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PREPARATION AND SPECTRAL CHARACTERIZATION OF NEW THIAZOLYLAZO LIGAND WITH SOME TRANSITION METAL COMPLEXES

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Abstract

Some transition metal complexes of Fe(ш),Co(п),Ni(п),Cu(п),Zn(п)and Ag(I) with new benzothiazolylazo ligand 2-[(6-nitro-2^{-}-benzothiazolyl)azo]-4-nitro phenol(6-NO_2BTAP=LH)were prepared and characterized by elemental analysis ,magnetic susceptibility at room temperature ,molar conductance measurements, infrared and electronic spectra. The isolated solid complexes are found to have the general formula $[ML_2]Cl_n.{}_mH_2O$, where n=1,m=1 when M=Fe (ш), Co(п) and n=0, m=0 when M= Ni(п) and Cu(п) or [MLX]. $_mH_2O$ when x= Cl ,m=1 ,M= Zn(п) and x=H_2O,m=0,M= Ag(I).Electronic spectra and magnetic susceptibility data has supported the proposed octahedral geometry of Fe(ш),Co(п) Ni(п) and cu(п) complexes , but tetrahedral geometry of Zn(п) and Ag(I) complexes .The coordination number of all ions are found to be six ,except of Zn(п) and Ag(I) were found four ,with bonding through the phenolate O ,azo N and with thiazole N .The mole ratio method of the metal:ligand (M:L) has showed 1:2 for all the prepared complexes except of Zn(п) and Ag(I) complexes were found 1:1.

Introduction

Thiazolyl azo phenols ligands and its derivatives are described as heterogenous compounds and investigated for many purposes.(1-3) Thiazolyle azo and benzothiazolyl azo dyes have attracted much attention as they are sensitive chromogenic reagents in addition to being important complexing agents(4-6). They have been used for spectrophotometric and extraction photometric determination of many metal ions(7,8).These dyes are applied for dyeing fibers(9,10)and different biological industrial fields of life (11,12). The azo dyes give colored complexes with most metals ,especially with some transition metal ions(13,14).Thiazolylazo molecule being a π-acidic azo imine group (─N=N─C=N─) for this reason a number of these compounds were prepared as chelating ligands(15-18).

This work describe the preparation and characterization of some transition metal complexes , using the new thiazolyazo ligand (6-NO_2BTAP) .

Experimental

1- Materials and Instruments

All chemicals were of highest purity and used BDH, Aldrich and Fluk except of 2-amino-6-nitro benzothiazole was prepared as described in the literature(19).

Electronic absorption spectra in the visible and ultraviolet regions were measured with a shimadzu UV-1650 spectrophotommeter using ethanol as solvent .Infrared spectra were measured with FT-IR-8000 shimadzu , in the 4000-400 cm^{-1} range using C_SI disc .

Atomic absorption spectrophotometer –AA-160shimadzu was used .

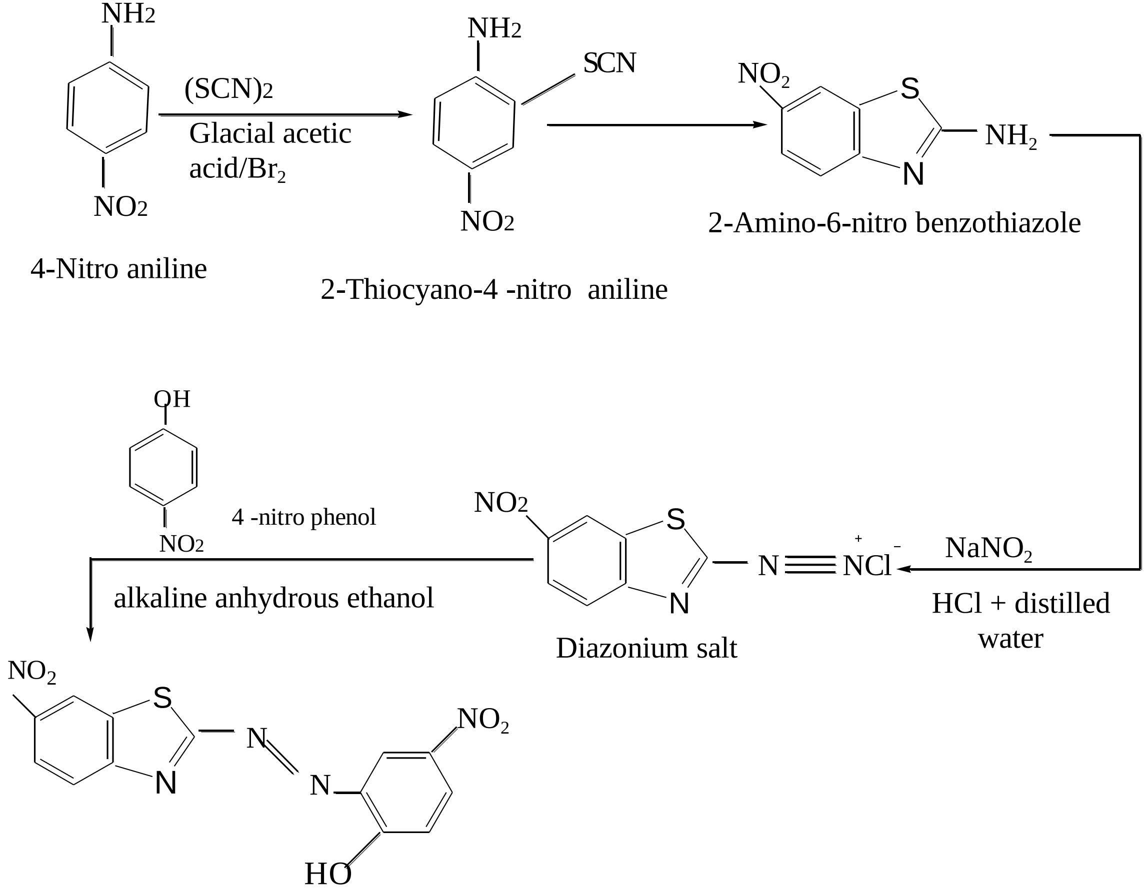
Elemental C.H.N analysis were carried out by Perkin–Elmer 2400 elemental analyzer .The magnetic susceptibility of the prepared complexes were obtained at room temperature using Farady method for this purpose ,balance magnetic MSB-MI had been employed .The pH values were determined with a Philips PW 9421 pH meter (pH $\mp$0.001) .

Electronic molar conductivity measurement were carried out at room temperature by conductivity bridge model Ec 219 with solute concentration (10^{-3} M) in DMF. Electro thermal melting point 9300 was used to measure the melting point of ligand and their complexes.

2. Preparation of ligand (6-NO_2BTAP)

The azo ligand (6-NO_2BTAP) was prepared by dissolving (1.95 gm, 0.01 mol) 2-amino-6-nitro benzothiazole in 50 ml of distilled water and 10ml of concentrated hydrochioric acid. The filtered solution was cooled below 5°C. To this mixture a solution of (0.75 gm, 0.01 mol) of sodium nitrate in 25 ml of distilled water was added dropwise at 0-5 °C and the mixture was stirred for 40 min. This diazonium chloride solution was added dropwise in 500 ml beaker containing (1.39 gm, 0.01 mol) of 4-nitro phenol dissolved in 200ml anhydrous ethanol and cooled to 0-50 °C.

