Synthesis and Characterization Studies of Complexes of Co(III), Ni(II), Cu(II), Zn(II),Cd(II) and Hg(II) with new azo ligand 2-[2-(6-Methyl benzothiazolyl)azo]-4-Hydroxy phenol.

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Abstract

In this work the new azo ligand prepared was 2-[2-(6-Methyl benzothiazolyl)azo]-4-Hydroxy phenol (MeBTAHP) by coupling reaction between 6-Methy-2-benzo thiazolyl diazolyl diazonium chloride with 4-hydroxy phenol in alkaline alcoholic sulotion.New six complexes of Co(III),Ni(II),Cu(II),Zn(II),Cd(II) and Hg(II) were synthesis and characterized by Uv-vis spectra , in Frred spectra ,electronic spectra,magnetic susceptibility and molar conductance measurements. Measurements were conducted appint a constant stability the complexes and spectral methods were stability in the following order Co(III)> Cd(II) >Cu(II)>Ni(II) >Hg(II) > Zn(II).Through mesurments above general formula were identified for complexes $[M(LH)_2]Cl.H_2O$,the analytical data show that the metal to ligand ratio in all complexes are (1:2) in complexes Co(III),Ni(II) and Cu(II) and (1:1) in complexes Cd(II),Zn(II) and Hg(II) .

Keywords*:*2-[2-(6-Methyl benzothiazolyl)azo]-4-Hydroxy phenol,Characterization ,*spectrophotometry , determination.*

1- Introduction

Used orgnic ligands in many fields[1,2]. Including inorganic chemistry of characteristics to contain aggregates effective qualify to interact with most of the elements of the periodic table and prefor orgnic ligands from other because weights moleculer and high selectivity and solubility in organic solvents and give deposits with colors characteristic of the presence of groups effective and seen from studies in literature[3,4].The azo dyes of the most important orgnic ligands because of its sensitivity and selectivity[5], and the presence of more than one location for consistency .Large nuber of thaizolyl azo phenols and its derivatives as ligand have been prepared and studied.These compounds are useful and important in many directions[6].This is based the presence of the azo group(-N=N-) as wall as other substituted chromophoric[7].In this work prepared and characterized new thiazolyl azo ligand 2-2[(6-Methyl benzothiazolyl)azo]-4-Hydroxy phenol (MeBTAMP)

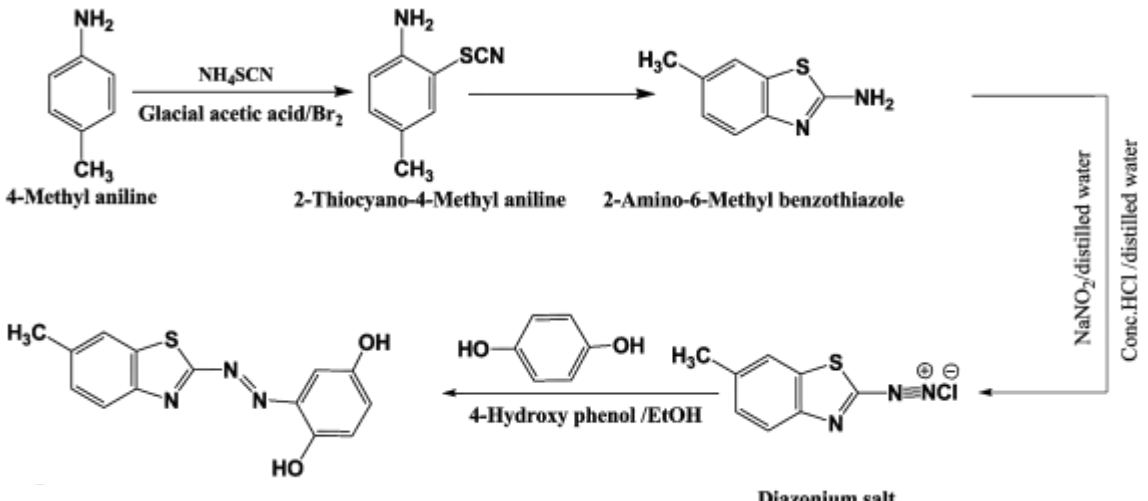
2- Experimental

2-1. Apparatus and materials

UV-Vis.spectra of ligand and their complexes were recoreded with UV-1650 PC shimadzu with 1 cm cells using methanol as solvent, Elemental analyses were obtained by using micro analytical unit, a C.H.N.O.S. Euro EA 300 elemental analyzer and the FT-IR spectra for all compounds were recorded with FT-IR-8400S shimadzu spectrophotometer were used for spectral measurement in the (4000-400)cm^{-1} rang using KBr disc . Electronic conductivity was measured by using digital conductivity meter 214 HANNA (stuart melting point) apparatus was used to measure the melting point of ligand and its complexes and the pH measurement of this compound is recorded by pH meter 210.The chemicals used were BDH and Fluka expect of 2-amino-6-methyl benzo thiazole wes prepared as described in literature[8].And the organic solvents in cluding hydrochorid ethanol and DMF are of hights purity and used as supplied by manfactures.

