Synthesis And Spectrophotometer Study 2-[(2-Sulfopheny)Azo]-4,5-Diphenylimidazole With Some Transition Metal Complexes

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الخلاصة

تضمن البحث تحضير مجموعة من المعقدات الكوبلت (III) والنيكل (II) والنحاس (II) والخارصين (II) والكادميوم (II) والزنبق (II) مع ليكاند الازو ٢– (٢- سلوفنيل) ازو ، -٤ و ٥– ثنائي فنيل اميدازول (SAI). جرى دراسة الظروف المثلي لتكوين تلك المعقدات كتحديد التراكيز المولارية للمعقدات، تأثير الزمن للمعقدات وتحديد أفضل دالة حامضية تم اقتراح التراكيب المتوقعة للمعقدات المدروسة باستخدام طريقة النسبة المولية إذ أشارت النتائج الى ان جميع المعقدات المحضرة تمتلك نسبة مولية (١ : ٢) (فلز : كاشف) ما عدا النحاس يمتلك نسبة مولية (١:١) (فلز : كاشف) كذلك تم قياس درجات الانصهار للكاشف ومعقداته أما بالنسبة الى أطياف الاشعة تحت الحمراء والاشعة فوق البنفسجية المرئية فقد أظهرت أطياف المعقدات المدروسة اختلافاً واضحاً فيهما مقارنة يطبق الكاشف الحر .

Abstract

This study is concerned the synthesis of Co(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complex of 2-[2-sulfophenyl) azo] -4,5- diphenyl imidazole (SAI). Complexes has been studied, such as, molar concentration, effect of time on a formation of the complexes and pH values. The expected structure of these complexes were by mole Ratio method, the results showed that all of these complexes have a mole ratio (1:2) (metal: reagent) except Cu+2 which have amole ratio (1:1) and melting points measurement of these complexes showed high stability. IR and UV-Vis spectra of free reagent showed some changes comparing with high reagent changes comparing the spectra of complexes.

Key words: *Co(III), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complex, 2-[2-sulfophenyl) azo] -4,5- diphenyl imidazole (SAI).*

Introduction

Imidazole is of considerable interest as a ligand in that its presence in chemical and biological systems[1-3]. In addition to used it's as reagents for extraction photometric , determination of many metal ions[4-7] . Imidazole has two nitrogen atoms, respectively of the pyridine and pyrrole type; high reactivity with metals is expected due to the strong, basicity of C, the pyridine- type nitrogen in comparison with pyridine it self[8]. (the molecule being the azoimine group (-N=N-C=N-) which is π - acidic function for this reason a number of these compounds were prepared and abilities as chelating ligands[9-11]. In this work we describe here the synthesized and identification of some metal complexes, using the imidazole azo ligand (SAI).

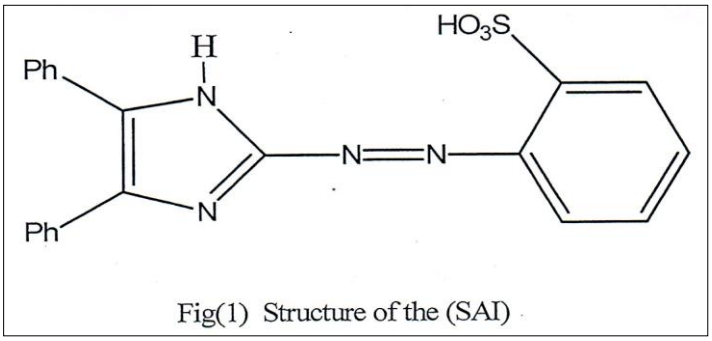
Experimental

Measurements and Materials

Elemental analysis was carried out using perkin Elmer 2400 elementary analyzer. IR spectra were recorded on (pye-Unicom sp3-300) spectrophotometer, in the 4000-200 cm^{-1} range using kBr disc. Electronic spectra were measured using (shimadzu-160A) range using spectrophotometer. The metal amounts were determined using, atomic absorption

technique by (shimadzu-AA-160). pH measurements were carried out using, pH meter model (H1932). Stuart melting point apparatus was used measure the melting point of ligand and its complexes . All chemicals used Fluka, Merck and BDH. Except of 4, 5- diphenyl imidazole was prepared as procedure[12] .

Synthesis of the 2-[(2-sulfophenyI)azo] -4,5- diphenylimidazole (SAI): For the synthesis of (SAI) ligand, the general procedure[13] is followed 2-aminobenzene sulfonic acid (1g) was dissolved in (11.5M) hydrochloric acid (2 ml) with (20 ml) of distilled water, (10 ml) ethanol was added. To this mixture a solution of 0.7 gm (0.01 mole) of sodium nitrite in 30 ml of distilled water was added dropwise at (0-5)C°. A 2.2 gm (0.01 mole) form 4,5 diphenyl imidazole was dissolved in 300 ml of ethanol, then added 50 ml of 10% sodium hydroxide and 50 ml of 10% sodium carbonate. The diazonium solution prepared was then added dropwise to this solution for coupling at (0-5) C° for three hours with sitirring. The mixture was stirred for additional 3 hrs, in an ice-bath allowed to stand overnight and acidified with dilute hydrochloric acid to (pH=6). The precipitated dye was filtered, dried and recrystillized twice from hot ethanol and dried over anhydrous $CaCl_2$. The structural formula of this ligand is show in **Figure 1.**



Fig(1) Structure of the (SAI)

Preparation of complexes: The complexes have been obtained by adding (2 mmol) from ligand dissolved in hot ethanol (50 ml) drop-wise with vigorous stirring to stoichiometric amounts (2:1) for Co(III), Ni(II), Zn(II), Cd(II) and Hg(II)chloride and (1:1) for the Cu(II) chloride, dissolved in 15 ml hot distilled water. The mixture was heated to (50C°) for 30 min, until the solid complexes precipitated. They were filtered off washed with ethanol and dried in desiccators over anhydrous $CaC1_2$.