The mixture was stirred for an additional 4 hours, in ice-bath allowed to stand over night and acidified with dilute hydrochloric acid to pH =6.0. The precipitate crude dyes were collected by filtration and recrystallization from hot ethanol and dried in a vacuum desiccator over anhydrous $CaCl_2$. A dark red crystals melting at 102 °C. The preparation of this ligand is shown in Scheme (1).



Scheme (1) Methods of preparation of the ligand 2-[(6-Nitro-2-benzothiazolyl)azo]-4- nitro phenol (6-NO_2BTAP=LH).

3- Prepartion of Complexes

The complexes were prepared by adding (0.345gm, 0.001 mol) of ligand (6-NO_2BTAP) dissolved in 50 ml hot anhydrous ethanol to a hot solution of metal chloride(0.0005 mol); $FeCl_3.6H_2O$, $CoCl_2.6H_2O$,$NiCl_2.6H_2O$ and $CuCl_2$ while (0.001 mol) of $ZnCl_2$ and $AgNO_3$ dissolved in 30ml buffer solution (ammonium acetate) at optimal pH for each metal ions. The mixture was stirring and heated to 50 °C for 1 hr., then left overnight where the solid complexes precipitated. They were filtered off, washed with ethanol 10 ml to remove the remaining unreacted substances and dried in a desiccators over anhydrous $CaCl_2$.

3.1-Result and Discussion

1- Characterization of ligand and

The azo dye ligand (6-NO_2BTAP) was drak red crystals but the coordination complexes of this ligand with Fe(ш),Co(п),Ni(п),Cu(п), Zn(п) and Ag(I) ions vary in color from purple, green and blue .The ligand and their solid complexes are stable in air ,insoluble in water but soluble in most organic solvents such as methanol ,ethanol ,acetone ,DMF and MSO. The result of elemental analysis and physical properties of prepared ligand and their complexes are given in Table (1).

Table (1)

Physical properties and analytical data of the ligand (6-NO_2BTAP=LH) and their complexes.

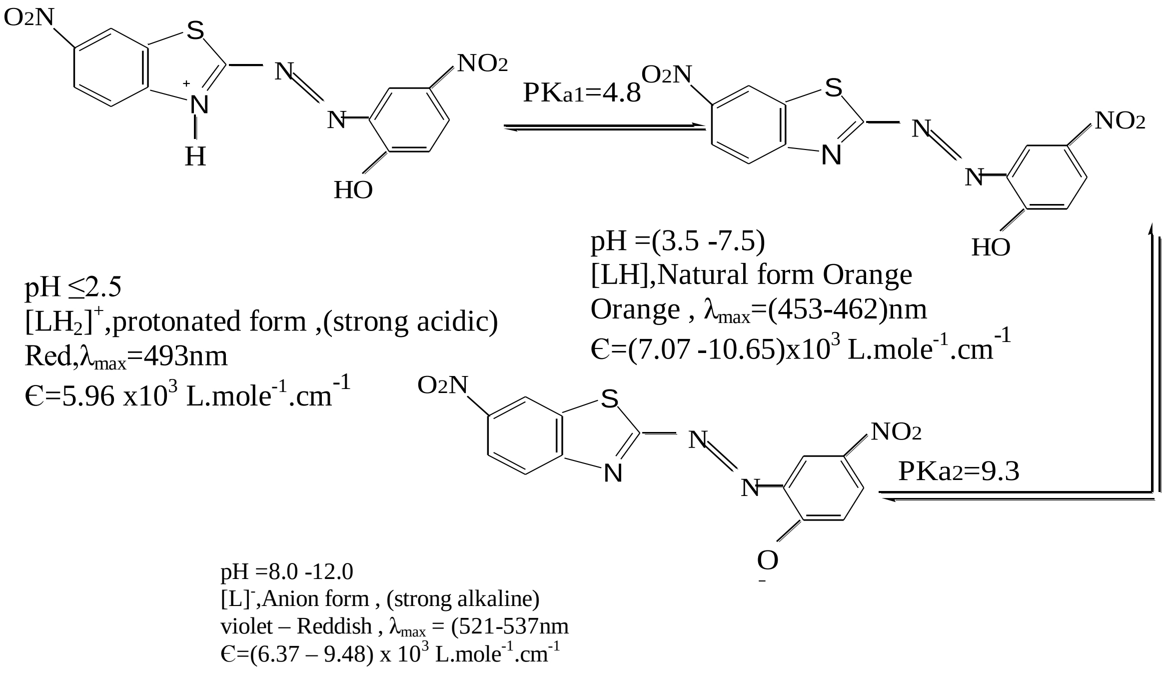
No.	Compound	Color	m.P C°	Yield %	Molecular formula (Mol.Wt)	Found (Calc.)%			
						C	H	N	M
1	LH	Dark red	102	67	$C_{13}H_7N_5O_5S$ (345.29)	45.31 (45.22)	1.95 (2.04)	20.43 (20.28)	——
2	$[FeL_2]Cl.H_2O$	Blue	167	73	$C_{26}H_{14}N_{10}O_{11}S_2ClFe$ (797.87)	39.23 (39.14)	1.66 (1.77)	17.44 (17.56)	6.79 (6.99)
3	$[CoL_2]Cl.H_2O$	Purple	194	61	$C_{26}H_{14}N_{10}O_{11}S_2ClCo$ (800.96)	38.87 (38.99)	1.63 (1.76)	17.67 (17.49)	7.59 (7.36)
4	$[NiL_2]$	Dark Purple	210 d.	58	$C_{26}H_{12}N_{10}O_{10}S_2Ni$ (747.25)	41.87 (41.79)	1.69 (1.62)	18.56 (18.74)	7.62 (7.85)
5	$[CuL_2]$	Green	186	72	$C_{26}H_{12}N_{10}O_{10}S_2Cu$ (752.10)	41.43 (41.52)	1.55 (1.61)	18.78 (18.62)	8.63 (8.45)
6	$[ZnLCl].H_2O$	Purple	218 d	65	$C_{13}H_8N_5O_6SClZn$ (463.13)	33.85 (33.72)	1.66 (1.74)	14.95 (15.12)	13.88 (14.12)
7	$[AgL(H_2O)]$	Purple redash	148	53	$C_{13}H_8N_5O_6SAg$ (470.16)	33.08 (33.21)	1.63 (1.71)	15.03 (14.90)	-

d = decompose

2- Acid base dissociation behavior of the ligand

The ligand (6-NO_2BTAP) showed acid-base indicator properties and were red in strongly acidic, orange in neutral solution but Violet–Reddish in strong alkaline solution.