2-2. Preparation ligand(MeBTAHP)

Can be prepared the ligand by dissolving of amin thiazol 2-amino-6-methyl benzo thiazole 0.481 gm (0.01 mol) in 40 ml of distilled water and 5 ml of concentrated hydrochloric acid added sodium nitrate solution 0.75 gm (0.01 mole) in 30 ml of distilled water dropwise untit the midum be can alkaline .The prepared diazonium solution was droping in to 500 ml beaker dissolving 1.1 gm (0.01 mole) of hydroxphenol dissolved in 150 ml alkaline ethanol .This mixture stirred for two hours thermal degree below zero and then left to settle over night.A red precipitate appears filtered and dried .Tue ligand was brown crystals and highy soluble in orgnic solvent .The yield was 70%, m.p 163 ^{0}C



2-[2-(6-Methyl benzothiazolyl)azo]-4-Hydroxy phenol. (MeBTAHP)

2-3. Preparation of metal complexes

All the complexes were prepared by dissolved (0.285gm,0.001mol) from ligand (MeBTAHP) in ethanol (100ml) and added with stirring to an aqueous solution of metal ions Co(III),Ni(II),Cu(II),Zn(II),Cd(II) and Hg(II) (0.05 mole) in 20 ml of suitable buffer solution.This mixture was stirred and left for stilled .These complexes were filtered and the precipitates were washed with distilled water and dried.

3- Results and Disicussion

The table(1) refered to some physical properties and several analytical data of the prepareded ligand and its complexes .

Table(1):Elemental analyses and some physical properties for ligand (MeBTAHP) and their metal complexes

Compound	m.p	Color	Yield (%)	Molecular formula (Mol.Wt)	Found Calc.(%)					
					C	H	N	S	O	M
LH=Ligand	130	Dark brown	71	**$C_{14}H_{11}N_3O_2S_1$ (285.32)**	59.00 (58.87)	3.88 (3.92)	14.72 (14.31)	11.23 (11.43)	11.20 (10.81)	——
$[Co(LH)_2]$ $Cl.H_2O$	168	Dark Purple	63	**$C_{28}H_{22}N_6O_5S_2Cl_1Co$ (681.02)**	49.37 (49.62)	3.25 (2.98)	12.34 (12.01)	9.41 (9.02)	11.73 (11.32)	8.66 (8.79)
$[Ni(LH)_2].H_2O$	150	Purple	52	**$C_{28}H_{22}N_6O_5S_2Ni$ (645.33)**	52.12 (51.83)	3.43 (3.71)	13.02 (13.32)	9.93 (9.73)	12.38 (12.03)	9.09 (9.21)
$[Cu(LH)_2].H_2O$	143	Purple redish	69	**$C_{28}H_{22}N_6O_5S_2Cu$ (650.18)**	51.72 (52.02)	3.40 (3.28)	12.92 (12.81)	9.86 (10.11)	12.29 (12.13)	9.77 (9.62)
$[Zn(LH)Cl].H_2O$	138	Purple	75	**$C_{14}H_{12}N_3O_3S_1Cl_1Zn$ (403.16)**	41.70 (41.91)	2.99 (3.07)	10.42 (10.31)	7.95 (8.12)	11.89 (11.97)	16.21 (16.02)
$[Cd(LH)Cl].H_2O$	140	Purple	60	**$C_{14}H_{12}N_3O_3S_1Cl_1Cd$ (450.19)**	37.34 (37.09	2.68 (2.97)	9.33 (9.61)	7.12 (6.98)	10.65 (10.47)	24.96 (24.78)
$[Hg(LH)Cl].H_2O$	139	Dark purple	81	**$C_{14}H_{12}N_3O_3S_1Cl_1Hg$ (538.37)**	31.23 (31.36)	2.24 (2.18)	7.80 (7.93)	5.95 (5.87)	8.91 (9.07)	——

LH=(MeTAMP)