Results and Discussion

Characterization of Ligand and its Complexes

The azo dye ligand was red crystal, but the coordination complexes of this ligand with ligand Co(III), Cu(II), Zn(II), Cd(II) and Hg (II). Vary in color from purple to brown. The ligand and its complexes were insoluble in water but soluble in most organic solvent. The result of element analyses and metal content reported in **Table 1** are in agreement with calculated values of (C.H.N) and (M) based on the mentioned molecular formula of

the ligand and its complexes.

Table1: Analytical And physical Data of The Ligand And its Complexes

No	Compound	M.P.C	Yield%	Formula	Found (called)%			
					C	H	N	M
1	SAI	>305	75	$C_{21}H_{16}N_4SO_3$	49.8	3.4	11.0	
					49.8	3.4	11.1	
2	$[CoL_2]Cl.H_2O$	285	68	$(C_{21}H_{15}N_4SO_3)_2.ClC_O$	27.4	3.4	6	2.9
					26.4	2.9	5.6	2.5
3	$[NiL_2].H_2O$	290	73	$(C_{21}H_{15}N_4SO_3)_2.Ni\ .\ H_2O$	28.5	3.6	6.3	3.1
					27.6	3.7	5.5	2.9
4	$[CuLCl].H_2O$	280	78	$(C_{21}H_{15}N_4SO_3)\ .ClCu\ .$	28.3	3.6	6.3	3.2
				H_2O	27.6	2.7	5.4	2.5
5	$[ZnL_2]$	265	65	$(C_{21}H_{15}N_4SO_3)_2.Zn$	28.9	3.4	6.4	3.4
					27.5	2.8	5.9	2.8
6	$[CdL_2]$	292	60	$(C_{21}H_{15}N_4SO_3)_2.Cd$	27.4	3.2	6	5.2
					26.8	2.7	5.8	4.8
7	$[HgL_2]$	270	55	$(C_{21}H_{15}N_4SO_3)_2.Hg$	25	2.9	5.5	7
					24.5	2.2	4.9	7.9

Absorption Spectra

The absorption spectra UV-of the reagent (SAI) and complexes with Co(III), Ni(II), Cu(II), Zn(II), Cd(II), Hg(II) are shown in **Figures 2-8**. The absorption spectra in aqueous ethanolic solution 50% (V/V) were studied for the prepared complexes showed a thochromic shift ranging between (21-72)nm ending an the metal ion.

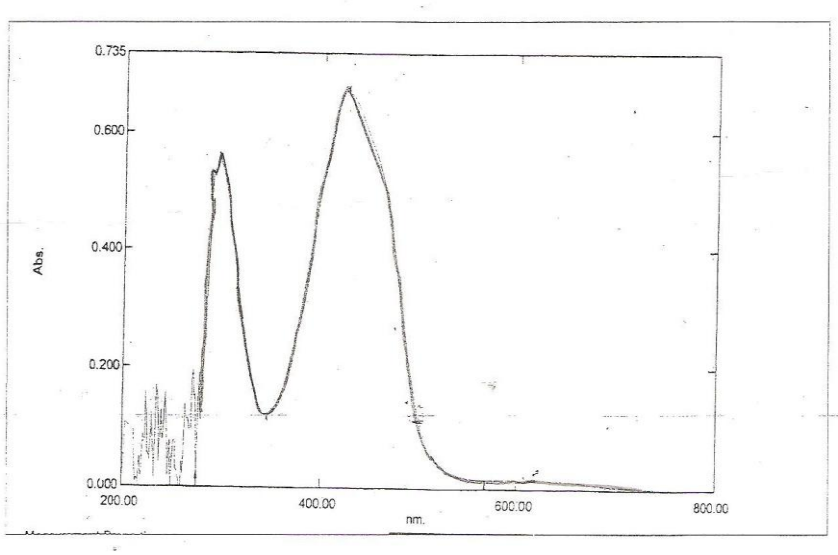


Fig. 2: The Absorption Spectra of SAI

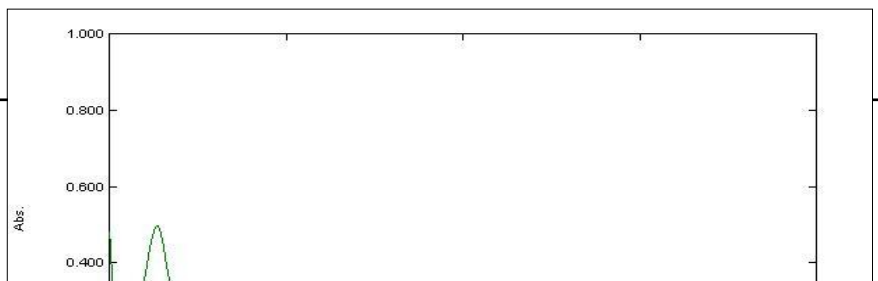


Fig. 3: The Absorption Spectra of ligand (Co^{+3})