Three species of the ligand, $[LH_2]^+$, [LH] and $[L]^-$are involved in its acid-base behavior. (20,21). The Pka values obtained by spectrophotometric method**.** The dissociation of ligand (6-NO_2BTAP) may formula is shown in Scheme (2).



pH ≤2.5
$[LH_2]^+$,protonated form ,(strong acidic)
Red,λ_{max}=493nm
Є=5.96 x10^3 L.mole^{-1}.cm^{-1}

pH =(3.5 -7.5)
[LH],Natural form Orange
Orange , λ_{max}=(453-462)nm
Є=(7.07 -10.65)x10^3 L.mole^{-1}.cm^{-1}

pH =8.0 -12.0
$[L]^-$,Anion form , (strong alkaline)
violet – Reddish , λ_{max} = (521-537nm
Є=(6.37 – 9.48) x 10^3 L.mole^{-1}.cm^{-1}

Scheme (2) Acid–base dissociation behavior of ligand (6-NO_2BTAP).

3- Infrared spectra

The infrared spectroscopic data of ligand and their complex with Fe(ш),Co(п),Ni (п),Cu(п),Zn(п) and Ag(I) are summarized in Table (2) .These spectra are complicated owing to the extensive overlap of number of bands arising due to υ(O─H), υ(C═N), υ(N═N) and other bands originate due to phenyl and thiazole rings appeared in the region below 1650 cm^{-1}, the comparison between spectra of the ligand with those of there coordination complexes have revealed certain characteristic :-

1- The IR spectrum of ligand (6-NO_2BTAP) gives characteristic broad band at 3438 cm^{-1} assigned to the phenolic υ(O─H). This suggests a strong intermolecular hydrogen bonding (15,16). In the spectra of Fe(ш), Co(п),Zn(п) and Ag(I) complexes show broad and weak bands around (3170-3417)cm^{-1} indicate the presence of water molecule in these complexes(22-24). But this band was disappeared in the spectra of rest complexes.

2- This weak band had been observed at 3115 cm^{-1} in the spectrum of the free ligand which was due to υ(C─H) aromatic. This band was stable in position as well as in intensity in both ligand and metal complexes.

3- The spectrum of ligand shows absorption band at 1605 cm^{-1} which is considered to be υ(C═N) of thiazole ring(15,25).This band shifts to lower frequency (1550-1597) cm^{-1} with a little change in shape in the metal complexesc spectra. These different suggest the linkage of metal ion with nitrogen of hetrocyclic ring. (23,26,27)

4- The azo group intens bands at 1519cm^{-1} and 1345 cm^{-1} are due to asymmetric and symmetri stretching vibrations of the ─N═N─ group ,respectively(15).The band appearing at (1451-1493) cm^{-1} and (1327-1350) cm^{-1} respectively with some decrease in intensity of metal complexes spectra. Both band shift and reduced in intensity may indicate that azo group is coordinated to the metal ions to the formation complexes (27,28).

5- The υ(C─S) of thiazole ring appear at 1248 cm^{-1} and 854 cm^{-1} in the spectrum of free ligand. this band unchanged in all complexes means that the sulfur atom of hetero cyclic ring does not participate in coordination (23,26,29,30).

6- The presence of coordinated water molecule in the Ag(I) complexes is further indicated by weak bands at 763 cm^{-1} and 732 cm^{-1}.

7- New weak bands in the region (420-563) cm^{-1} which are never been observed in the free ligand spectrum this may attributed to υ(M─O), υ(M─N) and υ(M─Cl) bands.(27,31,32).

The IR spectra data lead to suggestthat ligand behaves as tridentate chelating agent coordinating through the positions of phenolic oxygen, nitrogen of azo group and thiazole ring nitrogen. Representative example for their spectra are given in Figs. (1-4).

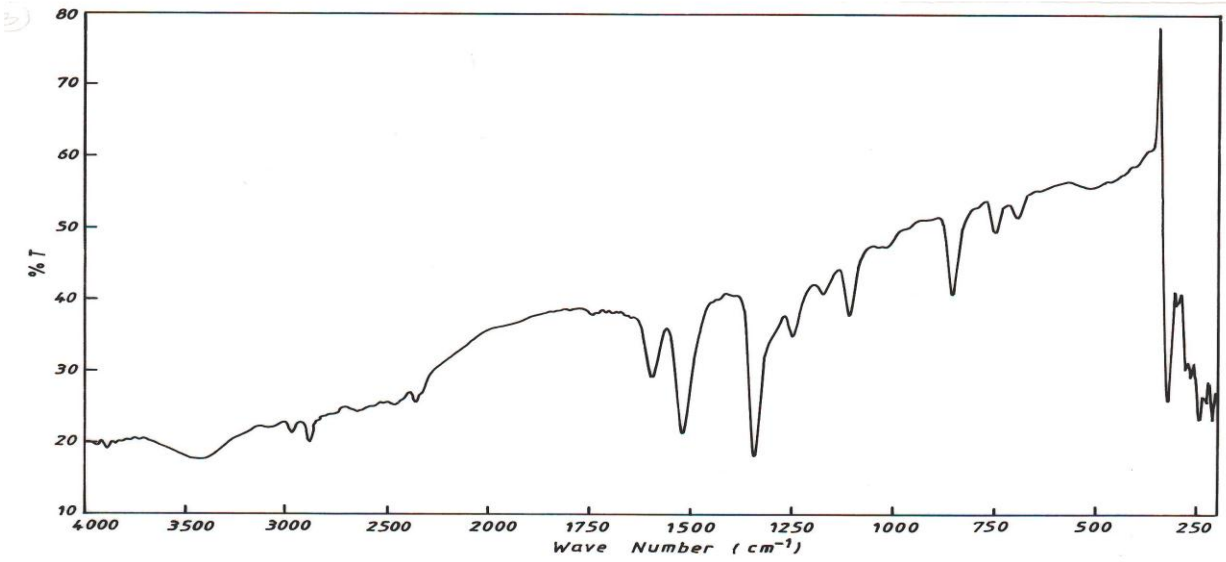


Fig. (1) : IR spectrum of the ligand (6-NO_2BTAP=LH).

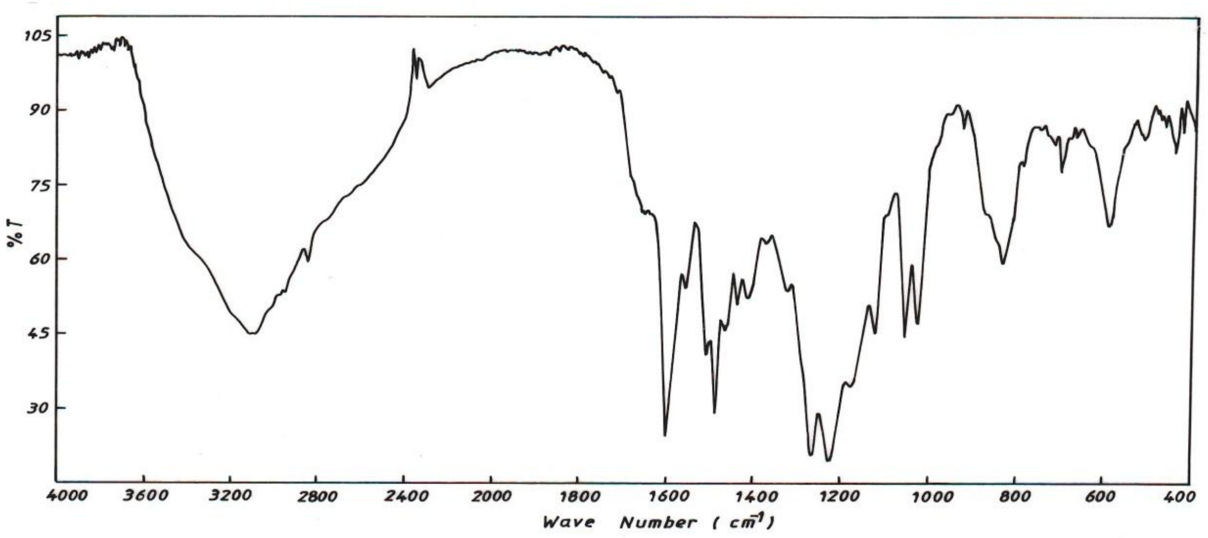


Fig. (2) : IR spectrum of the complex [FeL_2]Cl.H_2O.