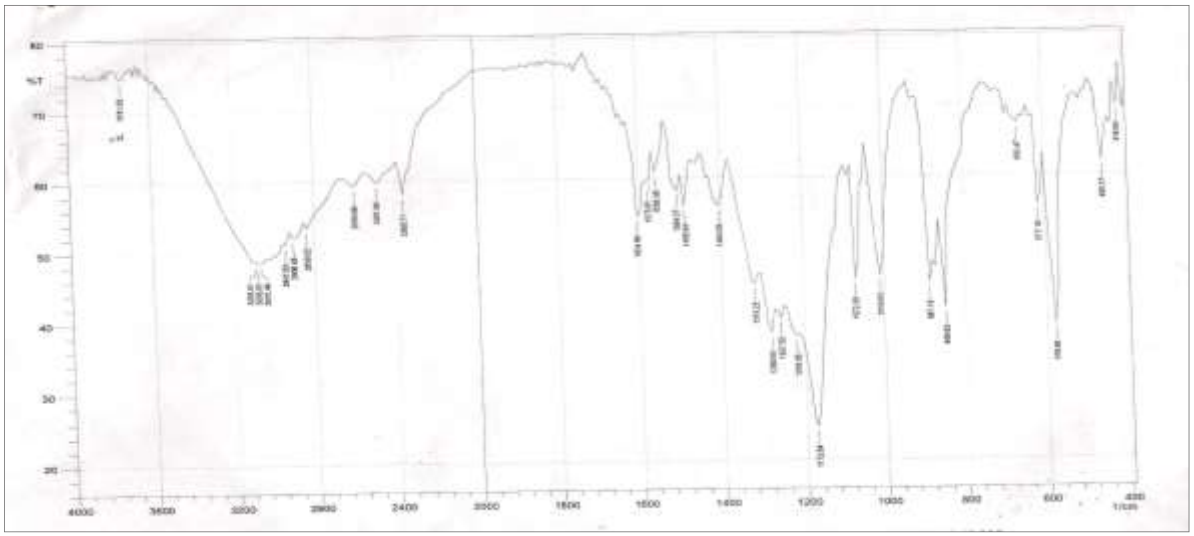
3-1 Infrared spectra

Adopt through the study of IR spectrum of ligand (MeBTAHP) and its complexes emergence packages absorption characteristic C=N,C=C, C=N and N=N group in addition fother bands from phenyl and thizol ring appeared in the region 4000-400 cm^{-1} .The shifts in the position and intensity referes to link ligand with metal ions to form chalate complexes .The spectrum of ligand (MeBTAHP)shews broad and weak absorption band at 3742 cm^{-1} refer to vibration (O-H), the band due to υ(C-H) aromatic bands are stable in position in both ligand and its complexes[9].In the free ligand the band at 1604 cm^{-1} due to υ(C=N) of thiazol ring[10].This band is undergo to lower shift at 1585cm^{-1} in the prepared complexes spectra the two bands at 1520 cm^{-1} and 1489 cm^{-1} due to υ(N=N) these bands shifted to lower frequnce at 1434 cm^{-1} and 1404 cm^{-1} in the spectra of complexes [11].In the edition that the band at 850 cm^{-1} in the spectrum of ligand due to υ(C-S) of thiazol ring [4,12].This band is stable in all metal complexes reafers that the atom sulpher in the thiazol ring does not participete in coordination[15,16].The IR spectra data lead to suggest that the ligand behaves as atridentate chelating ligand coordination through the positions of oxygen ,nitrogen of azo group and thiazol ring nitrogen. Figuers(1-3) shows the spectra of ligand (MeBTAHP), Ni(II)-complex and Zn(II)-complex

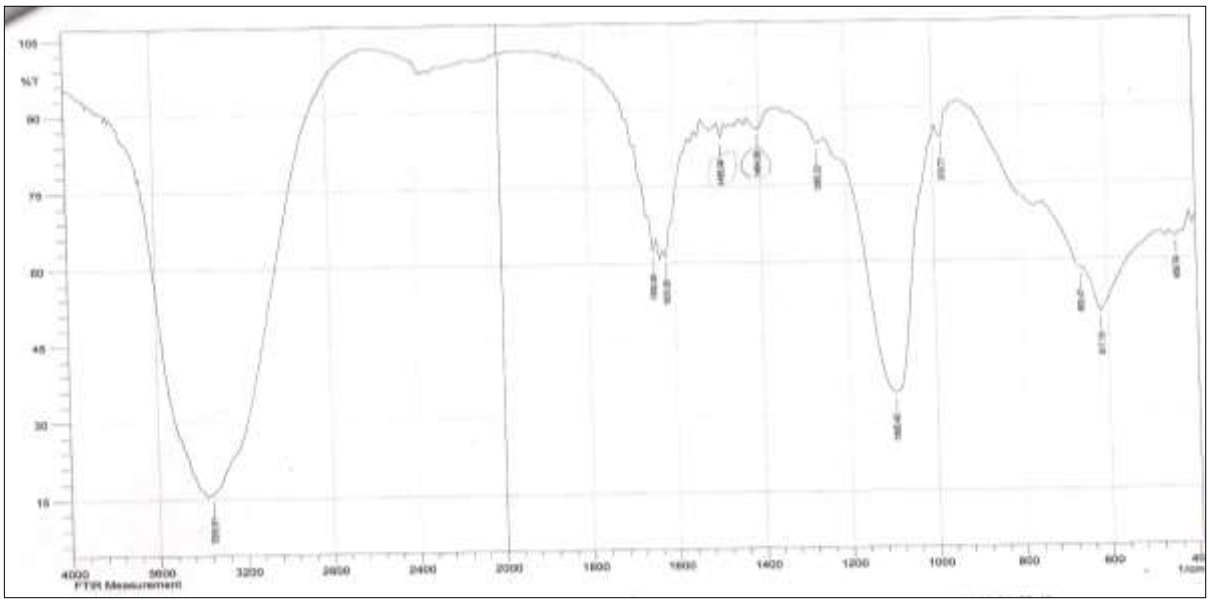
Table (2);-Some IR frequencies (in cm^{-1}) of the thiazolylazo ligand (MeBTAHP) and its metal complexes