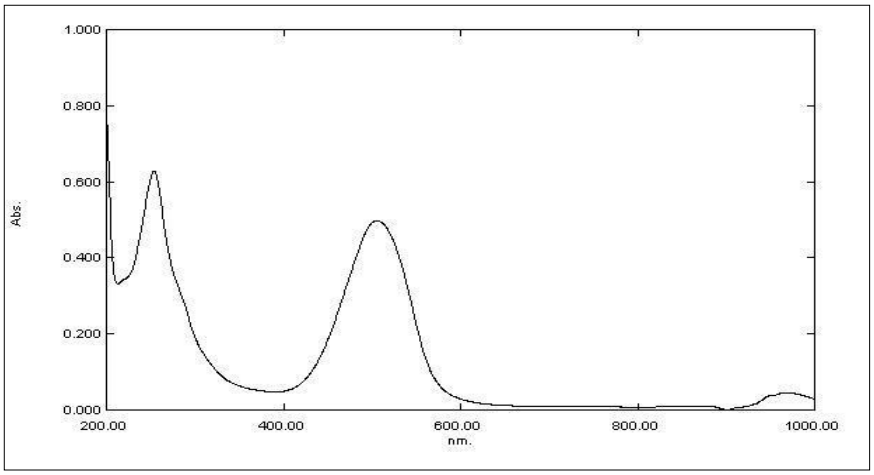


Fig. 4: The Absorption Spectra of ligand (Ni^{+2})

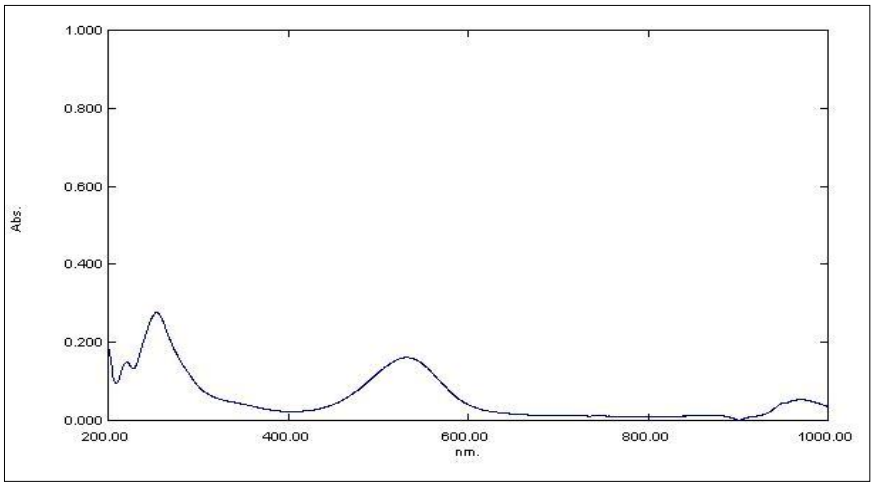


Fig. 5: The Absorption Spectra of ligand (Cu^{+2})

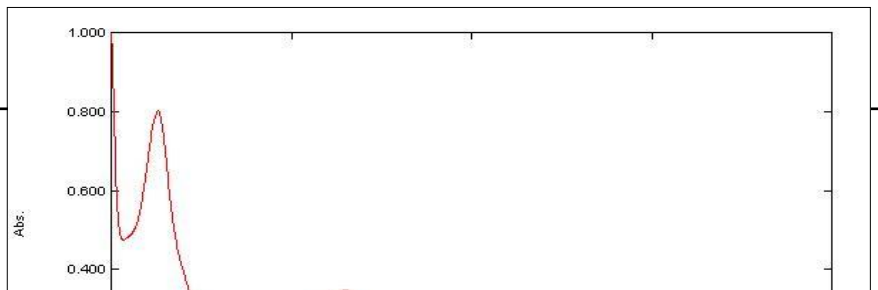


Fig. 6: The Absorption Spectra of ligand (Hg^{+2})

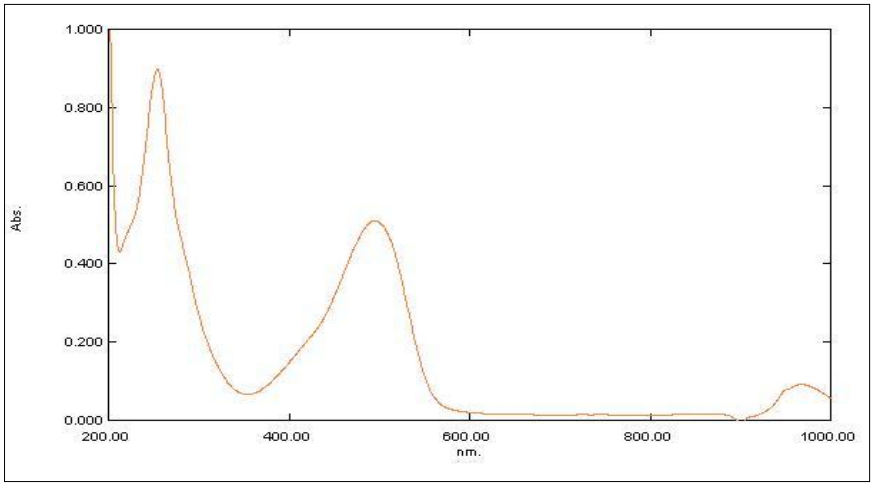


Fig. 7: The Absorption Spectra of ligand (Cd^{+2})