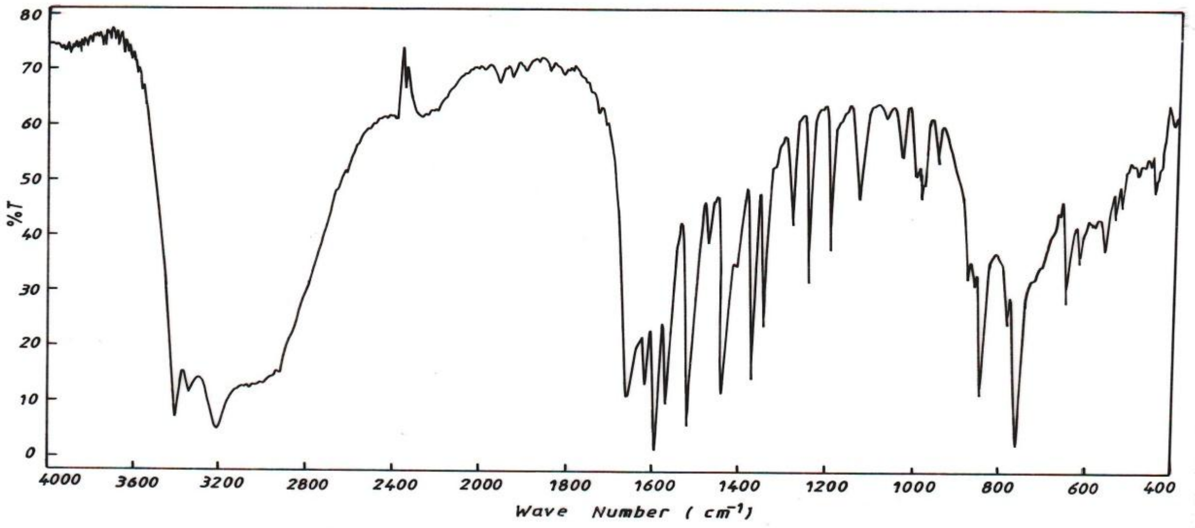


Fig. (3) : IR spectrum of the complex [ZnLCl].H_2O.

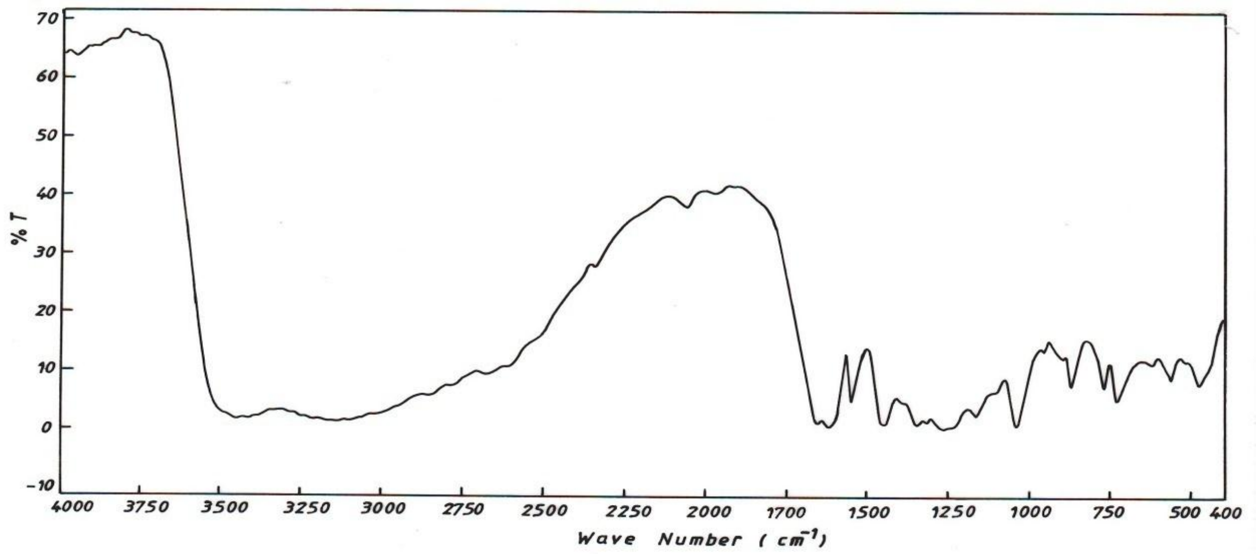


Fig. (4) : IR spectrum of the complex $[AgL(H_2O)]$.

Table (2)
Selected IR absorption bands of the ligand (6-NO_2BTAP) and their complexes in cm^{-1} units (CsI disc).

No.	Compound	υ(O─H)	υ(C═N)	υ(N═N)	υ(C─S)	υ(M─OH_2)	υ(M─O)	υ (M─N)	υ (M─Cl)
1	LH	3438 w.br.	1605 m	1519 m. 1345 s.	1248 w. 854 m.	──	──	──	──
2	$[FeL_2]Cl.H_2O$	3170 w.br.	1597 s.	1480 m. 1340 w.	1252 m. 850 m.	──	535 w.	440 w.	──
3	$[CoL_2]$ $Cl.H_2O$	3235 w.br.	1578 s.	1485 S. 1335 w.	1247 m. 855 w.	──	540 w.	425 w.	──
4	$[NiL_2]$	──	1583 m.	1470 m. 1327 w.	1250 m. 851 m.	──	557 w.	460 w.	──
5	$[CuL_2]$	──	1595 s.	1487 S. 1345 m.	1248 w. 851 m.	──	545w.	435 w.	──
6	[ZnLCl] .H_2O	3350 w.br.	1593 s.	1493 m. 1342 m.	1247 m. 850 s.	──	553 w.	455 w.	420w
7	$[AgL(H_2O)]$	3417 w.br.	1550 m.	1451 m. 1350 w.	1265 w. 857 m.	763.w 732.w	563 w.	471 w.	──

LH= ligand(6-NO2BTAP),
W=weak,
S=strange,
m= medium,
br=broad,
sh= shoulder.

4-Absorption spectra

The absorption spectra of ligand (6-NO_2BTAP) and their complexes with Fe(ш),Co(п),Ni(п),Cu(п),Zn(п)and Ag(I) ions were studied an aqueous ethanolic solution 50% (V/V). The absorption maxima (λ max) of the free ligand is 457 nm.