Compound	υ(O─H)	υ(C=C)	υ(C=N)	υ(N=N)	υ (C-S)	υ (C–N=N–C)	υ(M-O)
LH=Ligand	3742 m.br.	1404 w.	1604 s.	1489 vs.	1281 vs.	1172 s.	—
$[Co(LH)_2]$ $Cl.H_2O$	3733m.br.	1404 m.	1585s.	1434m.sh.	1265 vs.	1141 s.	849 w.
$[Ni(LH)_2].H_2O$	3355 m.br.	1404w.	1620s.	1475 vs	1265 vs.	1095 m.	663 w.
$[Cu(LH)_2].H_2O$	3410 s.br.	1396m.	1512 m.	1478 m.	1203 s.	1118 m.	586 w.
$[Zn(LH)].H_2O$	3217 w.br.	1396 m.	1512 m.	1419 m.	1157 m.	1157m.sh.	879 w.
$[Cd(LH)].H_2O$	3394 m.br.	1434 w.	1620 m.	1465 m	1380 vs.	1257 s.	671w.sh.
$[Hg(LH)].H_2O$	3525 w.br.	1393 m.	1612m.sh	1504 s.	1265 vs.	1103 vs.	810w.sh.

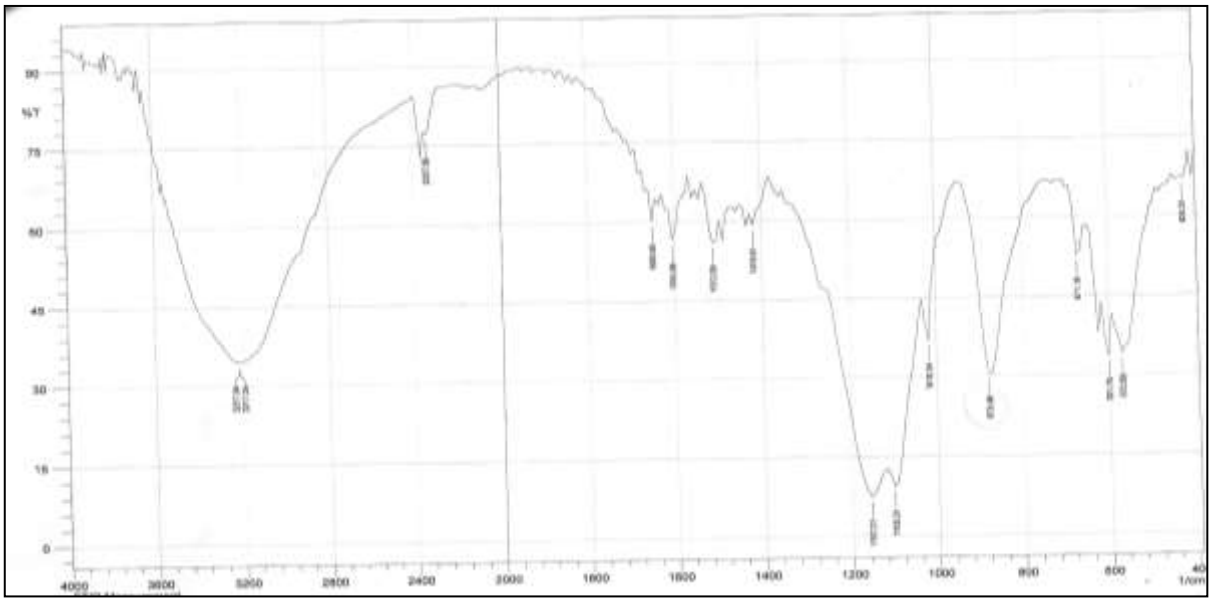
HL=ligand (MeBTAHP);W=weak , S=stronge ,m= medium , br=broad , sh= shoulder,vs=very strong



Figure(1);-Infrared spectra of ligand (MeBTAHP).