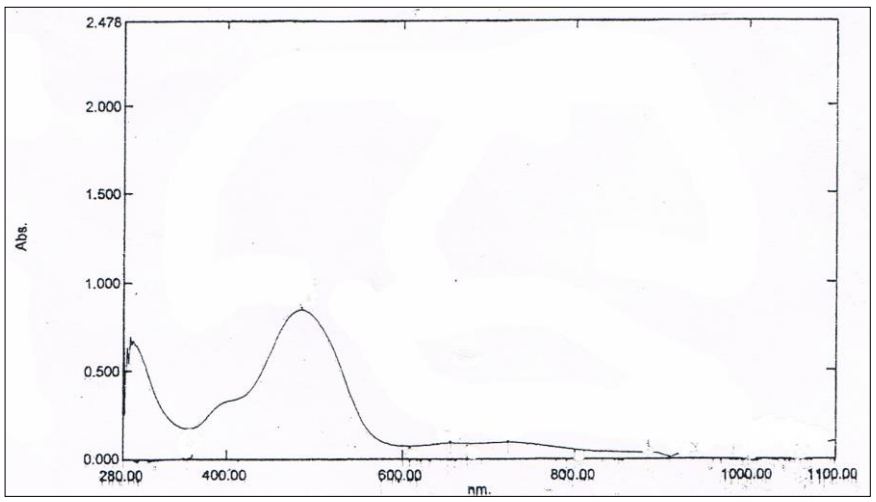


Fig. 8: The Absorption Spectra of ligand Zn^{+2}

Effect of pH

The effect of pH on the absorbance of metal complexes solutions were studied .The absorption of metalion –ligand solution of all complexes approach maximum at pH=(6.5-7.5) this results are agree with earlier work[14]he optimal pH , wave length (λmax) and molar absorptivity (∈) of Zn(II) , Cd(II) , Hg(II) , Co(III) , Ni(II) , Cu(II) complexes are calculated from beer-Lambert rule as equation (1), this value is shown in **Table 2** and **Figures 9 And 10.**

A = ε b c ……..(1)

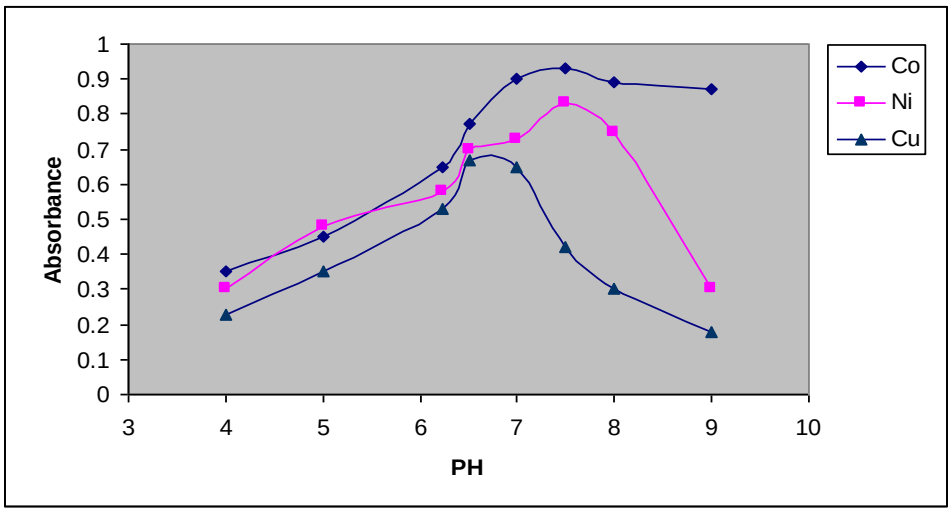


Fig. 9: The Effect of pH on The Absorbance(SAI) Metal Chelats

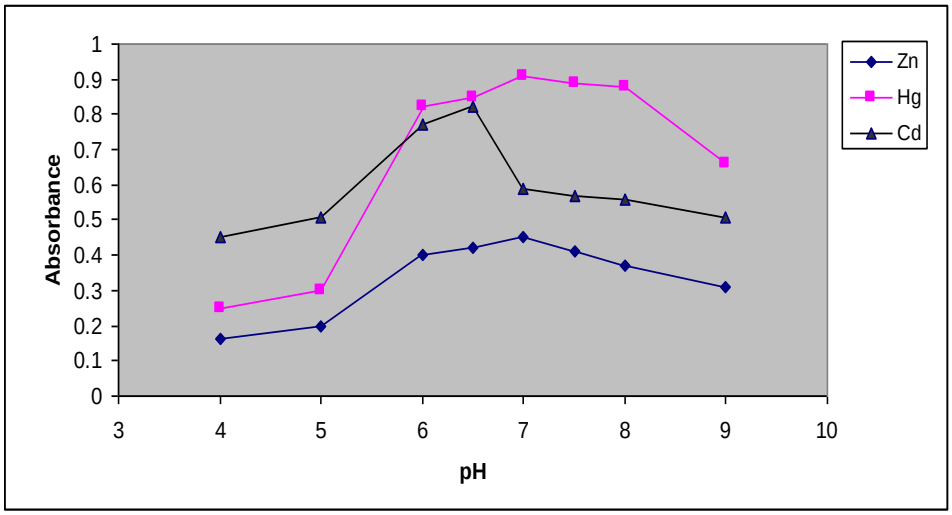


Fig. 10: The Effect of pH on The Absorbance (SAI) Metal Chelats

Table 2: The Optimal pH Values and WaveLength (λ max) with Absorptivity ($\in$) of Metal Ion