A btho chromic shfit ranging between (46-256) nm depending on the metal ion .The absorption spectra of the free ligand and their complexes are shown in Figs. (5 and 6).

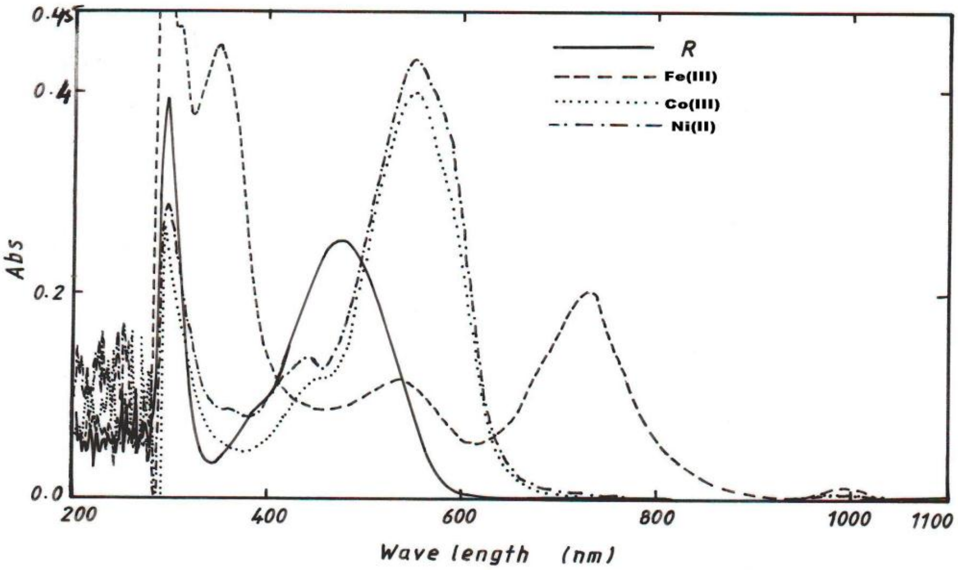
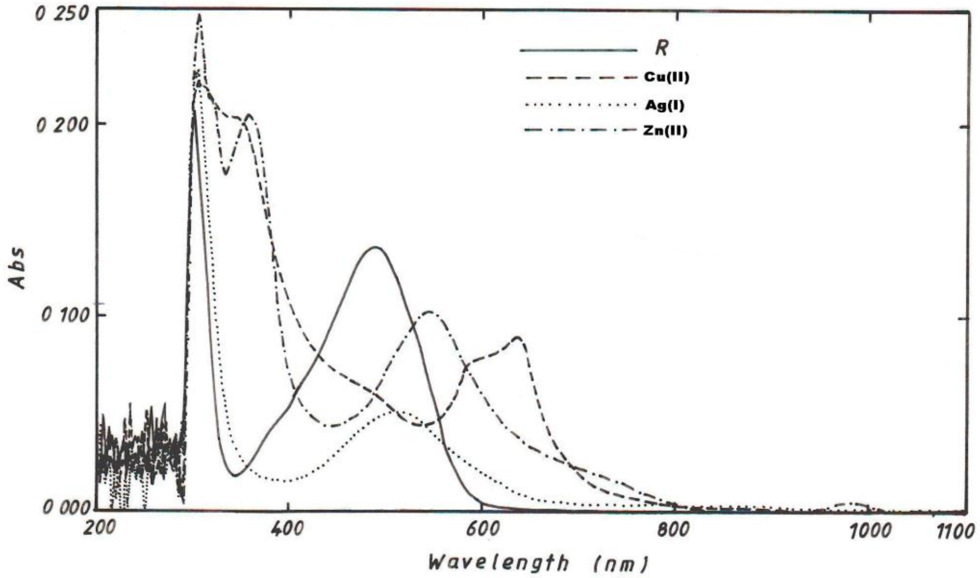


Fig. (5) : The absorption spectra of free ligand (LH) and their complexes in a suitable pH;Conc.=(1.75-2.50)x 10^{-4}M in aqueous ethanolic solution 50% (V/V);LH=(6-NO_2BTAP).



Fig(6) : The absorption spectra of free ligand (LH) and their complexes in a suitable pH;Conc.=(1.25-1.75)x 10^{-4}M in aqueous ethanolic solution 50% (V/V);LH=(6-NO_2BTAP).

5-Magentic susceptibility measurements

Magnetic susceptibility for all metal complexes were measured except Zn(п)and Ag(I) complexes due to the configuration d^{10} gave (μ_{eff} =0.0BM) these complexes have dia magnetic moment. The other metal complex showed the following values of magnetic moment in Table (3).

1- Iron (ш) complex absorbed magnetic moment value of μ_{eff}=1.83 B.M which suggest a low spin octahedral geometry ($t_2{}^5g\,\overset{0}{e}$g)(33).

2- The magnetic moment of the cobalt(п) complex gave a value of μ_{eff} =0.0B.M because the low spin behavior of this complex indicates that Co(п) is oxidized to Co(ш) during complexation to produce a diamagnetic propertics and octahedral geometry($t_2\overset{6}{g}\,\overset{0}{e}\overset{}{g}$).The change of the oxidation state agrees with earlier absorption that the aqueous solution of Co(п)salts are spontaneously oxidized to Co(ш) i n the presence of strong ligand such as thiazolylazo compounds(23,26).

3- Nickel(п) complex showed a magnetic moment value of μ_{eff} =2.97 B.M which can be a normal value for octahydral geometry high-spin($t_2{}^6g\,\overset{2}{e}$g)(23,33).

4- Copper(п) complex gave a value of magnetic moment μ_{eff}=1.76 B.M which suggest the presence of one unoaired electron in this complex and that suggest octahydral geometry ($t_2\,\overset{6}{e}\,\overset{3}{e}$g)(34).

6- Electronic Spectra

The prepared free ligand (6-NO_2BTAP), three absorption bands were detected, first and second bands located at 264 nm (37879 cm^{-1}) and 296 nm(33784 cm^{-1}) respectively referring to the $\pi \rightarrow \pi^*$ transitions while the third band located at 457nm(21882 cm^{-1}) is dueto the charge transfer characters(35,36). For the spectra of metal complexes the following results were obtained :

1- **Iron(ш) Complex**

The electronic spectrum of Fe(ш)-complex showed three bands at 979 nm (10214 cm^{-1}), 713 nm (14025cm^{-1}) and 536 nm (18657 cm^{-1}) attributed to

$${}^{4}A_{1}g \xrightarrow{\nu_1} {}^{4}T_{1}g(G),$$

$${}^{4}A_{1}g \xrightarrow{\nu_2} {}^{4}Eg$$

And

$${}^{4}A_{1}g \xrightarrow{\nu_3} {}^{4}T_{1}g(P)$$

transitions respectively.These bands suggest low spin octahedral geometry(37) and that agree with the value of magnetic moment (1.83 B.M).