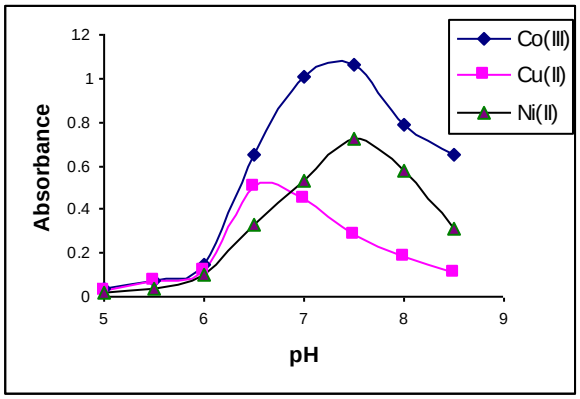
Figure(2);-Infrared spectra Ni(II)-complex.



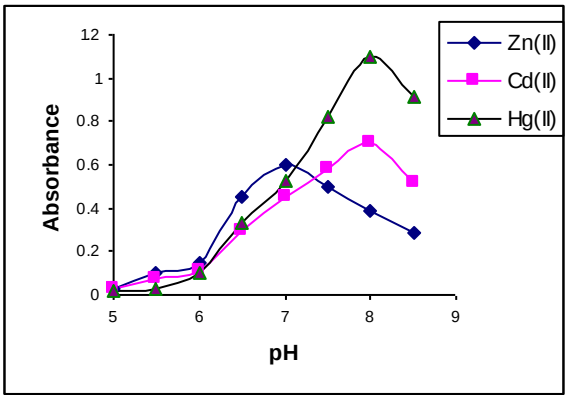
Figure(3);-Infrared spectra of |Zn(II)-complex.

3-2 Effect of pH

For evaluation of optimal pH values for determinations of Co(III),Ni(II),Cu(II).Zn(II),Hg(II) and Cd(II).The effects of pH on the absorbance were studicd with the results shown in Figure 4 and 5 ,in casecs of Co(III),Ni(II),Cu(II),Zn(II),Hg(II) and Cd(II) complexes.The absorbance spectra for them did not change over the whole range .The optimal pH concentration and wave length λ_{max} with mole absorpitivily of complexes are shown in Table 2.



Fig(4):-Effect of pH on absorbance values of chelate complexes.



Fig(5):-Effect of pH on absorbance values of chelate complexes.

3-3 Metal:Ligand ratio

The composition of chelat complexes were determined by molar ratio method at fixed pH and concentration at wavelength of maximum absorption .The azo ligand (MeTAHP) was found to from 1:2 chelates withCo(III),Cu(II) and Ni(II) metal ions but with Zn(II),Cd(II) and Hg(II) the complexes was found 1:1 ,these reslts are in agreement with the values reported for some thiazolylazo phenol complexes [4,8,16-18]. The results of this study are shown in figures (6) and (7).

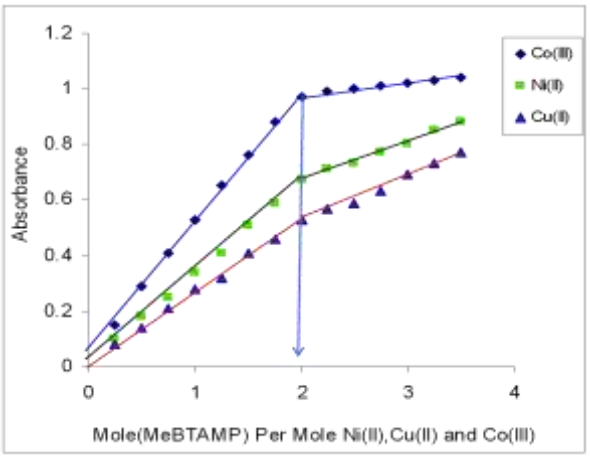


Fig.(6):-Mole ratio method (M:L) (MeBTAHP)-metal chelates Cu(II),Co(III) and Ni(п)

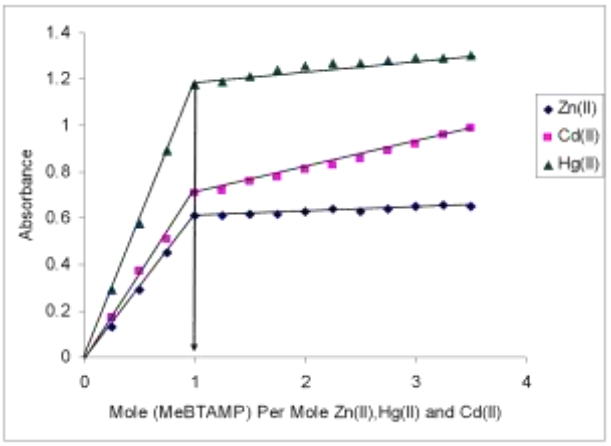


Fig.(7):- Mole ratio method (M:L) (MeBTAHP) -metal chelates Zn(п),Cd(п) and Hg(II).