Ligand	Metal ion	Optimal pH	Molar Absorptivity ($\in$) X 10^3	Wave length λ max	Metal ligand
SAI(425 nm)	Co(III)	7.5	46	497	1 : 2
	Ni(II)	7.5	8.41	484	1 : 2
	Cu(II)	6.5	5.4	4٤5	1 : 1
	Zn(II)	7.0	2.66	475	1 : 2
	Cd (II)	6.5	2.95	486	1 : 2
	Hg(II)	7.0	5.07	488	1 : 2

Metal : Ligand Ratios

The metal: ligand ratios of the complexes were deter mimed by the method of mole ratio [15]fixed pH, and at wavelengths of maximum absorption. The results are summarized in table (2). The ligand was found to form (2:1) chelates with Co(III), Ni(II), Cd(ll), Zn(ll) and Hg(II) and (1:1) chelates with the Cu (II). The results are in agreement with the values reported for some Imidazole complexes [16]. results indicate the formation (M: L) for complexes as shown in **Figures 11 and 12.**

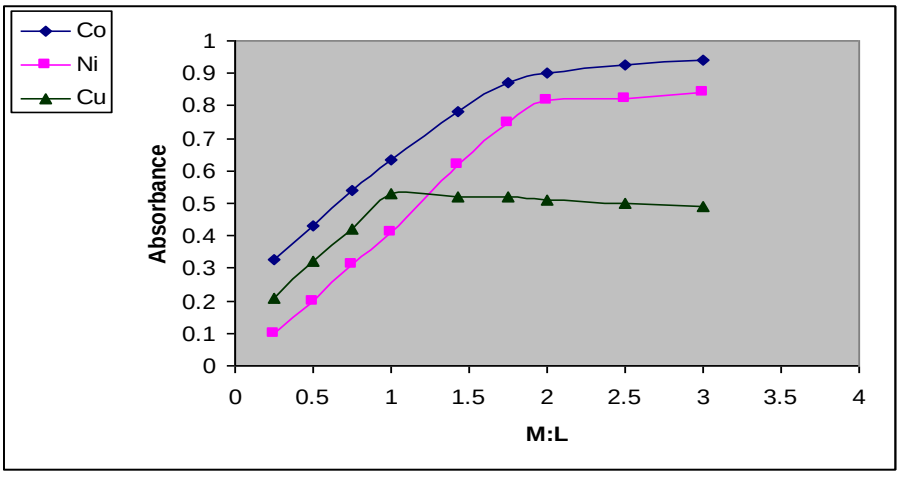


Fig. 11: Mole Ratio (M:L) of SAI – Metal Chelats

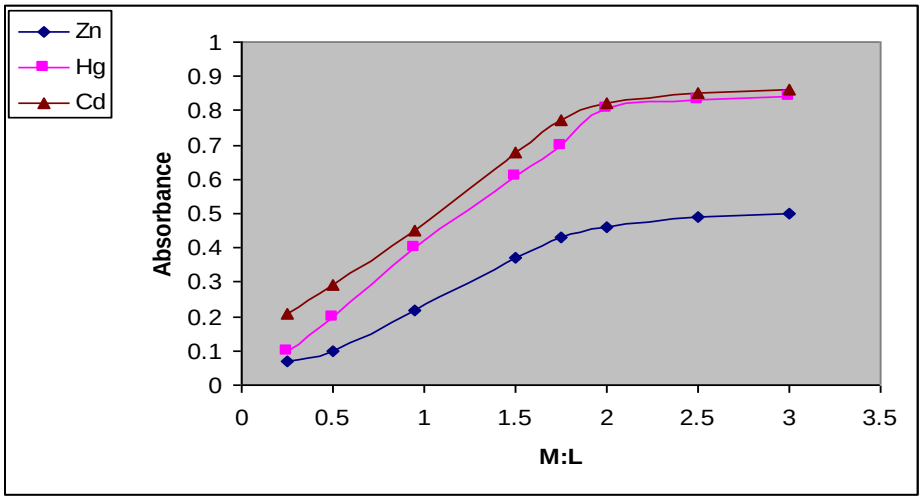


Fig. 12: Mole Ratio (M:L) of SAI – Metal Chelats

Infrared spectra

The I.R. spectrum of ligand (SAI) in (Table 3)) shown a characteristic broad band at 3370 cm due to the amine hydrogen and hydroxyl of sulfuric acid [17].e bands at 2940 hydrogen 3060 are due to (C-H) aliphatic and aromatic respectively. The band at 1625 is due to (C=N) of imidazole ring [18]. band at 1440 and 1510 to (N=N) azo group[19-21].The bands(470-570) to ν(M-0) and ν (M-N)[22-24]ased on the. Results presented above lead to suggest that the ligand behaves as tridentate chelating regent, coordinatine, with metal ion by ahydroxy oxygen of sulfonic group azo nitrogen and nitrogen coordinating nitrogen imidazole ring.