2- Cobalt(ш) Complex

The Cobalt(ш) complex , two bands were observed at 561 nm (17825 cm^{-1}) and 306 nm(32680 cm^{-1}) corresponding to

$${}^{1}A_{1}g \xrightarrow{\nu_1} {}^{1}T_{1}g$$

And

$${}^{1}A_{1}g \xrightarrow{\nu_2} {}^{1}T_{2}g$$

transitions respectively .The complex was found to be diamagnetic behavior of this complex indicates that Co(п) is oxidized to Co(ш) during complication. These result with (0.0 B.M) suggest a low spin octahedral geometry (23,38) .

3- Nickel (II) Complex :

The electronic spectrum of this complex showed a three bands at 973 nm (10277m^{-1}), 559 nm (17889 cm^{-1}) and 440 nm (22727 cm^{-1}) attributed to

$${}^{3}A_{2}g \xrightarrow{\nu_1} {}^{3}T_{2}g(F),$$

$${}^{3}A_{2}g \xrightarrow{\nu_2} {}^{3}T_{1}g(F),$$

$${}^{3}A_{2}g \xrightarrow{\nu_3} {}^{3}T_{1}g(P)$$

transitions with an octahedral geometry(23,35,39).

4-Copper (II) Complex

The electronic spectrum of Cu(п)complex show abroad band at around 637(15698cm^{-1}) due to ${}^{2}Eg \rightarrow {}^{2}T_{2}g$ transition. It is reasonable to assign distorted octahedral structure(16,27,40).

5-Zinc(II) and Silver(I) Complexes

The electronic spectra of these complexes do not show any d-d transition band. The spectral data and magnetic moments are listed in Table (3).

7- Molar conductivity measurements

The molar conductivity were measured for all complexes using DMF as a solvent with the concentration of 10^{-3}M at room temperature. Most complexes showed no or very weak conductance which means non ionic nature(16,17,41).But the lower conductivity values for the Fe(ш) and Co (ш) complexes appeared to be a good electrolyte 1:1 with ionic nature Table (3) and that was approved by using a solution of silver nitrate and a white colloidal precipitate of silver chloride obtained.

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

Stability constants of all complexes prepared are obtained spectraphotometrically by measuring the absorbance of solutions of ligand and metal mixture at fixed wavelength (λ max) and pH values.

The degree of formation of the complexes is obtained from the relation ship(42), $\beta=(1-\alpha)/(\alpha^2c)$ for Ag(I) and Zn(п) complex (1:1=M:L),but$\beta=(1-\alpha)/4\alpha^3c^2$),for remaining metal complexes (1:2=M:L), and $\alpha = A_m - A_s / A_m$, where A_m and A_s are the absorbance of the partially and fully formed complex respectively at optimum concentration.

The calculated log β values for the prepared complexes are given in Table (3). The stability constants follows the sequence Cu(п)>Co(п)>Fe(ш)>Ni(п)>Ag(I)>Zn(п). The high stability constant of ligand (6-NO_2BTAP) to ward Cu(п) is remarkable over the other ions .This implies a considerably higher affinity toward this ion.

Table (3)

Electronic spectra, magnetic moment measurements and stability constant values (β).

No.	Complexes	λmax n.m	Absorption bands ν cm^{-1}	Transition	Conductivity S.mol^{-1}.cm^2	*μeff* (B.M)	β L^2. Mol^{-2}	Logβ
1	[FeL_2]Cl.H_2O	979	10214	${}^4A_1g \xrightarrow{\nu_1} {}^4T_1g(G)$	85.31	1.83	4.266x10^9	9.630
		713	14025	${}^4A_1g \xrightarrow{\nu_2} {}^4Eg$				
		536	18657	${}^4A_1g \xrightarrow{\nu_3} {}^4T_1g(P)$				
2	[CoL_2] Cl.H_2O	561	17825	${}^1A_1g \xrightarrow{\nu_1} {}^1T_1g(G)$	79.53	dia	5.364x10^9	9.729
		306	32680	${}^1A_1g \xrightarrow{\nu_2} {}^1T_2g(G)$				
3	[NiL_2]	973	10277	${}^3A_2g \xrightarrow{\nu_1} {}^3T_2g(F)$	9.25	2.97	1.583x10^9	9.199
		559	17889	${}^3A_2g \xrightarrow{\nu_2} {}^3T_1g(F)$				
		440	22727	${}^3A_2g \xrightarrow{\nu_3} {}^3T_1g(P)$				
4	[CuL_2]	637	15698	${}^2Eg \rightarrow {}^2T_2g$	8.12	1.76	8.992 x 10^{10}	10.953
5	[ZnLCl].H_2O	529	——	——	7.53	(0)dia	7.095 x 10^5	5.850
6	[AgL(H_2O)]	503	——	——	5.93	(0)dia	8.394 x 10^5	5.924

To evaluate optimal pH values on the absorbance for the metal complexes solution were studied in the 50% (V/V) ethanolic solution as shown in Figs. (7 and 8). The ligand (6-NO$_2$BTAP) formed a very stable complex with metal ions Fe(ш), Co(п), Ni(п), Cu(п), Zn(п) and Ag(I) a wide pH range.

The absorption spectra did not change over the whole range. The optimal pH, optimal concentration and wavelength (λ max) with molar absorptivity (Є) of Fe(ш) ,Co(ш), Ni(п), Cu(п), Zn(п) and Ag(I) complexes are shown in Table (4).

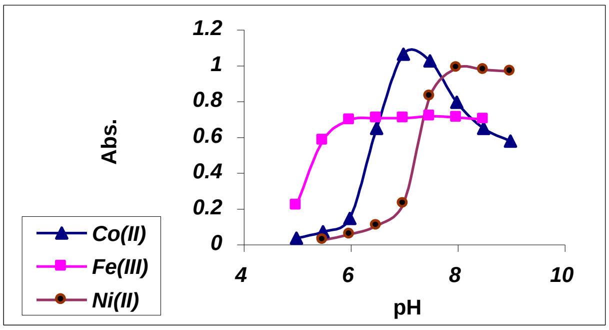


Fig.(7) : The absorption spectra of 6-NO2BTAP metal chelats (1.75-2.50) x10^{-4} M, in aqueous ethanolic solution 50% (V/V).

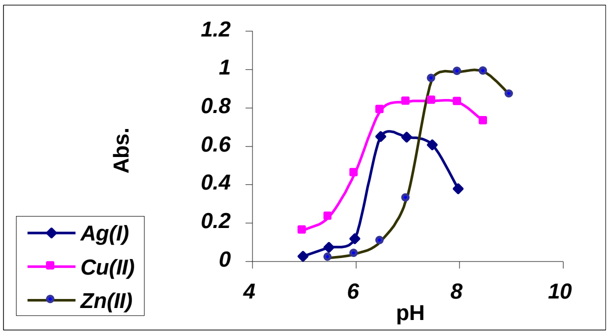


Fig. (8) : The absorption spectra of 6-NO2BTAP metal chelats (1.25-1.75) x10^{-4} M, in aqueous ethanolic solution 50% (V/V).

Table (4)

Absorptivity (Є) of metal ions in aqueous ethanolic solution 50% (V/V).

