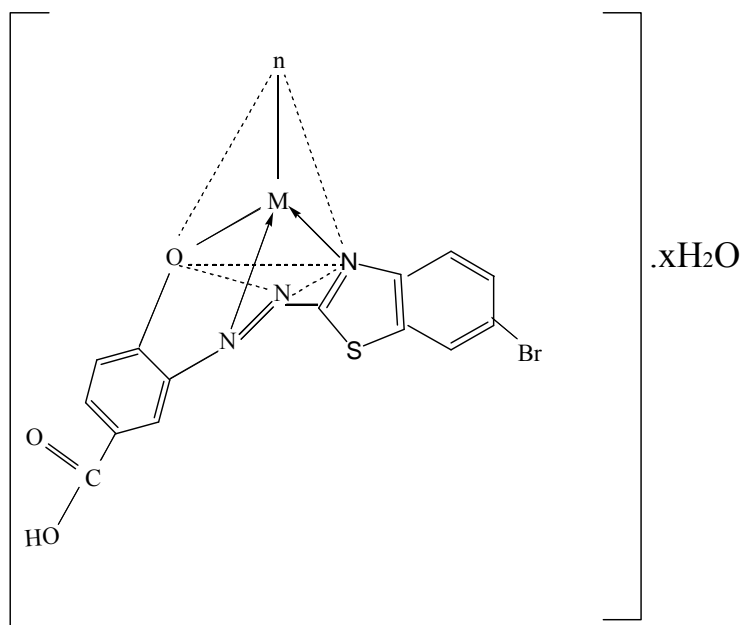
Table(4): The optimal pH values, optimal concentration, mole ratios, stability constants (β and $\log\beta$) and wavelengths(λ_{max}) with molar absorptivity(ϵ) of metal ions.

Ligand	Metal Ions	Optimal pH	Optimal molar conc. x 10^{-5} M	Metal : ligand	Molar absorptivity (ϵ)x 10^4 L. mol ⁻¹ .cm ⁻¹	Optimal wave length (λ_{max})nm	β L ² .mol ⁻²	Log β
6-BrBTABA , $\lambda_{max}= 416$ nm $\epsilon=7.22 \times 10^4$ L.mol ⁻¹ .cm ⁻¹ Conc.= 1.25x 10^{-5} M	Cr(III)	7.5	2.25	1:2	3.70	521	36.79×10^{10}	11.56
	Co(II)	7.0	1.75	1:2	3.57	630	82.09×10^{10}	11.91
	Ni(II)	6.0	2.00	1:2	4.63	516	7.87×10^{10}	10.89
	Zn(II)	7.5	1.50	1:1	6.25	520	21.51×10^5	6.33
	Cd(II)	8.0	1.25	1:1	7.34	531	1.17×10^5	5.07
	Ag(I)	6.5	1.75	1:1	5.21	515	12.64×10^5	6.10

According to above data the structural formula of chelat complexes may be proposed figs.13 and 14 .



Fig(13):-The proposed structural formula of Cr(III),Co(II) and Ni(II) complexes .



Fig(14):-The proposed structural formula of Zn(II), Cd(II) and Ag(I) complexes .

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تحضير ودراسة تشخيص بعض معقدات العناصر الانتقالية مع ليكاند الازو الجديدة 5 - [6-برومو-2-بنزو ثيازوليل (ازو) -4-هايديروكسي حامض البنزويك .

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الخلاصة :-

تضمن البحث تحضير صبغة ثيازول ازو جديده 5- [6-برومو-2-بنزو ثيازوليل (ازو) -4-هايديروكسي حامض البنزويك (6-BrBTABA=LH₂) وذلك بواسطة تفاعل الازدواج بين كلوريد (6-برومو-2-بنزو ثيازوليل الديدازونيوم) و 4-هايديروكسي حامض البنزويك في المحيط القاعدي . كما يتناول البحث تحضير ودراسة معقدات مخلبيه لا يونات الكروم (III) و الكوبلت (II) و النيكل (II) و الخارصين (II) و الكادميوم (II) والفضة (I) مع الليكاند المذكور . شخص الليكاند ومعقداته بواسطة التحليل الدقيق للعناصر والتوصيليه المولاريه و قياسات الحساسيه المغناطيسيه عند درجة حرارة الغرفة والاشعة تحت الحمراء والاطياف الالكترونيه وقد بينت النتائج التحليليه ان نسبة (الليكاند : الفلز) هي (1:2) لمعقدات الكروم (III) و الكوبلت (II) و النيكل (II) ولكن (1:1) لمعقدات الخارصين (II) و الكادميوم (II) والفضة (I) .