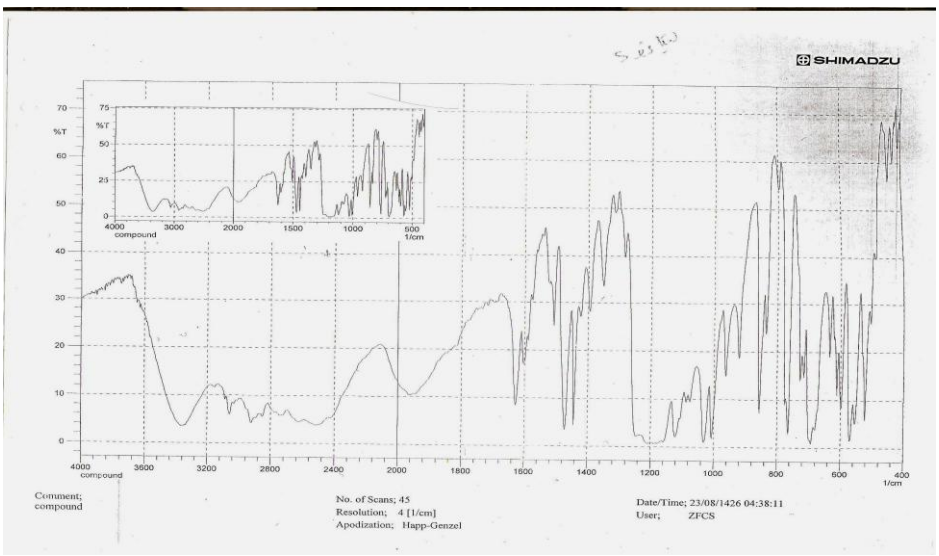


Fig. 13: The FTIR of The Ligand

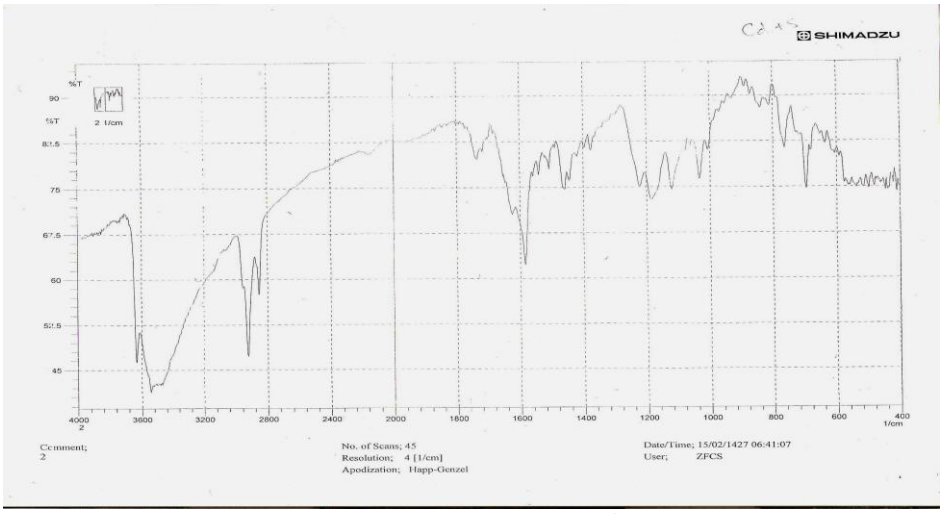


Fig. 14: The FTIR of The Cd^{+2} Complex

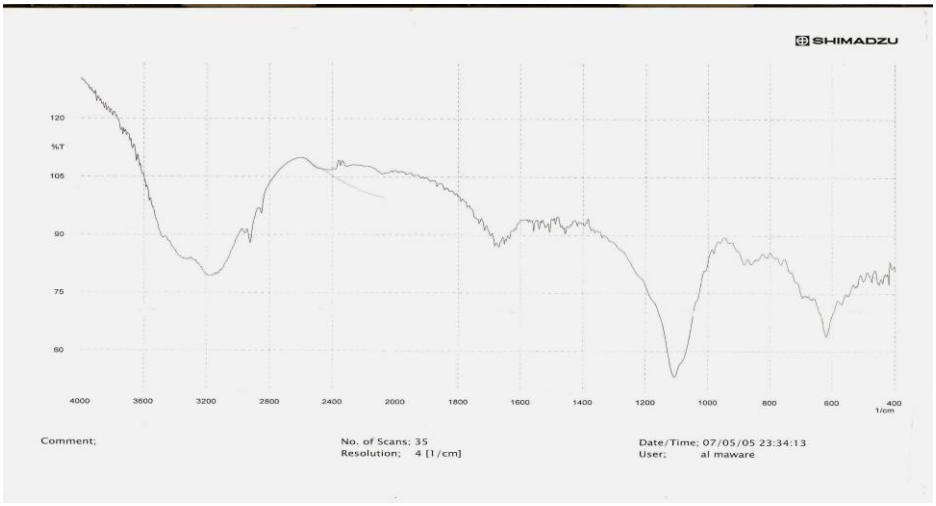


Fig 15: The FTIR of The Cu^{+2} Complex

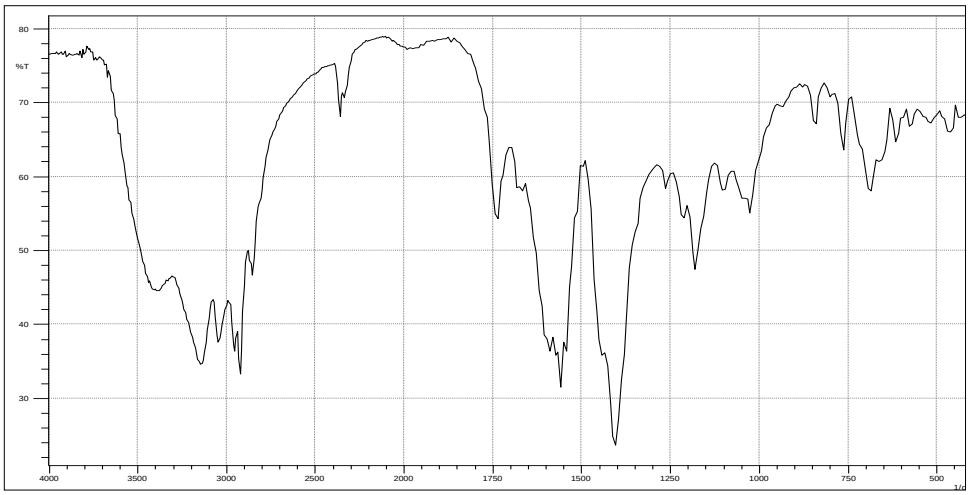


Fig. 16 :FTIR of The Ni^{+2}Complex

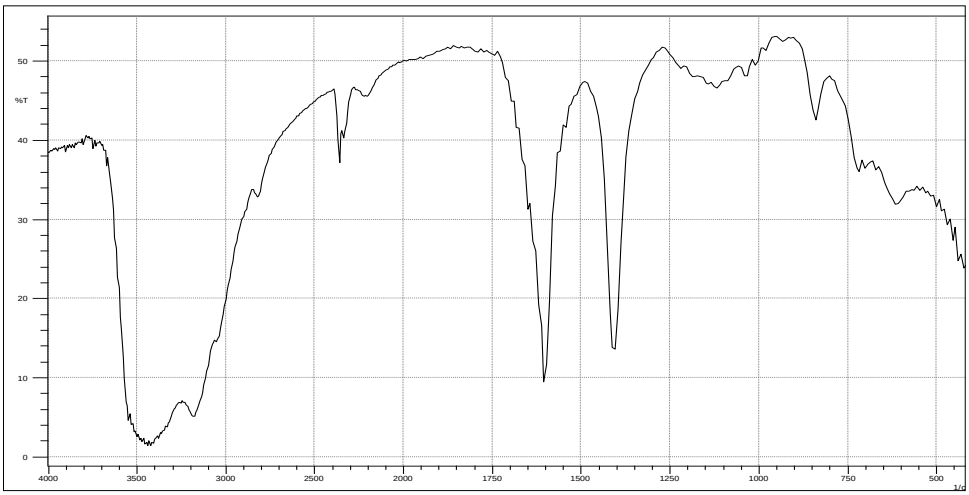


Fig. 17: The FTIR The Co^{+3}Complex

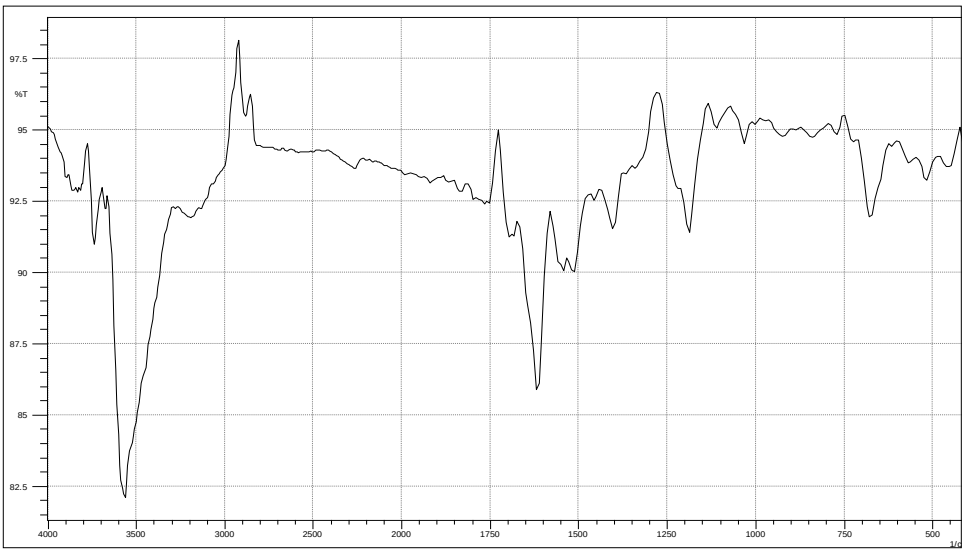


Fig. 18: The FTIR of The Hg^{+2}Complex