Ligand	**Metal Ions**	**Optimal pH**	**Optimal molar conc. x 10^{-4} M**	**Metal: ligand**	**Molar absorptivity (Є)x10^{3}L.mol^{-1}.cm^{-1}**	**Optimal wave length (λ_{max})nm**	**$\Delta\lambda^{a}_{max}$ nm**
6-NO$_2$BTAP ,λ_{max}=457nm Є=2.41 x 10^{3} L.mol^{-1}.cm^{-1}	Fe(ш)	7.5	1.75	1:2	1.15	713	256
	Co(ш)	7.0	2.50	1:2	1.72	561	104
	Ni(п)	8.0	2.25	1:2	1.6	559	102
	Cu(п)	7.5	1.5	1:2	0.64	637	180
	Zn(п)	8.5	1.25	1:1	0.86	529	72
	Ag(I)	6.5	1.75	1:1	0.35	503	46

10- Effect of time

The effect of time on the absorbance of the metal complexes were studied in ethanolic solution maximum value within 10min at room temperature and remains stable for about 24 hour. The result are shown in Figs. (9 and 10).

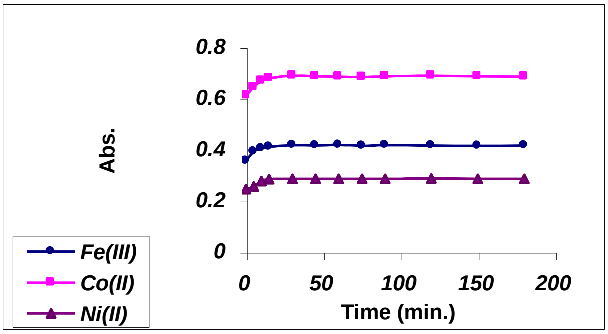


Fig. (9) : Effect of time on the absorbance of metal complexes ;M=Fe (ш),Co(ш) and Ni(п).

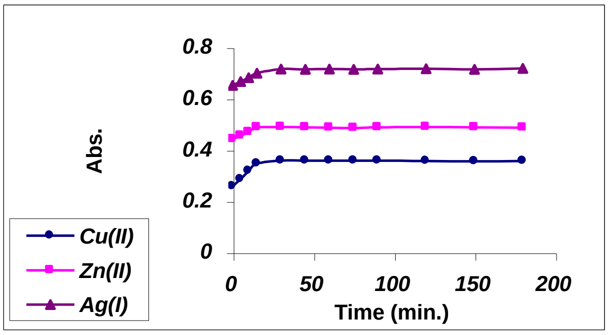


Fig. (10) : Effect of time on the absorbance of metal complexes; M=Cu(п),Zn(п) and Ag(I).

11- Effect of temperature

The effect of temperature on the absorbance of the metal complex were studied Figs.(11 and 12) show this effect the study was performed at temperature at the range (10-70) °C and the maximum absorption was obtained when the temperature was varied between 10 °C and 30 °C at temperature higher than 30 °C the absorbance gradually decreased with increasing temperature until it reaches 70 C° which may be due to dissociation of the metal complexes.

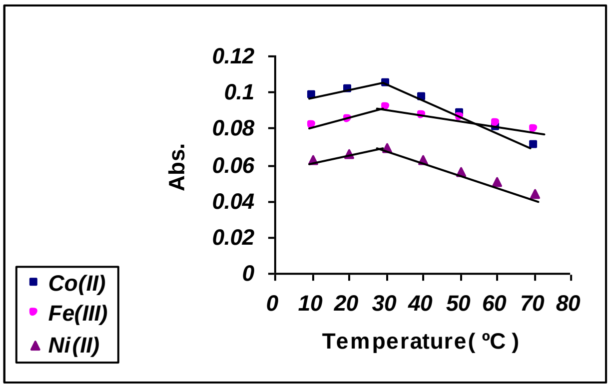


Fig.(11) : Effect of temperature on the absorbance of metal complexes M=Fe (ш), Co(ш) and Ni(п).

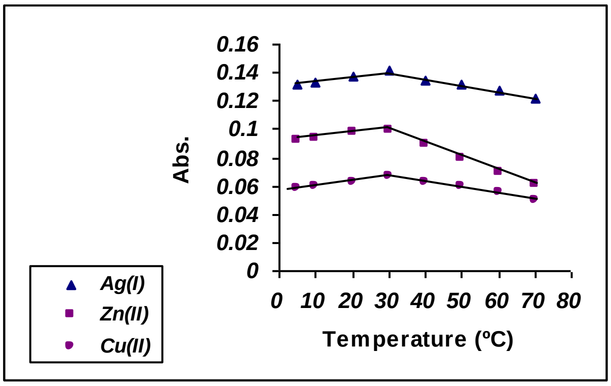


Fig. (12) : Effect of temperature on the absorbance of metal complexes; M=Cu(п),Zn(п) and Ag(I).

12- Metal :Ligand Ratios

The metal :ligand ratios(M:L) of complexes were determined by the method of molar ratio at the wavelength of maximum absorption ,molar concentration and fixed pH in aqueous ethanolic solution50% (V/V). The result are summarized in Table (4).

The ligand (6-NO_2BTAP) was found to from 1:2 (M:L) chelates with all metal ions except of Zn(п) and Ag(I) complexes was found 1:1 chelates as shown in Fgs.(13 & 14).

These results are in agreement with values reported for some thiazolylazo phenol complexes.$^{(16,17,21,23,27)}$

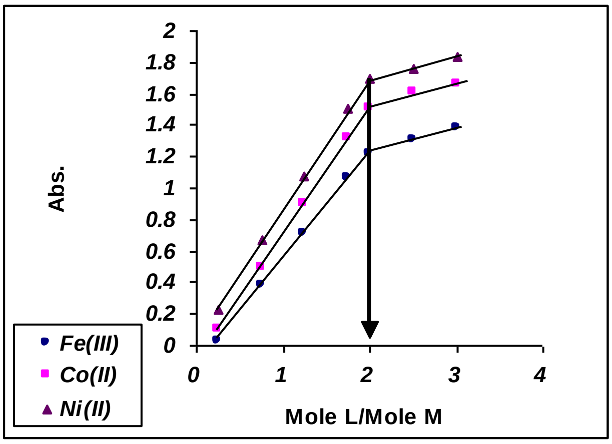


Fig. (13) : Molar ratio method (M:L) (6-NO_2BTAP)-meatal chelates at optimal pH and concentration.