3-4 Calculation of the metal complexes stability constant

Table-3 show the stability constants have been measured spectrally for prepared complexes ,were calculated by absorbance values ments at fixed wavelength (λ_{max}) , and optimum pH values. according to the following equation $\beta=(1-\alpha/4\alpha^3C^2$) whene the mole raito 1:2 (M:L) metal complexes and $\beta=(1-\alpha/\alpha^2C)$ when the mole ratio 1:1 (M:L) metal complexes[1,22,23] .The stability follows the sequence Co(III)> Cd(II) >Cu(II)>Ni(II) >Hg(II) > Zn(II).. The hight stability is Co(III)-complex.

3-5. Molar conductivity measurements

Were measured conductivity for solution of Co(III),Cu(II),Ni(II),Zn(II) and Cd(II)–complexes in DMF solvents (10^{-3} M) at laboratory temperature,included the results in Table-3.The values of molar conductivity of the complexes prepared for the lack of capacity ion for these complexes and this is consistent with the literature[4,20]. Except complex of Co(III)-complex his value condictivty top which indicates these the existence of such ionc.

Table(3):-Stability constant values (β and Log β),molar conductivity optimal concentration ,maximum wavelength(λ_{max}) and molar absorpitivity(Є) of chelate complexes.

Ligand	Metal ion	Optimal molar conc. x (10^{-5} M)	Optimal wave length nm λ_{max}	Molar absorpitivity (Є)x10^3L.mol^{-1}.cm^{-1}	Moler Conductivity (S.cm^2.mol^{-1})	Stability constant β (L^2.mol^{-2})	Logβ
MeBTAMP λ_{max}= 461 nm Є=3.56 x 10^3 L.mol^{-1} .cm^{-1} Conc.=1.25x10^{-5}M	Co(III)	2.5	540	3.66	37.54	1.24x10^{12}	12.09
	Ni(II)	2.0	520	3.42	6.81	3.53x10^{10}	10.54
	Cu(II)	1.75	513	2.81	9.38	7.47x10^{10}	10.87
	Zn(II)	1.25	536	2.71	6.33	2.01x10^7	7.30
	Cd(II)	1.25	544	2.40	7.56	7.22x10^{11}	11.85
	Hg(II)	1.5	543	1.25	5.52	4.07x10^8	8.61

3-6. Electronic spectra and magnetic properties

Adop taple (4) the data optained from the measurements of electronic spectra and magnetic properties.

3-6-1. Co(III) –Complex

The electronic spectrum of Co(III)-complexes gives d-d transition at 540 nm (18918 cm^{-1}) and 441 nm (22675 cm^{-1}) these bands due to transition $^1A_1g \rightarrow {}^1T_1g$ (υ_1) and $^1A_1g \rightarrow {}^1T_2g$, ($\upsilon_2$) .They were octahedral geometry and diamagnetic and low spin (17).

3-6-2. Ni(II)-Complex

Characteristic the electronic spectrum of Ni(II)-complex presence three bands were observed at 925nm (10810 cm^{-1}) attributed to $^3A_2g \rightarrow {}^3T_2g_{(F)}$ (υ_1) transition and the second one was strong and broad band at 520 nm(19230 cm^{-1}) due to $^3A_2g \rightarrow {}^3T_1g_{(F)}$ (υ_2) transition while the third one detected at 332 nm (30120 cm^{-1}) due to there are assigned to $^3A_2g \rightarrow {}^3T_1g_{(p)}$ (υ_3) transition[4,17]. These results with the value 3.29 B.M of magnetic moment suggest a high spin octahedral geometry ($^6t_2g\ ^2eg$) and hybridization sp^3d^2.

3-6-3. Cu(II)-Complex

The electronic absorption spectrun of Cu(II)- complex give band centered at 640nm (15625cm^{-1}) this band due to transition $^2Eg \rightarrow {}^2T_2g$ the Cu(II)-complex exist in octahedral environment (19). This complex give magnetic moment value of is 1.67 B.M

3-6-4. Zn(II),Cd(II) and Hg(II)-Complexes

The electronic spectrum of these complexes show bands are mainly due to charge transfer (M→L,CT). All these complexes diamagnetic moment.