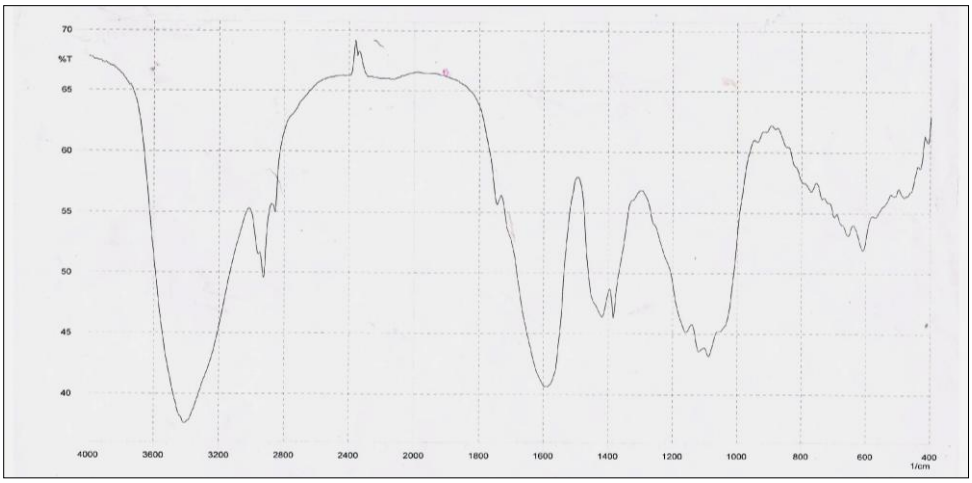


Fig. 19 : The FTIR of The Zn^{+2}Complex

Table 3: Important IR Frequencies for The Ligand and Its Complexes SO_3-H

Compound	ν (O-H)	ν (C=N)	ν (N=N)	ν (SO_3-H)	ν (M-O)	ν (M-N)	SO_3
SAI		1615	1500	1210			
$[CoL_2]Cl \cdot H_2O$	3402	1573	1456		526	-	-
$[NiL_2]$	3396	1588	1453		517	469	1175
$[CuL] Cl. H_2O$	3403	1576	1462		509	473	1183
$[ZnL_2]. H_2O$	-	1582	1457		521	487	1192
$[CdL_2]$	-	1593	1462		527	482	1160