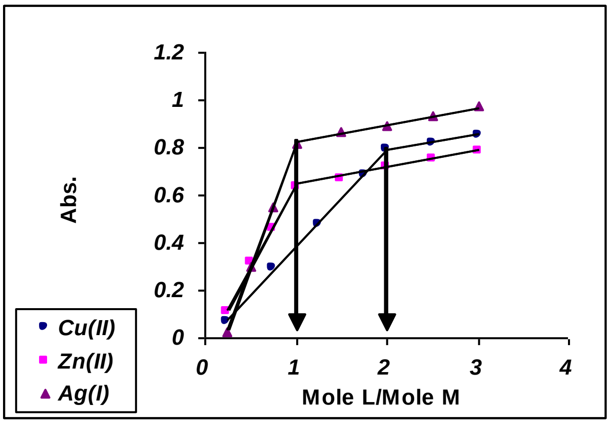
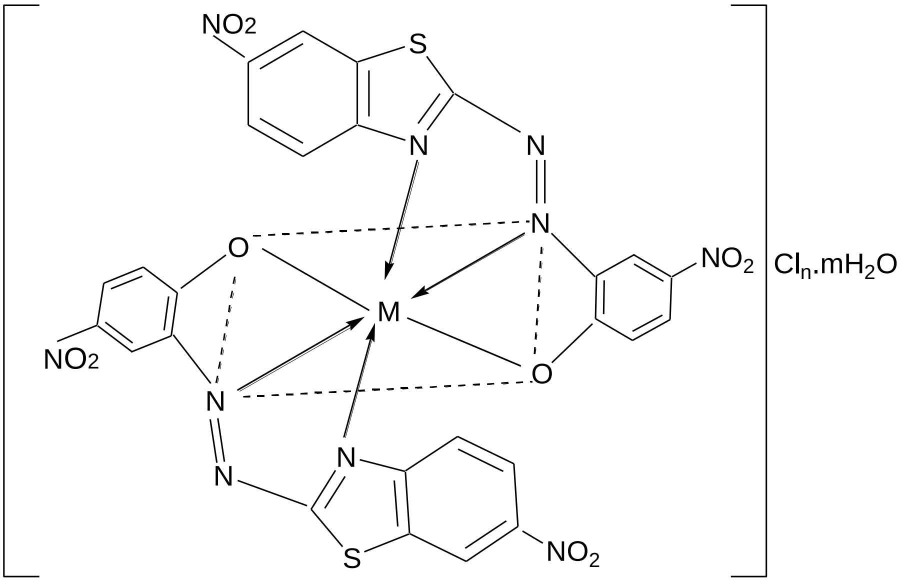


Fig. (14) : Molar ratio method (M:L) (6-NO_2BTAP)-meatal chelates at optimal pH and concentration.

According to these results the structural formula of prepared complexes in this work may be proposed composition of the complexes in the following Figs.(15, 16 and 17).



M=Fe(III),Co(III),n=1,m=1
M=Ni(II),Cu(II), n=0,m=0

Fig. (15) : The proposed structural formula of Fe(III),Co(III),Ni(II) and Cu(II) complexes .

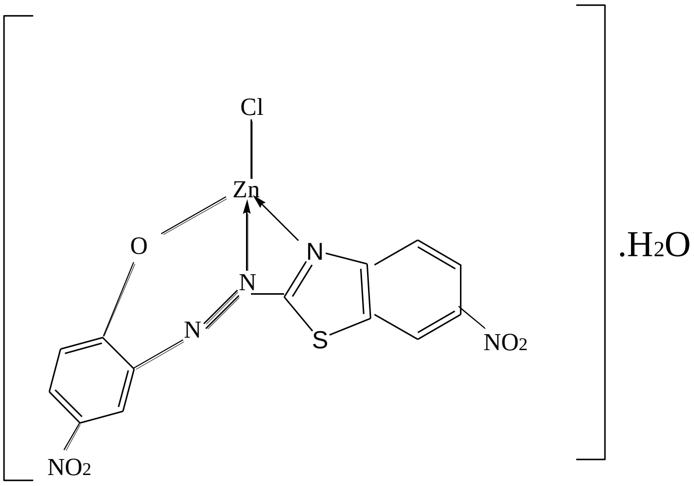


Fig. (16) : The proposed structural formula of Zn(II) -complex .

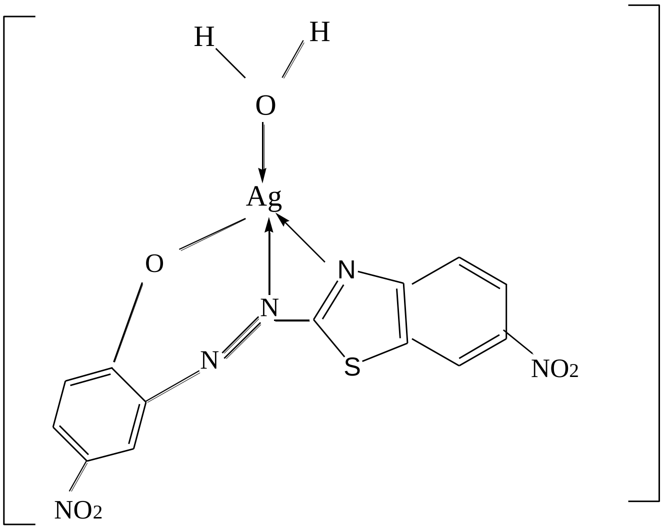


Fig.(17) : The proposed structural formula of Ag(I) complex .

13-Conclusions

The preparation of ligand (6-NO$_2$BTAP)and their complexes are simple .After combining all the physical measurement ,the following molecular formular for the complexes can be suggest octahydral configuration for Fe(ш), Co(ш), Ni(п) and Cu(п) complexes, but tetrahedral for Zn(п) and Ag(I) complexes. Stability constants refer to the high stability of all complexes. These complexes under optimum conditions are stable to more than 24 hour.

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الخلاصة

تم تحضير بعض معقدات العناصر الانتقالية لايونات الحديد (III) و الكوبلت (II) و النيكل (II) و النحاس (II) و الخارصين (II) والفضة(I) مع الليكاند الجديد ٢-[(٦-نايترو-2-بنزوثيازوليل)آزو]-٤-نايترو فينول (6-NO_2BTAP=LH) وشخصت بوساطة التحليل الدقيق للعناصر والحساسية المغناطيسية عند درجة حرارة الغرفة ، والتوصيليه المولارية وأطياف الأشعة تحت الحمراء والأطياف الالكترونية. تم اقتراح الصيغ التركيبية للمعقدات الصلبة استنادا" إلى معطيات النتائج التحليلية المذكورة أعلاه وكانت $[ML_2]Cl_{n\cdot m}H_2O$ وكانت n=١ ، m= ١لكل من الحديد (III) و الكوبلت (II) فيما كانت n=٠ و m=٠ لكل من النيكل (II) والنحاس (II). أما معقد الخارصين (II) فقد أتخذ الصيغة $[ZnLCl].H_2O$ فيما إتخذ معقد الفضة(I) الصيغة $[AgL(H_2O)]$. أثبتت بيانات الأطياف الالكترونية والحساسية المغناطيسية شكل ثماني السطوح لمعقدات الحديد (III) و الكوبلت (II) والنيكل (II) والنحاس (II) بينما أتخذ معقدي الخارصين (II) والفضة(I) شكل رباعي السطوح. إن عدد التناسق ستة لجميع الأيونات ماعدا أيوني الخارصين (II) والفضة (I) اربعة وذلك نتيجة لأرتباط الأيونات مع مواقع التناسق المتاحة في جزيئة الليكاند وهي أوكسجين مجموعة الهيدروكسيل للفينول وإحدى ذرتي نيتروجين مجموعة الآزو وذرة نتروجين حلقة الثيازول الملتحمة .تم ايجاد النسبة المولية للمعقدات المحضرة وقد وجد إن نسبة الفلز : الليكاند هي ٢:١ لجميع المعقدات المحضرة ماعدا معقدي الخارصين (II) والفضة(I) كانت ١:١.