Table(4):- Electronic Spectra (in nm and cm^{-1}) , geometry and hybridization of metal complexes

Complexes	λ_{max} (nm)	Absorption bands (cm^{-1})	Transition	Geometry	Hybrdization
$[Ni(LH)_2].H_2O$	925	10810	**$^3A_2g_{(F)} \rightarrow {}^3T_2g_{(F)}$ (υ_1)**	Octahedral	sp^3d^2 (high spin)
	520	19230	**$^3A_2g_{(F)} \rightarrow {}^3T_1g_{(F)}$ (υ_2)**		
	332	30120	**$^3A_2g_{(F)} \rightarrow {}^3T_1g_{(p)}$ (υ_3)**		
$[Co(LH)_2]\ Cl.H_2O$	540	18918	**$^1A_1g \rightarrow {}^1T_1g$ (υ_1)**	Octahedral	d^2sp^3 (low spin)
	441	22675	**$^1A_1g \rightarrow {}^1T_2g$ (υ_2)**		
$[Cu(LH)_2]\ .H_2O$	510	19607	**$^5T_2g \rightarrow {}^5Eg$**	Octahedral (distorted)	sp^3d^2 (high spin)
$[Zn(LH)].H_2O$	536	18656	**M→L,CT**	Teterahedral	sp^3 (high spin)
$[Cd(LH)].H_2O$	544	18382	**M→L,CT**	Teterahedral	d^2sp^3 (high spin)
[ZnL Cl].H_2O	543	18416	**M→L,CT**	Teterahedral	sp^3 (high spin)

3-7. Absorption spectra

The absoptio spectra of ligand (6-MBTAHP) and its complexes are give absorpan band at the wavelength for the maximum (λ_{max}) at 461 nm and its complexes undergo shift to longer wavelength .The absorption spectra of the azo ligand and its complexes are shown in figure(8) and (9).

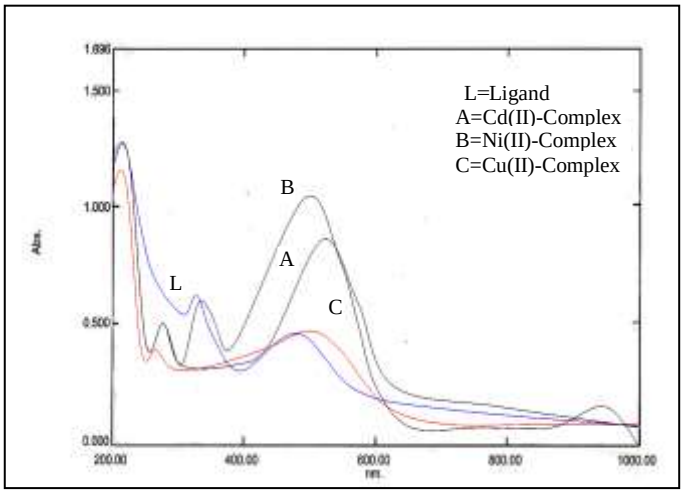
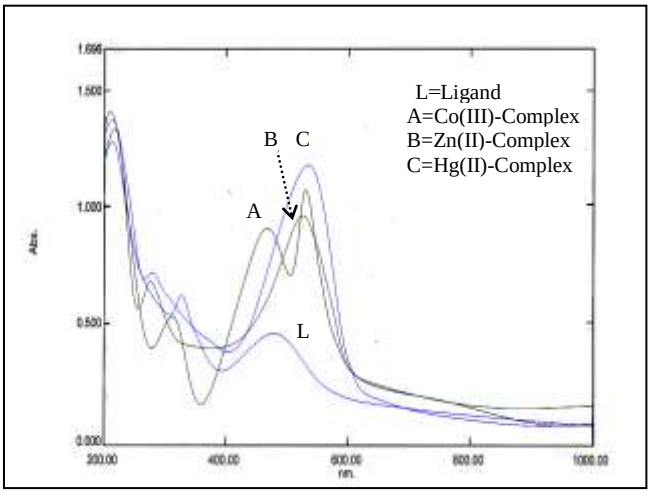


Figure (8):-The absorption spectra of MeTAHP–metal chelats(1.75, 2.0)x10^{-5}M in aqueous solution 50% (V/V).



Figure(9):-The absorption spectra of MeTAHP–metal chelats(1.25, 2.5)x10^{-5}M in aqueous solution 50% (V/V).

3-8. Composition of the complexes

The suggest formula of complexes were determined by the method of mole ration at optinal pH conceration the curves in dicated the formation a(1:2) metal :ligand were obtained as shown in figure 10 and the formation a (1:1) metal:ligand were obtained in figure 11.