$[HgL_2]$	-	1585	1452		514	477	1168

According to these results the structural formula of prepared complexes in this work may be proposed in **Figure 20** show below .

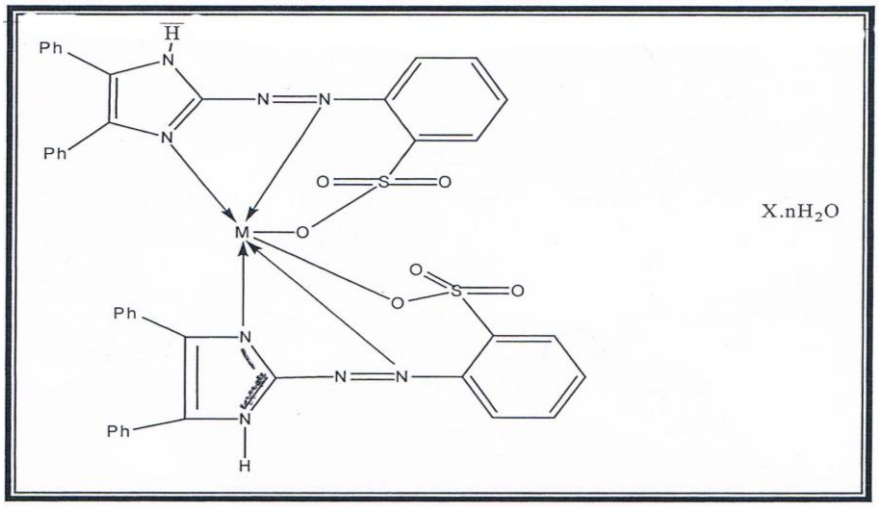
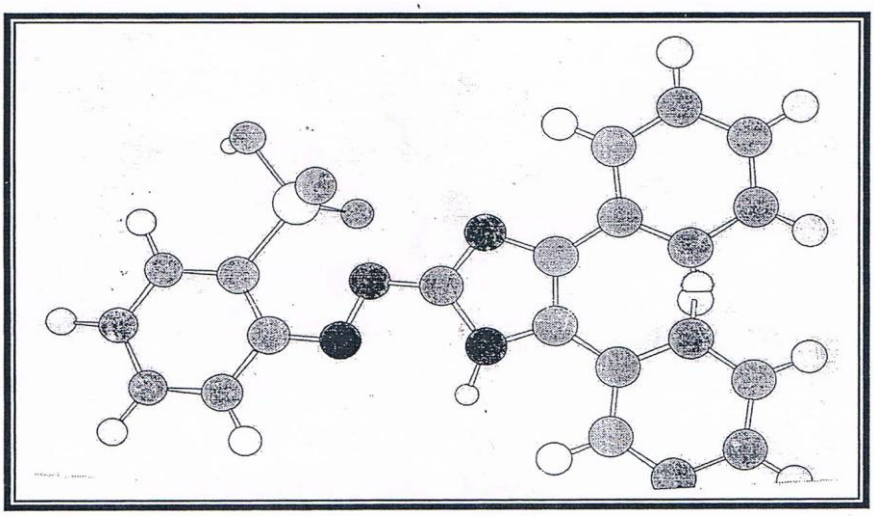


Fig 20 : The Proposed True Trued Formula of Prepared Complexes

M=Co(III) , Cu(II) , X = 1 , n = 1

M = Zn(II) and, X=0,n=1

M=Ni(II) , Cd(II) and Hg(II) , X=0,n=0



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