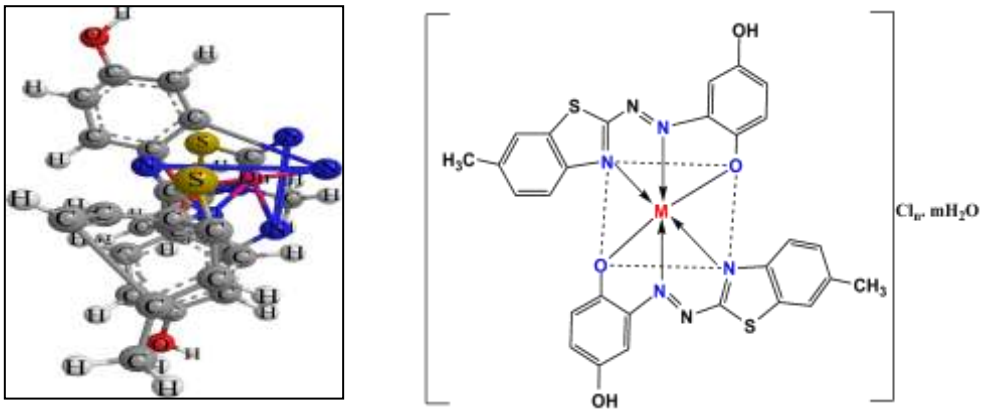


Figure (10):-The proposed chemical structure of Co(III), Ni(II) and Cu(II) chelet complexes when:-
M=Cu(II) and Ni(II) ;n=0 ; m=1
M= Co(III) ; n=1 ;m=1

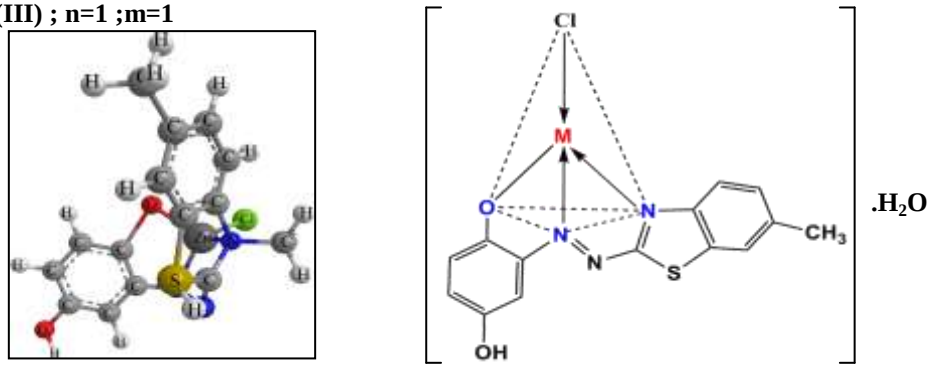


Figure (11):-The proposed chemical structure of Zn(II),Hg(II) and Cd(II)-complex

4-Conclusion

Although the ligand and its complexes are very simple and the proposed method is more simple.These compounds seem to be promising because of the remarkably hight molar absorptivity and large bathochromic shifts prodced on chelation and stability constants refer to the high stability of complexes.

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تحضير ودراسة تشخيص معقدات(Co(III و(Ni(II و(Cu(II و(Zn(II و Cd(II) و Hg(II) مع ليكاند الازو 2-[2-(6- ميثيل بنزو ثيازوليل)إزو]-4-هايدروكسي فينول .

زينب محسن الحمداني
قسم الكيمياء/كلية التربيه/جامعة القادسيه

الخلاصه :-

تضمن هذا البحث تحضير ليكاند ازو جديد 2-[2-(6-مثيل بنزوثيازوليل)أزو]-4- هيدروكسي فينول (MeBTAHP) وتم ذلك من تفاعل الأزدواج بين محلول ملح الديازونيوم للمركب 6-امينو ميثل بنزوثيازوليل مع هيدروكسيد الفينول في محلول قاعدي كحولي .تم تحضير ستت معقدات جديدة مع ايونات (Co(III و(Ni(II و(Cu(II و(Zn(II و(Cd(II و(Hg(II و تم تشخيص هذا الليكاند ومعقداته بوساطة الاشعة فوق البنفسجية (.UV-visb)واطياف الاشعة تحت الحمراء(FT-IR) والاطياف الالكترونية ودراسة الخواص المغناطيسية والتوصيلية المولارية ولقد تم تعين ثابت الاستقرارية للمعقدات المحضرة بالطريقة الطيفية والتي اتخذت الترتيب التالي(Zn(II <Hg(II <Ni(II)>Cu(II)> Cd(II)>Co(III). من النتائج والقياسات اعلاة تم اقتراح العامه للمعقدات وكانت ثمانية السطوح لمعقدات (Co(III و(Ni(II و(Cu(II و رباعية السطوح لمعقدات (Zn(II و (Cd(II و (Hg(II ومن خلال نتائج القياسات التحليلية كـــانت النـــسبة الليكاند:الفلز(1:2) لمعقدات (Co(III و(Ni(II و(Cu(II و (1:1) لمعقدات (Zn(II و(Hg(II و(Cd(II .